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Frontiers in Environmental Catalysis

Symposium in recognition of 20 years with the Competence Centre for Catalysis

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1. Introduction

This symposium was organised by Chalmers University of Technology, Sweden, to commemorate the first 20 years of research at Competence Centre for Catalysis (KCK). The Frontiers in Environmental Catalysis conference was held on 24th September 2015 at Chalmers University of Technology. All previous and current KCK employees were invited, together with representatives of KCK's member companies and few invited speakers. About 50% of the invited people attended, resulting in about 120 participants. Among them were four Johnson Matthey delegates (including the present reviewer, having been a post-doctoral fellow at KCK). Although Johnson Matthey is no longer part of KCK, a collaboration project on the study of methane oxidation is ongoing between Johnson Matthey Technology Centre, Sonning Common, UK and Professor Per-Anders Carlsson (KCK, Sweden) resulting in two poster presentations at the symposium.

The aim of this review is to summarise the oral presentations relevant for emission control applications and provide the reader with useful references for further reading. The topics covered by the poster presentations will also be mentioned to give an overview of the current research at KCK.

2. Oral Presentations

2.1 Twenty Years with KCK

An introductory talk to celebrate the history of KCK, an interdisciplinary research centre within heterogeneous catalysis since 1995, was given by the director of KCK, Professor Magnus Skoglundh (Chalmers University of Technology). The diversity of the centre was emphasised: it was originally composed of Chemical Engineering, Chemical Reaction Engineering and Applied Physics departments at Chalmers University of Technology, and recently it was further expanded by Eva Olsson's microscopy group. The research is focused on catalysis for emission control with a growing interest in energy related areas. KCK is financially supported by Chalmers University of Technology, the Swedish Energy Agency and the member companies: AB Volvo, ECAPS AB, Haldor Topsøe A/S, Scania CV AB, Volvo Car Corporation AB and Wärtsilä Finland Oy.

On a similar note, Pär Gabrielsson's (Haldor Topsøe, Denmark) talk on 'The Impact of KCK from an Industrial Perspective' stressed the role played by KCK on students' education and how it prepares them for employment in the catalysis and aftertreatment industry. This is confirmed by statistics, with 70% of PhDs employed by industry of which 45% are member companies. The remaining 30% of PhDs are employed by other organisations.

2.2 Automotive Aftertreatment

Galen Fisher (University of Michigan, USA) presented 'Progress and Challenges in Automotive Emission Control'. Fisher is one of the members of the KCK's international advisory board. His talk concentrated on current challenges facing the automotive emission control industry such as improving the low-temperature activity of three-way catalyst (TWC) and nitrogen oxides (NOx) traps. Moving the TWC design from a supported metal to a metal core surrounded by an inert shell was shown to prevent poisoning and metal sintering (1). Johnson Matthey was cited in relation to the development of palladium/cerium based low-temperature NOx adsorbers, characterised by lower nitrous oxide (N_2O) production compared to platinum-based catalysts and preferential storage of nitrogen oxide (NO) *vs.* nitrogen dioxide (NO_2) (2). Fisher discussed how the new aftertreatment technologies use layering/zoning strategies as well as diffusion effects to decrease emissions.

Jonas Jansson (AB Volvo, Sweden) presented 'Exhaust Aftertreatment for Heavy Duty Diesel Engines – Current Trends and Future Challenges'. The evolution of the aftertreatment systems for heavy duty diesel vehicles at Volvo was discussed. The original configuration diesel oxidation catalyst (DOC) + diesel particulate filter (DPF) + selective catalytic reduction (SCR) has been recently substituted by close-coupled DOC + SCR on filter (SCRF®) (or passive NOx adsorber (PNA) + SCRF®), allowing an enhancement of the light-off performances. The location of the catalysts and of the urea tank depends on the geographical area where the vehicle is commercialised.

2.3 Advanced Characterisation

Stig Helveg (Haldor Topsøe) presented 'Electron Microscopy Advances for Catalysis'. Helveg introduced the cutting-edge technology of *in situ* and *operando* transmission electron microscopy (TEM) imaging (3). A nanoreactor was designed at Haldor Topsøe in collaboration with TU Delft, The Netherlands, and was functionalised with a micrometre-sized gas-flow channel, transparent windows to allow the electron beam to reach the sample and with a heating device (4). This device allows the collection of images at 1 bar, solving the pressure gap issue typical of traditional TEM imaging. The time resolved TEM images and measurement of the outlet gas composition by mass spectrometry (MS) results in a powerful way of studying correlations between a catalyst structure and its activity. The research of oscillatory catalytic reactions, such as carbon monoxide oxidation, was reported as an example of successful application of this technique (5). In this case a link between catalyst activity and shape of platinum nanoparticles has been found (shape dynamics from squared to circular). Sintering mechanisms and kinetics can also be investigated with the same technique.

Anders Nilsson (Stockholm University, Sweden) presented 'Fundamental X-ray Studies of Catalytic Reactions'. The understanding of the nature of the interaction between water and metals, which is of interest in heterogeneous catalysis, was described (6). Professor Nilsson developed a library of X-ray absorption spectroscopy (XAS) and X-ray Raman scattering (XRS) spectra that spans the liquid part of the water phase space and several important aqueous solutions. This was used as a reference to identify hydroxyl species involved in catalytic reactions such as hydrogen oxidation in fuel cell applications.

Per-Anders Carlsson presented 'Studies of Catalysts at Work'. This talk focused on the use of synchrotron facilities (European Synchrotron Radiation Facility (ESRF), France; MAX IV, Sweden and PETRA III, Germany) to examine catalytic reactions. Some examples were given of various spectroscopic techniques (extended X-ray absorption fine structure (EXAFS), high-energy X-ray diffraction (HEXRD), Fourier transform infrared (FTIR) and MS) to distinguish the adsorbed species and simultaneously coordinate catalytic activity to changes in the catalyst oxidation state (7, 8) (**Figure 1**). The possibility of exploiting the structure gap, from ideal surfaces to big particles, small clusters and single atoms, to improve the understanding of catalytic reactions was also mentioned. Active areas of interest are total methane oxidation and partial selective methane oxidation to methanol.

2.4 Reaction Engineering and Molecular Modelling

Louise Olsson (Chalmers University of Technology) presented 'Studies of Aging Mechanisms for NH_3-SCR Catalysts using Experiments and Kinetic Modelling'. Sulfur poisoning and regeneration on copper-SSZ13 were studied and performed in collaboration with Cummins Inc. A three-site kinetic model was necessary to describe ammonia storage and oxidation during temperature programmed desorption (TPD) experiments (9). A connection was

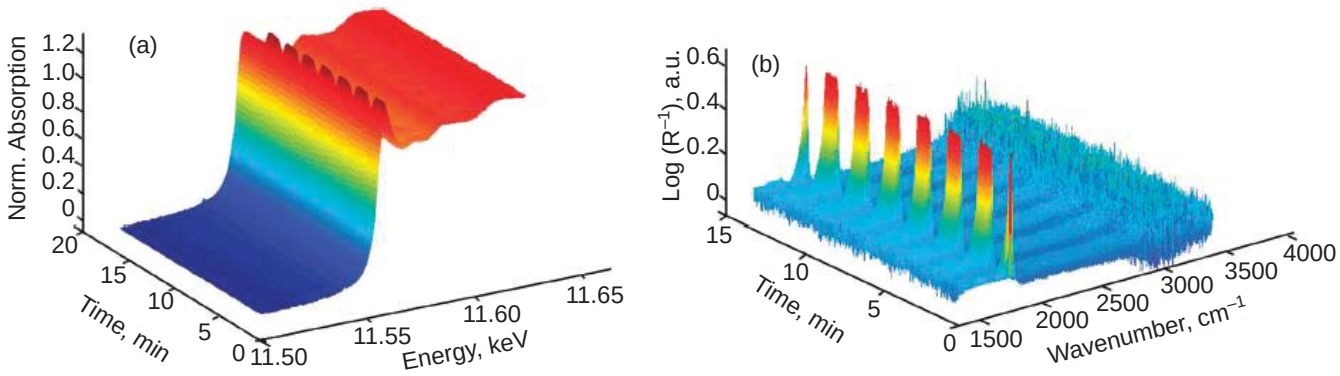

Fig. 1. (a) Evolution of X-ray absorption near edge structure (XANES) Pt LIII-edge spectra; and (b) IR bands in the interval 1500–4000 cm^{-1} for a 4% Pt/Al_2O_3 catalyst exposed to 1000 ppm CH_4 in He while periodically switching the O_2 concentration between 0 (60 s) and 1.5% (60 s) at 280ºC (Reprinted with permission from (7). Copyright (2011) American Chemical Society)

also found experimentally between the rate of SCR reaction and Cu loading, that was introduced in the kinetic model. A sulfur exposure study showed that sulfur dioxide (SO_2) can be adsorbed on Cu sites (S1-SO_2), resulting in a decreased catalytic activity. The experimental observation of more NH_3 stored in the presence of sulfur was elucidated with the formation of adsorbed ammonium-sulfur species (S1-$(NH_3)_2$-SO_2). The gradual decomposition of these species leads to catalyst regeneration and also provides an alternative route to the SCR reaction. This mechanism was successfully included in a kinetic model.

Henrik Grönbeck (Chalmers University of Technology) presented 'Catalysis from First-Principles Calculations'. A recent work combining X-ray photoelectron spectroscopy (XPS) measurements and first-principle calculations suggests that the most active phase for methane oxidation on Pd-based catalyst is a double layered PdO(101) structure (10). Density functional theory (DFT) calculations show that CH_4 repulsion from the surface is quite strong when only one monolayer of PdO is present, but it can be overcome after a second monolayer is created therefore explaining the better activity observed experimentally. A micro-kinetic model for CH_4 oxidation was also built from first principles, able to predict reaction orders in methane, water, and oxygen as well as apparent activation energies in good agreement with a range of experimental findings (11). Interestingly, different reaction steps were found to be limiting depending on the temperature: water inhibition, CH_4 desorption, CH_3 dissociation or CH_4 dissociation with increasing temperature. Different activation energies depending on the temperature were found also experimentally, which supports the modelling results.

3. Poster Presentations

29 posters were presented during the poster session, covering two main research areas: emission control and energy conversion.

One of the main focuses in emission control research was the understanding of ageing and sulfur poisoning mechanisms as well as deactivation during operation, for lean NOx trap (LNT), SCR and hydrocarbon oxidation catalysts. The SCR of NOx in the presence of excess oxygen by NH_3/urea (NH_3-SCR) or hydrocarbons (HC-SCR), and NOx storage reduction (NSR) using mixed lean/rich operation were explored. Posters on passive SCR and SCR coated DPFs were also presented. Another subject of interest is the catalytic oxidation of soot and methane in particular the inhibiting effect of H_2O on the latter.

Moving to the energy conversion theme, research is ongoing in the synthesis of methanol from direct selective oxidation of methane on Cu-zeolites as well as selective hydrogenation of oxygenates.

In many cases activity studies were accompanied by kinetic modelling and/or first principles calculations to support the interpretation of the experimental results.

4. Conclusions

The contribution by representatives from both academia and industry to the symposium made it an overall successful event. The range of presentations was diverse and covered the most relevant topics in environmental catalysis, with an emphasis on future challenges. The Chalmers' KCK demonstrated once again to be one of the leading groups in environmental catalysis research.

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The Reviewer

Djamela Bounechada graduated in Chemical Engineering at Politecnico di Milano, Italy, in 2008 with a thesis combining experimental and modelling studies of SCR of NOx by ammonia (NH_3-SCR) for automotive applications. She obtained a doctorate degree from the same university in 2012, with a thesis on strategies for enhanced methane oxidation in the exhausts of natural gas vehicles. After two years as a post-doctoral Fellow at Chalmers University of Technology, she joined Johnson Matthey Technology Centre (Sonning Common, UK) in 2014, as part of the reaction engineering research team.