

International Symposium on Zeolites and Microporous Crystals 2015

Recent advancements in zeolite research

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The International Symposium on Zeolite and Microporous Crystals 2015 (ZMPC2015) was held at the Sapporo Convention Center, Japan, from 28th June to 2nd July 2015 and had 435 attendees from 32 countries, with 75% from Japan, China, Korea or Taiwan. 396 presentations covered all aspects of zeolites and microporous crystals over four days. Catalysis and synthesis were the two main themes (46% of all presentations) with the others being: new porous materials; membranes and films; adsorption and diffusion; characterisation; novel applications; industrial applications; layered materials; computational chemistry; post-synthetic treatment; crystallography; and ion exchange. There were six plenary talks along with 17 keynote and 94 oral presentations that took place in three parallel sessions. There were two poster sessions for 250 posters and recent research reports.

Synthesis

'Innovations in Zeolite Synthesis and Applications at UOP' was presented by John Qianjun Chen (UOP,

USA). Using the charge density mismatch (CDM) approach, UOP scientists have invented and patented more than 50 new zeolite materials referred to as UOP zeolitic materials (UZMs). The CDM approach starts with a clear reaction mixture that cannot crystallise. A couple of economical structure-directing agents (SDAs) are then added, such as alkali or tetramethylammonium cations. Strict control over the concentration of the crystallisation SDAs allows one to have great control over the rates and extent of condensation, often resulting in nanocrystals and crystals of unique morphologies. Crystallite dimensions are typically 500 Å to 20 Å.

Tsuneji Sano (Hiroshima University, Japan) presented 'High Potential of Hydrothermal Conversion Route as an Alternative Method for Zeolite Synthesis'. Based on the hydrothermal conversion of one zeolite type into another type this presentation described recent investigations of the synthesis of several types of zeolites by hydrothermal conversion in the presence and absence of organic structure-directing agents (OSDAs). FAU could be converted to RUT, *BEA, CHA or OFF; USY to CHA; and FAU to LEV or MAZ. The presence of seeds sped up the conversion and led to a core/shell structure. The structural similarity between the starting zeolite and the final crystallised zeolite is a crucial factor for hydrothermal conversion, for example all having 4MR. Separately, a tetraethylphosphonium (instead of nitrogen based) cation was used to synthesise a high-silica AEI zeolite with high thermal/hydrothermal stability.

'Green Sustainable Science and Technology Supported by Worldwide Researchers' Community for Micro- and Meso-porous Materials' was presented by François Fajula (CNRS, University of Montpellier, France). Fajula is the current president of the International Zeolite Association (IZA) and spoke about the conversion of methanol to olefins through reaction intermediates and coke precursors, the identification of the active sites responsible for the carbonylation of methanol on mordenite and of the selective reduction of nitrogen oxides (NO_x) on Cu-SSZ-13. He also spoke about preparation of zeolite nanocrystals or crystals with multimodal hierarchical porosity, pulse field gradient NMR and the need for further advanced characterisation of zeolites.

Manuel Moliner (Instituto de Tecnología Química, Spain) presented 'Rationalizing the Synthesis of Small Pore Zeolites with Large Cavities'. The ability to place the silicon atoms selectively in isolated form (desired due to higher acid strength) will mostly depend on the properties of the OSDA selected for the SAPO synthesis, such as size, shape, rigidity or charge distribution. Therefore, extracting an 'SAR' value from ²⁹Si NMR spectra makes no sense as two SAPOs could have the same framework SAR but different distributions due to different OSDAs. A second part of the talk discussed Cu-SAPO-34, the hydrothermal stability of which has been considerably increased by properly modifying the synthesis conditions to favour the selective distribution of isolated Si species in the framework positions by direct synthesis methodologies (1).

Cong-Yan Chen (Chevron Energy Technology Co, USA) presented 'Investigation of Shape Selective Properties of SSZ-87 and Other Zeolites via Hydrocarbon Adsorption and Catalytic Test Reactions'. This talk from Chevron contained two interesting pieces of information. First, there was a new synthesis approach to yield alkali-free borosilicate zeolites using boric acid and ammonium fluoride, with both boron and fluoride as part of the synthesis product (2). Al can substitute B in zeolite frameworks if the pores are large enough to allow the hydrated Al cations to enter. As a result, the borosilicate zeolites can be converted to their aluminosilicate counterparts with acid sites strong enough to catalyse various hydrocarbon transformation reactions. Second, 2,2-dimethylbutane adsorption has proven to be a useful tool to provide valuable information for the determination of the unknown structures of many new zeolites. The initial rate of adsorption and

subsequent slower adsorption rate gives information on ring sizes and spatial restrictions.

Toshiyuki Yokoi (Tokyo Institute of Technology, Japan) presented 'Control of Location of Al atoms in the Pores of ZSM-5 Based on the Rational Choice of Organic and Inorganic Cations'. The type of OSDAs and the presence or absence of Na cations during crystallisation affects the location of Al atoms in the framework; for example the acid sites in tetrapropylammonium [TPA] are selectively located at the intersections because the negative charges of Al atoms in the MFI framework are balanced by large TPA cations, which is located in the intersections during the crystallisation of ZSM-5 (3).

Shaheen Anis (Masdar Institute of Science and Technology, Abu Dhabi) presented 'Fabrication of Micro and Nanozeolite Fibers Through Electrospinning'. Anis fabricated zeolite-Y microfibrils (>600 nm) and zeolite LTL nanofibrils (<100 nm) through electrospinning, which is an economic and versatile method for fabricating fibres. SEM images reveal a rough morphology for both zeolite-Y microfibrils and LTL nanofibrils, which is highly desirable for strong catalytic activity. The ratio of zeolite: polyvinylpyrrolidone (PVP):ethanol was 1:1:8 by weight. Calcination in a furnace at 475°C for 2 h removed the polymer without affecting the zeolite, characterised by BET and XRD.

Jorge Gascon (Delft University of Technology, The Netherlands) presented 'Rational Design of Structured Catalysts and Membranes'. Polymer membranes and inorganic membranes both have their pros and cons; mixed matrix membranes offer the best of both (4). Gascon also introduced the use of metal-organic frameworks (MOFs) as hard templates for the direct synthesis of carbon-metal nanoparticle composites displaying unrivalled stability in different conversions involving C₁ molecules, from Fischer-Tropsch synthesis to the electroreduction of CO₂ (5).

Characterisation

Yuriy Roman-Leshkov (Massachusetts Institute of Technology, USA) presented 'Lewis Acid Zeolites for Biomass Conversion: Insights on Reactivity, Characterization, and Stability'. Roman-Leshkov used dynamic nuclear polarisation (DNP) to characterise Sn-Beta zeolites without isotopic enrichment in a matter of hours, instead of a weekend. DNP was also used to obtain complex 2D spectra for elucidating adsorption geometry between nuclei from adducts and active sites in zeolites. Titanium, zirconium, tin and hafnium were

probed as Lewis acid sites, however the DNP results from Zr and Hf were not great. bCTbk dissolved in 1,1,2,2-tetrachloroethane was used as the DNP radical and solvent. Finally, results on TMPO as an acid-site probe molecule were presented. ^1H - ^{31}P heteronuclear correlation (HETCOR) experiments differentiated between open and closed sites.

Matthias Thommes (Quantachrome Instruments, USA) presented 'Progress and Challenges in the Physical Adsorption Characterization of Mesoporous Zeolites'. This talk from Quantachrome was on state-of-the-art physical adsorption techniques based on argon 87 K adsorption, applied to hierarchically structured zeolites and other materials. A novel methodology for the analysis of the adsorption hysteresis was applied to argon isotherms from a surfactant templated mesoporous Y zeolite in order to quantify the percentage of 'open' and 'blocked' mesoporosity.

Emiel Hensen (Eindhoven University of Technology, The Netherlands) presented 'Design of Hierarchical SSZ-13 Zeolite by Fluoride-modulated Growth'. Creating mesoporosity in SSZ-13 results in improved catalytic performance in the MTO reaction. However, the characterisation employed was of the most interest; SEM, TEM, confocal fluorescence microscopies, CO_{ads} FT-IR, MTO activity testing, methanol/propylene adsorption and positron emission tomography (PET) of ^{11}C -methanol. This last technique was used to observe, *in situ*, a methanol pulse moving through a fixed bed reactor.

' H_2 -Activation Ability of Zn^{2+} Caused by MFI: Effects of Al-Al Distance and Curvature Originated from MFI-Pore-Structure' was presented by Akira Oda (Okayama University, Japan). Oda reported that the H_2 activation ability of Zn^{2+} ion-exchanged in MFI is controlled by the two dominant factors derived from the ion-exchangeable site in MFI: Al-Al distance and specific nature endowed by the curvature originated from pore-structure. This was achieved using molecular orbital theory and observation of the $\text{Zn}4s$ and $\text{O}2p$ XPS peaks.

Kaname Yoshida (Japan Fine Ceramics, Japan) presented 'High Resolution Imaging of Zeolites with Aberration Corrected (S)TEM'. Aberration-corrected high resolution TEM (AC-HRTEM) imaging is very effective in imaging of zeolitic frameworks consisting of comparatively light elements such as Si, Al and O. Each crystalline sample was crushed in an agate mortar with ethanol, and collected on a TEM microgrid

support. Two C_s values of $\pm 15 \mu\text{m}$ were employed to AC-HRTEM imaging. Imaging with positive (PCS) and negative (NCS) values form dark and bright atomic images, respectively. In order to compensate the very low signal-to-noise ratio (SNR) of image contrast, all images were processed with a Bragg filter. The heavy element Cs^+ captured at the centre of S8R was clearly seen in all images; however, Na^+ delocalised near the centre of S8R could not be visualised absolutely in high-angle annular dark field (HAADF)-STEM mode.

Silica

Giuseppe Bellussi (Eni SpA, Italy) presented 'Hybrid Organic-inorganic, Crystalline or Pseudo-ordered, Porous Silicates'. Bellussi talked about periodic mesoporous organosilica (PMO) and eni carbon silicate (ECS) materials (6). The synthesis of ECS is often promoted by the presence of boric acid. Boron does not enter in the crystalline framework, but boric acid promotes the hydrolysis of the silica precursor thus accelerating the formation of pure crystalline phases. The silica to alumina ratio (SAR) of the materials obtained so far is low, close to 1, and this composition has prevented the obtainment of the acidic form of ECS materials. Interestingly, the structure of ECS-3 was determined by automated diffraction tomography (ADT) and ECS-20 contains an O_3 environment.

'Synthesis and Structural Study of the Complex Macroporous Photonic Structure by Electron Microscopy' was presented by Lu Han (Shanghai Jiao Tong University, China). To solve the complex hollow structure, the three-dimensional (3D) electrostatic potential map of the macroporous silica was obtained from the Fourier synthesis of the crystal structure factors taken from transmission electron microscopy (TEM) images. A 3D reconstruction was obtained from 160 reflections. TEM images were simulated using a 3-term nodal equation. These studies demonstrate that electron crystallography is the only way to solve the complex structure at such length scale.

Atsushi Fukuoka (Hokkaido University, Japan) presented 'Low-Temperature Oxidation of Ethylene by Platinum Nanoparticles supported on Mesoporous Silica'. The researchers studied platinum catalysis of ethylene oxidation at low temperature. The effect of supports was investigated using 5% Pt at

25°C, catalytic activities were ranked as follows: Pt/MCM-41 > Pt/SiO₂ > Pt/Al₂O₃ > Pt/TiO₂ > Pt/ZrO₂. A mechanism for the oxidation of ethylene by supported Pt catalysts was also proposed.

Catalysis

Michael Tsapatsis (University of Minnesota, USA) presented '2-Dimensional Zeolites: from High-quality Exfoliated Nanosheets for Thin Film Formation to Self-pillared Nanosheets for Catalysis and Adsorption'. Scale-up of membranes to separate *para*-/*ortho*-/*meta*-xylene is a big hurdle. Tsapatsis introduced an approach to hierarchical zeolite catalysts and adsorbents, which does not rely on sacrificial hard or soft templates and can be accomplished by single-step synthesis. The approach relies on rotational intergrowths and produces self-pillared nanosheets, which exhibit performance similar to other reported 2D assemblies. Thickness of the 2D nanosheets were determined by rel-rod mapping using TEM diffraction patterns over a tilt-series, see **Figure 1** (7).

Raul Lobo (University of Delaware, USA) presented 'Novel Active Sites and New Opportunities in Zeolite Catalysis'. Lobo spoke about methane oxidation on small-pore copper-zeolites and noted that diffuse-reflectance ultraviolet-visible (UV-Vis) spectroscopy revealed that the structure of the Cu sites is similar between the three zeolites investigated (SSZ-13, SSZ-39 and SSZ-16) but different from Cu-ZSM-5. Another topic was on the synthesis of benzene from methane using MoC_x nanoparticles embedded in the pores of H-ZSM-5. They decoupled the chemistry that occurs

on the MoC_x nanoparticles from the oligomerisation/aromatisation reaction by preparing a variety of catalysts in non-acidic zeolites.

Zhongmin Liu (Chinese Academy of Sciences, China) presented 'Recent Progress on Fundamental Researches of MTO Reaction'. The hydrocarbon pool mechanism, in which organic species confined in the zeolite cage or at the intersection of channels act as co-catalysts, has been regarded as a rational explanation for formation of C–C bonds in methanol conversion (8). Methylbenzenium cations and methylcyclopentenyl cations have been speculated to be the most important active intermediates involved in the 'hydrocarbon pool' mechanism. Although a reaction network was proposed, there still remain many scientific challenges, such as how the first C–C bond forms, what happens in the induction period, what are the exact relations among different reaction routes, how coke forms, and how to control the coking reaction in the reaction network.

Shang-Bin Liu (Institute of Atomic and Molecular Sciences, Taiwan) presented 'Brønsted-Lewis Acid Synergy during Selective Catalytic Reduction of Nitric Oxide over Lanthanide-metal Incorporated Iron-based ZSM-5 Zeolite'. The catalysts were characterised by X-ray diffraction (XRD), Brunauer, Emmett and Teller (BET) surface area analysis, electron microscopy (EM) and X-ray photoelectron spectroscopy (XPS), whereas their acidic properties were analysed by ammonia temperature-programmed desorption (NH₃-TPD), pyridine infrared (IR), and ³¹P magic-angle spinning nuclear magnetic resonance (MAS NMR) of adsorbed trimethylphosphine oxide (TMPO) as a probe molecule. CeFe-ZSM-5 catalyst exhibited the optimal NO

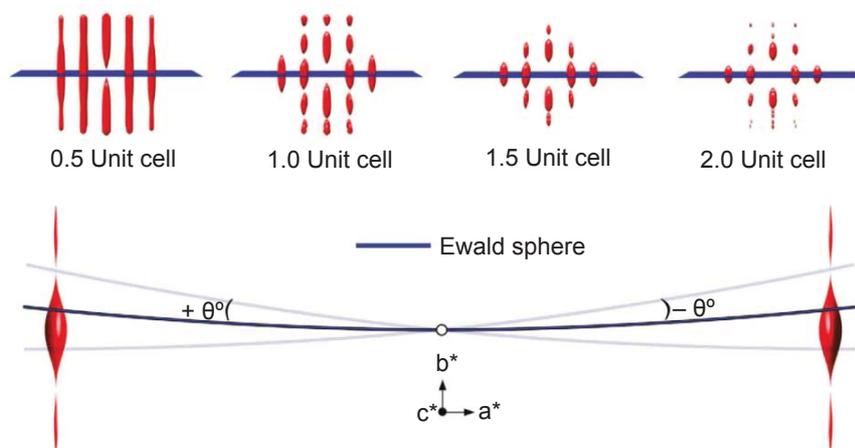


Fig. 1. Thickness dependence of rel-rods (7)

conversion exceeding 95% over a temperature range of 300°C to 500°C. The superior selective catalytic reduction (SCR) activity observed for the CeFe-ZSM-5 has been attributed to the synergistic effect from the Brønsted acidity of MFI zeolites and strong Lewis acidity induced by the presence of incorporated active Fe³⁺, Ce³⁺ and/or Ce⁴⁺ ion species.

Kristof De Wispelaere (Ghent University, Belgium) presented 'Combined Theoretical and Experimental Study on the Influence of Zeolitic Acid Strength on the Methanol Conversion Process'. Two AFI catalysts with different acid strength, H-SSZ-24 and H-SAPO-5, were tested for methanol to hydrocarbons (MTH) catalysis (9). It was found that the strongly acidic H-SSZ-24 is more selective towards aromatic products and light alkenes than the moderately acidic H-SAPO-5. Furthermore, it was found that while aromatic hydrocarbon pool species appear to play an important role in H-SSZ-24, these are of less importance in the weaker acid H-SAPO-5. AFI was chosen over the more typical CHA (SAPO-34) as AFI can be fed aromatics, which cannot enter the CHA supercages.

Javier Ruiz-Martínez (Utrecht University, The Netherlands) presented 'The Role of Methoxy and Aromatic Species during the Methanol-to-Olefins Reaction over SAPO-34'. The authors presented a novel operando approach combining UV-vis and IR spectroscopy with online mass spectrometry to investigate the chemistry of the species formed during the methanol to olefins (MTO) reaction (10). It was found that the accessibility of SAPO-34 is linked with the amount of methoxy species, whereas the formation of polyaromatic species that block the pores is the main cause of deactivation. Furthermore, the reaction pathways responsible for the formation of olefins and polyaromatics coexist and compete during the whole MTO process.

Ferdi Schüth (Max-Planck-Institut für Kohlenforschung, Germany) presented 'Porous Polymers as Catalysts and Catalyst Support'. Several syntheses, gas adsorption properties and catalytic performance of porous polymers were discussed. Notably, a 1000 m²g⁻¹ Pd/polyphenylene catalyst proved a very good solid catalyst for the Suzuki coupling of substrates which are very difficult to activate, such as methane to methanol (11). Hollow graphitic spheres containing platinum were also investigated for oxygen reduction reaction in fuel cells. This Pt@C catalyst does not deactivate with cycling and the hollow sphere is essential in a real fuel cell for effective mass transport, see **Figure 2** (12).

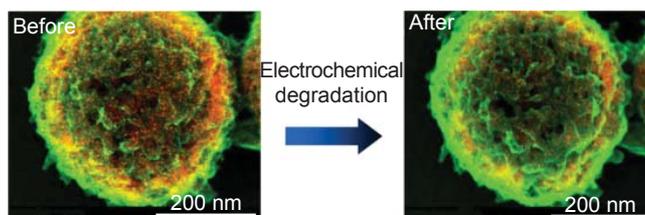


Fig. 2. Identical location scanning electron microscopy-scanning transmission electron microscopy (IL-SEM/STEM) micrographs of Pt@C after 0 and after 3600 electrochemical degradation cycles (Reprinted with permission from (12). Copyright (2012) American Chemical Society)

Conclusions

From a characterisation perspective, XRD, TEM and MAS NMR were the most popular techniques, all of which were presented in at least 15 separate talks attended by the reviewer. The TEM was especially advanced, incorporating electron crystallography and tomography. SEM and FTIR were also well represented, followed by UV-vis. AFM and XPS data were only shown in three talks, whilst Raman appeared once, suggesting that these techniques have potential to be further exploited by the community.

Overall, ZMPC2015 was well attended and well organised. We saw an excellent array of talks and posters that covered all the latest developments in the field of zeolites and microporous crystals, especially regarding catalysis and synthesis. The next conference will be held in Yokohama, Japan, in 2018.

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The Reviewer



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