

Active Species and Dynamic Structures for Selective Catalysis on Designed Surfaces and Nanoparticles

Yasuhiro Iwasawa*

Department of Chemistry, Graduate School of Science, the University of Tokyo, Hongo,
Bunkyo-ku, Tokyo 113-0033 (Japan)

*iwasawa@chem.s.u-tokyo.ac.jp; iwasawa@pc.uec.ac.jp

Introduction

Tremendous catalysis can appear with 2D aspect and unique ensemble on surfaces/pore walls and nanoparticles, which may be hard to produce in homogeneous and 3D bulk systems. New strategy and concept lead to tailor-made catalyst design for a target reaction in green sustainable processes, where in situ characterization of the surfaces is inevitably important for understanding the origin and mechanism of the tremendous catalysis and dynamic surface events. Multi-functional catalysis for innovative chemical processes is created by rational molecular design of surfaces and nanoparticles and by modifying solid surfaces with adsorbates and precursors to form new surfaces under catalytic reaction conditions. Dynamic structures on the surfaces relevant to selective catalysis are characterized by in-situ time-resolved analysis techniques. The talk documents active species and dynamic structures for several selective catalyses including direct phenol production from benzene with molecular oxygen on Re/ZSM-5 catalysts, surface events at a Pt/C cathode catalyst in a PEM fuel cell system, methane reforming on Ni/CeO₂-ZrO₂ with oxygen storage capacity, NO reduction on a Co ensemble/Al₂O₃ catalyst, selective oxidation on V/oxides and Ru/SiO₂, and H₂-O₂ reaction on Pt(111), characterized by means of time-resolved XAFS, time-resolved Raman, time-resolved micro-XPS, and DFT calculations [1-4].

Materials and Methods

The catalysts used in this study involve Re clusters in ZSM-5 zeolite pores with additive metals, Co₄ ensembles on γ -Al₂O₃, V oxides on SiO₂ and Al₂O₃, and Ni nanoparticles on CeO₂-ZrO₂ solid solution. These catalysts were prepared by an impregnation method and a CVD technique. Pt(111) surface was also employed. Time-resolved XAFS spectra were measured at KEK-PF and SPring8 at a time resolution of 2 ms – 1 s, depending on the reaction systems (Fig. 1). Micro-XPS spectra were measured at KEK-PF to monitor spatial distribution of oxygen species on Pt(111) (Fig.2). Time-resolved Raman was applied to measure Ni/CeO₂-ZrO₂ in situ under OSC processes. DFT calculations were made for active structures and reaction paths.

Results and Discussion

A novel N-interstitial Re₁₀ cluster was suggested to be active species for the selective benzene oxidation with O₂, whose structure was determined by EXAFS, DFT calculations, etc. Molecular oxygen was the oxidant for the phenol synthesis and the maximum phenol selectivity 87.7% at 5.8% conversion was achieved with a CVD catalyst. We suggested a concerted mechanism for the selective benzene oxidation: benzene C-H bond activation, O=O bond activation, and O insertion to the C-H bond concerted at a transition state on the novel Re₁₀ cluster. The decomposition of the active Re₁₀ cluster with O₂ was dominant under the reaction conditions. If the stability of the active Re₁₀ cluster increases, the concentration of the

active Re₁₀ cluster increases under steady-state reaction conditions, resulting that the benzene conversion can improve maintaining the high phenol selectivity. The catalyst prepared by an impregnation method showed a very low conversion of 0.2% and a low selectivity of 42%. The conversion increased to 27% by Pt addition to the impregnation catalyst, while keeping a good selectivity of 92%.

The timescale of the proton transfer from H₂O to OH in the 2D hydrogen-bonding network on a Pt(111) surface was determined to be 5.2 ± 0.9 and 48 ± 12 ns, respectively, at 140 K from micro-XPS observations of spatiotemporal changes in the patterned distribution OH+H₂O/H₂O/OH+H₂O. Obtained spatiotemporal changes were explained based on the diffusion equation, taking account of two different pathways; the direct proton transfer to the neighbor site and the H₃O⁺-mediated proton transfer to the next-nearest site. The understanding of proton dynamics at the 2D interfaces will be important to the protonics at interfaces like fuel-cell electrodes and biological membranes.

The active species and dynamic structures in the PEM fuel cell catalyst, the Ni/CeO₂-ZrO₂ CH₄ reforming catalyst and the other catalysts will also be reported.

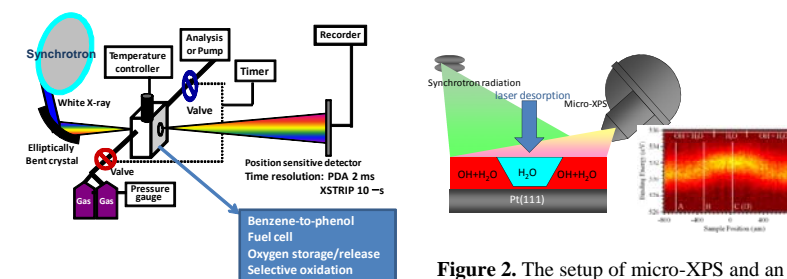


Figure 1. Time-resolved energy-dispersive XAFS system for monitoring dynamic processes. OH+H₂O/H₂O/OH+H₂O structure.

Significance

In situ time-resolved characterization provides the information on active species and dynamic structures for understanding the catalysis and achieving highly efficient processes.

References

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