APXPS 2018

5th Annual Ambient Pressure X-ray Photoelectron Spectroscopy Workshop 2018

Booklet of Abstracts

December 11th to 14st 2018

Berlin, Germany

Conference Venue:

Harnack House

Ihnestr. 16-20 - 14195 Berlin
Phone: +49 30 8413-3800
Fax: +49 30 8413-3801
Email: info@harnackhaus-berlin.mpg.de

Scientific Advisory Committee

- **Luca Artiglia** Paul Scherrer Institute, Switzerland
- **Hendrik Bluhm** Lawrence Berkeley National Laboratory, USA
- **Georg Held** University of Reading, UK
- **Axel Knop-Gericke** Fritz-Haber-Institut der MPG, Germany
- **Hiroshi Kondoh** Keio University, Japan
- **Zhi Liu** ShanghaiTech University, China
- **Simon Mun** Gwangju Institute, South Korea
- **Virginia Perez-Dieste** ALBA Synchrotron, Spain
- **Tulio Rocha** Brazilian Synchrotron Light Laboratory, Brazil
- **Francois Rochet** Sorbonne Université, France
- **Joachim Schnadt** Lund University, Sweden
- **Sven L. M. Schroeder** University of Leeds, UK
- **Ira Waluyo** Brookhaven National Laboratory, USA
- **Yaw-Wen Yang** NSRRC, Taiwan

Local organizers

- Dorothea Damm
- Alexander Klyushin
- Axel Knop-Gericke

Supported by

SPECS™
Innovation in Surface Spectroscopy
and Microscopy Systems

MAX-PLANCK-GESELLSCHAFT

AC
FHI

Table of Content

time	session	Tuesday December 11th	session	Wednesday December 12th		session	Thursday December 13th		session	Friday December 14th		time
9:00-9:10			Electrochemistry	welcome		Catalysis	K2	Papp	Instrumentation	O19	Masuda	9:00-9:10
9:10-9:20												9:10-9:20
9:20-9:30				K1	Rossmeisl					O20	bin Kaderi	9:20-9:30
9:30-9:40												9:30-9:40
9:40-9:50							I4	Ganduglia-Pirovano		O21	Schroeder	9:40-9:50
9:50-10:00												9:50-10:00
10:00-10:10				I1	Savinova					O22	Nemsak	10:00-10:10
10:10-10:20							coffee					10:10-10:20
10:20-10:30										coffee		10:20-10:30
10:30-10:40				coffee			I5	Ma				10:30-10:40
10:40-10:50										T6	Bluhm (cross contamination)	10:40-10:50
10:50-11:00												10:50-11:00
11:00-11:10				O1	Mao		O10	Bukhtiyarov				11:00-11:10
11:10-11:20										Workshop discussion		11:10-11:20
11:20-11:30				O2	Mom		O11	Held				11:20-11:30
11:30-11:40												11:30-11:40
11:40-11:50				O3	Mueller		O12	Escudero				11:40-11:50
11:50-12:00										Closing remarks		11:50-12:00
12:00-13:30				lunch			lunch			lunch		12:00-13:30
13:30-13:40			Interfaces	I2	Michaelis		I6	Osterwalder		Transfer to BESSY		13:30-13:40
13:40-13:50												13:40-13:50
13:50-14:00												13:50-14:00
14:00-14:10		registration		O4	H. Yang		O13	Kratky				14:00-14:10
14:10-14:20												14:10-14:20
14:20-14:30				O5	Favaro		O14	Y.-W. Yang				14:20-14:30
14:30-14:40										BESSY tour		14:30-14:40
14:40-14:50				O6	Stoerzinger		O15	Mun				14:40-14:50
14:50-15:00												14:50-15:00

15:00-15:10					coffee			coffee				15:00-15:10
15:10-15:20												15:10-15:20
15:20-15:30					I3	Cuenya	Material	I7	Yu			15:20-15:30
15:30-15:40												15:30-15:40
15:40-15:50												15:40-15:50
15:50-16:00												15:50-16:00
16:00-16:10	Technical	T1	Crumlin (Tender X-ray)		O7	Artiglia		O16	Reinke			16:00-16:10
16:10-16:20					O8	Bluhm		O17	Timm			16:10-16:20
16:20-16:30												16:20-16:30
16:30-16:40		T2	Zeller (spatially resolved XPS)		O9	Villar-Garcia		O18	Waluyo			16:30-16:40
16:40-16:50												16:40-16:50
16:50-17:00					Poster session and coffee							16:50-17:00
17:00-17:10		T3	Specs									17:00-17:10
17:10-17:20												17:10-17:20
17:20-17:30												17:20-17:30
17:30-17:40		coffee										17:30-17:40
17:40-17:50												17:40-17:50
17:50-18:00		T4	Karslioglu (charge compensation)									17:50-18:00
18:00-18:10												18:00-18:10
18:10-18:20												18:10-18:20
18:20-18:30		T5	Velasco-Velez (1bar AP-XPS)									18:20-18:30
18:30-18:40												18:30-18:40
18:40-18:50												18:40-18:50
18:50-19:00												18:50-19:00
19:00-21:00		Dinner get together			Conference dinner							19:00-21:00

🟥 Technical session 🟨 Keynote contribution 🟩 Invited contribution 🟦 Oral contribution ▨ Poster contribution

Program overview

11th, December

14:00-16:00	**Registration**
16:00–17:30	**Technical session 1**
17:30–17:40	**Coffee break**
17:40–19:00	**Technical session 2**
19:00-21:00	**Dinner get together**

12th, December

09:00–10:30	**Electrochemistry 1** 9:00-9:20 **Opening remarks** 9:20-10:00 **J. Rossmeisl** K1: *“Electro-Catalysis at the atomic scale”* 10:00-10:30 **E. Savinova** I1: *“Combining Near-Ambient Pressure Photoemission Spectroscopy with the Density Functional Theory Calculations for Understanding the Mechanism of Water Oxidation”*
10:30–11:00	**Break**
11:00–12:00	**Electrochemistry 2** 11:00-11:20 **B. Mao** O1: “*Operando Ambient Pressure X-ray Photoelectron Spectroscopy Studies of Sodium-Oxygen Redox Reactions*” 11:20-11:40 **R. Mom** O2: *“Electrochemical XPS Using Confined Electrolyte: Au and Pt Oxidation”* 11:40-12:00 **D. N. Mueller** O3: *“High temperature oxygen exchange of mixed conducting perovskite oxides”*
12:00–13:30	**Lunch**
13:30–15:00	**Interfaces 1** 13:30-14:00 **A. Michaelides** I2: *“Water at Surfaces”* 14:00-14:20 **H. Yang** O4: *“The hydrogen bonding structure of adsorbed water on ice nucleation active solid substrates”* 14:20-14:40 **M. Favaro** O5: *“Ambient Pressure XPS Investigation at the Solid/Liquid Interface of a Model System for Carbon Dioxide Capture”* 14:40-15:00 **K. A. Stoerzinger** O6: *“Impact of Sr-Incorporation on Cr Oxidation and Water Dissociation in* $La_{(1-x)}Sr_xCrO_3$*”*
15:00–15:20	**Break**

15:20–16:50	<u>**Interfaces 2**</u> 15:20-15:50 **B. Cuenya** I3: *"Dynamic Nanocatalysts: Environmental Effects* 15:50-16:10 **L. Artiglia** O7: *"Time-resolved APXPS characterization of catalysts under reaction conditions"* 16:10-16:30 **H. Bluhm** O8: *"Propensity of Ions for the Liquid/Vapour Interface Observed by APXPS"* 16:30-16:50 **I. J. Villar-Garcia** O9: *"Combined NAP XPS and NAP Core hole clock studies of polymer/TiO_2 hybrids for artificial photosynthesis"*
16:50-19:00	**Poster Session**
19:00-	**Conference dinner**

13th, December

09:00–10:10	<u>**Catalysis 1**</u> 9:00-9:40 **C. Papp** K2: *"From classical model catalysts to liquids"* 9:40-10:10 **M. V. Ganduglia-Pirovano** I4: *"Theoretical and in situ studies for the reactivity of metal-ceria (111) surfaces:Importance of strong metal-support interactions"*
10:10–10:30	**Coffee break**
10:30–12:00	<u>**Catalysis 2**</u> 10:30-11:00 **D. Ma** I5: *"Atomic layered Au clusters on α-MoC as catalyst for water gas shift reaction"* 11:00-11:20 **V. I. Bukhtiyarov** O10: "*CO oxidation on the model Pd-Au/HOPG catalysts: NAP XPS and MS study*" 11:20-11:40 **G. Held** O11: *"A NAP-XPS study of Methane Oxidation over supported Pd catalysts"* 11:40-12:00 **C. Escudero** O12: *"In situ AP-XPS and XANES of Co-Based Catalysts during Ethanol Steam Reforming"*
12:00–13:30	**Lunch**

13:30–15:00	**Catalysis 3** 13:30-14:00 **J. Osterwalder** I6: *“New APXPS endstation at the SLS for the study of model catalysts”* 14:00-14:20 **T. Kratky** O13: *“Performance of co-precipitated NiAlOx catalysts during CO2 methanation”* 14:20-14:40 **Y.-W. Yang** O14: *“Hydrogenation of CO_2 on NiGa polycrystalline thin films”* 14:40-15:00 **B. S. Mun** O15: *“Investigation of interfacial Pt-NiO1-x nanostructures on $Pt_3Ni(111)$ surface under CO oxidation”*
15:00–15:20	**Coffee break**
15:20–16:50	**Material** 15:20-15:50 **Y. Yu** I7: *“Towards Understanding the Fundamentals at the Electrochemical Interfaces”* 15:50-16:10 **P. Reinke** O16: *“Evolution of the Oxide Layer on Ni-Cr as a Function of Alloy Composition”* 16:10-16:30 **R. Timm** O17: *“Self-cleaning and surface chemical reactions during HfO_2 atomic layer deposition on InAs revealed by AP-XPS”* 16:30-16:50 **I. Waluyo** O18: *“In Situ Surface Characterization of Pt-Cu Single-Atom Alloy Model System in Ambient Pressure of Gases”*

14th, December

09:00–10:20	**Instrumentation** 9:00-9:20 **T. Masuda** O19: *“In situ X-ray photoelectron spectroscopy by using an environmental cell and Al Kα source”* 9:20-9:40 **A. bin Kaderi** O20: *“Mn, Cr-spinel Oxide’s Formation from APXPS’ Perspectives”* 9:40-10:00 **S. L. M. Schroeder** O21: *“The Removal of Surface Contaminants from Organic Crystals by Anti-Solvent Surface Treatment”* 10:00-10:20 **S. Nemšák** O22: *“Advances in analysis of Bragg-reflection standing wave photoemission”*
10:20–10:40	**Coffee break**
10:40–12:00	**Workshop discussion and closing remarks**
12:00–13:30	**Lunch**
13:30–17:00	**BESSY tour**

Poster Program

	Electrochemistry
P1	**L. Frevel, T. Jones, R. Mom, J. Velasco-Veléz, A. Knop-Gericke, R. Schlögl** ”Reactive oxygen species on iridium: testing hypotheses from DFT in situ”
P2	**C. Jiang, B. Mao, Q. Li, Y. Li, Z. Liu** ”A Rechargeable All-Solid-State Sodium Peroxide (Na_2O_2) Battery with Low Overpotential”
P3	**Q. Li, B. Mao, C. Jiang, Y. Li, Z. Liu** ”Study the All-solid-state Na-O_2 Battery Using Cerium Oxide as Oxygen Electrode by Ambient Pressure X-ray Photoelectron Spectroscopy”
P4	**K. Skorupska, T. Jones, R. Mom, D. Teschner, L. Xi, K. M. Lange, J. Melder, P. Kurz, M. Hävecker, Ch.-H. Chuang, A. Knop-Gericke, R. Schlögl** ”Manganese oxides at OER conditions by In-Situ Synchrotron Based Spectroscopy”
	Interfaces
P5	**A. H. de Abreu, A. N. Brito, T. C. R. Rocha** ”Atmospheric relevant molecules at aqueous interfaces probed with APXPS”
P6	**M. Ahmad, R. Prakash, H. Raschke, N. Esser, R. Hergenröder** “NAP-XPS of Functionalized GaN Surface for Biomolecular Sensing”
P7	**J. Cai, Y. Han, E. Crumlin, Y. Li, Z. Liu** ”Probing the surface states of Nickel single crystals under CO_2 by Ambient Pressure XPS”
P8	**S.-Y. Chang, B. Tayler-Barrett, E. A, Willneff, E. J. Shotton, C. Escudero, V. Perez-Dieste, S. L. M. Schroeder** ”Non-Destructive Depth Profiling of an Organic Crystal Surface Covered in Water by Variable Energy NAP-XPS”
P9	**G. D’Acunto, P. Shayesteh, M. Van Daele, F. Rehman, A.R. Head, F. Rochet, F. Bournel, R. Tsyshevskiy, C. Detavernier, C. Dendooven, J.-J. Gallet, J. Schnadt** ”ALD of HfO_2 on SiO_2 and TiO_2: Identification of Surface Species by Ambient Pressure XPS and IR Spectroscopy”
P10	**T. Duchoň, D. N. Müller, G. Held, C. M. Schneider** ”Probing hydroxylation of oxides via ambient pressure resonant photoemission”
P11	**W. T. Figueiredo, G. B. Della Mea, C. Escudero, V. Pérez-Dieste, F. Bernardi** ”Strong Metal Support Interaction (SMSI) in $CuxNi_{1-x}/CeO_2$ Nanoparticles”
P12	**D. Grinter, R. Hamlyn, F. Xu, D. Stacchiola, S. Senanayake, J. Rodriguez** ”Ambient Pressure Spectroscopy and Imaging of Molecular Interactions with Reducible Oxide Surfaces”
P13	**M. Jung, Y. Yu, B. Jeong, B. S. Mun** ”Measurement of work function on Pt(110) surface during CO oxidation”
P14	**C.-H. Lin, C.-H. Wang, Y.-J. Wang, W. Ting, Y.-W. Yang** “Ambient Pressure XPS Studies of NO_2 Sensing Mechanism of Titanyl Phthalocyanine”
P15	**F. Rehman, P. Shayesteh, A. Troian, G. D’Acunto, S.Yngman, E. Kokkonen, J. Knudsen, S. Urpelainen, F. Rochet, F. Bournel, J.-J. Gallet, R. Timm, J. Schnadt** ”Watching Atomic Layer Deposition with Synchrotron-based real time Ambient Pressure XPS: Towards Millisecond Time Resolution”
P16	**A. Shavorskiy, X. Ye, O. Karslıoğlu, A. D. Poletayev, M. Hartl, I. Zegkinoglou, L. Trotochaud, S. Nemšák, C. M. Schneider, E. J. Crumlin, S. Axnanda, Z. Liu, P. N. Ross, W. Chueh, H. Bluhm** ”Direct Mapping of Band Positions in Doped and Undoped Hematite during Photoelectrochemical Water Splitting”

P17	**R. H. Temperton, J. N. O’Shea** ”High pressure XPS analysis of the atomic layer deposition of aluminium oxide on titanium dioxide”
P18	**T. Yang, Y. Han, J. Cai, Q. Dong, Z. Liu** ”Interaction of CO$_2$ with Cu(111) and Cu(110) Studied with Ambient Pressure X-ray Photoelectron Spectroscopy: Structural Sensitivity and Pressure Dependence”

Catalysis

P19	**L. R. Baker, Y. Mueanngern, X. Yang, Y. Tang, F. Tao** ”Catalysis at Multiple Length Scales: Bifunctional Activation at Nanoscale and Mesoscale Interfaces in Platinum–Cerium Oxide Catalysts”
P20	**R. Castillo, J. C. Navarro, C. Escudero, V. Perez-Dieste, M. A. Centeno, M. Daturi, J. A. Odriozola** ”The evolution of APXPS as a tool for catalyst investigation: surface dynamics under preferential CO oxidation flow reaction conditions”
P21	**C.-H. Chuang, Y.-F. Wang, T.-W. Chiu, A. Knop-Gericke, J. J. Velasco-Vélez** ”Operando Observation of Cu-based Catalyst for Methanol Steam Reform-ing Process by Ambient-Pressure X-ray Photoelectron Spectroscopy”
P22	**P. Concepción, J. Cored, L. Liu, A. V. Puga, V. Pérez-Dieste, H. García, A. Corma** ”Sunlight-assisted Hydrogenation of CO$_2$ into ethanol and C2+ Hydrocarbons by Sodium-promoted Co@C Nanocomposites”
P23	**F. Huang, Y. Deng, Y. Chen, X. Cai, M. Peng, Z. Jia, P. Ren, D. Xiao, X. Wen, N. Wang, H. Liu, D. Ma** ”Atomically dispersed Pd on nanodiamond/graphene hybrid for selective hydrogenation of acetylene”
P24	**O. Karslıoğlu, A.R. Head, J. Raso, T. Gerber, Y. Yu, L. Trotochaud, P. Kerger, H. Bluhm** ”CO+NO+O$_2$ Reaction on Pd(100): New Insights From APXPS”
P25	**K.-J. Lee, Y. Ye, H. Su, D.-J. Yun, M. Sun, B. S. Mun, E. J. Crumlin** ”CO$_2$ conversion on Ni(100) probed with ambient pressure XPS”
P26	**J. J. Velasco-Vélez, D. Teschner, F. Girgsdies, M. Hävecker, V. Streibel, M-G. Willinger, J. Cao, M. Lamoth, E. Frei, R. Wang, A. Centeno, A. Zurutuza, S. Hofmann, R. Schlögl, A. Knop-Gericke** “The role of adsorbed and subsurface carbon species for the selective alkyne hydrogenation over a Pd-black catalysts: An operando study of bulk and surface at 1 bar”
P27	**M. Younas, H. Hartmann, J. Pasel, J. Dornseiffer, A. Besmehn** ”Combined time-resolved AP-XPS and TAP study on Pd for methane oxidation”
P28	**F. García, M. Ilyn, V. Pérez-Dieste, C. Escudero, B. Hagman, S. Blomberg, J. Gustafson, E. Lundgren, A.L. Walter, I. Waluyo, F. Schiller, J. E. Ortega** ”In-situ oxidation of CO on a curved Pt(111) surface”
P29	**J. E. Ortega, M. Ilyn, V. Pérez-Dieste, C. Escudero, C. Huck-Iriart, N. Ruiz del Arbol, B. Hagman, S. Blomberg, J. Gustafson, E. Lundgren, F. Schiller** ”Spatial variation of the active phases during the catalytic oxidation of CO measured on a curved Pd(111) surface”

Material

P30	**M. Andrä, R. Dittmann, H. Bluhm, C. Schneider, R. Waser, D. N. Mueller, F. Gunke** ”Origin and control of the surface space charge layer in donor doped SrTiO$_3$”
P31	**A. Boucly, L. Artiglia, H. Yang, M. Ammann** ”Ferrihydrite Acid Attack”
P32	**J. T. Diulus, S. P. Lorona, G. S. Herman** ”Investigation of the Initial Stages of SiGe(001) Thermal Oxidation Using Ambient Pressure X-ray Photoelectron Spectroscopy”

P33	**E. González, A. Echavarría, A. Santa, O. Arnache, D. Stacchiola, J. Llorca, C. Ostos** ”Co 2p APXPS investigation of Co_3O_4/Si films grown and monitored under in operando conditions”
P34	**M. Huber, M. Rötzer, M. Krause, H. Bluhm, M. Döblinger, S. Günther, U. Heiz, F. Esch, B. A. J. Lechner** ”Charge effects in the oxidation of size-selected Pt clusters”
P35	**T. A. Kathyola, E. A. Willneff, S. L.M. Schroeder** ”Combined NAP-XPS and XANES Analysis of Calcium Compounds“
P36	**M. Kjærvik, P. Dietrich, A. Thissen, K. Schwibbert, A. Nefedow, C. Wöll, W. Unger** ”Exploring the capabilities of NAP-XPS: Application to biofilms, suspended nanoparticles and metal-organic frameworks“
P37	**H. Lim, D. Kim, Y.Yu, G. Kim, M. Jung, C. J. Yoon, J. Y. Jo, B. S. Mun** ”Investigation on polarization switching behavior of $SrMnO_3$ ferroelectric thin film with Ambinet Pressure-XPS“
P38	**C. Ostos, A. Santa, A. Echavarria, A. Scott, J. Niño** ”Ce 3d APXPS investigation of ceria powder under in operando conditions”
P39	**L. P. Ramirez, J.-J. Gallet, A. Boucly, F. Bournel, F. Rochet** ”Room Temperature Silicon Oxidation: Longstanding Questions and New Experimental Findings from Near Ambient Pressure XPS”
P40	**C.C. da Silva, M. Rohwerder** ”Internal oxidation of iron-silicon model alloys during simulated annealing after hot rolling”
P41	**C. Volders, V. A. Avincola, G. Ramalingam, I. Waluyo, J. Perepezko, P. Reinke** ”The Impact of Mo and W on the oxide evolution of Ni-Cr Alloys”

Instrumentation

P42	**M. Amati, P. Zeller, L. Gregoratti** ”Toward Near Ambient Pressure Scanning Photoemission Imaging and Spectromicroscopy for in situ and in operando characterization of Fuel Cell components”
P43	**D. C Oliveira, F. Vicentin, T. C. R. Rocha** ”APXPS activites at LNLS: present and future”
P44	**E. Pellegrin, V. Perez-Dieste, C. Escudero, J. Fraxedas, P. Rejmak, N. Gonzalez, A. Fontsere, J. Prat, S. Ferrer** ”Water/methanol solutions characterized by liquid μ-jet XPS and DFT – the methanol hydration case”
P45	**R. Temperton, J. O’Shea, L. Johnson, D. Walsh, R. Jones** ”An electrochemical cell on a SPECS/Omicron sample plate?”
P46	**S. L.M. Schroeder, E. A. Willneff** ”The University of Leeds Near-Ambient Pressure XPS Facility “
P47	**L. Walczak, M. Dzierżęga, Ch. Kirschfeld, M. Bugla, M. Florek, S. Żuk, A. Stanik, L. Nittler, A. Szatkowski** ”Recent development in XPS and Ambient Pressure XPS techniques”
P48	**E. A. Willneff, S.-Y. Chang, S. L.M. Schroeder** ”Libraries of Core Level Binding Energies: The Added Value of NAP XPS for Analysing Chemical Shifts in Organic Systems”
P49	**Y. Ye, H. Su, K.-J. Lee, N. Andressen, M. Blum, Z. Hussain, E. J. Crumlin** ”Revitalization of ALS Tender X-ray APXPS Beamline”
P50	**P. Zeller, M. Amati, L. Gregoratti** ”Spatially resolved XPS measurements at NAP conditions”
P51	**S. Zhu, A. Shavorskiy, J. Kundsen, J. Schnadt** ”HIPPIE, The new ambient pressure X-ray photoelectron spectroscopy beamline at MAXIV”

Keynote talks

Electro-Catalysis at the atomic scale.

Jan Rossmeisl

Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen, Denmark

...

* *jan.rossmeisl@chem.ku.dk*

The chemical industry should in the future be based on renewable energy. Therefore, material development for environmentally friendly, electrocatalytic production of valuable chemicals is needed.

Chemicals could be produced using safe, cheap, more environmentally friendly and more abundant reactants than today. The products could be provided on demand at the place where they are needed, reducing expensive and hazardous transport of chemicals. However, stable, efficient and selective catalysts have to be discovered. This requires insight into the surface chemistry at the atomic scale.

Surface chemistry can be revealed based on density functional simulations. However, there are presently no atomic scale simulations or analysis that capture all the essential parts of the nature electrochemical interface. Thus the electrochemical solid/liquid interface represents one of the frontiers of atomic scale simulations.

I will give examples where the insight from simulations might pave the way for rational discovery of new catalyst materials and new electrocatalytic processes for sustainable production of fuels and chemicals. Some examples are: oxygen reduction to H_2O_2[1], Oxygen evolution [2] and CO_2 reduction reaction [3].

[1] Enabling direct H_2O_2 production through rational electrocatalyst design. Siahrostami, Samira; Verdaguer-Casadevall, Arnau; Karamad, Mohammadreza; et al. NATURE MATERIALS, 12, 1137-1143, 2013.

[2] Beyond the top of the volcano? - A unified approach to electrocatalytic oxygen reduction and oxygen evolution. Busch, Michael; Halck, Niels B.; Kramm, Ulrike I.; et al NANO ENERGY, 29, 126-135, 2016

[3] Understanding activity and selectivity of metal-nitrogen-doped carbon catalysts for electrochemical reduction of CO_2. Ju, Wen; Bagger, Alexander; Hao, Guang-Ping; et al. NATURE COMMUNICATIONS 8, 944, 2017.

From classical model catalysts to liquids

Christian Papp

Physikalische Chemie 2, FAU Erlangen, Egerlandstraße-3, 91058 Erlangen, Germany

...

* *christian.papp@fau.de*

XPS at near ambient pressures provides insight into different types of chemical reactions, as will be illustrated with three examples. In the first, we investigate the effect of higher pressures in the platinum-catalyzed CO oxidation and the formation of platinum oxides, and discuss the effect of particle size and substrate. While we observe the formation of disordered platinum oxides at elevated oxygen pressures [1], the dominant phase in CO oxidation was found to be metallic platinum. The second example discusses the liquid-gas reaction of an amine-functionalized ionic liquid with CO_2 [2]. We determined the amount of captured CO_2 in the near-surface region and identified the reaction products carbamate and carbamic acid. These results are compared to bulk measurements; the lower carbamic acid content in the bulk is assigned to differences in solvation. The third example concerns liquid binary alloys of transition metals and Ga [3] that are stable and selective alkane dehydrogenation catalysts. The beneficial effect of Ga is assigned to the catalyst being liquid during reaction. In XPS, we observe a temperature-dependent change in concentration, due to the formation of solid intermetallics, leading to the depletion of the catalytically active transition metal. In the Pd-Ga alloy, Pd is depleted at the surface [4].

[1] D. Fantauzzi, et al. Angew. Chem. Int. Ed. 56, 2594-2598 (2017)
[2] I. Niedermaier, et al. J. Am. Chem. Soc. 136, 436-441 (2014)
[3] N. Taccardi, et al. Nature Chemistry 9, 862–867 (2017)
[4] M. Grabau, et al. Chem. Eur. J. 23, 1-8 (2017)

Invited talks

Combining Near-Ambient Pressure Photoemission Spectroscopy with the Density Functional Theory Calculations for Understanding the Mechanism of Water Oxidation

V. A. Saveleva⊥, T. Jones[2], L. Wang[3], J.-J. Gallet[4,5], F. Bournel[4,5], A.S. Gago[3],
K. A. Friedrich[3,6], D. Teschner[2,7], R. Schlögl[2,7], and E. R. Savinova[1,**]

[1] ICPEES, UMR 7515, Université de Strasbourg, France
[2] Departement of Inorganic Chemistry, FHI der MPG, Berlin, Germany
[3] Institute of Engineering Thermodynamics, DLR, Germany
[4] LCPMR, Sorbonne Universités –CNRS, Paris, France
[5] Synchrotron-Soleil, Gif-sur-Yvette Cedex, France
[6] Institute of Energy Storage, University of Stuttgart, Germany
[7] Department of Heterogeneous Reactions, MPI für Chemische Energiekonversion, Mülheim a. d. Ruhr, Germany
…

* *Elena.Savinova@unistra.fr*

Water electrolysis in proton exchange membrane (PEM) cells is considered as the most promising means for converting the surplus electricity from renewable sources into the hydrogen fuel. However, the efficiency of the energy conversion is largely restricted by the sluggish oxygen evolution reaction (OER) at the anode of PEM electrolysers. Thus, wide dissemination of the PEM electrolysis technology largely depends on the progress in the understanding of the OER mechanism and on the replacement of expensive noble metal-based electrodes by cheaper and more abundant analogues.

We apply *operando* near-ambient pressure X-ray photoelectron spectroscopy and soft X-ray absorption spectroscopy (NEXAFS) to monitor the core-level XP and the O K-edge spectra during the OER on Ru- and Ir-based anodes. Density functional theory (DFT) calculations are performed for various surface terminations of RuO_2 and IrO_2 to aid in the assignment of the spectroscopic features to specific reaction intermediates. Armed with the experimental data and with the results of DFT calculations, we discuss the nature of the reaction intermediates and the mechanism of the OER on Ru- and Ir-based anodes.

We suggest that the OER occurs via the so-called cation and anion red-ox mechanisms on the Ru and Ir anodes respectively, and that the type of the mechanism depends on the d-band structure of the oxides. We compare oxides of various genesis and show that while strongly affecting the electrocatalytic activity, the type of oxide (thermal vs. electrochemical) has no impact on the nature of the OER mechanism. We finally make a link between the nature of the OER intermediates and the mechanism of the anode degradation.

⊥ Current address: Electrochemistry Laboratory, Paul Scherrer Institut, 5232 Villigen, Switzerland

Water at Surfaces

Angelos Michaelides

Thomas Young Centre, University College London

...

* *Angelos.michaelides@ucl.ac.uk*

There are few molecules, if any, more important than water. Yet remarkably little is known about how it interacts with solid surfaces, particularly at the all important atomic-level. This is true despite widespread general interest and compelling environmental and economic incentives. For example, water-solid inter-actions play a crucial role in the activity of fuel cells, the chemistry of the atmosphere, global warming, corrosion, catalysis, the operation of membranes, and so on. In this talk I will discuss some of our recent work in which we have been using classical and quantum molecular dynamics approaches as well as advanced electronic structure methods to better understand the structural and dynamical properties of water-solid interfaces. This will include work focused on understanding the formation of ice [1-3], confined water in nanocapiliaries [4], and water diffusion and friction [5-7].

[1] M. Fitzner, G. C. Sosso, S. J. Cox and A. Michaelides, J. Am. Chem. Soc. 137, 13658 (2015)
[2] G.Sosso et al., J. Phys. Chem. Lett. 7, 2350 (2015)
[3] A. Kiselev et al, Science 355, 367 (2017)
[4] J. Chen, G. Schusteritsch, C. J. Pickard, C. G. Salzmann and A. Michaelides, Phys. Rev. Lett. 116, 025501 (2016)
[5] G. Tocci, L. Joly and A. Michaelides, Nano Lett. 14, 6872 (2014)
[6] M. Ma, G. Tocci, A. Michaelides and G. Aeppli, Nature Materials 15, 66 (2016)
[7] L. Joly, G. Tocci, S. Merabia, and A. Michaelides, J. Phys. Chem. Lett. 7, 1381 (2016)

Dynamic Nanocatalysts: Environmental Effects

Beatriz Roldan Cuenya

[1]*Department of Interface Science, Fritz-Haber Institute of the Max Planck Society, 14195 Berlin, Germany*

...

* *roldan@fhi-berlin.mpg.de*

In order to comprehend the catalytic performance of metal nanostructures, their dynamic nature and response to the environment must be taken into consideration. The working state of a nanocatalyst might not be the state in which the catalyst was prepared, but a structural and/or chemical isomer that adapted to the particular reaction conditions. Furthermore, deactivation phenomena taking place under reaction conditions can only be understood, and ultimately prevented, if sufficient information is available on the catalyst morphology, structure, chemical state, and surface composition while at work.

I will first describe novel approaches for the synthesis of size- and shape-controlled nanoparticles (e.g. Cu, CuZn, CuNi, NiGa) and their functionalization/activation based on plasma treatments. Subsequently, I will illustrate how to follow the evolution of their morphology and surface composition under different gaseous environments in the course of a catalytic reaction, in this case, the hydrogenation of CO2, via NAP-XPS. Emphasis will be given to elucidating the role of the nanoparticle size, shape, composition, and chemical state of the catalysts in their activity and selectivity).

Theoretical and in situ studies for the reactivity of metal-ceria (111) surfaces: Importance of strong metal-support interactions

M. Verónica Ganduglia-Pirovano$^{\perp}$

Instituto de Catálisis y Petroleoquímica Consejo Superior de Investigaciones Científicas,
Calle Marie Curie 2, 28049 Madrid, Spain
...

* *vgp@icp.csic.es*

Metal-ceria catalysts are promising systems for industrially important reactions such as the water-gas shift reaction for hydrogen production, methane dry reforming (DRM: $CH_4+CO_2 \rightarrow 2H_2+2CO$), and the direct conversion of methane to methanol (DMTM: $CH_4+ \frac{1}{2} O_2 \rightarrow CH_3OH$). However, the complexity of real (powder) catalysts hinders the fundamental understanding of how they work, which is essential for their rational design. Specifically, the role of ceria in the catalytic activity of ceria-based systems is still not fully understood. To unravel it, well-defined ceria-based model catalysts consisting of metal nanoparticles deposited on a ceria surface are prepared experimentally or created theoretically and investigated.

In this talk, recent results on ceria-supported Ni, Co and Cu model catalysts will be discussed, as examples of catalysts for DRM.[1] The emphasis is here put on theoretical studies in combination with experiments using ambient pressure X-ray photoelectron spectroscopy, and special attention is given to the effects of ceria as catalyst support. The ability of ceria to stabilize oxidized species (MO_x: Co^{2+} and Ni^{2+}) on the CeO_2 surface, by relocalizing electrons on localized *f*-states, and metallic ones (Co^0, Ni^0) on the reduced CeO_{2-x} support, is essential for CH_4 activation —that occur at temperatures as low as 300 K— and its reforming at relatively low temperatures (~700 K). Also, the Ni/ceria system is considered for H_2O activation and methanol synthesis from methane and water.[2]

[1] Liu, Z. et al. *Angew. Chem., Int. Ed.* **2016**, *55*, 7455; Lustemberg, P. G. et al. *ACS Catal.* **2016**, *6*, 8184; Liu, Z. et al. *Angew. Chem. Int. Ed.* **2017**, *56*, 13041.

[2] Carrasco, J. et al. *Angew. Chem. Int. Ed.* **2015**, *54*, 3917; Lustemberg, P. G. et al. *J. Am. Chem. Soc.* **2018**, 140, 7681.

$^{\perp}$ The collaboration with P. G. Lustemberg, M. Nolan, Z. Liu, T. Duchoň, M. Vorokhta, V. Matolín, E. J. Crumlin, D. C Grinter, S. D. Senanayake, and J. A. Rodriguez is gratefully acknowledged.

Atomic layered Au clusters on α-MoC as catalyst for water gas shift reaction

Ding Ma

College of Chemistry and Molecular Engineering Peking University

...

* *dma@pku.edu.cn*

The water gas shift (WGS) reaction ($CO+H_2O=H_2+CO_2$) is an essential process for hydrogen generation/upgrading in various energy-related chemical operations. Normally for a chemical reaction, higher reaction temperature renders higher reaction rate. However, from a thermodynamic point of view, WGS is an equilibrium-limited reaction that is favored at low temperature. In particular, the potential application in fuel cells requires the commercial WGS catalyst to be highly active, stable and energy-efficient. Under these criteria, decreasing the reaction temperature will not only give a considerable rise in the CO equilibrium conversion but will also exhibit potential in reducing the energy consumption, and match the working temperature of on-site hydrogen generation and consumption units. Here by creating Au layered clusters on an α-MoC substrate, we have successfully constructed an interfacial catalyst system for the ultra-low temperature WGS reaction. Water is activated over α-MoC at 303 K, while CO adsorbed on adjacent Au sites is apt to react with surface hydroxyls formed from water splitting, leading to an unprecedented low-temperature WGS activity.

References

[1] S. Yao, X. Zhang, W. Zhou, R. Gao, W. Xu, Y. Ye, L. Li, X. Wen, P. Liu, B. Chen, E. Crumlin, J. Guo, Z. Zuo. W. li, J. Xie, L. Lu, C. Kiely, L. Gu, C. Shi, J. Rodriguez and D. Ma, *Science,* **2017**, 357, 389

[2] M. Xu, S. Yao, D. Rao, Y. Niu, N. Liu, M. Peng, P. Zhai, Y. Man, L. Zheng, B. Wang, B. Zhang, D. Ma, M. Wei, *J. Am. Chem. Soc***. 2018**, DOI: 10.1021/jacs.8b03117

New APXPS endstation at the SLS for the study of model catalysts

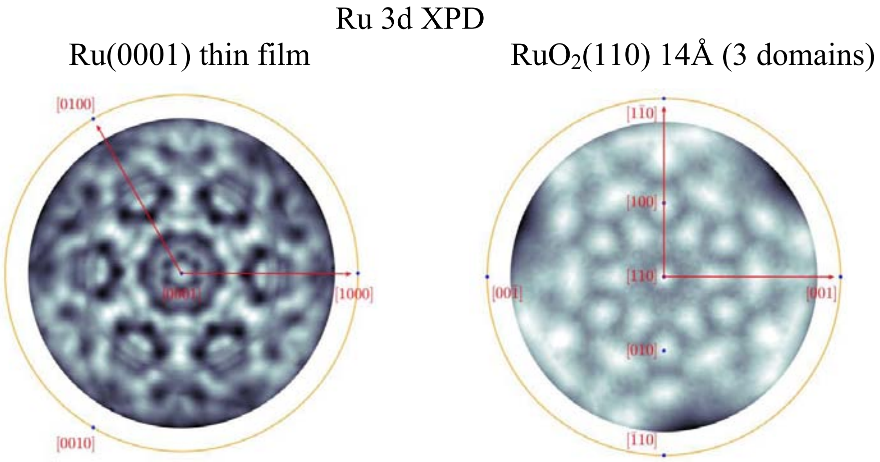
Zbynek Novotny[1,2], Benjamin Tobler[1], Jürg Osterwalder[1,*]

[1] *Department of Physics, University of Zurich, 8057 Zurich, Switzerland*
[2] *Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen, Switzerland*
...
* *osterwal@physik.uzh.ch*

Ambient pressure XPS offers great opportunities for the study of surface chemistry under reaction conditions. This applies both, for solid-gas and for solid-liquid interfaces. At the Swiss Light Source (SLS), a new endstation is currently being commissioned that combines such measurements with a facility for the preparation of model catalyst surfaces under UHV conditions.

The initiative is a next step in the current activities of our group in the study of model electrodes for pho-toelectrochemical cells for solar water splitting. We started out with UHV based studies of molecular catalysts immobilized on single-crystalline metal and oxide surfaces [1]. A chamber for wet chemical preparations and in situ transfer to the UHV chamber allows us to form self-assembled monolayers of larger molecules from solution [2].

The design of the new endstation combines a UHV preparation chamber with a UHV compatible analysis chamber for APXPS, connected via a transfer / load-lock chamber. In situ and operando studies at the solid-liquid interface will be carried out using the dip-and-pull method [3]. Single-crystal metal samples suitable for this technique are available in the form of ultrathin films grown on Si(111) wafers [4]. The figure demonstrates the formation of a highly ordered film of $RuO_2(110)$ prepared by oxidation of a Ru(0001) film.



Ru 3d XPD

Ru(0001) thin film

$RuO_2(110)$ 14Å (3 domains)

Figure: X-ray photoelectron diffraction data from a 150 nm thick, single crystalline Ru(0001) film before and after oxidation at 660K at 10^{-4} mbar oxygen pressure.

[1] D. Leuenberger et al., Nano Letters 17, 6620 (2017).
[2] W.-D. Zabka et al., J. Phys.: Condens. Matter 30, 424002 (2018).
[3] S. Axnanda et al., Sci. Rep. 5, 9788 (2015).
[4] M. Fischer et al., J. Appl. Phys. 104, 123531 (2008).

Towards Understanding the Fundamentals at the Electrochemical Interfaces

Yi Yu[1], Bryan Eichhorn[2], Hendrik Bluhm[3,4], Ethan Crumlin[4], Zhi Liu[1]

[1]*ShanghaiTech University, Shanghai, China*
[2]*Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, United States*
[3]*Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, United States*
[4]*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA, United States*
...

* *yuyi2@shanghaitech.edu.cn*

Understanding the electrochemical reactions at interfaces between different states of matter has been a long-term interest for both experimentalists and theorists in wide-range research areas of energy transfer and storage, heterogeneous catalysis, and electrochemistry. Revealing the fundamental chemistry at such interfaces is critical to the future designs of improved materials. In this talk, we will present a brief review on our in-situ and operando ambient pressure x-ray photoelectron spectroscopy investigations in several electrochemical interfaces, from the gas/solid interface of solid oxide electrochemical cells in redox reac-tions, to the liquid/solid interfaces of magnesium rechargeable batteries (non-aqueous) as well as the chemical composition profile on a cobalt metal electrode (aqueous). We will also introduce our newly commissioned beamline, Ambient Pressure Spectroscopy Beamline (APS), at Shanghai Synchrotron Ra-diation Facility. This bending magnet beamline covers an energy range of 40-2000 eV. The end-station allows measurements at pressures up to 20 mbar, and features a HIPP-3 analyzer equipped with spatial operation mode. This talk will also discuss our new lab-based APXPS system with a monochromatic Cr X-ray source for further in-depth investigations of the solid/liquid interfaces under operating conditions.

Oral contributions

A) Electrochemistry

Operando Ambient Pressure X-ray Photoelectron Spectroscopy Studies of Sodium-Oxygen Redox Reactions

Baohua Mao [a], Qingtian Li [a], Chenggong Jiang [a], Zhi Liu [ab]

[a] State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China,
[b] School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China
…

* *maobaohua@mail.sim.ac.cn*

Lower charge overpotential of sodium-oxygen (Na-O_2) batteries makes them a promising electrical storage technology. However, they have an undesirable discharge product, sodium carbonate (Na_2CO_3), which has widely been found in many previous studies. Whether and how the carbon components in the cathode are involved in the formation of Na_2CO_3 is still not well understood. Herein, an all solid-state Na-O_2 battery was constructed and its charge and discharge cycles were studied using ambient pressure X-ray photoelectron spectroscopy (APXPS). The operando XPS results clearly demonstrate the formation of Na_2CO_3 on the cathode during the discharge cycle. A fraction of the carbonate formed can be cycled while charging the battery. Transformation of the carbon-based cathode to Na_2CO_3 is a potential cause of capacity fading of the Na-O_2 battery. The potential loss over the discharge products is also directly observed using APXPS.

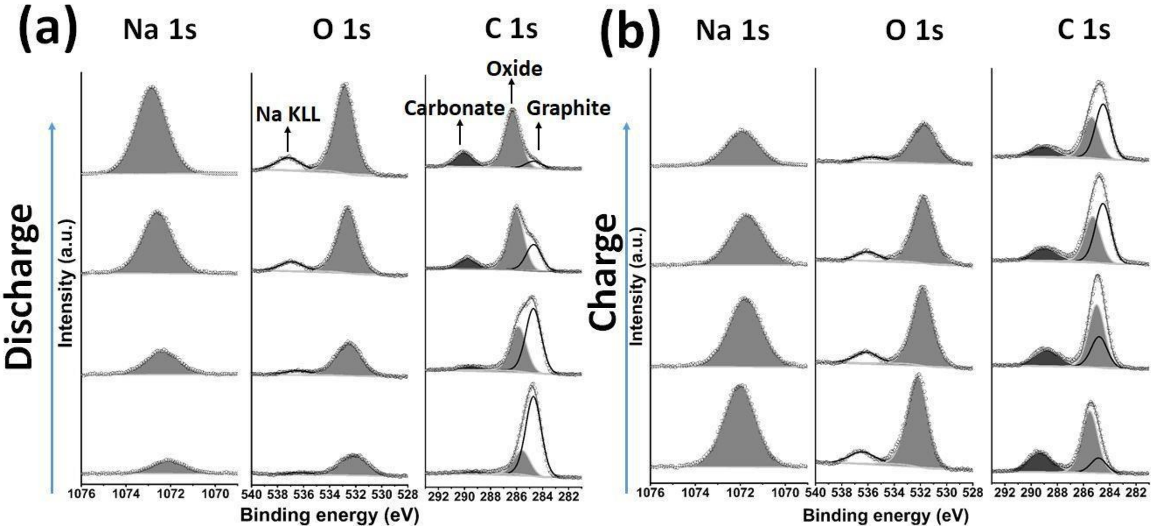


Fig. Operando APXPS results: the core-level spectra of Na 1s, O 1s, and C 1s on the cathode of Na-O_2 battery during (a) discharge and (b) charge

References

[1] Lu Y-C, Gallant BM, Kwabi DG, Harding JR, Mitchell RR, Whittingham MS, Shao-Horn Y (2013) Lithium– oxygen batteries: bridging mechanistic understanding and battery performance. Energy & Environmental Science 6 (3):750-768

[2] Kim J, Lim HD, Gwon H, Kang K (2013) Sodium-oxygen batteries with alkyl-carbonate and ether based electrolytes. Physical Chemistry Chemical Physics 15 (10):3623-3629

[3] Liu X, Yang W, Liu Z (2014) Recent Progress on Synchrotron-Based In-Situ Soft X-ray Spectroscopy for Energy Materials. Advanced Materials 26 (46):7710-7729

Electrochemical XPS Using Confined Electrolyte: Au and Pt Oxidation

Rik Mom*, Lorenz Frevel, Juan Velasco-Velez, Kasia Skorupska, Axel Knop-Gericke, Robert Schlögl

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

…

* *mom@fhi-berlin.mpg.de*

The need to understand the oxidation state of electrocatalysts under operating conditions has driven a rap-id development in electrochemical XPS methodology in recent years. Achieving the combination of proper electrode wetting, stability at high potential/reaction rate and good quality spectroscopy has proven challenging however. Here, we show that by sandwiching the electrocatalyst between a proton exchange membrane and a graphene layer, one can meet this challenge. As depicted in Figure 1, catalyst nanoparticles are deposited on a proton exchange membrane and subsequently covered with graphene. The electrolyte permeates from the backside through the membrane, providing a steady flow of water. The graphene layer on the other side greatly reduces the evaporation rate of the electrolyte into the vacuum chamber. We show that this can lead to the formation of a(n ultra)thin layer of liquid electrolyte between the graphene and the membrane. In addition, the graphene layer provides electrical contact to the catalyst nano-particles, enabling the study of isolated nanoparticles. Thus, electrocatalysts can be studied in an aqueous environment using XPS and NEXAFS, while maintaining accurate potential control.

Our studies on the potential-driven formation of platinum and gold oxides in 0.1 M H2SO4 show clear differences in the behavior of the two elements. While gold forms only Au^{3+} over the entire potential range up to 2.15 VRHE, Pt oxidation proceeds via a mixed surface oxide (Figure 1, right) to Pt^{4+}. Addition-al detail is obtained through O K-edge spectra, which allow for high time-resolution and identify (de)protonation and oxidation processes in the O anion network. Time-resolved measurements on Pt show that the oxidation process is fast: even bulk oxide growth occurs on the sub-minute timescale. This suggests that PtO2 may take part in the transient dissolution processes that dominate Pt electrode degradation. For Au, a transformation in the anion network under oxygen evolution reaction conditions is identified.

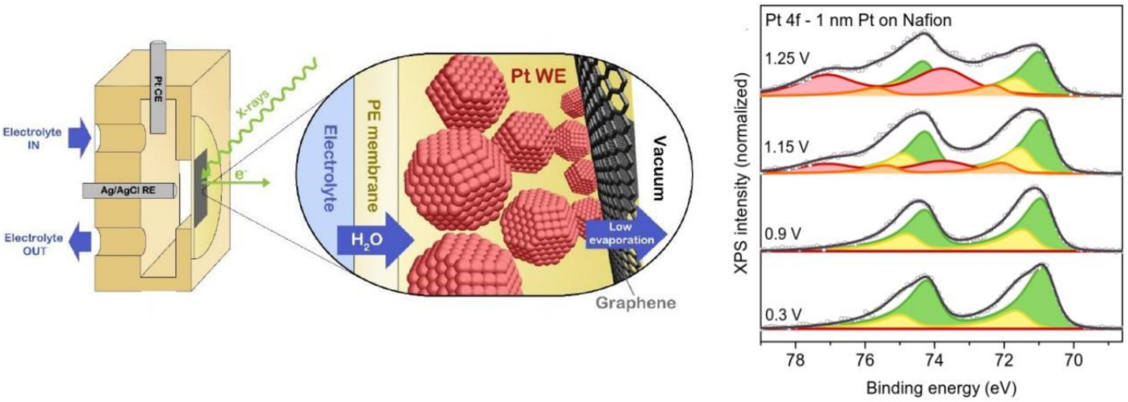


Figure 1: Schematic representation of the electrochemical cell (left) and Pt 4f spectra obtained by step-wise increase of the electrode potential vs. RHE (right).

High temperature oxygen exchange of mixed conducting perovskite oxides

David N. Mueller[1,*], T. Duchon[1], Y. Liu[2], Z. Guan[3], S. Baumann[2], H. Bluhm[4], S. Nemsak[4], W. C. Chueh[3], O. Guillon[2], C. M. Schneider[1]

[1] *Peter Gruenberg Institute 6, Forschungszentrum Juelich GmbH, Juelich, Germany*
[2] *Institute of Energy and Climate Research, Forschungszentrum Juelich GmbH, Juelich, Germany*
[3] *Department of Materials Science and Engineering, Stanford University, Stanford, CA, USA*
[4] *Advanced Light Source, Lawrence Berkeley National Laboratory,Berkeley, CA, USA*
...

* *dav.mueller@fz-juelich.de*

Mixed ionic electronic conducting oxides (MIEC) serve a plethora of high temperature applications such as oxygen separation membranes (OSM), cathodes for solid oxide electrochemical cells (SOEC) and oxy-gen storage catalysts. These applications rely to a large extent on the MIEC's ability to exchange oxygen with the surrounding atmosphere via redox reactions denominated the oxygen incorporation and evolution reactions, respectively. This facile exchange with a surrounding atmosphere leads to significant alterations of the defect chemistry and electronic structure both responsible for physical properties such as electronic and ionic conductivity, rendering the latter a function of temperature and *e.g.* oxygen partial pressure.

The family of perovskites of the general formula ABO_3 is a particularly interesting case, as utilization of elaborate substitution schemes of redox active 3d late transition metal cations such as Co and Fe on the B-site allow for a tailoring of physical properties to an application's need. In order to fully understand the effect of the B-site chemistry on the electronic structure at operating conditions, we employed in situ X-Ray absorption and photoelectron spectroscopy on the prototypical SOEC cathode and OSM materials $(La,Sr)(Ti,Co,Fe)O_{3-\delta}$ to elucidate how doping affects the evolution of the electronic structure with external thermodynamic stimuli. We found out that any evolving dynamics in the electronic structure centered around the oxygen derived electronic states, corroborating that the transition metals roles' in substitution strategies may be limited to providing a framework for the oxygen redox.

B) Interfaces

The hydrogen bonding structure of adsorbed water on ice nucleation active solid substrates

H.Yang[1,2], L.Artiglia[1], A.Boucly[1] and M.Ammann[1]

[1] Paul Scherrer Institut, Villigen, Switzerland
[2] ETH Zürich, Zürich, Switzerland
...

* *huanyu.yang@psi.ch*

The nucleation of ice is an important process in chemistry, physics and atmospheric science. Although ice nucleation has been studied since long, our understanding of ice nucleation is still far from complete, particularly from a molecular point of view. The hydrogen bonding structure of adsorbed water on a solid substrate may control deposition nucleation, which is a result of short and long range interactions between the substrate and the adsorbed water molecules.

As a first approach, we have measured electron yield NEXAFS spectra and XPS of adsorbed water on graphite and two mineral feldspar substrates under subsaturated conditions with respect to ice. Under isobaric conditions and by varying the temperature of the sample, we can change the relative humidity, which leads to varying amounts of adsorbed water in equilibrium between the substrate and water vapor. Preliminary results show that, under different relative humidity, the weakly and strongly coordinated OH bonds of adsorbed water on graphite and feldspars show different contributions to the Auger electron yield NEXAFS spectra, that is, the resonant transitions near the oxygen K-edge vary with relative humidity and temperature. We attribute this to the modification of the organization of water molecules in response to the interactions with the solid substrate. Moreover, chemistry composition of the sample is parallel addressed by XPS investigation. In view of the application of the NEXAFS technique, we believe it will open up a powerful tool to address the surface science of ice nucleation in the future.

Ambient Pressure XPS Investigation at the Solid/Liquid Interface of a Model System for Carbon Dioxide Capture

Marco Favaro[1,*], Ethan J. Crumlin[2], Roel van de Krol[1], David E. Starr[1]

1 Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institute for Solar Fuels
Hahn-Meitner-Platz 1, 14109 Berlin, Germany
2 Advanced Light Source, Lawrence Berkeley National Laboratory,
One Cyclotron Road, Berkeley, California 94720, USA
…

* *marco.favaro@helmholtz-berlin.de*

The optimization of CO_2 capture and reduction materials could be accelerated by the development of a molecular-level understanding of the adsorption and activation mechanisms. Using *in situ* ambient pressure hard X-ray photoelectron spectroscopy (AP-HAXPES) performed at 4 keV, we investigated the interfacial properties of an organic/inorganic hybrid system suitable for CO_2 capture.

Employing the "dip and pull" method combined with AP-HAXPES developed at the Advanced Light Source, we probed ~20 nm of aqueous electrolyte (in equilibrium with its vapor) in contact with an ~50 nm thick TiO_2 film functionalized with ~1 MLE of APTES (3-aminopropyl(triethoxysilane)). By systematically changing the pH of the electrolyte, we observe an increase in both the surface hydrophilicity, and stabilization of a thicker electrolyte layer at pH 14 compared to pH 7. We ascribe this to a deprotonation of surface hydroxyls which leaves negative charge on the TiO_2 surface at pH 14. Such a surface charge induces a change in the band bending in the TiO_2 as measured by shifts in the substrate and overlayer core level binding energies (Ti 2p, O 1s and Si 1s, N 1s). The findings obtained on such a model system show the possibility to tune the surface interfacial properties by properly adjusting solution properties. The knowledge gained in this investigation can be applied for the optimization of CO_2 capture systems in applied materials.

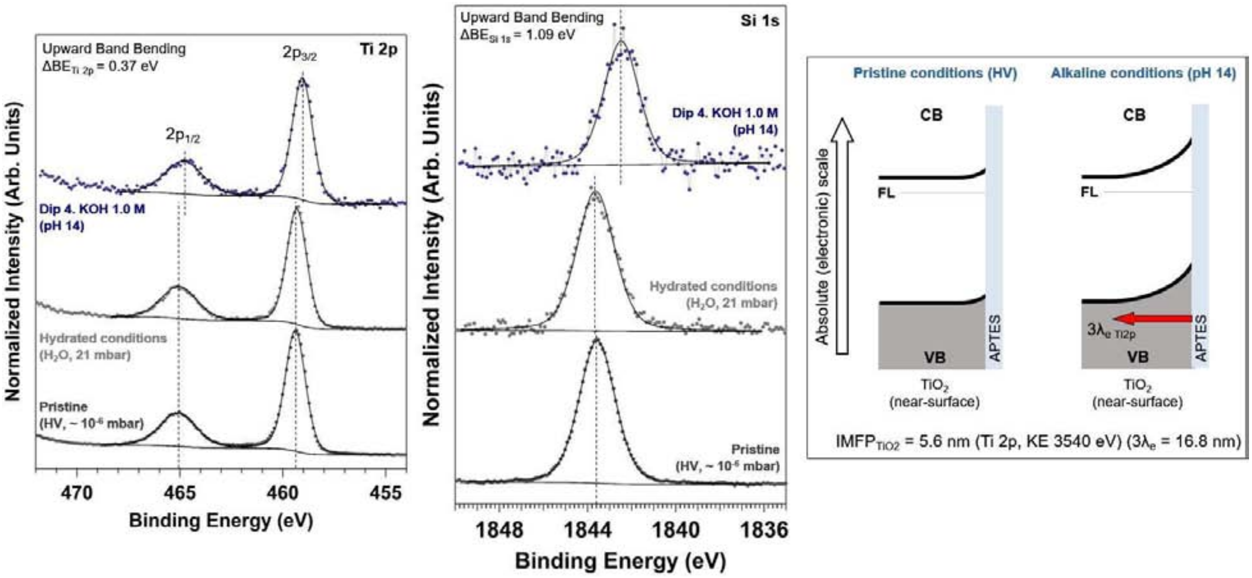


Figure 1. Band bending in APTES functionalized TiO_2 surface passing from pristine conditions to pH 14 in KOH aqueous solution (left, center: Ti 2p and Si 1s core levels. Right: schematization of the band bending).

Impact of Sr-Incorporation on Cr Oxidation and Water Dissociation in $La_{(1-x)}Sr_xCrO_3$

Kelsey A. Stoerzinger[1,2,*], Yingge Du[2], Kyuwook Ihm[3], Kelvin H.L. Zhang[4], Jun Cai[5,6], J. Trey Diulus[1], Ryan T. Frederick[1], Gregory S. Herman[1], Ethan J. Crumlin[6], Scott A. Chambers[1]

[1] School of Chemical, Biological and Environmental Engineering, Oregon State University, Corvallis, Oregon 97331, USA
[2] Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington 99352, USA
[3] Pohang Accelerator Laboratory, Pohang, Kyungbuk, Korea
[4] Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
[5] State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China
[6] Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
...

* *kelsey.stoerzinger@oregonstate.edu*

The oxidation and reduction of metal oxides and their interaction with the environment play a critical role in material stability and the ability to catalyze reactions. The local change in valence and formation of surface adsorbates affect the oxide electronic structure and chemical reactivity, yet are challenging to probe experimentally. Here we present a detailed study of the oxidation and reduction of Cr in the perovskite oxide family of $La_{(1-x)}Sr_xCrO_3$ using ambient pressure X-ray photoelectron spectroscopy.[1] The incorporation of Sr increases the propensity to oxidize at the surface, leading to the presence of Cr^{4+} and Cr^{6+} principally confined to the top unit cell when in equilibrium with O_2 gas. These acidic sites are readily reduced to Cr^{3+} in equilibrium with H_2O vapor, and the resultant amount of hydroxyls formed from the dissociation of H_2O is directly proportional to the density of surface sites which had been oxidized. Our quantification of the redox stability of $La_{(1-x)}Sr_xCrO_3$ and the relationship between the extent of oxidation, reduction, and hydroxylation with Sr yield important insight into the surface functionality during electrochemical applications.

[1] Stoerzinger, K.A. Du, Y. Ihm, K. Zhang, K.H.L. Cai, J. Diulus, J.T. Frederick, R.T. Herman, G.S. Crumlin, E.J. Chambers, S.A. “Impact of Sr-Incorporation on Cr Oxidation and Water Dissociation in $La_{(1-x)}Sr_xCrO_3$”. *Advanced Materials Interfaces* 5 (2018) 1701363.

Time-resolved APXPS characterization of catalysts under reaction conditions

Luca Artiglia[1,*], Kanak Roy[2], Olga Safonova[1], Jeroen A. van Bokhoven[1,2]

[1] *Paul Scherrer Institute, Forschungsstrasse 111, CH-5232 Villigen PSI, Switzerland*
[2] *ETH Zurich, Institute for Chemical and Bioengineering, Zurich, CH-8093, Switzerland*
...

* *luca.artiglia@psi.ch*

In-situ XPS and NEXAFS are efficient techniques to determine the local structure and chemical composition of heterogeneous catalysts. Despite this, the nature and role of the active species involved in catalytic reactions is still a matter of debate. This is due mainly to the low concentration of active sites, their short lifetime, and the requirement to distinguish them from inactive spectators. Operando time-resolved characterization tools are an important aid to acquiring snapshots of a catalytic reaction [1]. The time-resolved approach can be achieved under transient conditions, that is, modifying the gas or liquid feed concentration in an attempt to detect a modification of the population of active sites. Time-resolved XPS experiments performed on real catalysts are challenging due to the necessity of acquiring well-resolved spectra in milliseconds to seconds. Although ultrafast measurements were achieved on single crystals [2], measuring a working catalyst is still a challenge due to the low concentration of active sites, carbon contamination of the samples, and ambient pressure conditions. This presentation shows time-resolved measurements applied to catalysis obtained so far at the in-situ spectroscopy beamline at the Swiss light source synchrotron [3]. We investigated both planar samples (Pd foils) and powders (Pt nanoparticles supported on CeO2 and CeSnOx) as catalysts for the oxidation of CH4 and for the oxidation of CO, respectively. Photoemission spectra were acquired while switching from a gas mixture to another. By means of this approach, active sites involved in the reaction can be detected and the reaction meachanisms can be better understood.

[1] Weckhuysen, B. M. Chem. Commun. 2002, 97−110.
[2] Höfert, O. et al. Rev. Sci. Instrum. 2013, 84, 093103.
[3] Artiglia, L. et al. J. Phys. Chem. Lett. 2017, 8, 102-108.

Propensity of Ions for the Liquid/Vapour Interface Observed by APXPS

R.K. Lam,[1] J.W. Smith,[1] A.M. Rizzuto,[1] O. Karslıoğlu,[2,3] R.J. Saykally,[1,2] H. Bluhm[2,3,4]

[1] *Department of Chemistry, University of California at Berkeley CA, USA*
[2] *Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley CA, USA*
[3] *Fritz Haber Institute of the Max Planck Society, Berlin, Germany*
[4] *Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley CA, USA*
...

* *bluhm@fhi-berlin.mpg.de*

The fractionation of ions at liquid interfaces and its effects on the interfacial structure are of vital importance in many scientific fields. [1] Of particular interest is the aqueous carbonate system, which governs both the terrestrial carbon cycle and physiological respiration systems. We have investigated the relative fractionation of carbonate, bicarbonate, and carbonic acid at the liquid/vapor interface finding that both carbonate (CO_3^{2-}) and carbonic acid (H_2CO_3) are present in higher concentrations than bicarbonate (HCO_3^-) in the interfacial region. [2] While the interfacial enhancement of a neutral acid relative to a charged ion is expected, the enhancement of doubly charged, strongly hydrated carbonate anion over the singly charged, less strongly hydrated bicarbonate ion is surprising. As vibrational sum frequency generation experiments have concluded that both carbonate and bicarbonate anions are largely excluded from the air/water interface, the present results suggest that there exists a significant accumulation of carbonate below the depletion region outside of the area probed by sum frequency generation.

[1] O. Björneholm, M.H. Hansen, A. Hodgson, L. Limin, D.T. Limmer, A. Michaelides, Ph. Pedevilla, J. Rossmeisl, H. Shen, G. Tocci, E. Tyrode, M.-M. Walz, J. Werner, H. Bluhm, Chem. Rev. **116**, 7698 (2016).

[2] R.K. Lam, J.W. Smith, A.M. Rizzuto, O. Karslıog, H. Bluhm, R.J. Saykally, *J. Chem. Phys*. **146**, 094703 (2017).

Combined NAP XPS and NAP Core hole clock studies of polymer/TiO_2 hybrids for artificial photosynthesis

Alba García-Sánchez, Patricia Reñones, Elena Alfonso-González, Mariam Barawi, Raúl Pérez-Ruiz, Fernando Fresno, Marta Liras, Víctor A. de la Peña O´Shea and Ignacio J. Villar-Garcia*

Photoactivated Processes Unit IMDEA Energy Institute, Technological Park of Móstoles, Av. Ramón de la Sagra 3, 28935 Móstoles, Madrid, Spain

...

* *Ignacio.villar@imdea.org*

In this contribution, we will be introducing a combination of NAP XPS and NAP core hole clock experiments used to study the surface composition and related electron delocalisation times in a set of hybrid materials (semiconducting polymer+TiO_2) at CO_2 photocatalytic reaction conditions, *i.e.* under CO_2 and H_2O atmospheres (0.5mbar) and illumination (365 UV light). Initial data was acquired during commissioning time at the VERSOX beamline (Diamond, UK) and used to calculate electron delocalisation times from the area ratio of the characteristic signals of the spectator and non-resonant Auger channels in the S KLL Auger signal at resonant conditions (Figure 1) and using the life time of the core hole (1.3 fs)[3] as a reference (or internal clock). The calculated electron delocalisation times at UHV conditions were 2.3 fs and explain the low electron hole recombination rates observed for these polymers by TAS. Remarkably, electron delocalisation times changed when exposing the polymer to reaction conditions, *i.e.* dosing gases (H_2O and CO_2) and under illumination (365 nm LED). Moreover, the study of the NAP XPS data at the same conditions reveals the absorption and desorption of different species at the surface (H_2O and organic molecules such as CO or $HCOO^-$). To the best of our knowledge, this is the first study using the CHC method at near ambient conditions (NAP CHC) and in combination with NAP XPS shows a great potential to study both surface reactivity and charge transfer in photoactive materials at reaction conditions. The presentation will also include the results from the upcoming October run at VERSOX to study a set of hybrid materials.

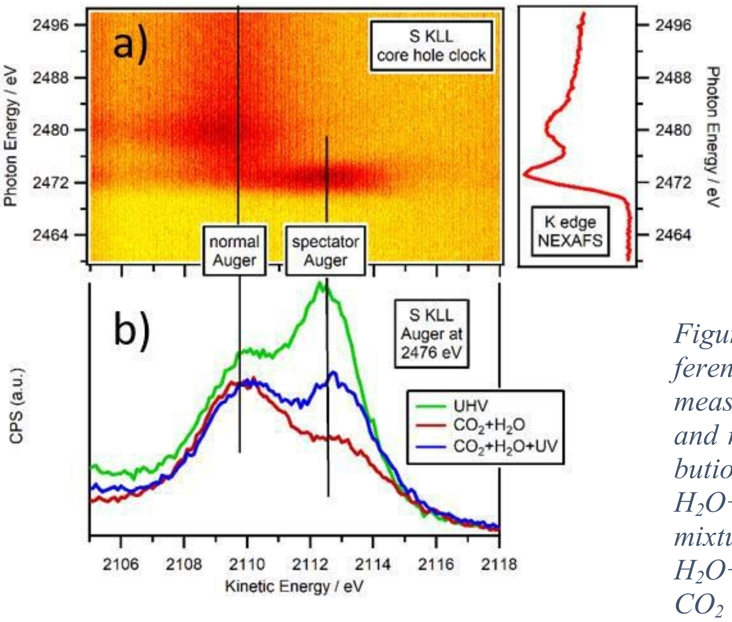


Figure 1 a) Counter plot of the S KLL at different photon energies. b) S KLL Auger measured at 2476 eV showing the spectator and normal (or non-resonant) Auger contributions for UHV (ultra-high vacuum), H_2O+CO_2 (under 0.5 mbar H_2O and CO_2 mixture (0.062 mbar H_2O) and H_2O+CO_2+UV under 0.5 mbar H_2O and CO_2 mixture (0.062 mbar H_2O) and illuminating with a LED source with 365 nm energy).

C) Catalysis

CO oxidation on the model Pd-Au/HOPG catalysts: NAP XPS and MS study

A.V. Bukhtiyarov[1], I.P. Prosvirin[1], M. Mamatkulov[1], I.V. Yudanov[1,2], A.Yu. Klyushin[3], A. Knop-Gericke[3], K.M. Neyman[4,5], V.I. Bukhtiyarov[1,*]

[1] *Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*
[2] *Institute of Chemistry and Chemical Technology SB RAS, Federal Research Center "Krasnoyarsk Scientific Center SB RAS", Krasnoyarsk, Russia*
[3] *Fritz-Haber-Institute der Max Planck Society, Berlin, Germany*
[4] *Departament de Ciència de Materials i Química Física and Institut de Quimica Teòrica i Computacional, Universitat de Barcelona, Barcelona, Spain*
[5] *ICREA (Institució Catalana de Recerca i Estudis Avançats), Barcelona, Spain*

...

* *vib@catalysis.ru*

Bimetallic systems attract the great interest of many scientific groups due to its ability to improve significantly catalytic properties in comparison with monometallic catalysts [1-2]. Good example proving this statement is the bimetallic Pd-Au catalysts, which exhibit extremely high activity in a number of industrially important reactions. This motivated researchers on numerous investigations of Pd-Au systems, which have shown that not only the ratio of the introduced metals, but also temperature of calcination will affect the surface composition causing the essential difference between Au/Pd atomic ratios in the bulk and surface [1-2]. Furthermore, surface composition can be varied under the influence of reaction mixture due to enrichment of the surface with one of the metals. It is evident that to clarify the influence of the above-mentioned effects on catalytic properties, the detailed *in situ* study of surface structure and composition of bimetallic Pd-Au catalysts is necessary to understand the nature of active sites and help to optimize the catalyst composition for the best activity, selectivity and stability.

Preparation of the model bimetallic Pd-Au/HOPG (highly oriented pyrolitic graphite) catalysts has been investigated with XPS and STM [3]. Initially, model "core–shell" type Pd–Au/HOPG catalysts with similar particle size distribution (5–8 nm) were prepared. Subsequent annealing of these samples in temperature range of 300–400°C leads to formation of Pd–Au alloyed particles.

Treatment of the alloyed Pd–Au/HOPG model catalysts under CO oxidation conditions destroys the alloy structure due to segregation of Pd over Pd–Au particle surface via formation of Pd-CO_{ads} bonds. Heating the samples restores the alloy structure due to CO desorption even under the reaction conditions. All these changes in the particle structure were identified using NAP XPS technique.

Density functional calculations combined with calculations using topological energy expression method (TOP method) were applied to reveal the mechanism of this phenomenon and to quantify the stability of different arrangements of metal atoms in bimetallic PdAu nanoparticles in the presence of CO adsorbate. According to results of this computational approach, adsorption of CO already at a rather moderate coverage is sufficient to make energetically feasible segregation of Pd at terraces of PdAu nanoparticles similar in size with experimentally studied ones.

Acknowledgements

The authors would like to thank Russian Science Foundation (Grant No. 14-23-00146) for the financial support of this work.

References

[1] C.W. Yi, K. Luo, T. Wei, D.W. Goodman, *J. Phys. Chem. B.,* 109, 18535 (2005)
[2] A. Wang, X.Y. Liu, C.-Y. Mou, T. Zhang, *J. Catal.,* 308, 258 (2013)
[3] A.V. Bukhtiyarov, I.P. Prosvirin, V.I. Bukhtiyarov, *Appl. Surf. Sci.,* 367, 214 (2016)

A NAP-XPS study of Methane Oxidation over supported Pd catalysts

Alexander Large[1], Rachel Price[1], Roger Bennett[1], Tugce Eralp-Erden[2], Agnes Raj[2], Sonia Garcia[2], Pilar Ferrer-Escorihuela[3], Federica Venturini[3], David Grinter[3], Rosa Arrigo[3], Georg Held[1,3*]

[1] Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK
[2] Johnson Matthey Technology Centre, Blounts Court Road, Sonning Common, Reading RG4 9NH, UK
[3] Diamond Light Source, Harwell Science & Innovation Campus, Didcot OX11 0DE, UK
...

* *g.held@reading.ac.uk*

Near ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS) was used to study the oxidation states of methane oxidation catalysts in-situ. Al2O3 and SiO2-supported Pd catalysts [1,2] were prepared with different particle sizes ranging from 4 to 10 nm. These catalysts were exposed to conditions similar to those used in the partial and complete oxidation of methane and simultaneously monitored by NAP-XPS and mass spectrometry. NAP-XPS data show changes in the oxidation state of the palladium as the temperature increases, from metallic Pd^0 to PdOx, and back to Pd^0. Mass spectrometry shows an increase in CO production (partial oxidation), whilst the Pd is in the oxide phase, and a switch to CO2 production (complete oxidation), when the metal is reduced again at higher temperature. A particle size effect is observed, such that CH4 conversion starts at lower temperatures with larger sized particles from 6 to 10 nm on both supports. The data show that the behavior is different from that of Pd foil in the same gas environment.

The second part of the talk will address the problem of charging of supported catalysts and ways how charging can be reduced in the experiment and/or accounted for in data fitting.

[1] Rachel Price, Tugce Eralp-Erden, Ethan Crumlin, Sana Rani, Sonia Garcia, Richard Smith Liam Deacon, Chanan Euaruksakul, Georg Held, Topics in Catalysis 59 (2016) 516 – 525
[2] Rachel Price, Tugce Eralp-Erden, Ethan Crumlin, Sonia Garcia, Agnes Raj, Georg Held, submitted

In situ AP-XPS and XANES of Co-Based Catalysts during Ethanol Steam Reforming

Carlos Escudero[1,*], Cristián Huck-Iriart[1,2], Lluís Soler[3], Albert Casanovas[3], Carlo Marini[1], Jordi Prat[1], Jordi Llorca[3]

[1] *ALBA Synchrotron Light Source, Carrer de la Llum 2–26, 08290 Cerdanyola del Vallès, Barcelona (Spain)*
[2] *Escuela de Ciencia y Tecnología, Universidad Nacional de San Martín (UNSAM), Campus Miguelete, 25 de Mayo y Francia, 1650 San Martín, Provincia de Buenos Aires (Argentina)*
[3] *Institute of Energy Technologies, Department of Chemical Engineering and Barcelona Research Center in Multiscale Science and Engineering, Universitat Politècnica de Catalunya, EEBE, Eduard Maristany 10-14, 08019 Barcelona, (Spain)*
...

* *cescudero@cells.es*

The Ethanol Steam Reforming (ESR) reaction is a well-known process used for hydrogen generation and especially interesting for the on-site production of this gas. Three different Co-based catalysts have been studied for the ESR reaction using *in situ* Near Ambient Pressure XPS (NAP-XPS) and X-ray Absorption Near Edge Structure (XANES) at the ALBA Synchrotron Light Source. The Co-based catalysts studied are Co_3O_4 (Co-spinel), $Co_3[Si_2O_5]_2(OH)_2$ (Co-talc) and $[Co_2Mg_4Al_2(OH)_{16}]CO_3{\cdot}4H_2O$ (Co-hydrotalcite or Co-HT). The use of Cobalt-based catalysts allows decreasing the reaction temperature since there is no methane generation in the intermediate reaction steps as opposed to other catalysts that do produce this gas, which can only be reformed at high temperature. Furthermore, the possibility to operate at lower temperatures shifts the water-gas shift reaction balance towards the formation of hydrogen. However, Co-based catalysts can be deactivated under ESR reaction conditions due to carbon deposition and this fact has been attributed to the formation of metallic Co [1]. Our recently published results [2] show that when using Co-spinel and Co-talc for ESR metallic Co is detected while for Co-HT, which exhibits an excellence performance for ESR, there is no formation of metallic Co. This interesting result allows designing cobalt-based catalysts for ESR without coke deposition by placing in appropriate environments $Co^{\delta+}$ active species.

[1] R. Espinal, E. Taboada, E. Molins, R.J. Chimentao, F. Medina, J. Llorca. *Cobalt hydrotalcite for the steam reforming of ethanol with scarce carbon production*, RSC Adv. 2 (2012), 2946–2956.
[2] C. Huck-Iriart, L. Soler, A. Casanovas, C. Marini, J. Prat, J. Llorca, Carlos Escudero, *Unraveling the chemical state of Cobalt in Co-based catalysts during Ethanol Steam Reforming: an in situ study by Near Ambient Pressure XPS and XANES*, ACS Catalysis 8 (2018), 9625−9636

Performance of co-precipitated $NiAlO_x$ catalysts during CO_2 methanation

Tim Kratky[1*], Moritz Wolf[1], Barbara A. J. Lechner[1], Thomas Burger[1], Federica Venturini[2], Georg Held[2,3], Olaf Hinrichsen[1], Sebastian Günther[1]

[1] *Department of Chemistry & Catalysis Research Center, Technical University of Munich, Lichtenbergstr. 4, 85748 Garching, Germany*
[2] *Diamond Light Source, Harwell Science & Innovation Campus, Didcot OX11 0DE, UK*
[3] *Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK*
...

* *tim.kratky@tum.de*

Low-cost pathways to CO_2 activation promise sustainable and green alternatives to current energy carrier formation. Ni-Al catalysts have long been used in methanation reactions, including more recently the methanation of CO_2. We found that Fe or Mn promoters improve the activity of a mixed $NiAlO_x$ oxide towards this reaction. In a recent near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) study at the Diamond Light Source synchrotron facility, we followed the chemical status during activation of a co-precipitated $NiAlO_x$ catalyst. Using the radiation delivered from the bending magnet line B07 (VerSoX), the evolution of the Ni 2p, Ni LMM, Al 2p, O 1s and C 1s signals was monitored. The reduction of the catalyst during activation in hydrogen at 723 K is evidenced by formation of Ni^0 while the Al 2p peak remains unaffected. Interestingly, impregnated Ni/AlO_x catalysts are reduced to a similar extent after activation under the same conditions but lead to a significantly lower activity. These findings indicate the importance of the structural differences of the decomposed mixed $NiAlO_x$ catalyst with respect to the ones of the impregnated Ni on a well separated AlO_x support. Difficulties occurring during *in situ* catalyst characterization of the activation process are discussed. Finally, CO_2 methanation of the activated catalyst in a 5 mbar reactive atmosphere (CO_2+H_2, 1:4) was monitored *in situ* by differentially pumped QMS in addition to NAP-XPS.

Hydrogenation of CO_2 on NiGa polycrystalline thin films

Pei-Shun Lin[1], Chia-Hsin Wang[2], Sun-Tang Chang[2], Yaw-Wen Yang[*,1,2]

[1] *Department of Chemistry, National Tsing-Hua University, Hsinchu, Taiwan 30013*
[2] *National Synchrotron Radiation Research Center, Hsinchu, Taiwan 30076*
...

* *yang@nsrrc.org.tw*

A successful catalytic conversion of carbon dioxide into high-value chemicals as a means of abating the global CO_2 emission has been a pressing challenge. A complete mechanistic understanding of hydrogenation of CO_2 holds the key toward an effective utilization of chemical reduction of CO_2. Herein, we report on an APXPS study of CO_2 hydrogenation reaction on bimetallic nickel-gallium thin films, with research objective aimed at identifying surface reaction intermediates and possibly altering chemical reactivity by varying the atomic ratio of alloy. The measurements were carried out in a newly constructed endstation located at a soft X-ray bending magnet beamline (BL24A) in Taiwan Light Source. Four types of NiGa films of different atomic ratios, Ni, Ni_3Ga, Ni_5Ga_3 and $NiGa_2$, were prepared via vacuum deposition in a UHV preparation chamber, and CO_2/H_2 gaseous mixtures up to 1 mbar were in use. Our results show that all four types of NiGa alloy films are quite reactive and capable of producing carbon-containing species such as $CO_2^{\delta-}$, CO, HCOO, CO_3, and HCO_3 at 300 K already. The addition of Ga into the alloy films alters the reaction pathway, producing more $CO_2^{\delta-}$ and HCOO for the films of increasing Ga content. Interestingly, for the highest Ga content film, $NiGa_2$, the oxidation of both Ni and Ga is simultaneously inhibited even after 600 K reaction, suggesting that a strong electronic structure modification of alloy films indeed occurs.

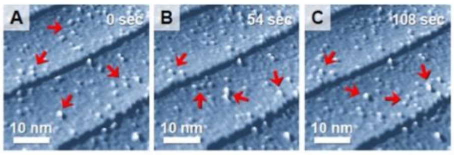
Investigation of interfacial Pt-NiO_{1-x} nanostructures on $Pt_3Ni(111)$ surface under CO oxidation

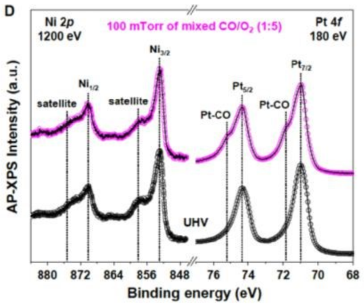
Jeongjin Kim[1,2], Woong Hyeon Park[1], Myung Cheol Noh[1,2], Si Woo Lee[1,2], Won Hui Doh[2], Jean-Jacques Gallet[3], Fabrice Bournel[3], Kondoh Hiroshi[4], Kazuhiko Mase[5], Yousung Jung[1], Jeong Young Park[1,2*], Bongjin Simon Mun[6,7*]

[1] *Graduate School of Energy, Environment, Water and Sustainability (EEWS), Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea.*
[2] *Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Daejeon 34141, Republic of Korea.*
[3] *Laboratoire de Chimie Physique-Matière et Rayonnement, Sorbonne Universités – Université Pierre et Marie Curie Paris 06 – CNRS, France.*
[4] *Department of Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-Ku, Yokohama 223-8522, Japan.*
[5] *Institute of Materials Structure Science, High Energy Accelerator Research Organization, SOKEN-DAI (The Graduate University for Advanced Studies), 1-1 Oho, Tsukuba 305-0801, Japan.*
[6] *Department of Physics and Photon Science, School of Physics and Chemistry, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, Republic of Korea.*
[7] *Center for Advanced X-ray Science, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, Republic of Korea.*
…

* *bsmun@gist.ac.kr*

With the combination of ambient pressure STM and ambient XPS, the presence of catalytically active interfacial Pt-NiO_{1-x} nanostructures are investigated. Under UHV condition, the surface forms Pt-skin layer. Then, as the oxygen pressure is introduced, NiO_{1-x} clusters forms on surface as Ni atoms segregate to the surface. During CO oxidation, the coexistence of NiO_{1-x} clusters on the Pt skin is observed. DFT calculation of $Pt_3Ni(111)$ also support that a CO molecule adsorbed on Pt-NiO_{1-x} nanostructures has a lower surface energy barrier than Pt surface.





References

[1] J. Kim et al., *Science Advances*, **4**,7 (2018)
[2] H. C. Lee *et al.*, *Catal. Today* **260**, 3 (2016)

D) Materials

Evolution of the Oxide Layer on Ni-Cr as a Function of Alloy Composition

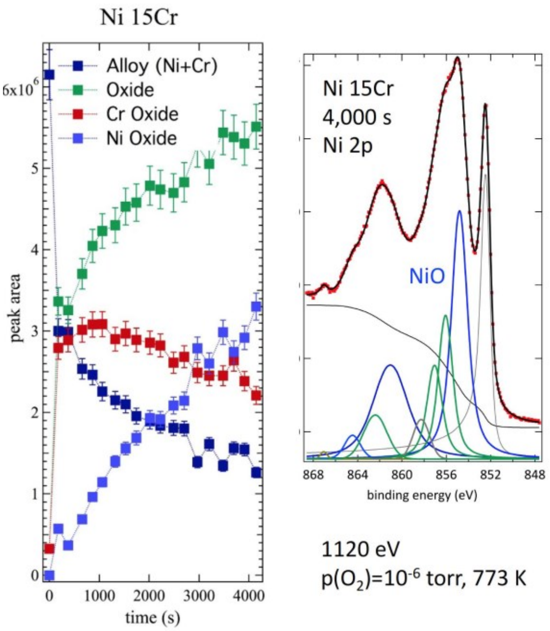
Cameron Volders,[1] Valentina Angelici Avincola[1], Evan Zeitchick[3], John Perepezko[3], Iradwikanari Waluyo[2], Adrian Hunt[2], Petra Reinke[1*]

[1] University of Virginia, Department of Materials Science and Engineering, 395 McCormick Rd., Char-lottesville, VA 22904, U.S.A.
[2] National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973
[3] University of Wisconsin-Madison, Department of Materials Science and Engineering, 1509 University Avenue, Madison, WI 53706
...

* *pr6e@virginia.edu*

Ni-based superalloys are highly coveted and their superb corrosion resistance is combined with excellent mechanical properties. The oxidation process is characterized by the competition between the formation of chromia, and the rapid nucleation and growth of NiO. We target in our work a temperature regime of where the competition between chemically distinct oxides (NiO, Cr_2O_3, $NiCr_2O_4$, non-stoichiometric) offers critical information to develop our understanding of NiCr alloy oxidation.

We observed the oxidation of Ni 5wt%Cr, Ni 15wt%Cr and Ni 30wt%Cr for p=0.1 mbar/ 10^{-6} mbar and followed the evolution of the oxide layer and alloy compositions at 773 K at NSLS II, beamline IOS/23-ID-2. The native oxide was removed by annealing to 1073 K leading to a slightly Cr-enriched surface. The rapid formation of an ultrathin Cr-oxide layer, whose thickness scales with the Cr-concentration in the alloy completely depletes the alloy surface layer of Cr, and is followed by rapid growth of Ni-oxide in an island growth mode. The most rapid growth is seen for Ni 15wt% and can be attributed to the Cr^{3+}-Vacancy complex which promote Ni-transport in the oxide (see Figure). Cr-oxide is retained at the alloy-oxide inter-face. NiO contribution to Ni-oxide component increases with time and saturates at 50% for all alloys; the remaining oxides are likely spinel, and a non-stoichiometric, highly defective oxide. The Cr2p peak likewise supports the formation of chromia and confirms the presence of a considerable amount of non-stoichiometric oxide. We will discuss the growth kinetics and modes in the context of oxide and alloy chemistry, and contrast them with NiCr alloys with minor alloying elements Mo and W.



The complexity of the Ni2p and Cr2p multiplet splitting poses a significant challenge in the interpretation of the oxide contributions and we present an analysis scheme, which progressively develops information from alloy-ox-ide signal contributions and growth kinetics to the fit of individual core levels. The fit process combines finger-printing with information from the pure oxides and a statistical analysis of the fit quality using correlation analysis of the residuals. We will discuss the feasibility of this approach for the study of complex oxide layers.

Self-cleaning and surface chemical reactions during HfO_2 atomic layer deposition on InAs revealed by AP-XPS

Andrea Troian[1], Giulio D'Acunto[1], Foqia Rehman[1], Sofie Yngman[1], Sarah McKibbin[1],
Samuli Urpelainen[2], Esko Kokkonen[2], Anders Mikkelsen[1], Joachim Schnadt[1], and Rainer Timm[1]

[1] *Synchrotron Radiation Research, Department of Physics, and NanoLund, Lund University, Sweden*
[2] *Max IV Laboratory, Lund University, Sweden*
…
* *Rainer.Timm@sljus.lu.se*

Atomic layer deposition (ALD) enables ultrathin high-quality oxide layers that are central to all modern metal-oxide-semiconductor circuits. However, the quality of the semiconductor-oxide interface is still limiting the performance especially of III-V semiconductor-based (opto)electronic devices due to a high defect density and remaining native oxide. X-ray photoemission spectroscopy studies performed at ultra-high vacuum revealed that the chemical reactions during the first ALD cycle are crucial for a successful self-cleaning effect, but the details and dynamics of these reactions are still partially unknown.

Here we present ambient pressure XPS (AP-XPS) studies of the ALD of HfO2 on InAs, using tetrakis-(dimethylamino)-Hafnium (TDMA-Hf) and water precursors: By performing subsequent half-cycle steps of the ALD process within the reaction cell of an AP-XPS system, we were able to monitor this techno-logically relevant ALD reaction and thus obtain fully in-situ and real-time XPS measurements of the high-k deposition on III-V semiconductors. From correlating time-resolved As 3d, In 3d, In 4d, and Hf 4f core-level spectra (Figure 1), we could reveal the temporal evolution of complete As-oxide and almost complete In -oxide removal, Fermi level unpinning, and formation of HfO_2. Furthermore, we observed an unexpected and previously unknown two-step reaction mechanism including molecular adsorption of the Hf-precursor, demonstrating that the previously widely accepted ligand exchange model has to be revised. These results have strong potential for improving interface quality and performance of III-V semiconductor-oxide based devices.

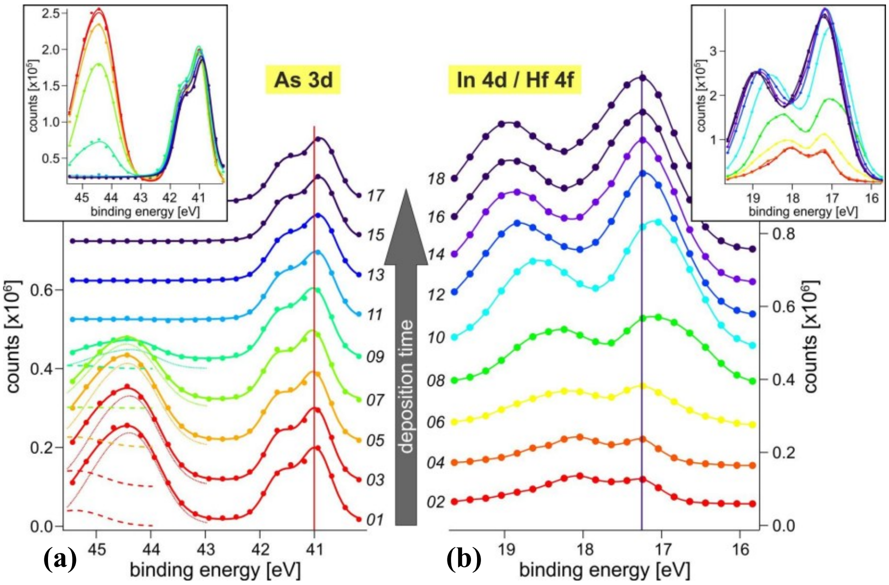


Figure 1:
Alternating (a) As 3d and (b) In 4d / Hf 4f core-level spectra acquired during the initial deposition of TDMA-Hf. The insets show the same spectra without being shifted along the y-axis. Red (a) and blue (b) lines indicate the binding energy position of (a) As-In bulk prior to the reaction and (b) Hf-Oxide after the reaction. From Ref [1].

[1] R. Timm et al., Nature Commun. **9**, 1412 (2018).

In Situ Surface Characterization of Pt-Cu Single-Atom Alloy Model System in Ambient Pressure of Gases

J. P. Simonovis[1], A. Hunt[1], R. M. Palomino[2], S. D. Senanayake[2], I. Waluyo[*1]

[1] National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973
[2] Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973
…

* *iwaluyo@bnl.gov*

In heterogeneous catalysis, the interaction between reactant molecules and the surface of the catalyst often causes changes in the surface composition and chemical state of the catalyst, which, in turn, may affect its chemical properties and reactivity. Therefore, it is important to systematically characterize such interactions using well-controlled model systems with *in situ* techniques such as ambient pressure XPS. Pt-Cu single-atom alloys, in which Pt forms highly dispersed, isolated atoms, have recently gained increased interest as an active hydrogenation catalyst that is tolerant to CO poisoning. In this talk, I will present recent AP-XPS results from the 23-ID-2 beamline at the National Synchrotron Light Source II in which we studied the interaction of common reactants (CO, H_2) with the Pt/Cu(111) single-atom alloy model system. By probing the Pt 4f core level, we were able to clearly distinguish Pt atoms in different chemical and physical environments as well as monitor their evolution in various experimental conditions. Ambient pressure of CO stabilizes surface Pt atoms at high temperatures and can draw out Pt that has diffused into the bulk back to the surface. However, restructuring of the subsurface layer due to heating causes changes in the Pt-CO interaction that has important implications in the catalyst's ability to activate H_2.

E) Instrumentation

In situ X-ray photoelectron spectroscopy by using an environmental cell and Al Kα source

Takuya Masuda[1,2], Raimu Endo[1,2]

[1] *National Institute for Materials Science, Japan*
[2] *Hokkaido University, Japan*
...

* *MASUDA.Takuya@nims.go.jp*

Utilization of environmental cells for in situ XPS measurements of solid/liquid interfaces has been much attention.[1-5] We previously constructed an in situ electrochemical XPS apparatus for electrochemical processes at solid/liquid interfaces under potential control using hard x-rays from synchrotron light sources and an environmental cell equipped with a 15 nm-thick silicon membrane as a X-ray/photoelectron window, and observed electrochemical growth of Si oxide in contact with water.[2] Because conventional XPS utilizing an Al Kα source is too surface sensitive to detect the photoelectrons generated at the Si membrane/water interface through the 15 nm-thick membrane, we utilized hard x-rays to effectively detect those photoelectrons. Here, we present our recent progress on the development of a lab-based in situ XPS apparatus which is equipped with an Al Kα source. By using a newly developed x-ray/photoelectron window, solution species encapsulated within the environmental cell are successfully observed.

References

[1] Kolmakov, A.; Dikin, D. A.; Cote, L. J.; Huang, J. X.; Abyaneh, M. K.; Amati, M.; Gregoratti, L.; Gunther, S.; Kiskinova, M. *Nat. Nanotechnol.* **2011**, *6*, 651.

[2] Masuda, T.; Yoshikawa, H.; Noguchi, H.; Kawasaki, T.; Kobata, M.; Kobayashi, K.; Uosaki, K. *Appl. Phys. Lett.* **2013**, *103*, 111605.

[3] Kraus, J.; Reichelt, R.; Gunther, S.; Gregoratti, L.; Amati, M.; Kiskinova, M.; Yulaev, A.; Vlassiouk, I.; Kolmakov, A. *Nanoscale* **2014**, *6*, 14394.

[4] Velasco-Velez, J. J.; Pfeifer, V.; Havecker, M.; Weatherup, R. S.; Arrigo, R.; Chuang, C. H.; Stotz, E.; Weinberg, G.; Salmeron, M.; Schlogl, R.; Knop-Gericke, A. *Angew. Chem., Int. Ed.* **2015**, *54*, 14554.

[5] Nemsak, S.; Strelcov, E.; Duchon, T.; Guo, H. X.; Hackl, J.; Yulaev, A.; Vlassiouk, I.; Mueller, D. N.; Schneider, C. M.; Kolmakov, A. *J. Am. Chem. Soc.* **2017**, *139*, 18138.

Mn, Cr-spinel Oxide's Formation from APXPS' Perspectives

Akbar bin Kaderi[1,2]

[1] Previously at ZEA-3, Forschungszentrum Jülich, 52428 Jülich, Germany.
[2] Graduate Student of the Faculty of Georesources and Materials Engineering, RWTH Aachen, 52056 Aachen, Germany
...

* *akb.kaderi@gmail.com*

Spinel oxide is a very interesting compound. The general formula for spinel oxides is AB_2O_4. The compound has interesting physical properties including electronic and magnetic as well as chemical properties including oxidation and catalysis. The unique properties of spinel oxide have found its use in many technological energy applications such as in solar cell, fuel cell and batteries. In this abstract, interests and works on Mn,Cr-spinel oxides are presented. Mn,Cr-spinel oxides has been known to prevent Cr_2O_3 evaporation in Solid Oxide Fuel Cell's operating environments. Normally, this Mn,Cr-spinel oxides would form a layer on the interconnector part of the solid oxide fuel cells during operations. Nevertheless, the formation mechanism of these Mn,Cr-spinel oxides has yet to be addressed clearly. In this work particular attention is given on the Mn,Cr-spinel oxides formation from the solid state reaction of MnO and Cr_2O_3 at 500 °C and 700 °C. The in-situ APXPS observations of the reaction was performed in $p_{O2} = 5$ mbar in the said temperatures. The in-situ observations has demonstrated the importance of Mn in preventing the evaporation of Cr_2O_3 at high temperature by means of Mn,Cr-spinel oxides formation. Additionally, Mn also has been shown to be more significant in regulating the oxidation of Cr.

The Removal of Surface Contaminants from Organic Crystals by Anti-Solvent Surface Treatment

Benjamin Tayler-Barrett[1],Alexandru A. Moldovan[1],Sin-Yuen Chang[2], Elizabeth Willneff[1,3],
Elizabeth Shotton[2], Sven L.M. Schroeder[1,2]

[1] *School of Chemical and Process Engineering, University of Leeds, Leeds, UK*
[2] *Diamond Light Source, Didcot, UK*
[3] *School of Design, University of Leeds, Leeds, UK*
...

* *s.l.m.schroeder@leeds.ac.uk*

Given the surface sensitivity of XPS, surface cleanliness is of paramount importance. Typical methods for removing contamination, for example, argon sputtering, heating or the use of ozone cleaning is destructive to organic crystals. We have developed an anti-solvent surface treatment method for the non-destructive removal of surface contaminant. Optimization of the cleaning protocol was performed initially by using atomic force microscopy (AFM), in which ultra-pure water, ethanol, methanol, isopropyl alcohol, and dichloromethane (DCM), as well as saturated solutions of all solvents, were examined. In the case of paracetamol crystals, the solvent that provided the best cleaning results was DCM. With the polar solvents all significantly altering the surface topology of the crystals. The optimized cleaning protocol was then taken forward for NAP-XPS experiments at the NSLS-II 23-ID-2 CDX-II beamline. Spectra were acquired before and after cleaning on the same facet of a crystal at 3 mbar water vapor pressure. Paracetamol C1s XPS spectra have a distinctive carbonyl shoulder at 287.7 eV binding energy, which was used to calibrate the energy positions and normalize the spectra intensities. Elemental analysis showed a 14% reduction in total C after cleaning. The total amount of paracetamol, as determined from the carbonyl shoulder, remained unchanged. No chlorine was detected in the survey spectra suggesting that there was no residual DCM solvent at the surface.

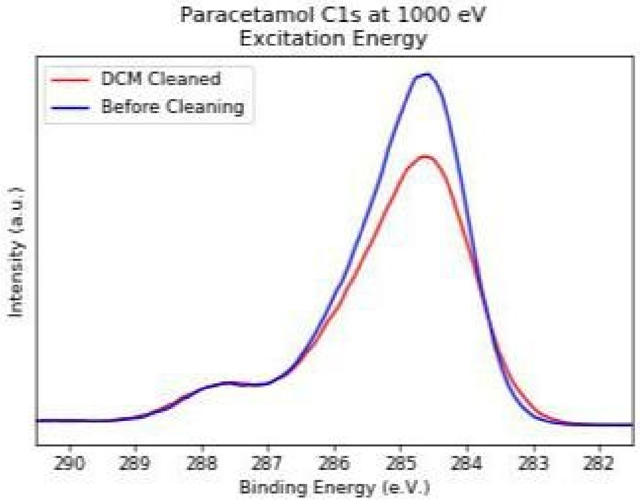


Figure 1. C1s high-resolution spectra of paracetamol obtained at 1000 eV excitation energy.

Advances in analysis of Bragg-reflection standing wave photoemission

S. Nemšák,[1] O. Karslıoğlu,[2] M. Gehlmann,[3,4] J. Müller,[5] H. Bluhm,[1,2,6] C.S. Fadley[3,4]

[1] *Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley CA, USA*
[2] *Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley CA, USA*
[3] *Material Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA, USA*
[4] *Department of Physics, University of California Davis, Davis CA, USA*
[5] *Computational Research Division, Lawrence Berkeley National Laboratory, Berkeley CA, USA*
[6] *Fritz Haber Institute of the Max Planck Society, Berlin, Germany*
…

* *snemsak@lbl.gov*

Standing-wave ambient pressure photoemission spectroscopy is a recently developed experimental tool possessing a huge application potential due to its superb depth resolution [1]. In comparison with conventional photoelectron spectroscopy, however, both data collection and subsequent data analysis are much more complex processes. Depth profiling in standard X-ray photoemission spectroscopy usually involves variation of the incident photon energy and/or electron emission angle to vary the effective information depth. From the complexity point of view, this is in stark contrast to standing-wave experiments, which use several tens of different angles/photon energies spread over the Bragg peak in order to capture the phase of the standing wave reliably.

The current level of automation at both soft X-ray endstations at beamlines 9.3.2 and 11.0.2 of the Advanced Light Source allow for rapid and relatively autonomous data collection of standing-wave scans, but the data analysis is still a very time consuming effort. Data analysis is performed via structure optimization process (that requires frequent user intervention), which compares experimental data to X-ray optical and photoemission simulations, where several thousands of iterations are usually required to converge the optimized structure.

Here we present a newly written code for the analysis of standing-wave data, called SWOPT, that automates this trial-and-error optimization process. The program includes an algorithm that has been developed for computationally expensive problems, i.e. a so-called “Black-box optimizer”. It also includes a more efficient version of the Yang X-ray Optics Program (YXRO) [2]. Apart from the initial setup of the optimization ranges and precisions, human interaction is not required during the optimization. Some examples of the optimization algorithm performance solving real and hypothetical problems will be discussed and we demonstrate that it finds better solutions significantly faster than a random search approach. The total optimization time depends on the sample structure and is typically of the order of tens of minutes to a few hours on a modern multi-core computer and is up to 100x faster than a corresponding manual optimization. These speeds make the SWOPT program an indispensable tool for real-time data analyses, which can in return enable more educated steering of the synchrotron ambient pressure photoemission experiments. [3]

[1] S. Nemšák et al., Nat. Comm. 5, 5441 (2014)
[2] S.-H Yang et al., J. Appl. Phys. 113, 1 (2013)
[3] O. Karslıoğlu et al., J. El. Spec. and Rel. Phenomena, submitted.

Poster contributions

A) Electrochemistry

Reactive oxygen species on iridium: testing hypotheses from DFT in situ

Lorenz Frevel*, Travis Jones, Rik Mom, Juan Velasco-Veléz, Axel Knop-Gericke, Robert Schlögl

Fritz-Haber-Institut der Max-Planck-GesellschaftFaradayweg 4-6, 14195 Berlin

…

* *frevel@fhi-berlin.mpg.de*

Reactive species of heterogeneous catalysts are difficult to identify with X-ray spectroscopy. They usually have a low steady state concentration, simply due to their reactivity, and appear only on the sur-face. The same applies to electrocatalysts active in the oxygen evolution reaction (OER), which are highly desired for their ability to produce hydrogen from water with excessive energy of renewable sources. In order to tackle this challenge we used two strategies: first, we enhanced surface sensitivity and, secondly, we used time resolved spectroscopy to avoid low steady state concentrations and track transitions from one species to another.

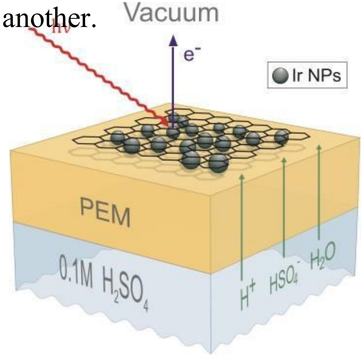


Figure 1: Schematic drawing of the methodology.

Firstly, we developed a methodology which facilitates surface sensitive X-ray spectroscopy on a working electrocatalyst. We achieve that by blanketing iridium nanoparticles on a permeable membrane with graphene. The thin carbon layer is the current collector and, in its function as an evaporation barrier for water, it leads to condensation and consecutively to a thin layer of electrolyte. In this way, we can perform electrochemistry and photoelectron spectroscopy at the same time.

Secondly, our ab initio calculations predicted the μ_1-O species to be most active in water oxidation and suggested that μ_1-OH is transferred into a μ_1-O species at the onset of oxygen evolution. By using time resolved spectroscopy we were, indeed, able to show a relationship between the electrochemical current (figure 2a) and an intensity shift from the distinctive spectroscopic feature of μ_1-OH (figure 2b) to the one of μ_1-O (figure 2c). It was confirming that full spectra of the catalysts steady state were in good agreement with the ab initio calculations, too.

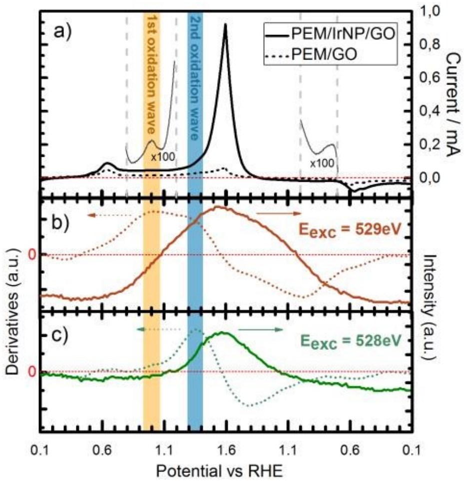


Figure 2: Tracking of the electrochemical currents and the absorption intensity of reactive oxygen species.

Rechargeable All-Solid-State Sodium Peroxide (Na_2O_2) Battery with Low

Chenggong Jiang[1], Baohua Mao[1], Qingtian Li[1], Yimin Li[12*], Zhi Liu[12*]

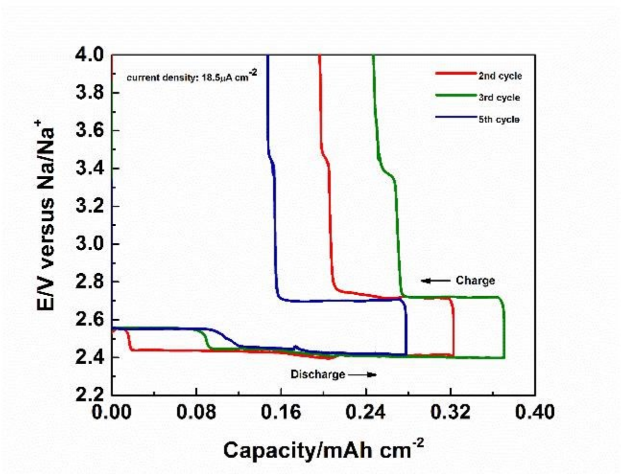
[1] Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai, 200050, China.

[2] School of Physical Science and Technology, ShanghaiTech University, Shanghai, 201210, China

...

** liyml@shanghaitech.edu.cn * zliu2@mail.sim.ac.cn*

The sodium superoxide (NaO_2) batteries have solved the problem of large overpotential in Li-O_2 batteries, nevertheless, the capacity is still limited by the one-electron transferring process comparing with the sodium peroxide (Na_2O_2) battery, which still suffers from the same issue as the Li-O_2 battery (large overpotential). Here we report a brand new type of an all-solid-state Na-O_2 battery using traditional nanoporous gold (NPG) material as the air electrode, ceramic Na-β″-Al_2O_3 as the solid electrolyte and sodium metal as the cathode. We found sodium peroxide (Na_2O_2) as the discharge product and can be reversibly cycled at a very low overpotential, which is different from previous reports. We conducted qualitative and quantitative studies on the discharge-charge products of the cell using in situ ambient pressure X-ray photoelectron spectroscopy (APXPS).



Key words: in situ, ambient pressure X-ray photoelectron spectroscopy, sodium-oxygen batteries, nanoporous gold.

Study the All -solid-state Na-O_2 Battery Using Cerium Oxide as Oxygen Electrode by Ambient Pressure X-ray Photoelectron Spectroscopy

Qingtian Li[1], Baohua Mao[1], Chenggong Jiang[1], Yimin Li[1], Zhi Liu[1,2]

1 Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences
2 School of Physical Science and Technology, ShanghaiTech University
...

* *qtli@mail.sim.ac.cn*

All-solid -state Na-O_2 batteries have attracted great attention recently due to their high theoretical energy densities and high security which make them attractive candidates for application in Evs. The major challenge of Na-O_2 battery is the chemical composition of product is still controversy. [1-3] Thus understanding the chemistry behind Na-O_2 batteries is critical towards enhancing their performance and advancing their development. [4] In this study, we built an all-solid-state Na-O_2 battery using porous cerium oxide as oxy-gen electrode, and studied the oxygen reduction reaction and oxygen evolution reaction during discharge and charge process using ambient pressure X-ray photoelectron spectroscopy (APXPS). The results indicate that the Na-O_2 battery using porous cerium oxide electrode can cycle well, and the porous cerium oxide electrode provides a suitable three-phase interface for the deposition of discharge products. The electrochemical reaction in the battery is the formation and decomposition of Na_2CO_3 based on the analysis of the spectra, while the large interfacial resistance lead to large discharge polarzation of ~0.5 V. This study has demonstrated that oxygen electrode using porous cerium oxide for all-solid-state Na-O_2 batteries shows potential for the battery development, while large resistance at the interface limit the cycle performance and coulomb efficiency in those batteries.

References

[1] Yadegari, H., Q. Sun, and X.L. Sun, Sodium-Oxygen Batteries: A Comparative Review from Chemical and Electrochemical Fundamentals to Future Perspective. Advanced Materials, 2016. 28(33): p. 7065-7093.

[2] Hartmann, P., et al., A rechargeable room-temperature sodium superoxide (NaO2) batery. Nature Materials, 2013. 12(3): p. 228-232.

[3] Lutz, L., et al., Operando Monitoring of the Solution-Mediated Discharge and Charge Processes in a Na-O2 Battery Using Liquid-Electrochemical Transmission Electron Microscopy. Nano Lett, 2018. 18(2): p. 1280-1289.

[4] Liu, Q., et al., In Situ Imaging the Oxygen Reduction Reactions of Solid State Na-O2 Batteries with CuO Nanowires as the Air Cathode. Nano Lett, 2018.

Manganese oxides at OER conditions by In-Situ Synchrotron Based Spectroscopy

K. Skorupska[1,2], T. Jones[1], R. Mom[1], D. Teschner[2], L. Xi[3], K. M. Lange[3], J. Melder[4], P. Kurz[4], M. Hävecker[1,2], Ch.-H. Chuang[5], A. Knop-Gericke[1,2], R. Schlögl[1,2]

[1] *Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck- Gesellschaft, Faradayweg 4-6, Berlin, 14195, Germany*
[2] *Department of Heterogeneous Reactions, Max-Planck-Institut für Chemische Energiekonversion, Stiftstr. 34-36, Mülheim a. d. Ruhr, 45470, Germany*
[3] *Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany*
[4] *Institut für Anorganische und Analytische Chemie and Freiburger Materialforschungszentrum (FMF), Albert-Ludwigs-Universität Freiburg, Albertstraße 21, 79104 Freiburg, Germany*
[5] *Department of Physics, Tamkang University, No. 151 Yingzhuan Rd. 25137 New Taipei City, Taiwan*
...

* *skorupska@fhi-berlin.mpg.de*

In nature the oxygen evolution reaction (OER) takes place at the oxygen evolving complex (OEC) in photosystem II 1. The [Mn_4O_x:Ca] core structure of the OEC resembles inorganic manganese oxides, making the latter interesting candidate OER catalysts 2, 3. Birnessite, a layered manganese based ox-ide, is well known to be active under OER conditions 4, 5. Here we compare the in-situ results obtained with different detection methods for K-Birnessite and an electrodeposited MnOx (Birnessite-like). These two materials are characterized by a high degree of amorphicity and porosi-ty. Their behaviors during the OER in 0.1M phosphate buffer pH7 as well as in 0.1M KOH solution are similar. The changes in O K-edge are correlated with the oxidation state of manganese. Un-der the OER most-ly Mn^{4+} was detected. At this condition the O K-edge resonance at 529.6 eV can be seen to increase with potential, which would suggest an increase in O 2p hole-character as a con-sequence of O-Mn hybridization 6. This leads to the conclusion that the active form of manganese oxide has more cova-lent character. The same phenomena were observed for neutral and alkaline solution and the results are confirmed with surface sensitive and bulk sensitive in-situ measurements 7, 8. It was also possible to detected oxygen during OER.

[1] Cox, N. et al. (2013), Accounts of Chem. Research 46, 1588.
[2] Wiechen, M. et al. (2014), Energy Eviron. Sci. 7, 2203.
[3] Armstrong, F. A. (2008), Phil. Trans. R. Soc. B, 363, 1263.
[4] Gonzalez-Flores, D. et al. (2016), ChemSusChem, 9, 379.
[5] Lucht, K. P. et al. (2015), J. Phys. Chem. C, 119, 22838.
[6] Tesch, M.F. et al. submitted
[7] Ch. Schwanke, L. Xi, K. M. Lange, (2016), J. Synchrotron Rad. 23, 1390.
[8] Streibel, V. et al. accepted for publication in Topics in Catalysis

B) Interfaces

Atmospheric relevant molecules at aqueous interfaces probed with APXPS

Anderson H. de Abreu, Arnaldo N. Brito[2] and Tulio C. R. Rocha[1*]

[1] Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research on Energy and Materials (CNPEM), Campinas-SP, Brazil
[2] Institute of Physics Gleb Wathagin (IFGW), State University of Campinas (UNICAMP), Campinas-SP. Brazil
…

* *tulio.rocha@lnls.br*

Environmental questions related with climate change are very important problems nowadays. Problems like, the role of atmospheric aerosol particles on the tropospheric chemistry and cloud formation are a great challenge for science. Atmospheric aerosols can affect the global radiative balance by light scattering and act like condensation clouds nuclei. The effects of aerosols have been identified by International Panel on Climate changes (IPCC) as an important source of uncertainty in climate models [1]. The liquid-gas interface is important for aerosols due to their small size, but surface effects are not generally taken into account in current climate models. To include surface effects in climate models, it is paramount to improve our molecular level understanding of atmospheric surface phenomena and processes. An effective way to study the composition of the surface of liquids at molecular level is by using X-ray photoelectron spectroscopy (XPS) associated with the liquid microjet technique [2,3]. Using a thin liquid jet (20 micrometers) we can study the chemical properties of the surface of solutions in a molecular level. In this work we will discuss the results of liquid jet XPS experiments of atmospheric relevant organic molecules (aminoacids, amines, carboxylic acids) and salts, obtained by an international collaboration between institutions of Sweden and Brazil. Particularly we will show that thermodynamic potentials that describe the structure and reactivity of interfaces can be obtained be careful analysis XPS spectra measured for liquid jets at variable like concentration, pH and temperature.

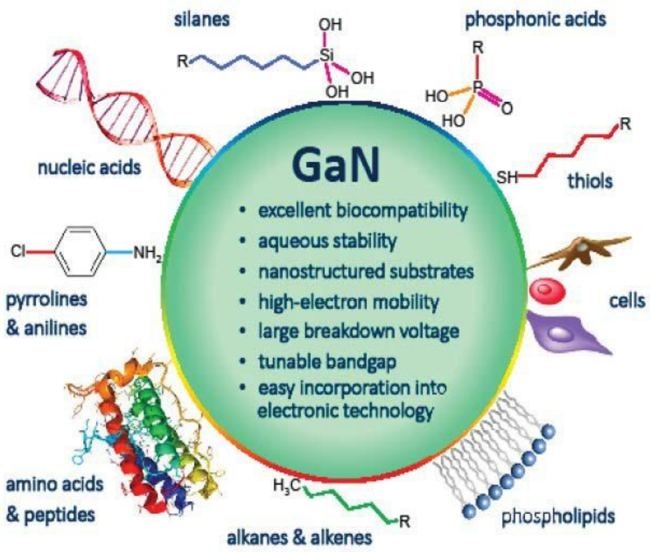
NAP-XPS of Functionalized GaN Surface for Biomolecular Sensing

Mais Ahmad[1], Ravi Prakash[1], Hannes Raschke[1], Norbert Esser[2], Roland Hergenröder[1]

[1] *Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V., Bunsen-Kirchhoff-Str. 11, 44139 Dortmund, Germany.*
[2] *Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V., Schwarzschildstr. 8, 12489 Berlin, Germany.*
...

* *mais.ahmad@isas.de*

The wide-band gap gallium nitride (GaN) semiconductor is nowadays considered as a favorable candidate for use in biological -based microelectronic and biosensing devices due to its many peculiar physical and chemical properties, in addition to its excellent natural living-cell biocompatibility and its ability to convert biological return directly into an electrical signal. The potency of GaN to detect biological species has been assessed via studying surface modification of priori-cleaned/annealed GaN surface upon its functionalization with few monolayers of low-pressure water and L-cysteine molecules by atomic force microscopy (AFM), low-energy electron diffraction (LEED), and near ambient pressure (NAP-) X-ray photoelectron spectroscopy (XPS). It has been noted that not much change took place in the chemical structure of studied water/GaN interface, but there was some evidence of surface modification and change of bonding mechanisms on L-cysteine/GaN interface related to the sulfur-group of amino acid, which may help to get more understanding of the bio-physical-chemical interactions and bonding processes active at functionalized organo/GaN interfaces.



Probing the surface states of Nickel single crystals under CO_2 by Ambient Pressure XPS

Jun Cai[1,2], Yong Han[2], Ethan Crumlin[3], Yimin Li[2], Zhi Liu[1,2]

[1] ShanghaiTech University,
[2] Shanghai Institute of Microsystem and Information Technology,
[3] Advance Light Source, Lawrence Berkeley National Laboratory
...

* *liuzhi@shanghaitech.edu.cn*

Nickel based catalysts play an important role in the chemical transformation of CO_2.[1-3] A fundamental understanding of the interfacial interaction between CO_2 and nickel at atomic level is necessary.[4,5] In this study, the interfacial reactions of CO_2 on Ni(111), Ni(110) as well as Ni(100) surfaces were studied using ambient pressure X-ray photoelectron spectroscopy (APXPS). On all surfaces, the chemisorbed CO_2 only appeared on Ni(110), being both a precursor for dissociation of CO_2 into CO^* and O^* and a reactive species that undergoes conversion in the CO2 hydrogenation process. The Ni(100) has the highest ability to dissociate CO_2 into CO^* and O^*. As the dissociated species CO^* desorbed from the Ni(111) surface, the Ni(111) is more easily to be oxidized with increasing temperature. In particular, the surface adsorbed carbon on Ni(100) is more stable than those on Ni(111) and Ni(110), which was thought to be the carbon sources in the dry reforming of methane. In addition, since the oxidation of nickel surfaces is obviously suppressed under the presence of adsorbed carbon species, it is proposed that the CO^* and graphite carbon species could inhibit the oxidation of nickel surfaces. Further investigation may be needed to confirm this view. Our findings improve our understanding of the CO_2 activation on nickel single crystal surfaces.

References

[1] Wang, W., et al., Recent advances in catalytic hydrogenation of carbon dioxide. Chemical Society Reviews, 2011. 40(7).
[2] Rahim, M.A., R.A. Hameed, and M. Khalil, Nickel as a catalyst for the electro-oxidation of methanol in alkaline medium. Journal of power sources, 2004. 134(2).
[3] Patera, L.L., et al., Real-time imaging of adatom-promoted graphene growth on nickel. Science, 2018. 359(6381).
[4] Heine, C., et al., Recycling of CO2: Probing the Chemical State of the Ni(111) Surface during the Methanation Reaction with Ambient-Pressure X-Ray Photoelectron Spectroscopy. Journal of the American Chemical Society, 2016. 138(40).
[5] Vesselli, E., et al., Carbon dioxide hydrogenation on Ni (110). Journal of the American Chemical Society, 2008. 130(34).

Non-Destructive Depth Profiling of an Organic Crystal Surface Covered in Water by Variable Energy NAP-XPS

Sin-Yuen Chang,[1,2] Benjamin Tayler-Barrett,[1] Elizabeth A, Willneff,[1] Elizabeth J. Shotton,[2]
Carlos Escudero,[3] Virginia Perez-Dieste,[3] Sven L.M. Schroeder[1,2*]

[1] School of Chemical and Process Engineering, School of Design, University of Leeds, LS2 9JT Leeds, United Kingdom.
[2] Diamond Light Source, Harwell Science and Innovation Campus, OX11 0DE Didcot, United Kingdom.
[3] ALBA Synchrotron, 08290 Cerdanyola del Vallès, Barcelona, Spain.
…

* *s.l.m.schroeder@leeds.ac.uk*

We have recently established that gas phase pair formation can be used to minimize surface charging in NAP XPS measurements on electrically insulating organic crystals. We have used this technique to examine the overlayer formed on a paracetamol crystal surface in the presence of 23% relative humidity (10℃, 3 mbar water) by variable photon energy NAP XPS. Assuming layer-by-layer growth of homogeneous phases we have modelled expected signal variations as a function of stoichiometry and thickness of the overlayer formed by water adsorption. Using least squares fitting against the experimental data we find that within the probing depth of XPS the system is dominated by an aqueous paracetamol solution layer, indicating that significant dissolution of paracetamol takes place, rather than condensation of a pure water overlayer. The best-fit model also suggests that adventitious hydrocarbon may rise to the surface of the solution. The study demonstrates that gas phase ionisation makes it feasible to examine electrically insulating organic crystals at ambient humidity conditions, i.e., in the absence of a dedicated charge neutralization system. The results also highlight the importance of cleaning of organic crystals surfaces before reliable quantitative conclusions can be drawn from surface analysis.

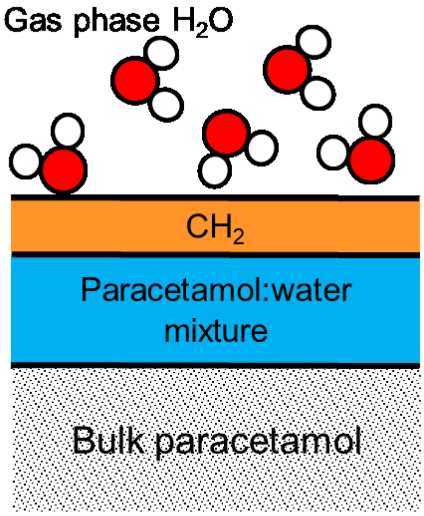


Figure 1. The proposed model for the overlayers covering the paracetamol crystal in the presence of 23% relative humidity at 10℃.

ALD of HfO_2 on SiO_2 and TiO_2: Identification of Surface Species by Ambient Pressure XPS and IR Spectroscopy

G. D'Acunto[1], P. Shayesteh[1], M. Van Daele[2], F. Rehman[1], A.R. Head[3], F. Rochet4, F. Bournel[4], R. Tsyshevskiy[5], C. Detavernier[2], C. Dendooven[2], J.-J. Gallet[4], J. Schnadt[1]

[1] Lund University, Sweden
[2] University of Ghent, Belgium
[3] Brookhaven National Laboratory,USA
[4] Sorbonne Université, Paris, France
[5] University of Maryland, USA
...

* *giulio.dacunto@sljus.lu.se*

Atomic layer deposition (ALD) is a powerful technique for deposition of thin film materials with atomic scale precision. Ideal ALD schemes, relying on the assumption of a self-limiting nature of the growth, provide guidelines to understand how ALD grows and which structures are produced. However, the surface chemistry in ALD process is not fully understood[1]. In our work, we explore possibilities to acquire exact understanding of the surface chemistry in ALD process from the application of *in situ* and *operando* methods, which allow the investigation of surfaces during the reaction.

The ALD of HfO_2 on a oxidized SiO_2/Si(111) surface and on an anatase TiO_2(101) surface from tetrakis(dimethylamido)-hafnium (TDMAHf) and H2O was studied using ambient pressure XPS (APXPS) and *in situ*-Fourier transform infrared spectroscopy (FTIR). The ALD was conducted at 280°C, and the surfaced species during the process were investigated. The FTIR data show that adsorption and reactions of TDMAHf and H_2O on the oxidized Si(111) surface is self-limiting at this temperature (Fig.1). Operando APXPS at high temporal resolution illustrates the evolution of the N1s and Hf4f core levels on SiO_2 (Fig.2) and high-resolution spectra for both the surface were acquired. The data from the two different substrates show different surface species involved in the reaction. On SiO_2 Hf-amido adsorbates and methyl-methyleneimine surface species were identified. A component in the N1s spectra on TiO_2 was identified as alkylammonium[2] (Peak A in Fig.2). Hence, surface sensitive *in situ* and *operando* methods provide detailed understanding of ALD surface process during growth.

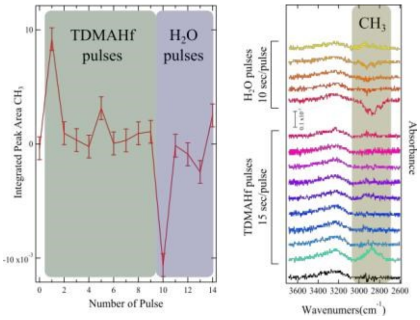


Fig.1 Left) Integrated peak area versus number of pulses for the CH_3 stretching modes (2650-3050 cm^{-1}). Right) FTIR differential absorbance spectra for ALD of HfO_2 on SiO_2/Si(111).

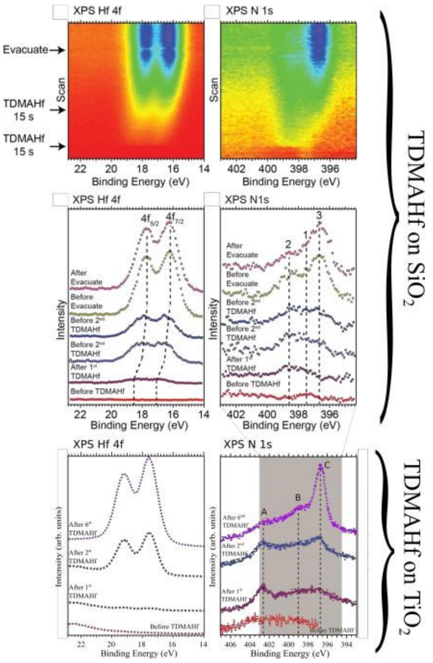


Fig.2 XPS analysis of the first half cycle of HfO_2 ALD on SiO_2/Si(111) and TiO_2(101).

[1] F. Zaera, Coord. Chem. Rev. **257**, 3177 (2013).
[2] A. R. Head et al., J. Phys. Chem. C **120**, 243 (2016)

Probing hydroxylation of oxides via ambient pressure resonant photoemission

Tomáš Duchoň[1*], David N. Müller[1], Georg Held[2,3], Claus M. Schneider[1]

[1] *Peter-Grünberg-Institut 6, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany*
[2] *Diamond Light Source Ltd., Harwell Science and Innovation Campus, Didcot, OX11 0DE, UK*
[3] *Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK*
…

* *t.duchon@fz-juelich.de*

Water interactions are among the most common natural and synthetic chemical processes. Of particular interest is the hydroxylation of oxides in a humid environment, an essential function of industrially relevant steam reforming reactions. While hydroxylation is typically probed via -OH signature in the O 1s core-level spectroscopy, the resonant photoemission offers unique ad-vantages for investigation of oxides. In this contribution, we illustrate these using a prototypical reducible oxide frequently utilized in water-based applications, namely cerium oxide. We carry out a resonant photoemission investigation at the Ce 3d → Ce 4f photoabsorption threshold in 100 mTorr of water. The results reveal an order of magnitude higher sensitivity towards surface hydroxyl groups compared to conventional core-level spectroscopy. Furthermore, the interatomic nature of the utilized resonant photoemission process directly probes the cation-anion hybridization in the system, providing valuable information about the nature of the Ce–OH bonding. As such, the resonant photoemission allows us to reveal the fact that c–f hybridization in cerium ox-ides extends to the surface hydroxyl groups. Our results highlight the utility of resonant photoemission, a technique accessible at conventional synchrotron-based APXPS systems, for investigation of relevant chemical processes in the ambient pressure regime.

Strong Metal Support Interaction (SMSI) in CuxNi1-x/CeO2 Nanoparticles

Wallace T. Figueiredo[1], Guilherme B. Della Mea[1], Carlos Escudero[2], Virginia Pérez-Dieste[2] and Fabiano Bernardi[1,*]

[1] *Programa de Pós-Graduação em Física, Instituto de Física, Universidade Federal do Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil*
[2] *ALBA Synchrotron Light Source, Carrer de la Llum 2-26, 08290 Cerdanyola del Vallès, Spain.*
…

* *bernardi@if.ufrgs.br*

The Strong Metal-Support Interaction (SMSI) effect plays a central role in many important reactions either hindering or enhancing the catalytic activity. In order to elucidate the nature and mechanisms of the SMSI effect on CeO_2-based nanoparticles, we have investigated Cu_xNi_{1-x}/CeO_2 $(0 < x < 1)$ nanoparticles under reducing (H_2) and oxidizing (CO_2) conditions at 500 °C by means of in-situ spectroscopic techniques. Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS) and X-ray Absorption Near Edge Spectroscopy (XANES) were used to probe the kinetics and mechanisms of both nanoparticle and support reduction and oxidation processes. In reducing conditions, Cu atoms migration towards the surface of the Cu-Ni bimetallic nanoparticles was observed, which was reversed under oxidizing conditions.

The core-shell-like structure changes with the Cu concentration in the nanoparticle. A capping layer from the support (CeO_{2-x}) surrounding the metallic nanoparticles after reduction treatment in H_2 atmosphere -characteristic of the SMSI effect- was detected in some specific cases, depending on the Cu concentration. The surface of the nanoparticles presenting the SMSI effect is recovered to the initial state, free of the capping layer, after exposure to CO_2 atmosphere. Regarding the mechanism of the SMSI, it was found that the capping layer interacts with the Cu and Ni atoms via $Ce3d^{10}O2p^6Ce4f^0$ and $Ce3d^{10}O2p^6Ce4f^1$ initial states, depending on the case.

As a consequence of the SMSI effect, the Cu atoms of the nanoparticles reduced at lower temperature than for similar nanoparticles not presenting the SMSI effect. Therefore a lower reduction temperature is directly related to the interaction between the CeO_{2-x} capping layer and Cu and Ni atoms.

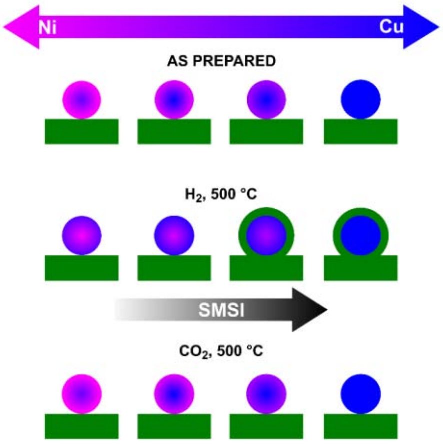


Figure 1. Schematic representation of the atomic arrangement and cerium oxide capping layer formation (SMSI effect) during reduction as a function of Cu concentration in Cu_xNi_{1-x}/CeO_2 $(0 < x < 1)$ nanoparticles. The CO_2 atmosphere reverts the nanoparticles surface to the state without capping layer.

Ambient Pressure Spectroscopy and Imaging of Molecular Interactions with Reducible Oxide Surfaces

David Grinter*[1], Rebecca Hamlyn[2], Fang Xu[2], Dario Stacchiola[2], Sanjaya Senanayake[2], Jose Rodriguez[2]

[1] *Diamond Light Source, Didcot, UK*
[2] *Brookhaven National Laboratory, New York, USA*
…

* *dave.grinter@diamond.ac.uk*

Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) and Scanning Tunneling Microscopy (AP-STM) have provided numerous important insights into the behaviour of materials under conditions out of reach of traditional surface science experiments. In my presentation I will highlight the application of AP-XPS and AP-STM to a number of model heterogeneous catalyst systems based on reducible oxide single crystals and ultrathin films (TiO_2 and CeO_2).[1-4] Catalysts composed of metal-oxide supported nanoparticles have wide ranging industrial uses with particular energy-related applications including alter-native fuel synthesis via methane reforming.[3,4] I will demonstrate how AP-XPS plays a vital role as part of a multi-technique approach into investigating molecular interactions with the surfaces of such materials. The figure below shows AP-XPS and AP-STM of the exposure of a $TiO_2(110)$ surface to 0.2 Torr CO_2 at 300K, leading to the formation of a weakly-absorbed condensate layer.

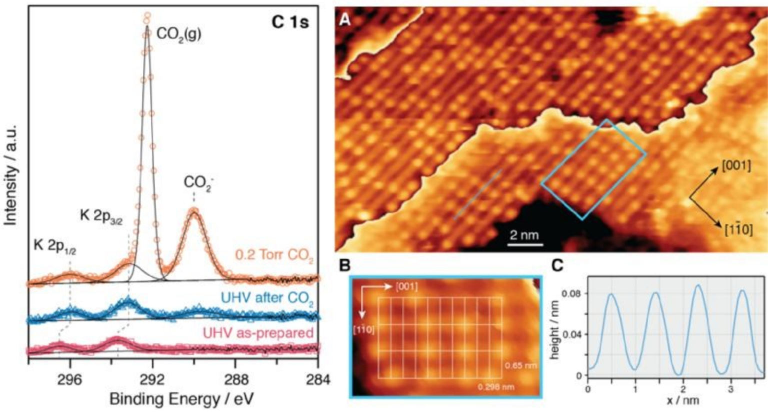


Figure 1. AP-XPS and AP-STM of 0.2 Torr CO2 on $TiO_2(110)$ at 300 K.

References

[1] J. Rodriguez, D. Grinter et al. *Chem. Soc. Rev.* 2017
[2] R. Hamlyn, D. Grinter et al. *PCCP* 2018
[3] P. Lustemberg, D. Grinter et al. *JACS* 2018
[4] Z. Liu, D. Grinter et al. *Angew. Chemie* 2017

Measurement of work function on Pt(110) surface during CO oxidation

Moonjung Jung[1], Youngseok Yu[1], Beomgyun Jeong[2], Bongjin Simon Mun[1*]

[1] *Department of Physics and Photon Science, Gwangju Institute of Science and Technology, Gwangju, 61005, Republic of Korea*
[2] *Division of Material Science Research, Korea Basic Science Institute, Daejeon, 34133, Republic of Korea*
...

* *bsmun@gist.ac.kr*

A work function is an intrinsic surface electronic property and has a close relation to surface reactivity. As a good example, the charge transfer between adsorbed molecules and reacting surface is critically related to the degree of surface work function.

An ambient pressure X-ray photoelectron spectroscopy (AP-XPS) has been applied to measure the work function on Pt(110) surface during oxygen-rich CO oxidation condition, $P(O_2) / P(CO) = 10$. Before the reaction, the surface is covered with CO and its work function is increased by 0.2 eV. At the onset of CO oxidation reaction, the surface oxide is formed and the surface work function is increased by 0.9 eV. The work function of surface oxide is higher than that of atomic oxygen surface. The formation of oxidic surface and its correlation to work function will be discussed.

Ambient Pressure XPS Studies of NO_2 Sensing Mechanism of Titanyl Phthalocyanine

Chia-Hsuan Lin[1], Chia-Hsin Wang[2,*], Yu-Jie Wang[1], Wei Ting[1], Yaw-Wen Yang[1,2,*]

[1] *Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan.*
[2] *National Synchrotron Radiation Research Center, Hsinchu, Taiwan*
…

* *wang.ch@nsrrc.org.tw* * *yang@nsrrc.org.tw*

Metal phthalocyanines (MPcs) have been demonstrated to be useful materials for gas sensing application due to their favorable transducer response, high resistance to oxygen and moisture interference, and good thermal stability. However, the sensing mechanism remains not completely clear. Here, we use a newly completed AP-XPS endstation to investigate the nitrogen dioxide (NO_2) sensing mechanism of titanyl phthalocyanine (TiOPc) and derive at how the electronic structure of TiOPc is modified during the gas sensing process. As the TiOPc film is exposed to NO_2 gas, an abrupt lower binding energy shift of 0.4 eV is noted when the gas pressure is increased above 0.025 mbar, in accord with the detection threshold of 25 ppm determined from OTFT measurements. This binding energy shift is interpreted as an evidence of hole-doping effect by NO_2 on TiOPc film. With XPS curve fitting, several N-containing surface species can be identified under NO_2 ambient. The surface adsorbed NO_2 undergoes a disproportionation reaction to produce NO_3^- and NO^+. Reduced nitrogenated species could bind to titanium central atom and increase its binding energy due to their electron withdrawing nature. In addition, the changes of unoccupied electronic state of Ti metal atom and the orientation of TiOPc molecule induced by NO_2 exposure are also revealed by means of Ti L edge XAS and N K-edge NEXAFS data.

Watching Atomic Layer Deposition with Synchrotron-based real time Ambient Pressure XPS: Towards Millisecond Time Resolution

F. Rehman[1], P. Shayesteh[1], A. Troian[1], G. D'Acunto[1], S.Yngman[1], E. Kokkonen[2], J. Knudsen[1,2], S. Urpelainen[2], F. Rochet[3], F. Bournel[3], J.-J. Gallet[3], R. Timm[1], J. Schnadt[1,2]

[1] *Department of Physics, Lund University, Lund, Sweden*
[2] *MAX IV Laboratory, Lund University, Lund, Sweden*
[3] *LPCMR, Sorbonne Université, Paris, France*
...

* *foqia.rehman@sljus.lu.se*

Atomic layer deposition (ALD) is a thin film deposition technique for depositing uniform and conformal layers on complex three-dimensional topographies. ALD is highly used in different fields of technology, e.g. in microelectronics for metal-oxide semiconductor field effect transistors. The understanding of the atomic and molecular surface processes underlying the ALD growth are, however, far from complete, which implies difficulties in further advancing the technology. A thorough investigation for the identification and role of surface species, surfaces defects, impurities and vapour phase reactions are therefore very much needed [1].

Here, we have applied ambient pressure x-ray photoelectron spectroscopy (APXPS) to study the ALD growth of metal oxides on the clean native oxide-covered surfaces with different time resolution. APXPS has the advantage that it can be carried out during thin film growth, i.e. under *operando* conditions. Our investigation focuses on the dynamic nature of the ALD process, and it is for the first time that APXPS has been applied to this subject with millisecond time resolution. This is illustrated in Fig. 1, which shows APXPS spectra taken during the ALD of HfO_2 on Si(111) substrate and on an InAs(100) surface at different time resolution. It is possible to follow the evolution the core levels during ALD in detail. For this suitable time resolution is important to choose.

Fig. 1. (a) As 3d spectra taken during the exposure of a native oxide-covered InAs(100) surface during exposure to TDMAT at 10^{-2} mbar. In total 1200 spectra were taken in around 70 s. (b) Hf 4f spectra taken in the same kind of experiment, measured at 0.07 Hz frequency using Si(111) substrate.

References:
[1] F. Zaera, Coord. Chem. Rev. **257**, 3177 (2013).

Direct Mapping of Band Positions in Doped and Undoped Hematite during Photoelectrochemical Water Splitting

Andrey Shavorskiy[1,2], Xiaofei Ye[3], Osman Karslıoğlu[1], Andrey D. Poletayev[3], Matthias Hartl[1], Ioannis Zegkinoglou[1], Lena Trotochaud[1], Slavomir Nemšák[1], Claus M. Schneider[4], Ethan J. Crumlin[5], Stephanus Axnanda[5], Zhi Liu[5], Philip N. Ross[6], William Chueh[3], and Hendrik Bluhm[1*]

[1] *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States*
[2] *MAX IV Laboratory, Lund University, Lund, Sweden*
[3] *Material Science and Engineering Division, Stanford University, Stanford, California 94305, United States*
[4] *Peter-Grünberg-Institut-6, Forschungszentrum Jülich, 52425 Jülich, Germany*
[5] *Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States*
[6] *Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States*
...

* *hbluhm@lbl.gov.*

We employ an Ambient Pressure Photoemission Spectroscopy as a noncontact local probe of electrical potential to investigate changes in the surface chemistry as well as the band alignment of the hematite at the semiconductor/KOH interface during photoassisted water splitting as a function of solar illumination and applied potential. With this tool we could demonstrate the absence of in-gap states, which is contradictory to previous measurements using indirect methods. We could also give a comprehensive description of shifts in the band positions and limiting processes during the reaction.

High pressure XPS analysis of the atomic layer deposition of aluminium oxide on titanium dioxide

Dr. Robert H. Temperton[1], Dr. James N. O'Shea[1]

[1] *School of Physics, University of Nottingham, UK*

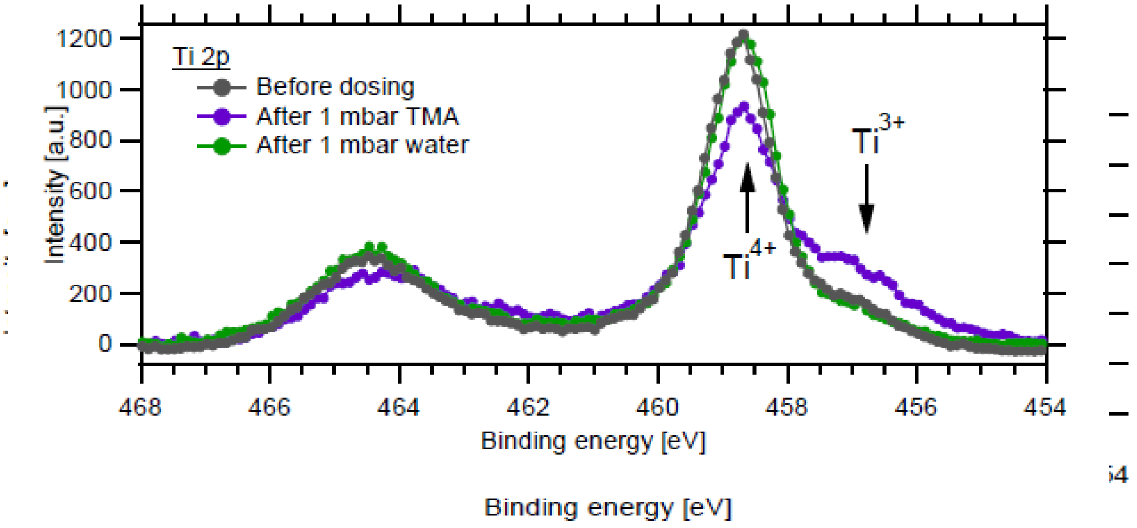
…

* *robert.temperton@nottingham.ac.uk*

Ultra-thin oxide layers can act as a tunneling barrier between the redox mediator and photoelectrode in photoelectrochemical devices. For example, in the now infamous dye sensitized solar cell[1], it has been shown that adding an ultra-thin aluminum oxide layer between the titanium dioxide surface and absorbed dye can reduce recombination effects increasing power conversion efficiency[2]. A tempting route to grow these ultra-thin films is atomic later deposition: for the case of aluminum oxide, tri-methylaluminium (TMA) and water can be dosed alternately producing high purity films to an easily controllable thickness.

This study uses NAP XPS to follow the growth of alumina, in situ, on a clean $TiO_2(110)$ rutile surface by alternate exposure to 1 mbar of TMA and water. We reveal interesting chemistry at the titania/alumina interface. For example, as shown in the figure below, exposure to the two precursors leads to the creation and healing of Ti^{3+} "defects" on the rutile surface. We find monitoring this can be used as a probe of when complete coverage of the titania surface is reached.

We also compare this data with a comparable experiment where the precursors were dosed in UHV conditions. This definitively shows using "high pressure" conditions to study this sort of process is critical to produce conclusions that are relevant to the realistic industrial conditions.



[1] O'Regan, B. & Grätzel, M. *Nature* **353,** 737–740 (1991).

[2] Ganapathy, V., Karunagaran, B. & Rhee, S. W. *J. Power Sources* **195,** 5138–5143 (2010).

Interaction of CO_2 with Cu(111) and Cu(110) Studied with Ambient Pressure X-ray Photoelectron Spectroscopy: Structural Sensitivity and Pressure Dependence

Tian Yang[1], Yong Han[2], Jun Cai[1], Qiao Dong[1], Zhi Liu[2*]

[1] *Shanghai Institute of Microsystem and Information Technology*
[2] *ShanghaiTech University*
...

* *liuzhi@shanghaitech.edu.cn*

The conversion of CO_2 into valuable chemicals and fuels has attracted extensive attention due to its significance in environment and industry. A detailed understanding of the sur-face-state changes during the initial step of CO_2 conversion is crucial for optimizing the performance of catalysts. Using ambient pressure X-ray photoelectron spectroscopy (APXPS), we find that the surface species and chemical states of Cu surfaces are structure sensitive and pressure dependent during the CO_2 activation. At the CO_2 pressure of 1×10^{-6} mbar, the Cu(111) is partially covered by dissociative oxygen while a complete coverage of oxygen atoms is observed on the Cu(110) surface, indicating that the Cu(110) is more active to dissociate CO_2 than Cu(111). As the CO_2 pressure increases from 0.01 to 1 mbar, the carbon-contained species undergo an evolution from chemisorbed CO_2 ($CO_2^{\delta-}$) to CO_3^{2-} on the Cu(111) surface. However, no carbon contained species are detected on the Cu(110) surface in this pressure range since the metallic Cu sites are completely occupied by oxygen atoms. When the CO_2 pressure is up to 0.01 mbar, both Cu surfaces gradually transform to Cu_2O as the temperature increase. Our findings unveil significant insights into the CO_2 activation on Cu surfaces and provides fundamental information for developing highly selective Cu-based catalysts for CO_2 reduction.

C) Catalysis

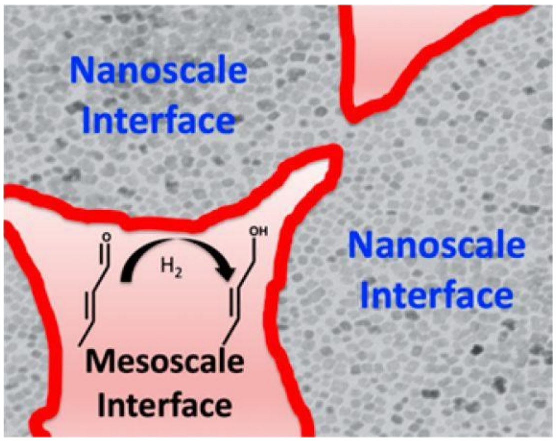
Catalysis at Multiple Length Scales: Bifunctional Activation at Nanoscale and Mesoscale Interfaces in Platinum–Cerium Oxide Catalysts

L. Robert Baker[1*], Yutichai Mueanngern[1], Xin Yang[1], Yu Tang[2,3], Franklin (Feng) Tao[2,3]

[1] *Department of Chemistry and Biochemistry, The Ohio State University*
[2] *Department of Chemistry, University of Kansas*
[3] *Department of Chemical and Petroleum Engineering, University of Kansas*
…

* *baker.2364@osu.edu*

Crotonaldehyde hydrogenation is carried out on Pt–CeO_2 catalysts to investigate the mechanism of enhanced C=O bond hydrogenation by the oxide–metal interface. We show that deposition of CeO_2 nanoparticles onto a Pt surface leads to two types of Pt–CeO_2 interfaces: 1) the nanoscale interface defined by the contact of individual CeO_2 nanoparticles with the Pt surface and 2) a larger, mesoscale interface de-fined by the boundary between domains of a self-assembled nanoparticles and the surrounding clean Pt substrate. Surprisingly, although the nanoscale interface accounts for greater than 90% of the total 3-phase boundary as shown by TEM analysis, C=O bond hydrogenation kinetics scale exclusively with the larger, mesoscale interface. These results indicate that production of unsaturated alcohols extends well beyond the actual oxide–metal interface. Using in situ ambient pressure XPS, we show that these kinetics are not the result of variations in the CeO_2 oxidation state due to H spillover or of Pt decoration by reduced Ce atoms during reaction. Instead, we hypothesize that reaction is rate limited by the surface migration of crotyl-oxy intermediates as they form on CeO_2 nanoparticles and subsequently diffuse and react on surrounding Pt. The surprisingly long length scale for bifunctional activity highlights challenges and opportunities in nanoscale design of selective catalysts.



J. Phys. Chem. C, 121, 13765–13776 (2017).

The evolution of APXPS as a tool for catalyst investigation: surface dynamics under preferential CO oxidation flow reaction conditions

R. Castillo[1,3], J.C. Navarro[1], C. Escudero[2], V. Perez-Dieste[2], M.A. Centeno[1], M. Daturi[3], J.A. Odriozola[1*]

[1] Inorganic Chemistry department, University of Seville and Institute of Material Science of Seville (US-CSIC), 41092 Seville, Spain 1
[2] Normandie Univ, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, 14000 Caen, France
[3] ALBA Synchrotron Light Source, Carrer de la Llum 2-26, 08290 Cerdanyola del Vallès, Spain
…

* *odrio@us.es*

Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) is usually employed in fundamental research in surface science. However, the pioneer work of the group of Salmeron and Somorjai has developed a new concept: "surface reaction-driven restructuring", which highlighted the reversible changes in the composition and the oxidation state of solids in response to the environmental atmosphere, so revolutionizing the concept of catalytic surfaces[1].

In the Hydrogen technology, the preferential oxidation of CO in excess of hydrogen (PrO_x reaction) is an important process for obtaining CO-free hydrogen for proton exchange membrane fuel cells (PEMFCs). PtCu based catalysts are one of the most studied systems for mobile devices because of their high activity/selectivity balance and their appropriate chemical and mechanical properties for the start-up/shut-down procedures during fuel processors operation conditions.

In this work, well-defined PtCu bimetallic alloy nanoparticles catalyst were synthetized and studied by *operando* APXPS in ALBA Synchrotron (Spain). These studies allowed understanding the surface electronic modifications in the solid-gas interface catalyst under PrOx reaction conditions, in particular from the point of view of surface dynamics and of the possible effects of reaction atmosphere and temperature on it. APXPS analyses carried out under model PROX reaction conditions confirm an appreciable surface copper enrichment as well as a modification of the active site electronic density.

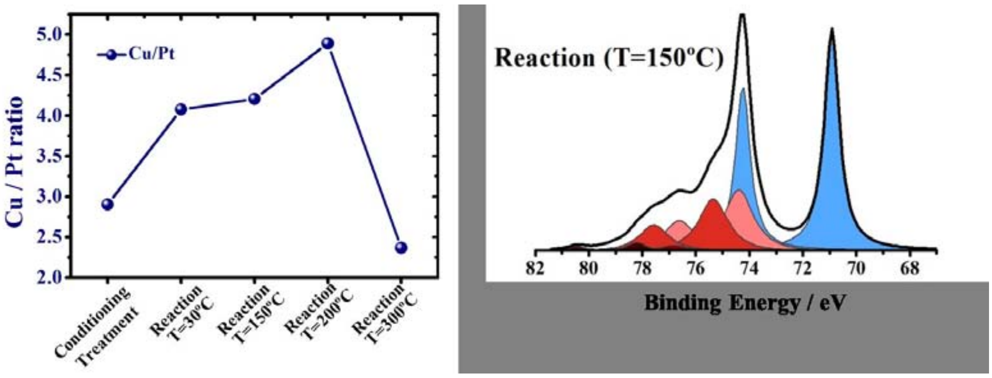


Figure 1. Surface copper/platinum atomic ratio as a function of the reaction temperature calculated by APXPS study of Pt 4*f* and Cu 3*p* photoelectrons (IMFPs = 4.5 Å).Reaction flow: 50% H_2, 10% H_2O, 10% CO_2, 1% CO, 1% O_2 and N_2 (balance).

[1] Tao, F.; Grass, M. E.; Zhang, Y.; Butcher, D. R.; Renzas, J. R.; Liu, Z.; Chung, J. Y.; Mun, B. S.; Salmeron, M.; Somorjai, G. A. *Science.* **2008**, *322*, 932–934.

Operando Observation of Cu-based Catalyst for Methanol Steam Reforming Process by Ambient-Pressure X-ray Photoelectron Spectroscopy

Cheng-Hao Chuang[1,*],Yu-Fu Wang[1], Te-Wei Chiu[2], A. Knop-Gericke[3], J. J. Velasco-Vélez[3,4]

[1] *Department of Physics, Tamkang University, Taiwan*
[2] *Department of Material and Mineral Resources Engineering, National Taipei University of Technology, Taiwan*
[3] *Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin 14195, Germany*
[4] *Department of Heterogeneous Reactions, Max Planck Institute for Chemical Energy Conversion, Mül-heim an der Ruhr 45470, Germany*
…

* *chchuang@mail.tku.edu.tw*

Hydrogen has been considered as a promising candidate for the future fuel cell due to the zero-pollutants emission and abundant resource, although the safety storage and transportation become the limitations. Methanol steam reforming (MSR) reaction become known for an attractive and rising process for the hydrogen production, which is commonly activated by copper-based catalyst. The guideline is that water gas reaction and methanol decomposition reaction are happened at the catalytic site, and the intermediate state as CO gas formation make the catalyst poisoned and inactive. The strategy to improve MSR process starts to observe the in-situ chemical reaction with the real environment, if only to compare the catalytic performance without the kinetics condition is not enough. Ambient pressure X-ray photoelectron spectroscopy offers the gas pressure (up to 1 torr range) and mixtures to study the catalytic reaction of $CuCrO_2$ and $CuFeO_2$ surface under the realistic conditions. The systematical investigation into the chemical state of heterogeneous surface and adsorbed/dissolved species is found with different probing depths and detection modes. The chemical state (Cu^{2+} and Fe^{3+}) of $CuCrO_2$ and $CuFeO_2$ under the working temperature is found to be reduced to less oxidation state by active gas species, which is corresponding to the increase of hydrogen gas production. Our project is to observe the chemical evolutions of $CuCrO_2$ and $CuFeO_2$ sur-face using the in-situ control and operando experiment, offering more comprehensive insights and useful information into the green energy application.

Sunlight-assisted Hydrogenation of CO_2 into ethanol and C2+ Hydrocarbons by Sodium-promoted Co@C Nanocomposites

Patricia Concepción*[1], Jorge Cored[1], Lichen Liu[1], Alberto V. Puga[1], Virginia Pérez-Dieste[2], Hermenegildo García[1] and Avelino Corma[1]

[1] Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas (UPV-CSIC), Avenida de los Naranjos s/n, 46022 Valencia, Spain
[2] ALBA synchrotron light source, 08290 Cerdanyola del Vallès, Barcelona, Spain
...

* *pconcepc@upvnet.upv.es*

Photocatalytic CO_2 reduction, commonly referred to as artificial photosynthesis, is one of the most challenging issues in chemical research. Actually low reaction rates and low selectivity to the more valuable C2+ hydrocarbons are obtained, being CH_4 and CO the actual main products. This is combined with an almost lack of knowledge about the reaction mechanism. Recently in our research group we reported the photoassisted hydrogenation of CO_2 into hydrocarbons with a selectivity to C2+ hydrocarbons >30% at nearly 100% CO_2 conversion, using Na-promoted Co@C nanocomposites as catalysts and working at atmospheric pressure [1]. The effect of light irradiation and the promoting effect of Na on the reaction mechanism has been studied by near ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) and *in situ* Raman spectroscopy. In this sense, Na-Co@C and Co@C samples in presence of CO_2 and H_2, un-der thermal (with buttom heater) and photothermal reaction conditions (using a solar simulator, view fig 1) has been studied in the NAP-XPS experiments. Based on the C1s spectra (fig.1), the direct role of light has been ascribed to an electronic effect where electrons generated by absorption of UV light are responsible for activating CO_2 to $CO_2^{\delta-}$, promoting CO_2 dissociation into CO, and the stabilization of CO on the catalyst surface (C1s component at 286.5eV). The stabilization of CO contributes to a higher selectivity toward ethanol by a CO insertion mechanism. Moreover carbonate species have been observed as spectator species (C1s component at 289.4eV).

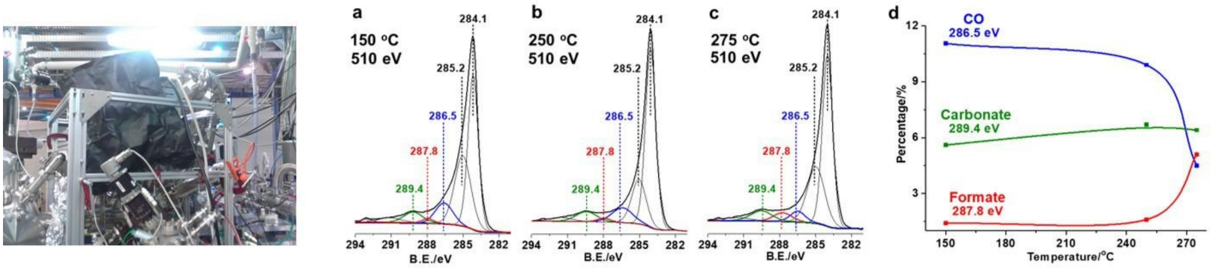


Fig.1 Ambient-pressure XPS spectra of Na-Co@C sample during CO2 hydrogenation reaction conditions (P_{CO2}= 0.1 mbar and P_{H2}= 0.5 mbar) under photothermal conditions. C1s spectra obtained with incident X-ray energy of *hv*=510 eV.

[1] L. Liu, A.V. Puga, J. Cored, P. Concepcion, V. Pérez-Dieste, H. García and A. Corma, Appl. Catal. B. Environ-mental, 235, 2018, 186-196

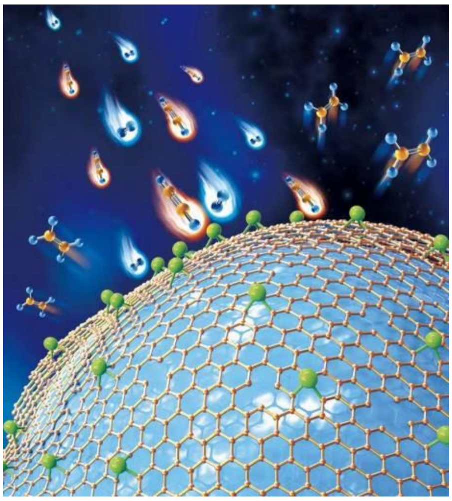
Atomically dispersed Pd on nanodiamond/graphene hybrid for selective hydrogenation of acetylene

Fei Huang,[1,2,#] Yuchen Deng,[3,#] Yunlei Chen,[4,5,#] Xiangbin Cai,[6,#] Mi Peng,[3] Zhimin Jia,[1,2] Pengju Ren,[4,7] Dequan Xiao,[8] Xiaodong Wen,[4,7] Ning Wang,[6] Hongyang Liu,[1,*] and Ding Ma[3,*]

[1] *Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of*
[2] *School of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, P. R. China*
[3] *Beijing National Laboratory for Molecular Engineering, College of Chemistry and Molecular Engineering and College of Engineering, BIC-ESAT, Peking University, Beijing 100871, P. R. China*
[4] *State Key Laboratory of Coal Conversion, Institute Coal Chemistry, Chinese Academy of Sciences, Tai-yuan 030001, P. R. China*
[5] *University of Chinese Academy of Science, No. 19A Yuanquan Road, Beijing 100049, P. R. China*
[6] *Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon,*
[7] *National Energy Center For Coal to Clean Fuel, Synfuels China Co., Ltd, Huairou District, Beijing 101400, P. R. China*
[8] *Center for Integrative Materials Discovery, Department of Chemistry and Chemical Engineering, Uni-versity of New Haven, 300 Boston Post Road, West Haven, Connecticut 06516, United States*
...

* *liuhy@imr.ac.cn* * *dma@pku.edu.cn*

- An atomically dispersed palladium (Pd) catalyst supported onto a defective nanodiamond-graphene (ND@G) is reported here for selective hydrogenation of acetylene in the presence of abundant ethylene. The catalyst exhibits remarkable performance for the selective conversion of acetylene to ethylene: high conversion (100%), ethylene selectivity (90%), and good stability (i.e., steady for at least 30 hours). The unique structure of the catalyst (i.e., atomically dispersion of Pd atoms on graphene through Pd-C bond anchoring) ensure the facile desorption of ethylene against the over-hydrogenation of ethylene to undesired ethane, which is the key for the outstanding selectivity of the catalyst.



CO+NO+O_2 Reaction on Pd(100): New Insights From APXPS

Osman Karslıoğlu[1], Ashley R. Head[1], Joseph Raso[1], Timm Gerber[1], Yi Yu[1,2], Lena Trotochaud[1], Philipp Kerger[1,3], Hendrik Bluhm[1,4,5*]

[1] *Chemical Sciences Division and* [4] *Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley CA 94720, USA*
[2] *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA*
[3] *Department of Interface Chemistry and Surface Engineering, Max Planck Institute for Iron Research, D-40237 Düsseldorf, Germany*
[5] *Fritz Haber Institute of the Max Planck Society, Berlin, Germany*
…

* *hbluhm@lbl.gov*

We used ambient-pressure X-ray photoelectron spectroscopy to study the CO+NO+O_2 reaction system on Pd(100). The surface was exposed up to ~1 Torr mixtures of the three gases, at temperatures ranging from 25 °C up to ~425 °C. In all the experiments O_2 was in excess, which—in most cases—led to the oxidation of the surface after light-off. When CO:O_2 ratio was 1, addition of NO up to 20% of O_2 had no effect on the light-off temperature. When CO:O_2 ratio was 0.01, addition of NO led to an increase in the light-off temperature and—in the case of 1:1 NO:O_2 ratio—the prevention of √5-surface-oxide and PdO formation. In that case, the surface was oxygen-covered-metallic, but never reached the critical coverage for the surface-oxide formation. Furthermore, mass spectrometry showed that CO oxidation was slow, most likely due to the lack of CO adsorption sites on the O-poisoned surface.

CO_2 conversion on Ni(100) probed with ambient pressure XPS

Kyung-Jae Lee[1,2], Yifan Ye[1], Hongyang Su[1], Dong-Jin Yun[1], Meiling Sun[1],
Bongjin S. Mun[*2], Ethan J. Crumlin[*1]
[1] *Advanced Light Source, Berkeley Lab, US*
[2] *Department of Physics and Photon Science, GIST, Korea*
...
* *bsmun@gist.ac.kr* * *ejcrumlin@lbl.gov*

CO_2 has attracted many attentions due to its possibility of the utilization as a feedstock for various valuable chemicals, such as CO, CH_4, and higher carbon products. Thus, many scientists have studied its conversion to other chemicals, and because of its stability, the use and understanding of catalysts are critical in CO_2 conversion.

In this study, the authors studied CO_2 conversion on Ni(100) with H_2 using ambient pressure XPS (APXPS), and mass spectrometer (MS), which is connected to the differential pump. Depending on the sequence of dosing gases, two different surfaces were observed, and these two different surfaces could affect CO_2 conversion rate, which was reported previously. (L. Dietz et al., J. Phys. Chem. C, 2011, 115, 1255) In addition, we observed the trends of surface components along the temperature and found how the dominant chemical reactions (CO_2 dissociation, CO desorption, and CO dissociation) changes as the temperature and the amount of surface components varied. This trend was compared with the calculation reported before (X. Hao et al., Phys. Chem. Chem. Phys., 2016, 18, 17606), and it helps to understand the reaction mechanism. And finally, with the help of MS, the real products (CO and H_2O) were observed along the reaction conditions, and we could correlate the surface components and the products to under-standing reaction mechanism.

These results provide that the combination of APXPS and MS could be a powerful tool for understanding the reaction with observing the change of surface components and the real reaction product simultaneously.

The role of adsorbed and subsurface carbon species for the selective alkyne hydrogenation over a Pd-black catalysts: An operando study of bulk and surface at 1 bar

J. Velasco-Vélez[1,2*], D. Teschner[1,2], F. Girgsdies[1], M. Hävecker[2], V. Streibel[1], M- G. Willinger[1], J. Cao[1], M. Lamoth[1], E. Frei[1], R. Wang[3], A. Centeno[4], A. Zurutuza[4], S. Hofmann[3], R. Schlögl[1,2,] A. Knop-Gericke[1,2]

[1] Department of Inorganic Chemistry, Fritz-Haber-Institute der Max-Planck-Gesellschaft
[2] Department of Heterogeneous Reactions, Max Planck Institute for Chemical Energy Conversion
[3] Department of Engineering, University of Cambridge
[4] Graphenea
…

* *velasco@fhi-berlin.mpg.de*

The selective hydrogenation of propyne over a Pd-black model catalyst (Figure b) was investigated under *operando* conditions at 1 bar making use of advanced X-ray diffraction (bulk sensitive, Figure c) and photoelectron spectroscopy (PES) (surface sensitive, Figure d) techniques. It was found that the population of subsurface species controls the selective catalytic semi-hydrogenation of propyne to propylene due to the formation of surface and near-surface PdC_x that inhibits the participation of more reactive bulk hydrogen in the hydrogenation reaction. However, increasing the partial pressure of hydrogen reduces the population of PdC_x with the concomitant formation of a β-PdH_x phase up to the surface, which is accompanied by a lattice expansion, allowing the participation of more active bulk hydrogen which is responsible for the unselective total alkyne hydrogenation. Therefore, controlling the sur-face and subsurface catalyst chemistry is crucial to control the selective alkyne semi-hydrogenation. Accordingly, these experiments at high pressure validate the previous reaction model demonstrated by *in situ* NAP-XPS at few mbar partial pressure and therefore close the "pressure gap" in the understanding of the hydrogenation of alkynes on Pd catalysts showing the evident difference between bulk and near-surface chemistry of the Pd catalyst in contact with both hydrogen and hydrocarbons. On the other hand, this work is an example for the value of true *operando* studies even and because it shows here the absence of a high-pressure gap due to a well understandable reason based in high sticking.

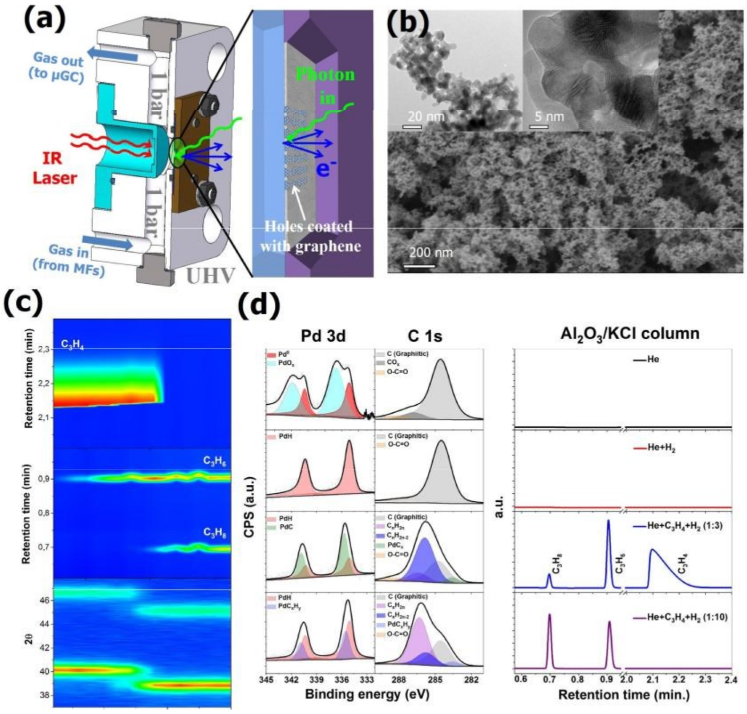


Figure: (a) Detection scheme. (b) TEM/SEM Pd-black characterization. (c) Operando at 1 bar (c) XRD and (b) XPS.

Combined time-resolved AP-XPS and TAP study on Pd for methane oxidation

Muhammad Younas[1], Heinrich Hartmann[1], Joachim Pasel[2], Jürgen Dornseiffer[3], Astrid Besmehn[1*]

[1] Central Institute of Engineering, Electronics and Analytics 3: Analytics
[2] Institute of Energy and Climate Research 3: Electrochemical Process Engineering
[3] Institute of Energy and Climate Research 1: Materials Synthesis and Processing
Forschungszentrum Juelich GmbH, D-52425 Juelich, Germany
...
* *a.besmehn@fz-juelich.de*

Natural gas vehicles (NGVs) are receiving more focus due to relatively clean exhaust products (CO_2, H_2, H_2O) as compared to gasoline or diesel powered engines. However, methane slip caused by incomplete combustion makes a catalytic exhaust treatment necessary. Palladium is the highest active catalyst for low temperature methane oxidation in the range of 200°C and 500 °C relevant for NGVs. Previous studies show that the activity of Pd based catalyst depends on the ratio of metallic Pd and PdO_x active sites as it is believed that methane attaches itself to both Pd^0 and PdO_x dual sites simultaneously in the dissociative adsorption and redox mechanism [1,2]. In this work, we will present results of a combined Ambient Pres-sure X-rays Photoelectron Spectroscopy (AP-XPS) and Temporal Analysis of Products (TAP) study to investigate the synergy of both chemical and well as physical processes involved in methane oxidation. AP-XPS and TAP experiments are carried out in continuous as well as alternative pulses mode (time-resolved). Reactant gases such as CH_4, O_2, CO_2, and CO were used to study the surface/gases interaction. In addition, AP-XPS is coupled with mass spectrometry to give a deeper understanding about different Pd species (Pd^0 and PdO_x) and their correlation to catalytic activity. Therefore a combination of time-resolved AP-XPS and TAP is believed to highlight the importance of the chemical and physical aspect of the catalytic methane oxidation.

[1] Huang, F.; Chen, J.; Hu, W.; Li, G.; Wu, Y.; Yuan, S.; Zhong, L.; Chen, Y. Appl. Catal. B Environ. 2017, 219, 73–81

[2] Tompos, A.; Margitfalvi, J. L.; Hegedus, M.; Szegedi, A.; Fierro, J. L. G.; Rojas, S.; Tomposa, A. A.; Heged, M. M.; Margitfalvi, J. L.; Heged, M. M. Comb. Chem. High Throughput Screen. 2007, 10 (1), 71–82.

In-situ oxidation of CO on a curved Pt(111) surface

F. García[1], M. Ilyn[1], V. Pérez-Dieste[2], C. Escudero[2], B. Hagman[3], S. Blomberg[3], J. Gustafson[3], E. Lundgren[3], A. L. Walter[4], I. Waluyo[4], F. Schiller[1], J. E. Ortega[1,5,6*]

[1] *Centro de Física de Materiales CSIC, San Sebastian (Spain)*
[2] *ALBA Synchrotron, Barcelona (Spain)*
[3] *Department of Physics, Lund University (Sweden)*
[4] *National Synchrotron Light Source, Brookhaven (USA)*
[5] *Departamento Física Aplicada I, Universidad del País Vasco, 20018-San Sebastian (Spain)*
[6] *Donostia International Physics Centre DIPC, 20018-San Sebastian (Spain)*
…
* *enrique.ortega@ehu.eus*

The study of the catalytic CO oxidation on Pt single crystals and nanoparticles has been a wide research field since long.[1] However, the role and the interplay among different coordination sites and facet planes has never been clarified. This is in part due to the fact that both crystal surfaces and nanoparticles undergo complex structural/chemical changes during catalytic reactions. In this context, using multi-facet samples, such as cylindrical crystals, for in-situ studies is highly desirable.[2] We have carried out near-ambient pressure X-ray photoemission (NAP-XPS) experiments of the CO oxidation using a curved Pt(111) crystal. The figure below shows the temperature evolution of the O 1s at the (335) plane, marking the ignition temperature at 505 K. Once this is known, we freeze the reaction at fixed temperatures around the ignition point and scan the surface with the synchrotron beam. This allows us to probe surface chemical species across different crystallographic planes in stationary conditions. As a way of example, the figure (left) shows the C 1s scan across the curved surface before the ignition (480 K, poisoned stage).

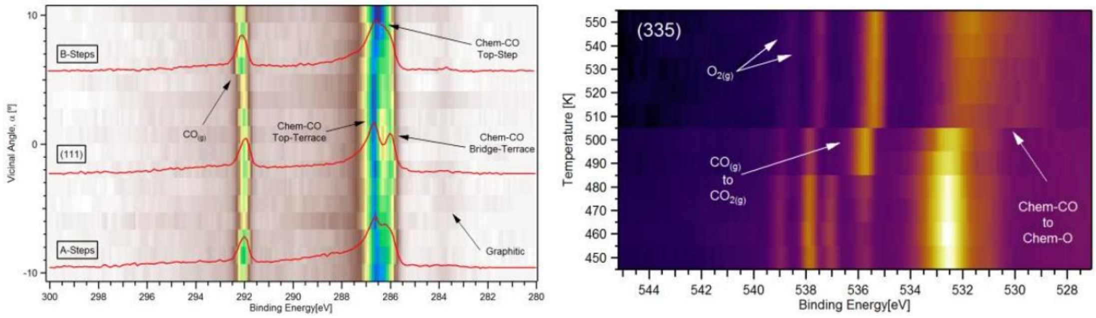


Figure 1. Right, temperature scan of the O1s peak at the (335) plane, marking the ignition of the CO oxidation reaction at 505 K. Left, C1s scan over the curved surface before ignition at 480 K.

The temperature scan at the (111) plane (right panel) shows that, below the onset of the catalytic reaction, the surface is covered with a variety of chemisorbed CO (Chem-CO) species, in the presence of CO and O_2 in the gas phase. When the ignition begins, Chem-CO is displaced by chemisorbed oxygen and Pt oxides, and this process is accompanied by the quenching of the CO gas signal, the emergence of CO_2, and the rightward shift of all gas phase peaks. The XPS scan in the left panel demonstrates that, in the poisoned stage, there is a vicinal-angle-dependent variety of Chem-CO species (terrace-top, terrace-bridge, step-top), similar in nature and concentration to those that saturate the c-Pt(111) crystal at 300 K in Ultra-High-Vacuum[3].

Acknowledgements. We acknowledge financial support from the Spanish Ministry of Economy (Grant MAT-2017-88374-P) and Basque Government (Grant IT621-13).

[1] Kinne et al.The Journal of Chemical Physics 120, 7113 (2004).
[2] Vendelbo, S. B et al. Nat Mater 13, 884–890 (2014).
[3] Walter, A. et al. Nat Comm 6, (2015).

Spatial variation of the active phases during the catalytic oxidation of CO measured on a curved Pd(111) surface

J. E. Ortega[1*], M. Ilyn[1], V. Pérez-Dieste[2], C. Escudero[2], C. Huck-Iriart[2], N. Ruiz del Arbol[3], B. Hagman[4], S. Blomberg[4], J. Gustafson[4], E. Lundgren[4], F. Schiller[5,6]

[1] Centro de Física de Materiales CSIC, San Sebastian (Spain) (frederikmichael.schiller@ehu.es)
[2] ALBA Synchrotron, Barcelona (Spain)
[3] Instituto de Ciencia de Materiales CSIC, Madrid (Spain)
[4] Department of Physics, Lund University (Sweden)
[5] Departamento Física Aplicada I, Universidad del País Vasco, 20018-San Sebastian (Spain}
[6] Donostia International Physics Centre DIPC, 20018-San Sebastian (Spain)
...
* *enrique.ortega@ehu.eus*

For decades, the study of chemical reactions on single metal surfaces has been aimed at identifying those active sites and crystal planes that feature nanoparticles[1].However, nanocrystal facets coexist in a reduced space, and are expected to simultaneously undergo chemical and structural transformations during catalytic reactions[2]. In ALBA we explore chemical-structural interplays among crystal planes using curved crystals and near-ambient X-ray photoemission (XPS) at CIRCE. As a test case for the approach, we recently used a curved Pd(111) surface, on which we freeze the CO oxidation reaction at the ignition temperature. By scanning the photon beam across the curved surface, we observe a smooth spatial variation of chemisorbed phases, demonstrating a different reaction stage at each crystallographic plane. As shown in the Figure, the XPS signal from chemisorbed CO reveals the linearly decreasing fraction of CO-poisoned areas, from the (111) direction up to a 10º critical angle, and at various temperatures around light-off. This behavior is explained as a collective structural response of the surface at the reaction onset, consisting in the weighted segregation of less-active (111) phase and highly-active (223) and (332) facets in A-type and B-type vicinal planes, respectively.

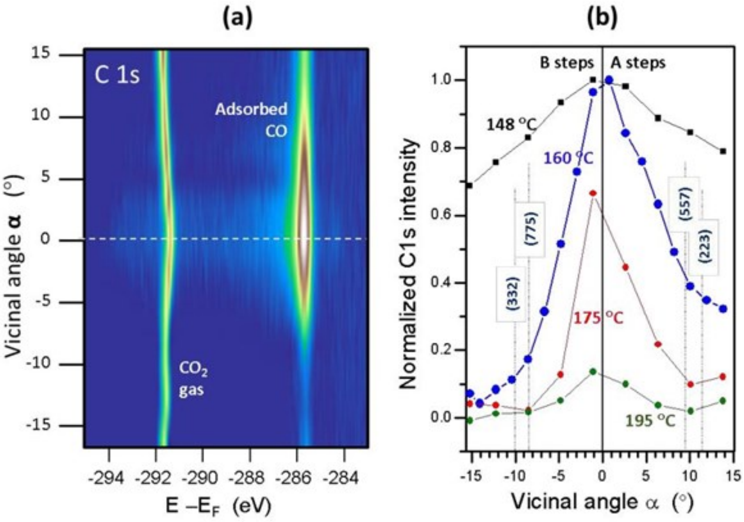


Figure: (a) C1s intensity (color scale) across a curved Pd(111) surface exposed to a 1:1mbar $CO:O_2$ gas mixture at 160ºC, when cooling off the CO oxidation reaction. (b) Normalized C 1s intensity for the adsorbed CO peak of (a), at different temperatures around light-off, and across the curved surface. The linear drop from the (111) center toward 10° miscut suggests segregation of vicinal planes into active [(332) and (223) at A and B sides] and less active (111) facets upon reaction light-off.

Acknowledgements. We acknowledge financial support from the Spanish Ministry of Economy (Grant MAT2013-46593-C6-4-P) and Basque Government (Grant IT621-13)

[1] Introduction to Surface Chemistry and Catalysis, edit. Somorjai, G.A. and Li, Y. John Wiley & Sons (2010).
[2] Vendelbo, S. B et al. Nat Mater 13, 884–890 (2014).

D) Materials

Origin and control of the surface space charge layer in donor doped $SrTiO_3$

M. Andrä[1], R. Dittmann[1], H, Bluhm[2], C. Schneider[3], R. Waser[1,4], D. N. Mueller[3,*], F. Gunkel[4]

[1] Peter Gruenberg Institute 7, Forschungszentrum Juelich GmbH, Juelich, Germany
[2] Advanced Light Source, Lawrence Berkeley National Laboratory,Berkeley, CA, USA
[3] Peter Gruenberg Institute 6, Forschungszentrum Juelich GmbH, Juelich, Germany
[4] Insitut fuer Werkstoffe der Elektrotechnik II, RWTH Aachen University, Aachen, Germany
...

* *dav.mueller@fz-juelich.de*

Donor-doped ternary transition metal oxides such as donor-doped strontium titanate (n-$SrTiO_3$) are of fundamental importance for oxide electronic devices as well as for electronic surface and interface engineering. Here we demonstrate the presence of a surface space charge layer defined by the surface redox chemistry of n-$SrTiO_3$. It is responsible for an oxygen partial pressure (pO_2)-dependent surface band bending and a thickness-dependent electron density in n-$SrTiO_3$ thin films. Synchrotron-based near ambient pressure X-ray photoelectron spectroscopy conducted on n-$SrTiO_3$ thin films under applied thermo-dynamic bias (T, pO_2) reveals the presence of a variable surface potential and a corresponding negative surface charge. pO_2-dependent surface potential profiles were mapped by spectroscopic depth profiling, revealing an electron depletion layer present at the surface of n-$SrTiO_3$ thin films in both nominally reducing (ultra high vacuum) and oxidizing conditions. Reversible pO_2 governing of the negative surface charge is obtained by exploiting surface defect equilibria controlling the formation and annihilation of strontium vacancy defects as concluded from in-situ strontium core level spectroscopy. Transient sheet resistance response to a change in ambient atmosphere was monitored to probe the impact of the altered negative surface charge on the electron density contributing to electrical transport in n-$SrTiO_3$ thin films. We correlate the resistance change to the varying concentration of strontium vacancies at the surface of n-$SrTiO_3$. As underlying process, we suggest a conversion of the charge-neutral strontium oxide surface termination into strontium oxide clusters accompanied by charged strontium vacancies in oxidizing conditions.

Ferrihydrite Acid Attack

A. Boucly[1*], L. Artiglia[1,2], H. Yang[1], M. Ammann[1]

[1] *Paul Scherrer Institut (PSI), Labor für Umweltchemie, CH-5232 Villigen PSI, Switzerland*
[2] *Paul Scherrer Institut (PSI), Laboratory for Catalysis and Sustainable Chemistry, CH-5232 Villigen PSI, Switzerland1Affiliation*
...

* *anthony.boucly@psi.ch*

Ferrihydrite is a form of Iron(III) Oxy-Hydroxide that exists in the form of nanoaggregate loosely cristaline.[1,2] It has no clear structure (it exists in two types: 2 lines and 6 lines), has no fixed composition and is metastable[1] as it will slowly transform into either Goethite or Hematite, the most stable form Iron(III) Oxy-Hydroxide species. Due to its porous nanostructure, Ferrihydrite has a high specific surface area[1] and offer a high number of accessible sites for adsorption and reaction. It is also consider to be the main source of Bio-Available iron[2] (Iron that can be leached from the mineral and adsorbed by organism) and thus as a huge impact on the marine life. Ferrihydrite mainly comes from dust particle emitted from desert sand such as the Sahara. Due to its oxide and non-conductive nature, few spectroscopic experiences have been carried out and in general few experiments have been made to study its reactivity as an aerosol particle. Yet it is part of an important redox couple which can interact with different species (most notably acid). Here I will show the first result on how acid interact with the Ferrihydrite and modify it. For these, two different acid have been used, ascorbic acid as it also an electron donor that can reduce Iron (III) and citric acid.

[1] Schwertmann et al. "From Fe(III) Ions to Ferrihydrite and then to Hematite." Journal of colloid and interface science. (1999)
[2] Rodriguez-Navarro, C., di Lorenzo, F., and Elert, K.: Mineralogy and physicochemical features of Saharan dust wet deposited in the Iberian Peninsula during an extreme red rain event, Atmos. Chem. Phys.

Investigation of the Initial Stages of SiGe(001) Thermal Oxidation Using Ambient Pressure X-ray Photoelectron Spectroscopy

J. Trey Diulus, Shane P. Lorona, Gregory S. Herman*

School of Chemical, Biological, and Environmental Engineering, Oregon State University, Corvallis, OR, 97331, USA

...

* *greg.herman@oregonstate.edu*

The combination of n-type strained silicon and p- type silicon germanium (SiGe) metal-oxide-semiconductor field effect transistors (MOSFET) are of considerable interest for next generation complementary circuits. SiGe has many useful properties including high carrier mobilities and compatibility with standard silicon based processing. However, controlling the semiconductor- dielectric interface for SiGe is more challenging than Si due to the different thermodynamic stabilities of SiO_2, GeO_2, and their alloys. In this study, we have performed laboratory- based ambient pressure X-ray photoelectron spectroscopy (AP-XPS) on SiGe(001) surfaces to better understand the initial thermal oxidation processes at the SiGe surface. Chemical state resolved AP-XPS was performed at temperatures up to 300 °C and O_2 pressures up to 1 mbar. We have found that both Si and Ge thermally oxidize with two distinct regions at 300 °C and 1 mbar. First there is a rapid oxidation regime, which is then followed by a quasi-saturation regime with a much slower oxidation rate. We find that the Si^{4+}/Si^0 and Ge^{4+}/Ge^0 ratios have very similar rates in both the rapid and quasi-saturation regime, but that the Si^{4+}/Si^0 ratio is always larger than the Ge^{4+}/Ge^0 ratios. To evaluate preferential SiO_2 growth we have also performed experiments at lower oxygen pressures at 300 °C. Prior studies have suggested that Ge can catalytically enhance the rate of oxidation, so we have performed similar oxidation experiments for Si(001) and Ge(001) surfaces under identical conditions and have characterized their oxidation rates. These studies indicate that AP-XPS provides valuable insight into processes relevant to the semiconductor industry.

Co 2p APXPS investigation of Co_3O_4/Si films grown and monitored under in operando conditions

E. González, [1] A. Echavarría[1*], A. Santa[1], O. Arnache[2], D. Stacchiola[3], J. Llorca[4], C. Ostos[1]

[1] NAP-XPS Lab, CATALAD Research Group, FCEyN, Universidad de Antioquia, Medellín, Colombia
[2] Solid State Research Group, FCEyN, Universidad de Antioquia, Medellín, Colombia
[3] Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973, USA
[4] Institute of Energy Technologies, Department of Chemical Engineering and Barcelona Research Center in Multiscale Science and Engineering, Universitat Politecnica de Catalunya, Eduard Maristany 10-14, 08019, Barcelona, Spain

...

* *adriana.echavarria@udea.edu.co*

The spinel oxide, Co_3O_4, has been recognized to be an excellent catalyst due to its high activity in oxidation processes, which is ascribed to the generation of oxygen vacancies through disruption of a weak lattice Co-O bond. This is possible because of Co_3O_4 has both octahedral Co^{3+} and tetrahedral Co^{2+} ions, which particularity leads to the formation of punctual surface defects; besides, Co^{2+}/Co^{3+} oxidation states stablish a relative variation in oxidative properties of the catalyst [1,2].

In this spirit, this work was focused to investigate how Co_3O_4 can be formed during a controlled oxidation process and monitored by means of NAP-XPS. Co thin films were successfully deposited on Si (100) substrate by DC-Sputtering technique, using Ar atmosphere and 1 in. metallic cobalt as target. The sample surface was pretreated before NAP-XPS analysis with Ar^+ ion gun sputtering to ensure a clean metallic coating (**Figure 1**). Next, the sample was positioned inside the in-situ cell chamber where XPS spectra were taken, firstly at UHV conditions and later the in-situ cell was filled with O_2, and next keeping a flux of 0.75 mL/min, in order to follow the oxidation process of Co by measuring the Co 2p XPS signal from RT to 873 K.

Oxidation process of Co coating was effectively monitored by in-situ XPS measurement of Co 2p signal. Changes in oxidation states of Co were successfully studied; this has allowed us to know in what way the Co_3O_4 spinel is formed through determination of Co^{2+}/Co^{3+} ratio states throughout the oxidation experiment (**Figure 1**).

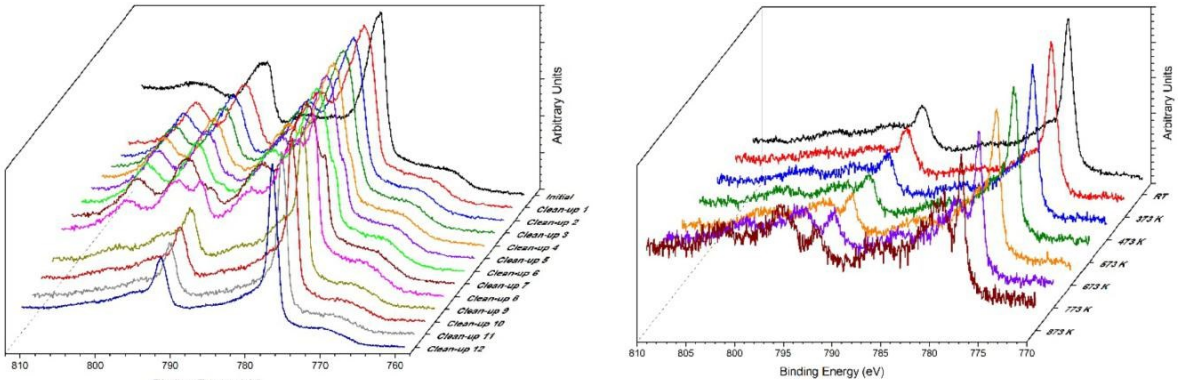


Figure 1. Clean-up cycles of Co/Si(100) sample (left) and monitoring of Co 2p signal in the oxidation process (right).

References

[1] S. A. Singh and G. Madras, "Detailed mechanism and kinetic study of CO oxidation on cobalt oxide surfaces," *Appl. Catal. A Gen.*, vol. 504, pp. 463–475, 2015.
[2] K. Shojaee, A. Montoya, and B. S. Haynes, "Insight into oxygen stability and vacancy formation on Co_3O_4 model slabs," *Comput. Mater. Sci.*, vol. 72, pp. 15–25, 2013.

Charge effects in the oxidation of size-selected Pt clusters

Maximilian Huber[1,2], Marian Rötzer[1], Maximilian Krause[1], Hendrik Bluhm[2], Markus Döblinger[3], Sebastian Günther[1], Ulrich Heiz[1], Friedrich Esch[1], Barbara A. J. Lechner[1,*]

[1] *Department of Chemistry, Technische Universität München, 85748 Garching, Germany*
[2] *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*
[3] *Department of Chemistry, Ludwig-Maximilians-Universität München, 81377 München, Germany*
…

* *bajlechner@tum.de*

We investigate the oxidation of size-selected Ptn clusters (n = 8–40) on the native oxide of n- and p-type Si(100). Scanning transmission electron microscopy of Pt clusters on oxidized silicon nitride films con-firmed that the size-selection is maintained during transport to a synchrotron and subsequent exposure to oxidizing and reducing conditions.

Pt clusters exhibit a markedly different oxidation behavior on p- and n-type Si in ambient pressure X-ray photoelectron spectroscopy. Upon exposure to ≤0.5 Torr O_2 at 300 K, we observed shifts to higher binding energies in the Pt 4f peaks of clusters on n-type Si. The magnitude of the shift increases with cluster size, yet remains small. The clusters are thus not fully oxidized, in agreement with re-ports that the oxidation of Pt nanoparticles is kinetically hindered[1] and exposure to atomic oxygen required for complete oxidation.[2] We find that the peaks shift back to lower binding energies after evacuation. Exposure to CO or H_2 does not result in further shifts, implying that the clusters are already fully reduced in vacuum.

In contrast, Pt clusters on p-type Si do not exhibit any significant binding energy shifts. As shown in the figure, the same Pt_{20} clusters show a shift of 0.23 eV on n -doped Si upon exposure to just $4x10^{-5}$ mbar O_2, but none on p-type Si. Our results suggest that negatively charged Pt clusters on n-type Si facilitate the dissociative adsorption of O_2, while positively charged Pt clusters on p-type Si do not.

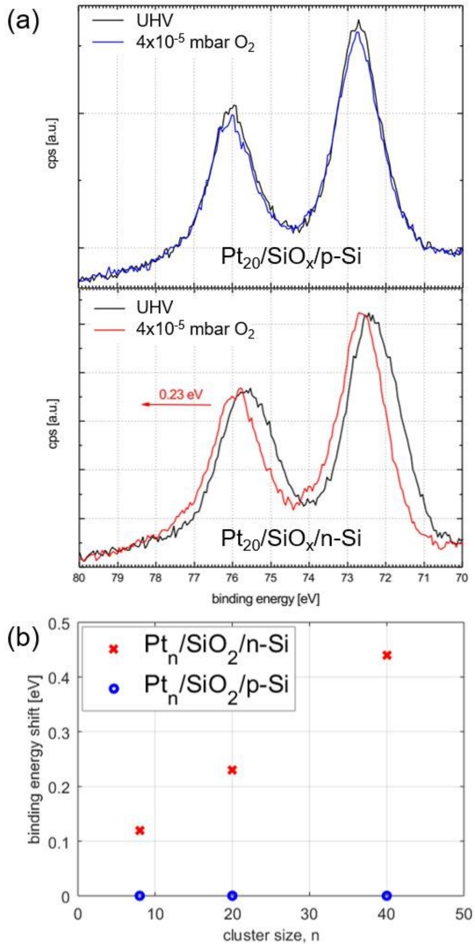


Figure: (a) Pt 4f spectra and (b) binding energy shifts of Pt_n on silica on p- and n-type Si.

[1] U. Hejral, A. Vlad, P. Nolte, A. Stierle, *J. Phys. Chem. C* **2013**, *117*, 19955.
[2] L. K. Ono, J. R. Croy, H. Heinrich, B. R. Cuenya, *J. Phys. Chem. C* **2011**, *115*, 16856–16866.

Mn, Cr-spinel Oxide's Formation from APXPS' Perspectives

Akbar bin Kaderi[1,2]

[1] *Previously at ZEA-3, Forschungszentrum Jülich, 52428 Jülich, Germany.*
[2] *Graduate Student of the Faculty of Georesources and Materials Engineering, RWTH Aachen, 52056 Aachen, Germany*
...

* *akb.kaderi@gmail.com*

Spinel oxide is a very interesting compound. The general formula for spinel oxides is AB_2O_4. The compound has interesting physical properties including electronic and magnetic as well as chemical properties including oxidation and catalysis. The unique properties of spinel oxide have found its use in many technological energy applications such as in solar cell, fuel cell and batteries. In this abstract, interests and works on Mn,Cr-spinel oxides are presented. Mn,Cr-spinel oxides has been known to prevent Cr_2O_3 evaporation in Solid Oxide Fuel Cell's operating environments. Normally, this Mn,Cr-spinel oxides would form a layer on the interconnector part of the solid oxide fuel cells during operations. Nevertheless, the formation mechanism of these Mn,Cr-spinel oxides has yet to be addressed clearly. In this work particular attention is given on the Mn,Cr-spinel oxides formation from the solid state reaction of MnO and Cr_2O_3 at 500 °C and 700 °C. The in-situ APXPS observations of the reaction was performed in $p_{O2} = 5$ mbar in the said temperatures. The in-situ observations has demonstrated the importance of Mn in preventing the evaporation of Cr_2O_3 at high temperature by means of Mn,Cr-spinel oxides formation. Additionally, Mn also has been shown to be more significant in regulating the oxidation of Cr.

Combined NAP-XPS and XANES Analysis of Calcium Compounds

Thokozile A. Kathyola[1], Elizabeth A. Willneff[2], and Sven L.M. Schroeder[*1,3]

[1] *School of Chemical and Process Engineering, University of Leeds, Leeds. LS2 9JT, UK*
[2] *School of Design, University of Leeds, Leeds. LS2 9JT, UK 3Diamond Light Source, Didcot, Oxfordshire, OX11 0DE, UK)*
...

* *s.l.m.schroeder@leeds.ac.uk*

Calcium carbonate ($CaCO_3$) is an extensively studied material due to its abundance in nature and wide application in industry, e.g. fuel, pharmaceuticals and construction sectors. Despite widespread scientific interest, there is still limited understanding of what governs $CaCO_3$ polymorph selection, polymorphic transformation dynamics, crystallinity and stability. We are addressing the molecular basis of these phenomena through time-resolved *in situ* experiments using X-ray absorption and photoelectron spectroscopy. Here, we present an *ex* and *in situ* near-ambient pressure XPS study of the C 1s, Ca 2p and O 1s emissions for the reactive crystallization of $CaCO_3$. NAP XPS provides information on the electronic structure of the reactants and products involved in the hydration and carbonation reactions (Fig. 1). Our results indicate for the reaction of calcium hydroxide ($Ca(OH)_2$) with CO_2 that the most stable $CaCO_3$ polymorph, calcite, is formed. Through the C 1s spectra we can differentiate and quantify the composition of the reactants and products and thereby determine interfacial reaction kinetics. The multi-element XPS results were complemented by *in situ* Ca K-edge XANES studies. *In toto* these studies provide deeper mechanistic understanding, which should ultimately provide predictive capability for controlling the nucleation and crystallisation of $CaCO_3$ products.

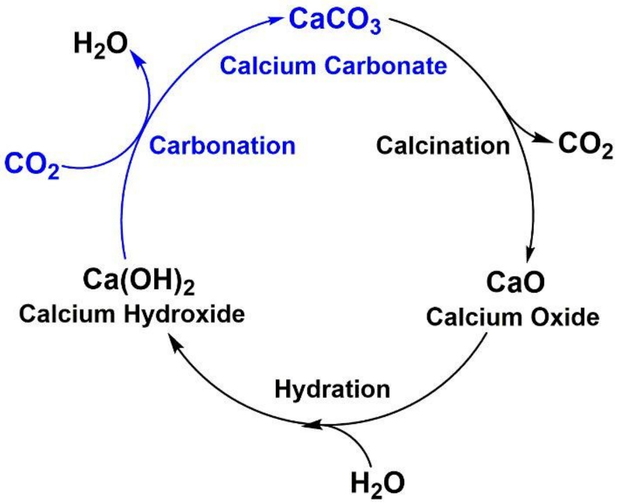


Fig. 1. Lime cycle highlighting the reactive crystallization of calcium carbonate ($CaCO_3$).

Exploring the capabilities of NAP-XPS: Application to biofilms, suspended nanoparticles and metal-organic frameworks

M. Kjærvik[1], P. Dietrich[2], A. Thissen[2], K. Schwibbert[1], A. Nefedow[3], C. Wöll[3], W. Unger[1]

[1] *Bundesanstalt für Materialforschung und -prüfung - Berlin (Germany)*
[2] *SPECS Surface Nano Analysis GmbH - Berlin (Germany)*
[3] *Karlsruhe Institute of Technology (KIT)- Eggenstein-Leopoldshafen (Germany)*
…

* *marit.kjaervik@bam.de*

Near-ambient pressure XPS makes it possible to characterise samples not compatible to ultra-high vacuum, and enables the study of liquid-solid, gas-liquid and gas-solid interfaces. NAP-XPS measurements of biofilms, suspended nanoparticles and metal-organic frameworks were performed with EnviroESCA developed by SPECS.

An interesting application is surface characterisation of biofilms, which are bacterial communities embedded in a self-produced polysaccharide matrix. Various model systems ranging from pure polysaccharides of alginate to biofilms harvested directly from the growth medium have been characterised in humid conditions [1].

NAP-XPS also makes it possible to characterise nanoparticles in solution. Silver nanoparticles in aqueous solution were characterised and the Ag 3d-spectrum compared to spectra obtained of dried nanoparticles in UHV-conditions [2]. The binding energy of the Ag 3d-core level peak was shifted 0.6 eV towards higher binding energy for suspended nanoparticles compared to the dried sample measured in UHV. This can be assigned to a change in surface potential at the water-nanoparticle interface.

Metal-organic frameworks (MOFs) are suitable materials for gas storage of small molecules due to their nanoporous, crystalline structure. However, instability in humidity remains an issue for many types of MOFs. XPS-measurements of the MOF-structure HKUST-1 were performed in various NAP-conditions to assess the stability of the sample and its interaction with the gas molecules as water, methanol and pyridine.

Acknowledgements

This project has received funding from the EMPIR program co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation program.

Reference

[1] M. Kjaervik, K. Schwibbert, P. Dietrich, A. Thissen, and W. E. S. Unger, "Surface characterisation of Escherichia coli under various conditions by near-ambient pressure XPS," Surf. Interface Anal., 2018.

[2] M. Kjærvik et al., "Detection of suspended nanoparticles with near-ambient pressure x-ray photoelectron spectroscopy," J. Phys. Condens. Matter, vol. 29, no. 47, p. 474002, 2017.

Investigation on polarization switching behavior of $SrMnO_3$ ferroelectric thin film with Ambinet Pressure-XPS

Hojoon Lim[1], Dongwoo Kim[1], Youngseok Yu[1], Geonhwa Kim[1], Moonjung Jung[1], Chang Jae Yoon[2], Ji Young Jo[2], Bongjin Simon Mun[1,3,*]

[1] *Department of Physics and Photon Science, GIST, Gwangju 61005, Korea*
[2] *Department of material science and engineering, GIST, Gwangju 61005, Korea*
[3] *Center for Advanced X-ray Science (SRC), Gwangju 61005, Korea*
...

* *bsmun@gist.ac.kr*

The research of ferroelectric thin film has received much attention due to not only its intriguing complex nature of condensed matter physics, but also potential industrial applications in the fields of semiconductor, catalyst, and nonvolatile memories. While electrical stimuli are the popular choices for controlling the polarizability of ferroelectric thin film, an external modification of surface chemical potential has proved to be also effective to make structural transition and local polarization. A spontaneous polarization switching of $PbTiO_3$ (PTO) ferroelectric thin film have been shown by controlling oxygen pressure and temperature via synchrotron-based *in situ* X-ray scattering. [1]

$SrMnO_3$ (SMO), a well-known ferroelectric material with ABO_3 type perovskite structure [2], has lower dipole moment and Curie temperature than PTO and is expected to show the polarization switching behavior under the variation of surface chemical potential. We investigate the chemically switchable polarization of SMO thin film with the application of ambient pressure XPS (AP-XPS). In addition, the presence and role of defect in SMO film has been characterized as a function of oxygen partial pressure.

Reference

[3] Wang, R. V. et al., "Reversible chemical switching of a ferroelectric film." Phys. Rev. Lett. **102,** 047601 (2009) (DOI:10.1103/PhysRevLett.102.047601)

[4] Lee, Jun Hee, and Karin M. Rabe., "Epitaxial-strain-induced multiferroicity in $SrMnO_3$ from first principles." Phys. Rev. Lett. **104**, 207204 (2010) (DOI: 10.1103/PhysRevLett.104.207204).

Ce 3d APXPS investigation of ceria powder under in operando conditions

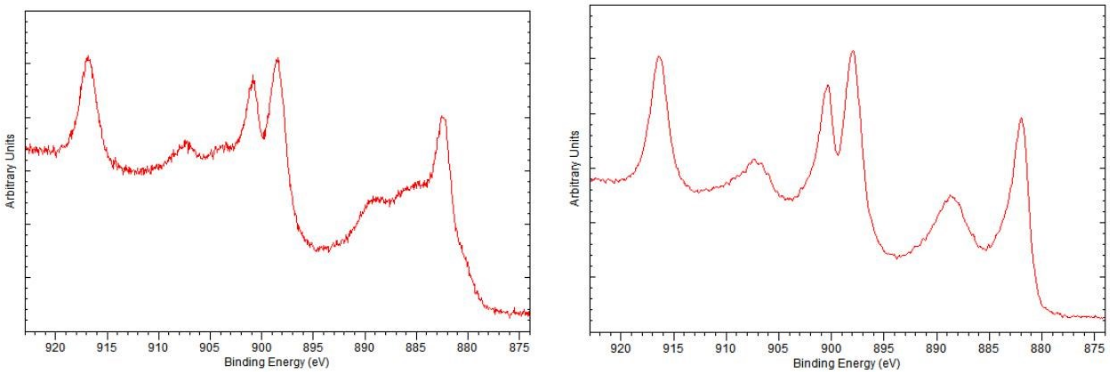
Ostos, C.[1], Santa, A[1], Echavarria[1], A, Scott[2], Niño, J.[2]

[1] *NAP-XPS Lab, CATALAD Research Group, Universidad de Antioquia, Medellín, Colombi*
[2] *Nino Research Group, Department of Materials Science and Engineering, University of Florida,*
100 Rhines Hall, Gainesville , FL 32611 , USA
…

* *carlos.ostos@udea.edu.co*

Ceria is one of the most important material in heterogeneous catalysis due to its high oxygen storage capacity based on the oxidation and reduction of cerium ions. It is used in the water-gas-shift reaction, for the oxidation of hydrocarbons, histochemistry, electrolytes for solid oxide fuel cells, ultraviolet absorbents, oxygen sensors, and automotive catalytic converters (1,2,3). Stoichiometric defects such as oxy-gen vacancies and their mobility on the oxide surface are of great importance for redox reactions involving gases and metal oxides with multiple oxidation states and are widely exploited in oxygen storage materials like CeO_2 by UHV XPS since this important property is related with the $Ce^{3+/}Ce^{4+}$ ratio (1,2).

In this study $Ce^{3+/}Ce^{4+}$ ratio was determined under in operando conditions analyzing Ce 3d and O 1s core levels by means of APXPS technique. CeO_2 powder was sited into the in-situ cell chamber and spectra were taken from RT to 873K at UHV conditions (Figure 1a). Next, this procedure was replied but now filling the in-situ cell chamber with 1 mbar of O_2 in order to follow the oxidation process (Figure 1b). $Ce^{3+/}Ce^{4+}$ ratio was successfully calculated and the results were compared with previous reported in literature under UHV conditions.



(a) (b)

Figure 1. Ce 3d heated at 873K under (a) UHV conditions and (b) 1 mbar O_2.

References

[1] C. Barth, C. Lafforn, R. Olbrich, A. Ranguis, Ph. Parent, and M. Reichling. Nature Scienfific Reports. 6:21165. 2016

[2] S. T. Hossain, E. Azeeva, K. Zhang, E. T. Zell, R. Wang. Applied Surface Science, Volume 455, 15 October 2018, Pages 132-143

[3] E. Beche, P. Chavrin, D. Perarnau, S. Abanades and G. Flamant. Wiley Interscience. 21 January 2008.

Room Temperature Silicon Oxidation: Longstanding Questions and New Experimental Findings from Near Ambient Pressure XPS

Lucia Perez Ramirez[1,*], Jean-Jacques Gallet[1,2], Anthony Boucly[3], Fabrice Bournel[1,2], François Rochet[1,2]

[1] *Sorbonne Université, CNRS, Laboratoire de Chimie Physique Matière et Rayonnement, Campus Pierre et Marie Curie – 4, place Jussieu, BC1140, F-75005 Paris, France*
[2] *Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, F-91192 Gif-sur-Yvette, France*
[3] *Paul Scherrer Institute, Villigen, Switzerland*
…

* *lucia.perez_ramirez@etu.upmc.fr*

The study of silicon oxidation has attracted considerable interest since the 1960s as silicon dioxide is the gate oxide of MOS technology. Phenomenological interpretations of the kinetics of silicon oxidation were accompanied by atomic transport studies and physicochemical analyzes of the Si/SiO_2 interface, in which synchrotron radiation X-ray photoemission spectroscopy (XPS)[1,2] had the most significant role. With the advent of near ambient pressure photoemission (NAP-XPS), real-time monitoring of the oxide growth was finally made possible.

Here, we present a NAP-XPS study of the oxidation of the Si(111)-7×7 surface under O_2 atmosphere using the set-up of the LCPMR (Sorbonne Université) installed at TEMPO beamline, SOLEIL. The clean reconstructed surface was exposed to dry oxygen at room temperature under pressures ranging from 10^{-7} to 1 mbar, and the Si 2p core-level (suboxide distribution and Fermi level position in the gap) and secondary electron energy distribution curve (work function) were monitored as a function of time. Two regimes are observed: a regime of low oxygen coverage where O_2 adsorption and decomposition on surface adatoms dominates the process, and a regime where a continuous SiO_2 layer has formed and O_2 seeks to fit into the free interstices of amorphous silica inducing a change of surface dipole probably due to ozonyl species stabilized by the dense SiO_2 network[3]. By solving longstanding questions that had previously been addressed only by theoretical calculations, this real-time XPS experiment illustrates the interest of giving a complete electron energy scheme of a surface being oxidized under "realistic" NAP conditions.

[1] Himpsel, F.; McFeely, F.; Taleb-Ibrahimi, A.; Yarmoff, J.; Hollinger, G. Microscopic Structure of the SiO_{2}/Si Interface. *Phys. Rev. B* **1988**, *38*, 6084–6096.
[2] Jolly, F.; Rochet, F.; Dufour, G.; Grupp, C.; Taleb-Ibrahimi, A. Oxidized Silicon Surfaces Studied by High Resolution Si 2p Core-Level Photoelectron Spectroscopy Using Synchrotron Radiation. *J. Non. Cryst. Solids* **2001**, *280*, 150–155.
[3] Bongiorno, A.; Pasquarello, A. Multiscale Modeling of Oxygen Diffusion through the Oxide during Silicon Oxidation. *Phys. Rev. B - Condens. Matter Mater. Phys.* **2004**, *70*, 1–14.

Internal oxidation of iron-silicon model alloys during simulated annealing after hot rolling

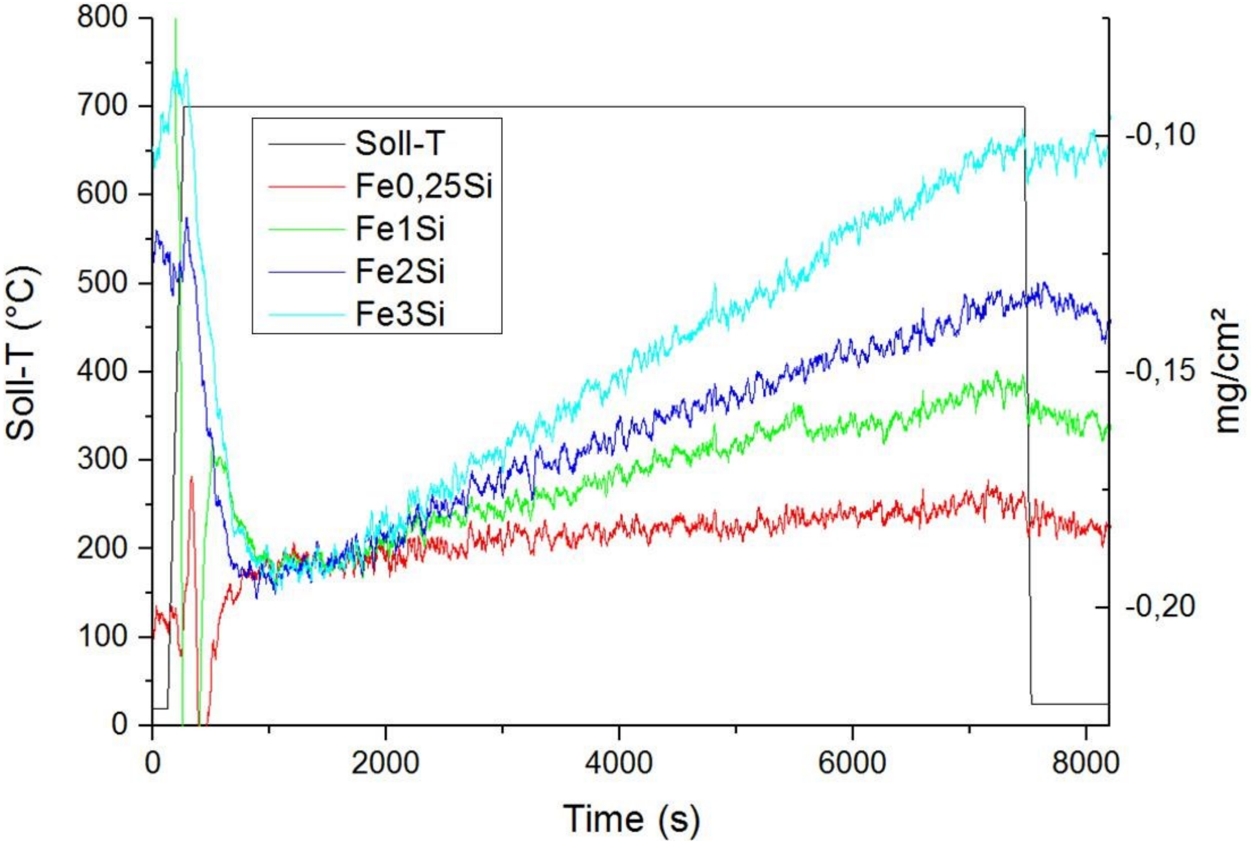
Cauê Corrêa da Silva[1*], Michael Rohwerder[2]

[1] *Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany*

...

* *c.dasilva@mpie.de*

Internal oxidation of lesser noble alloying elements occurs in several steel grades as a side effect of heat treatment, e.g. annealing, what might be harmful for the desired properties and further processing steps. Thermogravimetric analysis indicates that the internal oxidation of iron-silicon model alloys is determined by the oxygen uptake, which increases with the silicon content. Even when the oxygen uptake is boosted by a 5 nm-thick silicon coating, it remains linear across time. Nevertheless, the initial oxidation phenomena during annealing are concealed by apparent mass changes due to gas flow and surface roughness effects, that most likely are correlated to phase changes on the surface of the sample during heating. Therefore is NAPXPS the right technique to better assess the very first steps of native iron oxide reduction and more stable oxide formation, as well as to unveil the kinetics of the oxide formation during annealing and during cooling.



The Impact of Mo and W on the oxide evolution of Ni-Cr Alloys

Cameron Volders[1], Valentina Angelici Avincola[1], Gopalakrishnan Ramalingam[1], Irdawikanari Waluyo[2], John Perepezko[3], Petra Reinke[1*]

[1] University of Virginia, Department of Materials Science and Engineering, 395 McCormick Rd., Charlottesville, VA 22904, U.S.A.
[2] National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973
[3] University of Wisconsin-Madison, Department of Materials Science and Engineering, 1509 University Avenue, Madison, WI 53706
...

* *pr6e@virginia.edu*

Ni-Cr alloys are highly coveted as they exhibit a combination of superior corrosion resistance and high-temperature strength, which allow these alloys to be used in a number of challenging environments. The properties of this system are further enhanced by the addition of minor alloying elements such as Mo and W. In example, the addition of Mo is known to reduce catastrophic degradation events such as pitting and crevice corrosion. The current work performed a series of *in-operando* oxidation experiments with the use of Ambient Pressure-X-ray Photoelectron Spectroscopy (AP-XPS) on the following alloy concentrations; (1) Ni-15Cr, (2) Ni-15Cr-6Mo and (3) Ni-15Cr-6W by weight percent. The objective was to better understand how the addition of Mo and W affects the oxide evolution of NiCr alloys and how that contributes to enhancing corrosion resistance of this alloy system. The primary results to be discussed in this presentation will include a direct comparison of the nucleation and oxide evolution for Ni-15Cr and Ni-15Cr-6W at T = 500 °C and $p(O_2) = 10^{-6}$ torr. The addition of W in the alloy resulted in the suppression of any Ni-oxide species while enhancing the growth of the desired Chromia layer and different models to explain this impact will be presented. Another important result is the surface segregation of Cr for these alloys prior to oxidation as it controls the initial nucleation of the different oxide species.

E) Instrumentation

Toward Near Ambient Pressure Scanning Photoemission Imaging and Spectromicroscopy for in situ and in operando characterization of Fuel Cell components

Matteo Amati*[1], Patrick Zeller[1], Luca Gregoratti[1]

[1] *Elettra - Sincrotrone Trieste S.C.p.A. di interesse nazionale, Strada Statale 14 - km 163.5 in AREA Science Park, 34149 Basovizza, Trieste, ITALY*

…

* *matteo.amati@elettra.eu*

Fuel-Cells are electrochemical devices providing efficient and environmentally friendly production of electricity directly converting the electrons exchanged in a redox reaction into electric current. One of the still unresolved issues is the limited durability of components that deteriorate the performance.

The authors have developed photoemission imaging and spectromicroscopy methodology based on the Scanning PhotoEmission Microscope (SPEM) to simultaneously overcome the two limitations of the XPS technique, i.e. lack of spatial resolution and UHV requirements [1]. Those solutions allow chemical and morphological analysis of cell components, providing information under operation conditions.

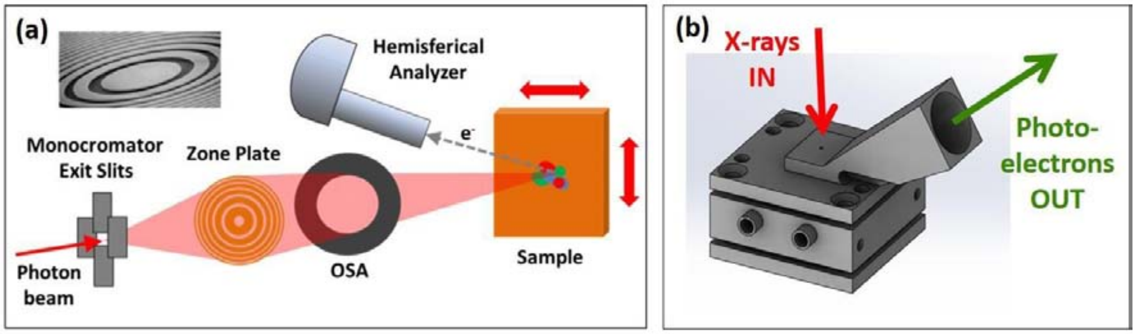


Figure: (a) SPEM Layout, (b) Effusive Cell for APXPS microscopy

SPEM (figure) uses a direct approach to add the spatial resolution to XPS i.e a small focused X-ray photon probe to illuminate the sample. The focusing of the X-ray beam is performed by Zone-Plates and samples surface is mapped by scanning the sample with the focused beam. X-ray beam can be downsized to a diameter of 130 nm, allowing imaging resolution of less than 50 nm with an energy resolution of 200 meV.

To overcome the UHV requirement an effusive cells (figure) where high- and low-pressure regions are separated by small apertures of few hundreds micrometers, for photons delivery and photoelectrons collection, was developed. The pressure inside the cell can be raised up to mbar while the pressure in the main chamber remains in UHV. Four isolated electrical connections are available for heating and biasing of sample.

Results on the in-situ and in-operando study of Fuel-Cell components performed at the Escamicroscopy beamline@ ELETTRA synchrotron will be presented.

[1] http://dx.doi.org/10.1002/cctc.201500637.

APXPS activities at LNLS: present and future

Daniela C. Oliveira[1], Flavio Vicentin[1] and Tulio C. R. Rocha[1*]

[1] *Brazilian Synchrotron Light Laboratory, Brazilian Center for Research on Energy and Materials, Av. Giuseppe Maximo Scolfaro, 10.000, Campinas, Brazil*

...

* *tulio.rocha@lnls.br*

The Brazilian Synchrotron Light Laboratory (LNLS) has an endstation dedicated to XPS of liquid-gas interfaces since 2010 based on a Scienta spectrometer, which is used at the undulator beamline U11-PGM. However, the measured spectra suffered from instabilities which limited its usability in atmospheric problems, which require reliable quantification. The stability of both intensity and energy scale of XPS measurements are of the utmost importance for quantitative measurements. This involves the stability of the spectrometer, the beamline, and the liquid jet sample introduction system. Recently, the whole endstation was upgraded to fulfill these stability requirements. In this work, we report the commissioning results of model experiments performed to investigate the stability, with the aim to estimate error bars on energies and intensities obtained from photoelectron spectra recorded with this setup. We also show results from our investigation of the surface propensity (partitioning) of certain molecules of atmospheric interest. We will also discuss the future plans for APXPS activities for Sirius, the new 4th generation storage ring under construction in Campinas.

Water/methanol solutions characterized by liquid μ-jet XPS and DFT – the methanol hydration case

E. Pellegrin[1*], V. Perez-Dieste[1], C. Escudero[1], J. Fraxedas[2], P. Rejmak[3], N. Gonzalez[1], A. Fontsere[1], J. Prat[1], and S. Ferrer[1]

[1] CELLS-ALBA, Carrer de la Llum 2-26, Cerdanyola del Valles, Barcelona, 08290, Spain
[2] Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, Barcelona, 08193, Spain
[3] Institute of Physics PAS, Lotnikow 32/46, Warsaw, 02-668, Poland
...

* *epellegrin@cells.es*

The advent of liquid μ-jet setups as proposed by Faubel and Winter – in conjunction with X-ray Photoemission Spectroscopy (XPS) – has opened up a large variety of experimental possibilities in the field of atomic and molecular physics. In this study, we present first results from a synchrotron-based XPS core level and valence band electron spectroscopy study on water (10^{-4}M aqueous NaCl solution) as well as a water/methanol mixture using the new ALBA liquid μ-jet setup (see Fig. 1). The experimental results are compared with simulations from density functional theory regarding the electronic structure of single molecules, pure molecular clusters, and mixed clusters configurations as well as with previous experimental studies. We give a detailed interpretation of the core level and valence band spectra for the vapour and liquid phases of both sample systems. The resulting overall picture gives insight into the water/methanol concentrations of the vapour and liquid phases as well as into the local electronic structure of the pertinent molecular clusters under consideration, with a special emphasis on methanol as the simplest amphiphilic molecule capable of creating hydrogen bonds.

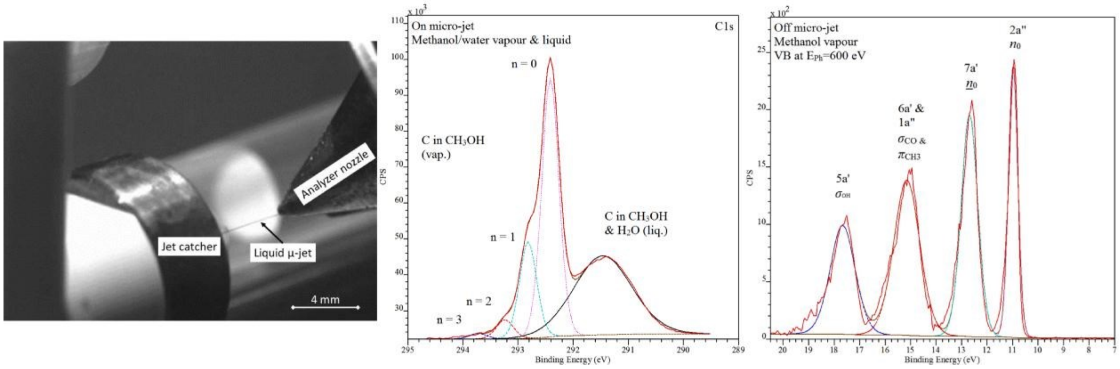


Fig. 1. Left: Photograph of the liquid μ-jet setup at the Circe NAPP end station. The conical electron analyzer entrance nozzle as well as the jet catcher can be seen on the right and left hand side, respectively. Center: C1s XPS lines of the methanol/water liquid μ-jet taken at 750 eV photon energy at a chamber pressure of 1 mbar. Right: Valence band XPS data from methanol vapour taken at 600 eV photon energy at a chamber pressure of 1 mbar.

An electrochemical cell on a SPECS/Omicron sample plate?

Dr. Robert Temperton[1*], Dr. James O'Shea[1], Dr. Lee Johnson[2], Dr. Darren Walsh[2], Dr. Robert Jones[2]

[1] *School of Physics, University of Nottingham, UK*
[2] *School of Chemistry, University of Nottingham, UK*
...

* *robert.temperton@nottingham.ac.uk*

In-operando AP-XPS, whereby a liquid-solid interface is under external electrochemical control, has so far relied on specialist apparatus, such as the dip and pull approach[1], or cells with a specialist electron-transparent electrodes, such as a graphene membrane[2]. Despite AP-XPS growing in popularity, these electrochemical strands of the technique remain inaccessible to many users, despite the increasing prevalence of lab-source instruments. A majority of these lab instruments have sample environments that are not inherently well suited to in situ electrochemical measurements without serious modification to the apparatus. This study presents preliminary in-progress work exploring the possibility of a low-cost two electrode electrochemical cell, mounted on a standard "flag" style sample plate, appropriate for use with standard lab-source AP-XPS instruments. Specifically, we investigate the viability of using very fine mesh or microporous working electrodes used to wet or contain a small liquid reservoir.

References

[1] Axnanda, S. *et al*. *Sci. Rep.* **5,** 9788 (2015).
[2] Velasco-Velez, J. J. *et al*. *Angew. Chemie Int. Ed.* **54,** 14554–14558 (2015).

The University of Leeds Near-Ambient Pressure XPS Facility

Sven L.M. Schroeder[1,2*], Elizabeth A Willneff[3]

[1] *School of Chemical and Process Engineering, University of Leeds, LS2 9JT Leeds, United Kingdom*
[2] *Diamond Light Source, Harwell Science and Innovation Campus, OX11 0DE Didcot, United Kingdom*
[3] *School of Design, University of Leeds, LS2 9JT Leeds, United Kingdom*
...

* *s.l.m.schroeder@leeds.ac.uk*

We will report initial results from a new laboratory NAP XPS facility that has been commissioned at the University of Leeds, UK. A flexible multi-user infrastructure for engaging new user communities has been established, which is configured around a Specs EnviroESCA system coupled to a multi-wavelength UHV XPS system. The EnviroESCA provides a modular, flexible instrument for NAP XPS on a wide variety of samples and environmental studies. The Leeds instrument features additionally a gas-cluster ion beam (GCIB) Ar source for gentle depth profiling a wide variety of samples with minimal ion beam damage of the surrounding substrate. The multi-wavelength XPS features Al, Zr, Ag and Cr anodes covering photon energies into the HAXPES range. Samples can be transferred between instruments, or from other sample preparation platforms, via either ultra-high vacuum or environmental suitcases. The EnviroESCA is particularly user-friendly, lowering barriers to entry and accommodating virtually any sample morphology, including liquids. Internal plasma cleaning of the analysis chamber minimizes cross-contamination between different materials and user experiments. The EnviroESCA also lends itself very well to high-throughput studies because multiple samples can be mounted on the sample plate and extremely short times are required for exchanging sample plates. For electrically insulating samples, charge neutralization is reliably and reproducibly achieved using the self-compensation via gas phase pair formation by energetic electrons emitted from the sample. Using examples from our facility commissioning we will outline the capabilities of the facility, discuss potential research areas, and show first results from the user community.

Recent development in XPS and Ambient Pressure XPS techniques

L. Walczak[1,*], M. Dzierżęga[1], Ch. Kirschfeld[1], M. Bugla[1], M. Florek[1], S. Żuk[1], A. Stanik[1], L. Nittler[1], and A. Szatkowski[1]

[1] *PREVAC Sp z o.o., Rogow, Poland*

...

* *l.walczak@prevac.eu*

Many important processes such as energy conversion, electrochemical, corrosion and biological processes take place at solid-gas and solid-liquid interfaces [1-3]. X-ray photoelectron spectroscopy (XPS) is the most powerful technique for understanding of these processes at the atomic level and it is the key to improving the performance of novel battery generation or renewable energy sources such as solar, wind or hydropower energy conversion devices. We would like to promote the latest equipment, technology solutions and innovations for the photoelectron spectroscopies field. Here it will be presented an innovative and compact spectrometers for the routine X-ray photoemission spectroscopy and ambient pressure photoemission spectroscopy for study of important phenomena in the current research. The design, construction, and technical parameters of new analyser will be presented. We will report the research results of XPS measurements conducted on the photovoltaic [4], catalytical [5] or bio-materials. Moreover, it will be demonstrated the analyser operation in ambient pressure. Also the results of interaction of oxygen and surface alloy will be presented, in order to permit complete characterization for the different pressure and temperature conditions.

References

[1] B. Lassalle-Kaisera et al. J. Electron Spectrosc. Relat. Phenom. 221, 18-27 (2017).
[2] Y. Takagi et al. Phys.Chem.Chem.Phys. 19, 6013 (2017).
[3] Z. Y. Ong el. al, Appl. Mater. Interfaces 9, 39259–39270 (2017).
[4] L. K. Preethi el al. Energy Technol., 5, 1-10 (2017).
[5] U. Filek el. al, Appl. Catal. A – submitted.

Libraries of Core Level Binding Energies: The Added Value of NAP XPS for Analysing Chemical Shifts in Organic Systems

Elizabeth A, Willneff,[2] Sin-Yuen Chang,[1,3] Sven L.M. Schroeder[1,3*]

[1] *School of Chemical and Process Engineering, University of Leeds, LS2 9JT Leeds, United Kingdom*
[2] *School of Design, University of Leeds, LS2 9JT Leeds, United Kingdom.*
[3] *Diamond Light Source, Harwell Science and Innovation Campus, OX11 0DE Didcot, United Kingdom*
...

* *s.l.m.schroeder@leeds.ac.uk*

An added value of laboratory NAP XPS is the ability to study organic materials with vapour pressures that are not compatible with UHV environments. We are assembling a growing library of N1s binding energies of small organic molecules. A total of 32 compounds have so far been measured as crystalline powders, including amino acids, aliphatic and aromatic carboxylic acids, and more complex nitrogen bases, such as imidazole and derivatives.[1-4] N1s is very sensitive to hydrogen bonding, polymorphism and Brønsted transfer of protons. Laboratory NAP XPS has allowed us to also characterize materials with significant vapor pressures at room temperatures, with much faster turnaround than in UHV systems. Imidazole for example would need careful preparation and constant cooling to maintain UHV conditions. Moreover, we will show that the use of approximately 10 mbar of Ar in the sample chamber reliably neutralizes surface charges, enabling high throughput studies of organic materials.

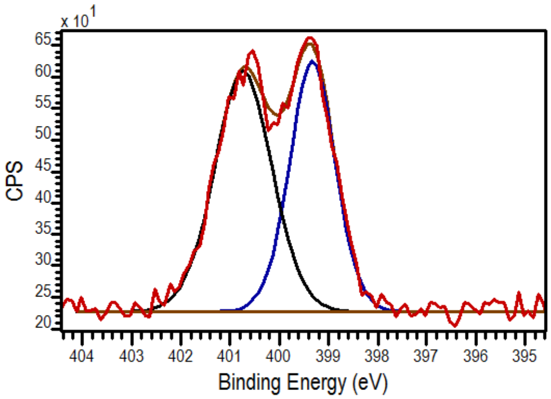


Figure 1. N1s spectrum of imidazole (vapour pressure: 3×10^{-3} mbar)

References

[1] J. S. Stevens, S. J. Byard, C. C. Seaton, G. Sadiq, R. J. Davey and S. L. M. Schroeder, *Phys. Chem. Chem. Phys.*, 2014, **16**, 1150-1160.
[2] J. S. Stevens, S. J. Byard, C. A. Muryn and S. L. M. Schroeder, *J. Phys. Chem. B*, 2010, **114**, 13961-13969.
[3] J. S. Stevens, C. R. Seabourne, C. Jaye, D. A. Fischer, A. J. Scott and S. L. M. Schroeder, *J. Phys. Chem. B*, 2014, **118**, 12121-12129.
[4] J. S. Stevens, A. Gainar, E. Suljoti, J. Xiao, R. Golnak, E. F. Aziz and S. L. M. Schroeder, *J. Phys. Conf. Ser.*, 2015, **712**, 012136.

Revitalization of ALS Tender X-ray APXPS Beamline

Yifan Ye[1,2,3], Hongyang Su[1,4], Kyung-Jae Lee[1,5], Nord Andressen[6], Monika Blum[1], Zahid Hussain[1], Ethan J. Crumlin[1,3*]

[1] *Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720*
[2] *Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, CA 94720*
[3] *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720*
[4] *Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China;*
[5] *Department of Physics and Photon Science, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, South Korea;*
[6] *The Center for X-ray Optics, Lawrence Berkeley National Laboratory, Berkeley, CA 94720*
...

* *EJCrumlin@lbl.gov*

APXPS brought new life to a 20+ year-old beamline at the Advanced Light Source (ALS). Beamline 9.3.1 is a bending magnet beamline that had a very fragile double crystal monochromator that was no longer operational as of late 2016. With the interest and excitement generated from the various new types of science that could be possible using APXPS at tender X-rays to probe solid/liquid interfaces we were able to procure the financial resources to upgrade all of the optical elements for the beamline: mirror one (M1), double crystal monochromator (DCM), and mirror two (M2). This talk will provide an overview of the beamline upgrade including the new optical layout, some lessons learned going through the upgrade. Additionally, we will show some of our initial commissioning results including scientific results from our initial experiments as we continue to optimize the beamline and start to reignite our science program. We will be opening access to this beamline on a limited basis through 2019 as we continue to optimize the beamline and expand the beamlines functionality.

Spatially resolved XPS measurements at NAP conditions

Patrick Zeller*, Matteo Amati, and Luca Gregoratti

Elettra - Sincrotrone Trieste ScPA, Area Science Park, SS14-Km163.5, 34149 Basovizza-Trieste, Italy

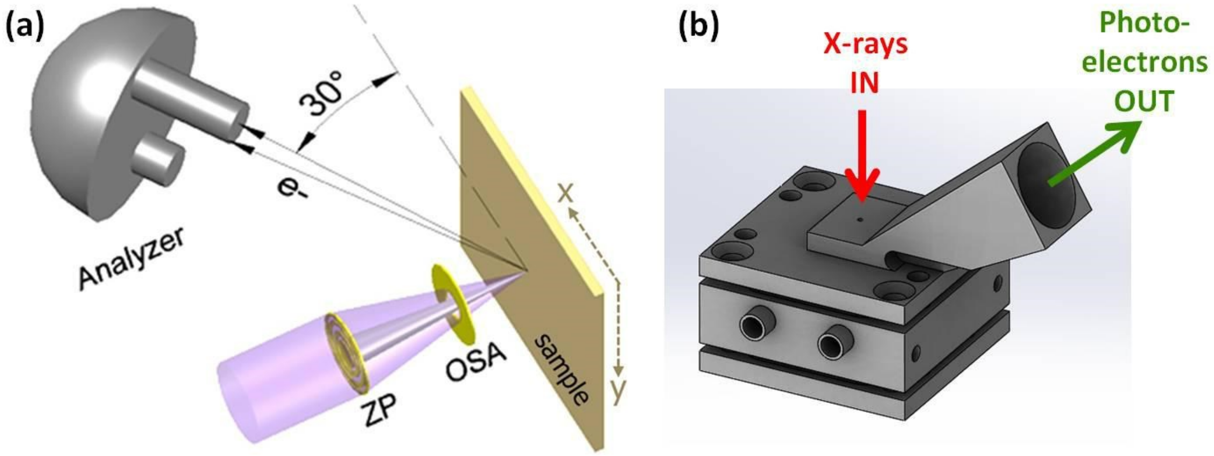
…

* *Patrick.Zeller@elettra.eu*

The investigation of complex systems in heterogeneous catalysis requires not only near ambient pressure (NAP) conditions but often the samples are inhomogeneous by exhibiting different grains or coexisting phases (materials gap) that must also be overcome. This can be achieved by combining NAP conditions with spatially resolved measurements. Recent examples of in situ, spatially resolved measurements at NAP conditions will be presented. [1, 2]

The Scanning Photoemission Microscope (SPEM), hosted at the ESCAmicroscopy beamline at the Elettra synchrotron light source, uses a focused, submicron X-ray probe to illuminate the sample. A Fresnel type Zone plate (ZP) in combination with an order sorting aperture (OSA) is used to focus the X-ray beam. The X-ray beam can be downsized to a diameter of 130 nm. The SPEM can be operated either in imaging mode or by acquiring XPS spectra from a microspot. The overall energy resolution is better than 200 meV.[3] To achieve NAP conditions a cell containing the sample can be placed within the SPEM chamber.[1, 2] The cell contains small pinholes with diameters of 200 - 400 µm fitting the geometry of the SPEM for the focused X-ray beam and the emitted photoelectrons, respectively. Their impedance allows pressures up to 0.1 – 1 mbar within the NAP cell while maintaining a suitable pressure in the SPEM chamber. Available sample temperatures are up to 600 °C.

[1] L. Gregoratti et al. Top. Catal. 61, (2018) 1274–1282
[2] H. Sezen et al. Surf. Interface Anal. (2017) doi:10.1002/sia.6276.
[3] https://www.elettra.eu/elettra-beamlines/escamicroscopy.html.



HIPPIE, The new ambient pressure X-ray photoelectron spectroscopy beamline at MAXIV

Suyun Zhu[1*], Andrey Shavorskiy[1], Jan Kundsen[1,2], Joachim Schnadt[1,2]

[1] *MAX IV Laboratory, Lund University, Box 118, 221 00 Lund, Sweden*
[2] *Division of Synchrotron Radiation Research, Department of Physics, Lund University, Box 118, 221 00 Lund, Sweden*
...

* *suyun.zhu@maxiv.lu.se*

HIPPIE is a state-of-the-art beamline for ambient pressure X-ray photoelectron spectroscopy (APXPS) at MAX IV laboratory in Sweden. The combination of the exceptional performance of the 3 GeV ring with an innovative design of the experimental station results in a beamline which is outstanding not just in a pure electron spectroscopy context, but which also significantly expands the scientific issues that can be addressed.

An APXPS endstation will permit in situ XPS and X- ray absorption spectroscopy (XAS) experiments at pressures up to 30 mbar as well as under ultrahigh vacuum (UHV) conditions. The photon energy range is 310 to 2000 eV with variable polarization and very high flux and resolution. HIPPIE endstation consists of an analysis chamber equipped with a hemispherical Scienta-Omicron HiPP-3 electron energy analyzer, an ambient pressure experimental cell (AP Cell) can be docked to the analyzer for ambient pressure experiments, when the AP cell is retracted UHV experiments can be performed. The analysis chamber is also equipped with a Bruker PM-IRAS instrument for simultaneous recording of APXP/APXA spectra and PM -IRA spectra; likewise, the composition of gas/vapour in the AP cell can be monitored by mass spectroscopy. Furthermore, different sample environments have been developed, including high pressure re-actor, electrochemistry cell, photo catalysis cell, high temperature cell and biological sample cell.

Notes

List of participants

Bluhm Hendrik
Artiglia Luca
Mun B. Simon
Ghafari Aliakbar
Rupprechter Günther
Eralp Erden Tugce
Waluyo Iradwikanari
Chuang Cheng-Hao
Lim Hojoon
Jung Moonjung
Kim Dongwoo
Prakash Ravi
Herman Gregory
Lee Kyung-Jae
Ahmad Mais
Walczak Lucasz
Ortega Enrique
Velsco-Vélez Juan
Gallet Jean-Jacques
Osterwalder Juerg
Coelho de Olivera Daniela
Reinke Petra
Besmehn Astrid
Younas Muhammad
Boucly Anthony
Corrèa da Silva Caué
Bukhtiyarov Valerii
Timm Rainer
Freitas de Isabel
Kokkonen Esko
He Yang
Rossmeisl Jan
Deng Yuchen
Song Fei
Held Georg
Zheng Jiang
Vogel Dirk
Peng Mi
Yang Hunayu
Pèrez-Dieste Virginia
Baker Robert
Pellegrin Eric
Kaderi Akbar bin
Perez Ramirez Lucia
Li Qingtian
Jiang Chenggong
Tayler-Barrett Benjamin
Kratky Tim
Duchoň Tomáš
Rehman Foqia
Rocha Tulio
Wang Chia-Hsin
Zhu Suyun
Yang Yaw-Wen
Michaelides Angelos
Ding Ma
Escudera Carlos
Bartling Stephan
Favaro Marco
Concepcion Patricia
Han Yong
Mao Baohua
Zhi Liu
Villar García Ignacio Jose
Mueller David
Zeller Patrick
Nemsak Slavomir
Bukhtiyarov Andrey
Amati Matteo
Lechner Barbara
Crumlin Ethan
Skorupska Katarzyna
Mom Rik
Paul Dietrich
Thissen Andreas
Hartwig Caroline
Sulzmann Frederick
Yu Yi
Willneff Elizabeth
Zhu Qingjun
Fraxedas Jordi
Ghafari Ali
Knop-Gericke Axel
Klyushin Alexander
Kathyola Thokozile
Freiberg Anna
Blomberg Sara
Nicholls Rachel
Temperton Robert
Sánchez Jaime
Schnadt Joachim
Haevecker Michael
Kjærvik Marit
Starr David
Jürgensen Astrid
Claussen Iris
Grinter David
Seymour Jake
Masuda Takuya
Stoerzinger Kelsey
Papp Christian
Ma Ding
Ganduglia-Pirovano Maria Veronica
Roldan Beatriz
Schlögl Robert
Savinova Elena
Frevel Lorenz
Tiedtke Marion
Damm Dorothea
Neeb Matthias
Clark Pip