

24th North American Catalysis Society Meeting

Highlights in emission control and zeolites from the biennial US event

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Introduction

The 24th North American Meeting of the Catalysis Society (NAM) was held from 14th to 19th June 2015 at the David L. Lawrence Convention Center in Pittsburgh, Pennsylvania, USA, with the Pittsburgh-Cleveland Catalysis Society as hosts (1). This biennial meeting is recognised as the premier conference about the science and applications of catalysis and catalytic processes and as a forum to explore their boundaries and shared concepts with homogeneous catalysis, electrocatalysis and photocatalysis.

There were approximately 1300 delegates from academia and a range of industries such as Chevron, BASF, Exxon Mobil, Synfuels China, Zeolyst, Dow, Sabic, Albemarle, Clariant, Haldor Topsøe, Dupont, BP, GM, Cummins and Velocys. It included three plenary lectures, presented by the recipients of the Michel Boudart, Eugene Houdry and Paul H. Emmett awards; 20 keynote addresses presented by the foremost leaders in the field; more than 400 oral presentations distributed along six parallel sessions; and about 600 posters on three of the days.

A wide range of topics were covered: Biomass Conversion; Catalysis for Fossil Energy; Coal, Petroleum, and Natural Gas; Catalyst Characterisation; Catalyst Design and Synthesis; Catalyst Modelling and Simulation; Environmental Catalysis; Fundamentals of Catalysis; Industrial and Fine Chemicals; Photocatalysis and Electrocatalysis; and Reaction Engineering. This selective review will focus on some highlights from Environmental Catalysis. There was not a specific programme for zeolites; however, there were various sessions dealing with zeolites.

Copper Zeolite Selective Catalytic Reduction

There were a large number of talks focusing on different aspects of Cu zeolite selective catalytic reduction (SCR) technology. A presentation by Feng Gao (Pacific Northwest National Laboratory (PNNL), USA) on 'Effects of Si/Al Ratios and Alkali Cocations on Cu/SSZ-13 NH₃-SCR Catalysts: Active Cu Species, Roles of Brønsted Acidity, and Hydrothermal Stabilities' claimed that with dehydrated Cu/SSZ-13, at low Cu loading, Cu was present in the D6Rs, while at higher loadings, Cu was present in both D6Rs and 8R. However, on hydration, all the Cu²⁺ is fully hydrated and less bound to the framework. It was shown that Cu-SSZ13 does not dehydrate until 200°C in flowing dry air. With a silica-to-alumina molar ratio (SAR) of 70, there was some evidence of Cu dimers, while at SAR 24, there was no evidence of Cu dimers. The presence of Brønsted acidity was shown to be essential for Cu location and it was proposed that

H⁺ was involved in the Cu redox process. Analysis of activity data indicated that although monodispersed Cu was best for SCR, it was poorer for NO oxidation, with dimers being more active.

In his presentation 'Molecular Elucidation of the Cu Redox Cycle Underlying NO_x Selective Catalytic Reduction in Cu-SSZ-13' Christopher Paolucci (University of Notre Dame, USA) described the use of modelling and extended X-ray absorption fine structure (EXAFS) analysis to show the state of the Cu under reaction conditions. Reduction to Cu⁺ is observed in the absence of molecular oxygen by 400°C and under SCR conditions a mixture of both Cu²⁺ and Cu⁺ is observed (2). With ammonia, modelling predicts that Cu⁺ will form a linear dimer (H₃N-Cu-NH₃)⁺, while Cu²⁺ will form a four-coordinated species with two framework oxygens and two ammonias. It was also claimed that the turn over frequency (TOF) for SCR is the same for Cu-chabazite (CHA) and beta polymorph A (BEA).

Atish Parekh (Purdue University, USA) presented 'Cu(I)-Cu(II) Redox Chemistry on Isolated Cu Ions for Ammonia Standard SCR', an X-ray absorption near edge structure (XANES) study on the effect of SCR feed components on Cu oxidation state. This was a complementary study to Paolucci's presentation. Using a nitric oxide, ammonia, oxygen, water and carbon dioxide feed, increasing the NO concentration led to an increase in Cu⁺ to a maximum of 50%. Removing the NH₃ led to only Cu²⁺ present and removing O₂ led to only Cu⁺.

Jean-Sabin McEwen (Washington State University, USA) gave a detailed study of XANES spectra through modelling in his talk 'Spectroscopic Properties of Cu-SSZ-13 in the SCR of NO_x: Computational IR and XANES Study'. He was able to show that the partial density of states (PDOS) is sensitive to the Cu location (dehydrated) and may be resolvable in XANES spectra. With hydrated spectra for both Cu⁺ and Cu²⁺ an increase in the XANES peak is expected due to the Cu having a higher symmetry as it is not bound to the framework. With NH₃, a change in the XANES peak is expected due to NH₃ coordination rather than Cu²⁺ reduction. This group has also studied Cu-silico-alumino-phosphate (SAPO)-34.

Peter Vennestrøm (Haldor Topsøe A/S Research & Development Kgs, Denmark) presented 'Solid-State Ion-Exchange of Cu into Zeolites by Ammonia at Low Temperatures'. Building on the observation that a mixture of copper(II) oxide and H-MFI zeolite under SCR conditions at 250°C gives active SCR catalysts, the work was extended to CHA and BEA, although

450°C was required for CHA to get good activity. *In situ* X-ray diffraction (XRD) showed that under NO+NH₃ and NH₃-only feeds, copper(I) oxide was formed. The presenter proposed that [Cu(NH₃)₂]⁺ is the active migration species. The catalyst showed similar SCR activity to ion-exchanged Cu-CHA with a solid state exchanged sample, but needed much higher amounts of Cu, suggesting the process is not 100% efficient.

Other SCR Systems

János Szanyi (PNNL, USA) discussed ion exchange of ammonium-CHA with iron sulfate under nitrogen to give Fe-SSZ-13 in his talk 'Kinetic and Spectroscopic Characterization of Fe-SSZ-13 NH₃ SCR Catalysts'. Ultraviolet-visible (UV-vis) spectroscopy shows that even fresh catalysts have FeO_x clusters and iron (III) oxide in addition to well-dispersed Fe. SCR activity is poorer than Cu-CHA with a full gas mix. This appears to be due to H₂O inhibition, with suppression of both NO and NH₃ oxidation by H₂O. On hydrothermal ageing, an increase in Fe oxide species is observed. Use of NO diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) shows formation of Fe²⁺-NO species, although initial vacuum treatment appears to reduce the Fe. The Fe is present in both D6R and 8R sites but only the Fe in 8Rs sites is able to take part in the redox cycle.

Erisa Saraci (Universität Leipzig Institute of Chemical Technology, Germany) presented 'SCR-DeNO_x on Mesoporous and Hierarchically Structured V₂O₅/TiO₂ Mixed Oxide Catalysts'. This covered the preparation of vanadium-titania catalyst by sol-gel with the inclusion of polyethylene glycol (PEG) to generate 1 μm macropores as well as normal 4 nm mesopores. The presenters found a 200% increase in SCR activity with added macropores overcoming significant mass transport issues in the non-PEG material.

Stanislaw Dzwigaj (Sorbonne University, France), in his presentation 'The Promotion of Co-BEA Zeolites by Copper for SCR of CO with NH₃', aimed to isomorphously substitute cobalt and Cu into BEA, by dealumination of aluminium-BEA to give SAR 1500 and then adding Co or Cu nitrates. He showed substitution by loss of silicon hydroxide nests and UV-vis showed no cobalt oxide species until 3.5 wt% Co loading. Hydrogen temperature-programmed reduction (H₂-TPR) showed very stable Co species not reducing until 1120 K. Pure Co-BEA only showed NH₃-SCR activity over 450 K with a peak at around 600 K. Addition of Cu brought this down to approximately

500 K. It was not clear whether this provides any advantage over standard ion-exchanged Cu BEA.

The presentation by Shijian Yang (Nanjing University of Science and Technology, China) titled 'Origination of N₂O from NO Reduction by NH₃ over MnO_x-CeO₂: Mechanism and Effect Factors' showed the MnO_x-CeO₂ system suffers from poor sulfur dioxide tolerance and low N₂ selectivity. N₂O formation appears to come from NH₃ oxidation rather than directly from the SCR reaction. H₂O inhibits the SCR at low temperature but improves N₂ selectivity.

There were also a number of hydrocarbon-SCR presentations generally concerned with silver-alumina catalysts.

NOx Storage and Reduction

Laura Righini (Politecnico di Milano, Italy) presented 'The Role of Pt/Ba Interaction on the NOx Storage and Reduction Processes over PtBa/Al₂O₃ LNT Catalysts'. It is commonly accepted that during the lean phase nitrogen oxides (NOx) are stored in the form of nitrites and nitrates over the platinum-barium on alumina lean NOx trap (LNT) catalyst. Nitrite and nitrate routes were reviewed and it was proposed that the reduction of stored NOx is not initiated by thermal decomposition but instead proceeds through a Pt catalysed pathway. When H₂ is used as reductant, it is activated by forming Pt-H species. Then the reductant spills from Pt to Ba, where stored NOx are converted to N₂ and other by products. Alternatively, a reverse spillover of stored NOx from Ba to reduced Pt sites may also occur. In these processes, a major role of the Pt/Ba proximity is expected. Fourier transform infrared (FT-IR) spectroscopy and transient reactivity experiments were carried out to gain information on the surface and gas phase species to be able to understand the relevance of the Pt/Ba interaction on both the adsorption and reduction pathways.

Other DeNOx Systems

Joseph Theis (Ford Motor Company, USA) highlighted disadvantages of the current LNT formulation based on alumina, ceria and high Pt loading in his talk: 'Assessment of Low Temperature NOx Adsorbers for Cold-Start NOx Control on Diesel Engines'. These formulations rely on the oxidation of NO to NO₂ and storage of the NO₂ as nitrates, which would be difficult

to purge completely at low temperatures. A 'new' formulation was presented based on palladium on ceria to store and release NO directly and this was compared to model catalysts Pt/CeO₂, Pt/Al₂O₃ and Pd/Al₂O₃. Data on Pd on ceria-zirconia demonstrated 38% NOx trapping efficiency. Effects of H₂O and hydrocarbons (C₂H₄) on the NOx storage were assessed. It was found that higher concentration of C₂H₄ improves the storage at lower temperatures (90°C–160°C) with 59% efficiency and shifts the release temperature to higher values. No N₂O was formed during the test, therefore HC-SCR reaction was ruled out. The formation of alkyl nitrates/nitrites was proposed. When H₂O was present during the test, a reduction in efficiency of 11% occurred and this was likely to be related to competition for storage sites at low temperature. If the storage temperature during the test was increased, H₂O did not show any effect. The effect of the rich purge was also presented. The catalyst was purged at 300°C and cooled down under 'neutral' conditions. The catalyst was completely deactivated due to a change in oxidation state. Additional data comparing to model catalysts was also presented. The mechanism of storage for Pt/Al₂O₃ is based on the oxidation of NO to NO₂. It showed good NOx storage above 200 seconds in the Federal Test Procedure (FTP) cycle, but is not suitable for low temperature applications. High N₂O formation due to HC-SCR reaction also occurred. The Pd/Al₂O₃ catalyst had poor storage performance, suggesting that ceria is important.

Jason Loiland (University of Delaware, USA) gave a talk titled 'NO Oxidation Reaction Mechanisms over Microporous Materials'. The NO oxidation reaction was studied over CHA, MFI and BEA zeolites, looking at the effect of the SAR and the extra framework cation (H⁺, Na⁺ and siliceous) on NO oxidation rates. Infrared experiments were performed to monitor N_xO_y surface species formed on the catalysts. The authors demonstrated that NO⁺ species are coordinated to framework aluminium sites. These species are directly involved in the catalysis at temperatures above 423 K, explaining the catalytic activity improvement.

Joon-Hwan Choi (Korea Institute of Materials Science, South Korea) presented a new catalyst coating technique with very strong adhesion strength to metal substrate and higher porosity in 'De-NOx SCR Catalyst Coating with Strong Adhesion to Metal Honeycomb Substrate'. The technique is based on aerosol deposition and no binder is needed.

Methane Oxidation

James B. Miller (Carnegie Mellon University, USA) discussed 'Support Roles in Pd Catalysts for Total Methane Oxidation'. In this kinetic study of Pd supported on Al_2O_3 , CeZrO_x and CeO_2 for methane oxidation, dynamic light-off data were used to generate pseudo-Arrhenius plots and determine activation energies. Hysteresis and activation effects were investigated with repeated ramps up and down in temperature. It was found that Al_2O_3 -supported catalysts showed good initial activity followed by slow deactivation, CeZrO_x -supported catalysts showed poor initial activity and slow activations and CeO_2 -supported catalysts showed poor activity and little activation. A Mars-van Kevelen mechanism requiring both neighbouring reduced and oxidised Pd sites was proposed.

Henrik Grönbeck (Chalmers University of Technology, Sweden), in his talk 'Methane Oxidation over Palladium Oxide from First Principles', showed that taking a Pd metallic surface and applying O_2 led to the formation of Pd-O species by 167°C and a full PdO surface by 333°C . On passing CH_4 , CO_2 formation was observed at 333°C which corresponded to a relatively thick film of PdO (ordered PdO (101)) (3) (**Figure 1**). Formation of an ordered PdO (111) film was unstable with CH_4 and loss of activity was observed. Density functional theory (DFT) calculations suggested that CH_4 adsorption on a one-layer PdO (101) surface is unfavourable, but becomes favourable over a two-layer PdO (101) surface. It was proposed that surface Pd sites needed a sub-surface O to bind CH_3 . A detailed micro-kinetic model of 80 reaction steps was shown.

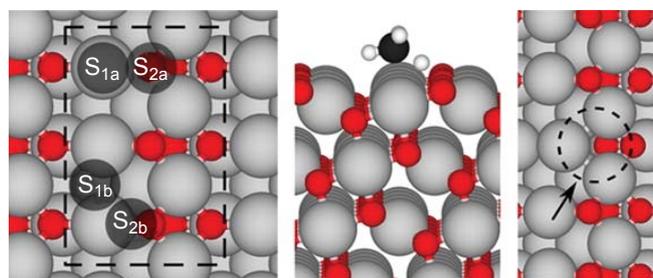


Fig. 1. (a) Top view of the PdO (101) surface with indication of the employed (3×1) surface unit cell and the different types of adsorption sites; (b) tilted view of the transition state for CH_4 dissociation; (c) structural model of a surface oxygen vacancy. Atomic colour codes: Pd (grey), O (red), C (black), H (white) (Reprinted with permission from (3). Copyright 2015 American Chemical Society)

Zeolites

Toshiyuki Yokoi (Tokyo Institute of Technology, Japan) discussed 'Improvement of Catalytic Activity in the MTO Reaction by Control of Location of Al Atoms in the Pores of ZSM-5'. Different structure-directing agents (SDAs) were used to control Al location in ZSM-5, for example the use of tetrapropylammonium (TPA) should only give Al at intersections. HC cracking (constraint index) was used to probe Al locations combined with ^{27}Al nuclear magnetic resonance (NMR) spectroscopy as differences in AlO_4 positions were observed.

Andrei Khodakov (Université Lille, France) presented a talk titled 'Influence of Zeolite Crystallite Size on the Activity and Stability of Hybrid Copper-Zeolite Catalysts for Direct Synthesis of Diethyl Ether', in which lutidene adsorption was used as a method to measure external zeolite acidity.

Trees de Baerdemaeker (KU Leuven Centre for Surface Chemistry and Catalysis (COK), Belgium) presented 'Introducing Catalytic Function in Zeolites Derived from Layered Precursors'. RUB-36, a ferrierite (FER)-like layer structure ($\text{SAR} = 200\text{--}\infty$), was used to introduce functionality and metal species. Addition of Fe *via* iron (III) chloride gave only isolated Fe species, which appear quite stable to reaction (benzylation of toluene). The crystals are dense, so mesoporosity can be introduced by base treatment, although this was shown to be quite damaging.

Manjesh Kumar (University of Houston, USA) gave a talk about the evolution of crystalline structure in zeolite gels, entitled 'Tailoring the Physicochemical Properties of Zeolite Crystals through Molecular Design'. With CHA, small amorphous particles are observed at short synthesis times, followed by aggregation, then crystallisation and conversion of small crystallites into large crystallites. It was shown that use of macromolecules could control crystal sizes, giving CHA crystals of 100 nm to 20 μm .

Jeffrey Rimer (University of Houston, Texas, USA) presented 'Time-Resolved *in situ* Imaging of Zeolite Surface Growth Reveals the Mechanism of Crystallization', a companion talk to the above. *In situ* solvothermal atomic force microscopy (AFM) was used to observe zeolite crystallisation and growth. Both molecular and nanoparticle deposition were observed on growing planes, with particle size being highly sensitive to the pH.

Michiel Dusselier (California Institute of Technology (Caltech), USA), in 'The Synthesis of SSZ-39 Using

Mixtures of Isomeric, Organic Structure Directing Agents', found SSZ-39 difficult to prepare at high yield and with the target SAR (for example 16 instead of 60). Also mordenite (MOR) and gismondine (GIS) impurities were found. A high SAR is desirable for methanol to olefins use as too many H⁺ sites lead to coking, but this was unsuccessful by direct synthesis.

Base Metal Catalysts for Emission Control Reactions

Masatoshi Sakai (Toyota Central R&D Laboratories, Aichi, Japan) presented 'Catalytic NO Reduction over Cu/CeO₂: Characterisation of Copper-Ceria Interface Active Sites'. Cu-CeO₂ catalysts prepared by Cu(OAc)₂ impregnation onto CeO₂ were studied in simple carbon monoxide-nitric oxide gas feeds. The onset of CO-NO reaction was observed at lower temperatures than over rhodium on ceria but full conversion did not occur until higher temperatures. There was no evidence of Cu incorporation into the CeO₂ lattice, although electron paramagnetic resonance (EPR) showed isolated Cu²⁺ at 0.5%, with formation of CuO clusters by 6%. TPR showed that isolated Cu²⁺ was stabilised towards reduction compared to CuO clusters and CO-NO light-off correlated with TPR reduction temperature. Small Cu(O) clusters formed by reduction of Cu²⁺ and local migration that 'wet' the CeO₂ were proposed as the most active Cu species (4) (**Figure 2**). At high Cu loading, pre-formed CuO particles are less active, possibly due to less interface sites.

Charles A. Roberts (Toyota Motor Engineering & Manufacturing North America, Inc, USA) presented a study of Fe-CeO₂ catalysts to see if they can mimic isolated Fe sites in zeolites with simple CO-NO reaction feeds in his presentation 'In Situ Spectroscopic Characterization of Highly Dispersed Fe-Oxide

Catalysts for NO_x Reduction'. Catalysts were prepared by sodium-iron-ethylenediaminetetraacetic acid (EDTA) impregnation onto CeO₂ and compared to Fe(NO₃)₃ + NaHCO₃. The EDTA based catalyst showed higher activity (although still modest compared to the above Cu example). DFT, XANES and NO DRIFTS were applied to study the systems but no real conclusions were drawn, with suggestions that the system can be significantly improved.

Stephen Golden (Clean Diesel Technologies Inc (CDTi), USA) gave a presentation on the development of the CDTi technology, entitled 'Spinel Mixed Metal Oxide with Enhanced Oxygen Storage Capacity for Zero-PGM Three Way Catalyst'. Initial targets have been to develop low platinum group metal (pgm) spinel catalysts with an ambition to move to zero-pgm. Also, there was an initial focus on underfloor applications, but this has now moved to close-coupled. Only the CuMn₂O₄ spinel system was mentioned. High oxygen storage capacity (OSC) was claimed for this material, but there was significant loss with ageing temperature. The use of ternary compositions improved fresh OSC further, but these still showed degradation on ageing. Good NO_x reduction under rich conditions was also claimed, but no lean NO_x reduction just above stoichiometric.

Andrew Binder (Oak Ridge National Laboratory (ORNL), USA) presented a talk entitled 'CuO-Co₃O₄-CeO₂ Ternary Oxide Catalyst with High CO Oxidation Capability Shows no Inhibition by Propene'. A Cu:Co:Ce (1:5:5) catalyst was investigated for diesel oxidation. For simple CO oxidation, T₉₀ was observed at 150°C with little inhibition by C₃H₆ in the feed (no SO₂ present). The ternary composition was more active than binaries. Characterisation suggests that Cu is dispersed over a Co₃O₄-CeO₂ composite.

Characterisation Techniques

Yuriy Roman (Massachusetts Institute of Technology (MIT), USA) presented 'Hyperpolarization NMR Methods for the Characterization of Isolated Lewis Acid Sites in Zeolites'. Dynamic nuclear polarisation-solid-state nuclear magnetic resonance (DNP-SSNMR) was used to characterise metal framework substituted zeolites with difficult NMR parameters. Most examples were with ¹¹⁹Sn and a chemical shift correlation plot with ¹⁵N pyridine adsorption was developed. Then ¹⁵N pyridine adsorption was used with quadrupole nuclei such as zirconium and hafnium to map onto the plot.

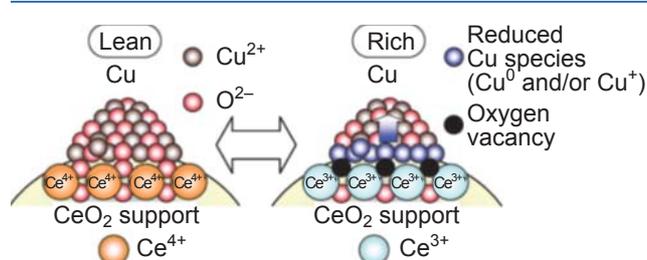


Fig. 2. Schematic representation of the redox behaviour of Cu and Ce in Cu/CeO₂ under periodic operation (Reproduced from (4) with permission of The Royal Society of Chemistry)

Korneel Cats (Utrecht University, The Netherlands) presented 'Active Phase Distribution Changes within a Catalyst Particle during Fischer-Tropsch as Revealed by Multi-Scale Microscopy' describing the use of hard X-ray transmission X-ray microscopy (TXM) (50 nm resolution, 3D), soft X-ray scanning transmission X-ray microscopy (STXM) (30 nm resolution, 2D) and scanning transmission electron microscopy-electron energy loss spectroscopy (STEM-EELS) (0.5 nm, 2D) to characterise a 15% Co/TiO₂ catalyst fresh and after testing. There was evidence that Co redistributes during reaction to give a 1–2 nm Co layer around the TiO₂ particles, together with carbon.

Libor Kovarik (PNNL, USA) presented 'Gamma-Alumina Platelets: Characterization and Comparative Study As a Model Catalyst Support'. Bulk and surface structures of transition aluminas are poorly understood due to low crystallinity, small particle sizes and the presence of multiple phases. In this presentation, the authors focused on δ -Al₂O₃ as a model system for fundamental studies of surface and structural properties. The morphological characteristics and surface properties were analysed by high-angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM), XRD and NMR. The structure was found to be highly complex and no clear conclusions were given at the end of the talk.

Ruigang Wang (Youngstown State University, USA) discussed 'Atomic-Level Interfacial Structure and Chemistry of Low-Temperature Active Metal-CeO₂ Nanocatalysts'. The CO oxidation activity over metal nanoparticle catalysts (Pt, Au, Ni, Cu, Ag) can be promoted, especially at low temperature, when using CeO₂ as support due to higher oxygen mobility *via* a redox reaction. The role of CeO₂ is believed to involve the adsorption and interaction of CO at the metal/CeO₂ interface. However, the interfacial structure and chemistry in metal-CeO₂ catalysts for CO oxidation is not well understood. Different shapes (nanorods, nanotubes or nanocubes) and reactive faces on the crystal surface were explored in the presentation by using high-resolution transmission electron microscopy (HR-TEM) and EELS. Nanorods and nanocubes possess higher OSC properties. Incorporation of Cu or Ni into ceria nanorods enhances the oxygen transfer between the metal and CeO₂. The interfacial structure and the surface area play a key role in the low temperature activity.

Patrick Wolf (Swiss Federal Institute of Technology (ETH) Zürich, Switzerland) presented 'Towards the Understanding of the Active Site-Distribution in

Sn-Beta'. This work gave fundamental insights into the nature of the active sites in tin-Beta zeolites. Sn-Beta zeolites were prepared according to different procedures. Several issues were found during *in situ* preparations; therefore a commercial Beta zeolite was used instead. Silanol nests were generated by acid treatments (HNO₃ at high temperature) and Sn was incorporated afterwards on the silanol nests. The structure of the material and the different types of active sites were determined by looking at the chemical shift in NMR (5).

Timothy D. Courtney (University of Delaware, USA) discussed 'Effect of Water Treatment on Sn-BEA Zeolite: Origin of 960 cm⁻¹ FTIR Peak'. It is known that conditions during calcination influence the concentration of open vs. closed sites in a metal-zeolite. In Sn-BEA the closed sites are the Sn species in tetrahedral coordination whereas open sites are related to Sn and Si bonds. IR spectroscopy was used to determine if the metal is incorporated into the zeolite framework. Typically, the 960 cm⁻¹ IR absorption band observed in Sn-BEA is associated with the incorporation of Sn in the zeolite framework. This is supported by the fact that by increasing the Sn loading the mentioned band displays a more significant perturbation. However, water can affect this band as well. IR and NMR spectra of calcined and water treated zeolites combined with first principles calculations indicate that the 960 cm⁻¹ band is not a vibration involving Sn but a result of isolated internal silanol groups. Thermogravimetric analysis and temperature-programmed desorption showed the silanol groups condense to form water at temperatures between 400°C and 700°C. Further water uptake experiments helped to elucidate the presence of sites that can be hydroxylated at relatively low temperatures and dehydrated at temperatures typically used for zeolite calcination.

In the presentation by Dmitry Doronkin (Karlsruhe Institute of Technology (KIT), Germany), 'Operando Spatially- and Time-Resolved XAS and Valence-to-Core-Xes to Study the Mechanism of the NH₃-SCR over Fe- and Cu-Zeolites', *operando* X-ray absorption spectroscopy (XAS) was applied under realistic reaction conditions to gain information such as oxidation state, coordination geometry, type and number of nearest neighbours or structural changes due to interaction with reactants. Changes occurring in the pre-edge and edge were monitored. Additionally, valence-to-core (V2C) X-ray emission spectroscopy (XES), allowed also to distinguish between atoms with close atomic numbers, like O and N. Brunauer, Emmett and Teller (BET)

surface area, atomic absorption spectrometry (AAS) and UV-vis spectroscopy were also applied to gain more information on the materials under study. Strong gradients of Fe and Cu oxidation state and a decrease of coordination number of the studied metal atom were observed along the catalyst bed for processes involving NO_x and NH₃. Re-oxidation of metal sites by oxygen is suggested to be the rate limiting step of the NH₃-SCR which is strongly inhibited by NH₃ at lower temperatures for Fe-zeolites (in contrast to Cu-zeolites). It was also observed that water inhibits the SCR reaction by coordination to the Fe-active centre. This was further supported by application of V2C-XES. The methodology applied provides evidence of the adsorption of NH₃ and NO in the presence of water and in combination with DFT calculations allowed the identification of potential reaction intermediates for the SCR process on metal-zeolite.

Daniel E. Resasco (University of Oklahoma, USA) presented 'Role of the Density of Zeolite Defects in the Instability of Zeolites in Hot Liquid Water'. The understanding of the susceptibility of different zeolites to hot liquid water allows the design of catalysts based on zeolites with higher stability and activity, for example for reactions of great importance in bio-oil refining such as fluid catalytic cracking (FCC), hydrocracking and alkylation. The thermal susceptibility of zeolites in liquid water is different from that in steam. While a pre-steamed zeolite can sustain treatments in the presence of steam at temperatures above 500°C, its crystal structure is completely destroyed after a few hours in liquid water at 200°C. It is believed that the susceptibility of the zeolite to hot liquid water depends on the structure and SAR, although this is still under

discussion. Here it was presented that the susceptibility of the zeolite to hot liquid water is related to the density of zeolite defects rather than to the SAR (6) (Figure 3). The role of zeolite structure, SAR, density defects, cation type, presence of mesoporosity and preparation parameters were analysed.

Jeffrey Rimer (University of Houston, USA) returned to give a presentation entitled 'Time-Resolved *in situ* Imaging of Zeolite Surface Growth Reveals the Mechanism of Crystallization'. Knowledge of zeolite growth mechanisms is helpful to design improved catalysts with physicochemical properties that can be determined *a priori*. *In situ* characterisation of zeolite crystal growth at length scale was presented. A dual mechanism is proposed, involving classical and non-classical mechanisms.

Single Site Catalysis

Preparation and characterisation of (non-zeolite) single-site catalysts appears to be a big topic in US catalysis at present and there were a number of interesting talks on this.

Aidan Mouat (Northwestern University, USA) discussed 'Highly Dispersed SiO_x/Al₂O₃ Materials: Catalytic Relevance of Isolated Silanol Active Sites'. Single mild acid sites are required on Al₂O₃ for aromatic dihydroxylation chemistry (biomass conversion). Atomic layer deposition (ALD) was used to deposit tetraethoxysilane (TEOS) onto γ-Al₂O₃ at a silicon loading below saturation of Al reactive sites (3.2 Si nm⁻²). Characterisation by X-ray photoelectron spectroscopy (XPS) (reduced binding energy compared to SiO₂) and ²⁹Si DNP-enhanced cross polarisation-magic angle

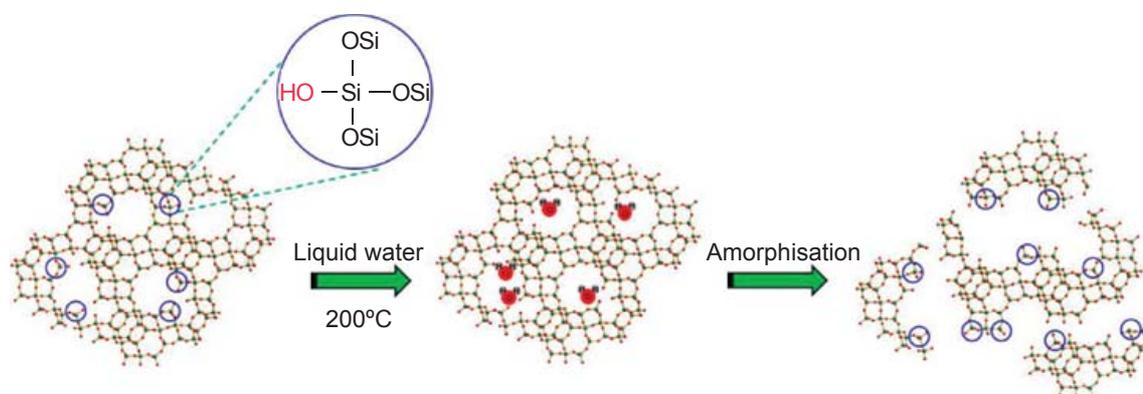


Fig. 3. The main characteristic of the zeolite that determines its susceptibility to hot liquid water is the density of silanol-terminated defects (Reprinted with permission from (6). Copyright 2015 American Chemical Society)

spinning (CP-MAS) NMR. NH_3 DRIFTS can be used to detect surface Si-OH and under-coordinated Al sites. Testing of samples for cyclohexane dehydration gave lower TOFs compared to 5% Si- Al_2O_3 but with much higher selectivity.

Luan Nguyen (University of Kansas, USA), in his presentation 'Catalysis on Singly Dispersed Bimetallic Sites', proposed that very small metal clusters will show higher selectivity for certain reactions. RhCo_3 clusters on CoO_x were prepared by first reducing Co_3O_4 and then adding Rh using deposition-precipitation. EXAFS shows the presence of Rh-Co metallic bonds and a coordination number ~ 1 . Testing with the CO+NO reaction showed high conversion to N_2 and CO_2 with no N_2O . This was compared to pre-formed CoRh nanoparticles which displayed very poor activity. However, only limited testing was done with no redox cycling or oxidative treatments. Also, it was unclear what the Rh loading was. The group is currently moving onto PtZn/ZnO at 0.05 wt% Pt and it was claimed that single-site reduced Pt was observed by XPS.

Christophe Copéret (ETH Zürich) covered the gap between classical homogeneous and well-structured heterogeneous surfaces in a plenary lecture entitled 'Controlled Functionalization and Molecular Understanding of Surfaces: Towards Supported Single-Site Catalysts and Beyond'. He started with the grafting of transition metal complexes onto SiO_2 to mimic commercial catalysts such as MoO_3 , WO_3 or Re_2O_7 on SiO_2 for alkene metathesis, then moved on to the characterisation of supports to understand reactivity differences between grafted complexes such as Re and Zr alkyl complexes. A good summary of the characterisation of Al_2O_3 surfaces using IR and N_2 , H_2 and CH_4 adsorption was given. He also discussed the role of adsorbed H_2O on Al_2O_3 in creating basic sites which provide binding sites for complexes and the role of DNP for surface enhanced NMR to investigate surface chemistry using an example of surface site characterisation of zeolites.

Materials

Tae-Sik Oh (University of Pennsylvania) presented 'Exsolution Behavior of Transition Metal Catalysts from Perovskite Host Lattices'. This group had previously investigated $(\text{La}_{0.4}\text{Sr}_{0.4})(\text{Ti}_{0.97}\text{Ni}_{0.03})\text{O}_{3-\delta}$ perovskites and found that Ni can be 'ex-solved' after reducing at 930°C in 5% H_2 /air followed by ageing at 900°C in 5% H_2 /Ar + H_2O for 20+60 hrs. It was determined that

Ni can only be segregated from the (110) surface as there need to be A cation vacancies, a B cation and B O vacancies. 'Ex-solved' Ni particles appear to show much less carbon nanotube formation as they are anchored more strongly (CNT formation requires 'lift-off' of the growth particles). $\text{LaFe}_{0.95}\text{Pd}_{0.05}\text{O}_{3-\delta}$ was also investigated and the formation of PdFe nanoparticles was observed on reduction.

Sibo Wang (University of Connecticut, USA) gave a talk entitled 'ZnO/Perovskite Core-Shell Nanorod Arrays Based Monolithic Catalyst for Hydrocarbon Oxidation at Low Temperature'. It had been previously shown that ZnO nanorods can be epitaxially grown on ceramic surfaces which is claimed to eliminate diffusion limitations. Nanoparticles of perovskite (LaMnO_3 , LaCoO_3 , La_2NiO_4) were coated onto the surfaces of the ZnO nanorods and the arrays tested for C_3H_8 oxidation. The perovskites on the ZnO showed a lower light-off when compared to the perovskites alone. The addition of Pt improved the low temperature oxidation further.

In her talk 'Ion Beam Surface Engineering for High Active Nanocatalysts' Nancy Artioli (Université de Caen, France) described the use of ion bombardment to improve the reducibility of CeZrO_x and Pt/CeZrO_x . IR spectroscopy was used to investigate vacancy formation in $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ through analysis of the surface OH vibrations. Ion beam treatment appears to form a higher number of O vacancies and higher O mobility.

Ming Li Ang (National University of Singapore) presented 'Highly Active Ni/xNa/CeO₂ Catalyst for Water-Gas Shift Reaction: Effect of Sodium on Methane Suppression'. Generally Ni is not a good candidate for water-gas shift as it has high methanation activity. The addition of Na inhibits methanation with Ni/CeO₂ catalysts. Up to a certain level Na appears to promote Ni reducibility, with XPS showing electron donation to Ni. *In situ* DRIFTS shows that Na inhibits the formation of Ni subcarbonyl species which are proposed to be key for methanation reactivity. It was also shown that Na promotes CeO₂ sintering up to 2 wt% after which there is no further effect. It was speculated that 2 wt% Na is the solubility limit of Na in CeO₂.

Yolanda A. Daza (University of South Florida, USA) discussed the use of H_2 reduction and CO_2 re-oxidation cycles for CO_2 capture studies on LaSrCoFeO_3 perovskites in her talk 'Intensified Reverse Water Gas Shift Chemical Looping on $\text{La}_{0.75}\text{Sr}_{0.25}\text{Co}_{(1-y)}\text{Fe}_y\text{O}_3$

Perovskite Oxides'. Under the cycling conditions (500°C reduction and >650°C re-oxidation) the pure Co containing perovskite is not stable, so Fe was added to stabilise it. Fe inhibits the Co reducibility. Although the LaSrCoFeO₃ is stable under repeated cycles, there is a loss in conversion attributed to both sintering and C (possibly CO₃²⁻) laydown. The addition of Cu improved H₂O formation from H₂ reduction but did not change CO formation from CO₂ re-oxidation. It was suggested that the extra vacancies formed by the addition of Cu are more stable.

Sean Hunt (MIT) presented 'Bimetallic Transition Metal Carbide Nanoparticles as Active, Stable, and Versatile Electrocatalysts'. Practical WC materials are often surface terminated with graphitic carbon which limits their usefulness. An alternative preparative method was shown that relied on forming WO_x nanoparticles, coating them in a porous SiO₂ shell, carburising and etching the SiO₂ with HF/EtOH to give WC nanoparticles. Similar nitrides can be made by substituting CH₄/H₂ for NH₃ in the carburising step. The route is also able to form carbides of other transition metals such as Mo and Ti. The WC nanoparticles supported on carbon are active for electrochemical MeOH oxidation, although less active than Pt.

Conclusions

This review has given a brief overview of the numerous talks and posters presented, largely in the area of

environmental catalysis but also some of those catalysts in zeolite and other structures, at the conference. A significant amount of work was focused on materials preparation and fundamental understanding, along with the development of new characterisation techniques. As shown in this review, there is also research into applications which do not utilise pgms for emission control reactions. Overall, the talks the reviewers attended were of a good quality and gave a good feel for the breadth of the US catalysis scene.

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