

Session summary report

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Session 1 “Fundamental and analysis” covering the topics 2-“Fundamentals: surface science and mechanism”, 7-“Characterization and in situ analyses of catalysts”

Kiyotaka Asakura, *Catalysis Research Center, Hokkaido University, West 21, East 10, Kita-ku, Sapporo 001-0021, Japan*

Fundamental and analysis session was dedicated to survey the way to understand the oxidation reaction mechanisms including surface science techniques and operando techniques.

I found three main topics in this session which were discussed by several authors; i.e., Au nanoclusters, epoxidation reaction and selective oxidation of hydrocarbons in all sections.

Au nanoclusters show high activity for CO oxidation reaction. The unique catalytic properties of Au nanoclusters were discussed here from various points of view, surface science (PL-1, KN1-2, OA1-05, P1-46), IR and TEM (OA1-046, P1-23, P1-31, P1-39), and effects of defect, additives and moisture (P1-02, P1-05, P1-42). TEM clearly shows the importance of the interface structure.

Epoxidation reaction is another interesting topic in this session. The reaction mechanism of epoxidation on Ag was studied by using isotope effect (OA1-03), model system prepared by EBL (electron beam lithography) (OA1-08) and density functional approach (P1-22). Au was also studied for the epoxidation (OA1-06).

Selective oxidation of hydrocarbons is one of the most important subjects in this conference. IR, XRD, SEM and TEM were used to characterize the catalyst but it still seemed to be difficult to apply surface scientific methods to this system because of complex structures with multicomponent and multiphase. The mostly studied system was a MoVTenb system and its related compounds for ammoxidation (OM1-02, P1-09, P1-19, P1-20, P1-36, P1-37, P1-41). Not a few presentations on partial oxidation of metals on oxides were found (OM1-03, OM1-04, P1-17, P1-21, P1-45).

We had one plenary lecture relating to this session, which was given by Prof. H.J. Freund. He reviewed recent surface science studies on well-defined oxide surfaces prepared by sophisticated ways, which aimed to figure out riddles hidden in real catalysts, i.e., the role of vacancies and defects, metal-oxide support interaction, and high activities on Au nanoclusters.

Operando and time-resolved spectroscopy are newly developed spectroscopy. Iwasawa presented recent developments in time-resolved XAFS techniques, which enabled us to obtain a structure change with less than 1 s time resolution. He discussed the reaction mechanism and energy diagrams of redox processes on CeO₂/ZrO₂ and Rh/Al₂O₃ in the CO adsorption and desorption process.

Wechhuysen emphasized the importance of the operando measurement. Operando is a new terminology from Latin meaning “working”. Operando spectroscopy is the spectroscopy of catalysts under working conditions. He also reported the important new X-ray spectroscopy technique called as AXAFS.

I was impressed that steady progress of this fundamental knowledge and analytical technique had been made in these days, which would evoke us new and key ideas for further development of oxidation catalysts with high activity and selectivity.

Session 2 “Molecular catalysis” covering the topics 3-“Molecular catalyst design”, 4-“Organic syntheses: selective and asymmetric oxidation”, 5-“Biocatalysts and biomimetic approaches”

Shunichi Fukuzumi, *Department of Material and Life Science, Division of Advanced Science and Biotechnology, Graduate School of Engineering, Osaka University, SORST, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan*

This session is focused on recent development of the oxidation of hydrocarbons of biological importance. Nature has evolved a variety of enzymatic processes capable of stereoselective oxidation of hydrocarbons. Prof. Que reported a family of bioinspired non-heme iron complexes capable of catalyzing stereoselective olefin oxidation with hydrogen peroxide to afford both epoxides and *cis*-diol products in varying ratios in his plenary lecture. The non-heme iron complexes are shown to generate Fe^{III}-OOH and/or formally Fe^V=O oxidizing species whose reactivity is finely controlled by tetradentate ligand topology, substrates, and additives. Prof. Newcomb has shown that such high valent transition metal-oxo intermediates can also be produced photochemically by ligand

cleavage reactions and by photo-oxidation of a lower valence metal-oxo species in his keynote lecture. The photochemical methods have provided highly reactive transients for detailed kinetic and mechanistic studies in which the identity of the oxidant can be determined directly in single turnover reactions, and direct kinetic studies can be conducted on microsecond timescales. Prof. Ishii has also given a keynote lecture on highly efficient and selective transformations of hydrocarbons to useful substances via the carbon radical generation from a C–H bond of a wide variety of compounds by the use of *N*-hydroxyphthalimide (NHPI) which serves as a carbon radical producing catalyst. On the other hand, an intriguing current controversy on the involvement of multiple oxidizing species in oxygen atom transfer reactions by cytochrome P450 and iron porphyrin models has been discussed by Prof. Nam in his invited lecture. The different products and/or product distributions observed in the catalytic oxygenations by iron porphyrin models are suggested to arise from the oxoiron(IV) porphyrin intermediates with a chameleon-like behavior rather than from the involvement of multiple oxidizing species in oxygen atom transfer reactions.

In addition to highlighted plenary and invited lectures mentioned above, a number of interesting reports have been given in oral and poster presentations in the present session. For example, Prof. Watanabe reported that an oxygen carrier (myoglobin) was engineered to efficiently perform peroxidase, catalase, and peroxygenase activities including a site-specific oxidation of aromatic ring by a myoglobin mutant and hydrogen peroxide. Prof. Kojima has shown that ruthenium(III) mononuclear complexes having tris(2-pyridylmethyl)amine (TPA) are capable of catalyzing alkane oxygenation with *m*-chloroperbenzoic acid at room temperature. Aliphatic C–H bond activation has also been shown to undergo by bis(μ -oxo) dinickel(III) complexes in an oral presentation by Prof. Suzuki who has succeeded in isolation and characterization of a series of the sequential reaction intermediate.

Bioinspired modeling of a number of enzymatic processes capable of stereoselective oxidation of hydrocarbons, discussed in this session, has been a challenging endeavor and the further extension beyond the scope of the bioinspired systems will be a more important objective in future.

Session 3 “Heterogeneous catalysis” covering the topics 8-“New developments in oxidants and oxidation catalysts”, 9-“New oxidation processes”, 11-“Selective oxidation for petrochemical intermediates”

Takashi Tatsumi, *Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

Upholding the great tradition of WCOG, Session 3, the Heterogeneous catalysis session, was the largest in the Congress. Actually among the 83 oral presentations, 38 papers were contained in Session 3. Because of this large number, Session 3 was forced to hold two parallel sessions on Monday afternoon. Of course, besides these submitted papers, two

plenary lectures, one featured lecture and one keynote lecture were delivered. The number of poster presentations rose to nearly 100.

Professor Sir Thomas delivered one of the plenary lectures. He emphasized the importance of “single-site heterogeneous catalysts” that will open up methods for the future avoidance of ecologically harmful conventional procedures. He demonstrated the innovative methodology of efficient and benign chemical conversions by the following examples: cyclohexane or cyclohexene to adipic acid, toluene to either benzaldehyde, benzoic acid or cresols, cyclohexanone with ammonia to ϵ -caprolactam, and secondary alcohols to ketones.

Professor Mizuno gave the other plenary lecture on molecular design of polyoxometalate catalysts for selective oxidation. Efficient H₂O₂ based olefin epoxidation systems with various polyoxometalates have been established. These systems have valuable features such as high activity and high H₂O₂ efficiency in the terminal olefin epoxidation, unique stereospecificity, regioselectivity, and diastereoselectivity in the epoxidation of *cis/trans* olefins, non-conjugated dienes, and 3-substituted cyclohexenes, respectively.

The keynote speech made by Prof. Panov was about various oxidation species on the surface of metal-oxide catalysts and their possible role in selective oxidation catalysis. He suggested that over FeZSM-5 zeolites so-called α -oxygen species are formed by the reaction of α -sites in the zeolites matrix with N₂O. This α -oxygen species was assumed to be similar to O⁻ anion radical, which abstracts hydrogen from methane and benzene.

Prof. Wan gave a featured lecture about mesoporous molecular sieves containing Fe sites for selective oxidation. Catalysts containing framework Fe showed higher selectivity for HCHO than catalysts containing extraframework FeO_x clusters in the oxidation of methane by O₂. However, the latter showed high conversion and epoxide selectivity in the oxidation of propylene by N₂O. Improvement in the catalytic performance was made by modification with various elements.

Besides these, Session 3 covered a wide variety of oxidation catalysis and processes. Catalysts based on Bi, Mo, V, etc. for selective oxidation of hydrocarbon continue to be of vital interest. Gold catalysts have been engaging the keen attention of people of science and technology in catalysis. As new catalytic materials, more and more zeolites and mesoporous materials have been applied to selective oxidation. As an alternative and green oxidant, H₂O₂ is gaining special interest and its synthesis and utilization are being developed. It seems that other intensively and extensively studied objects are oxidative dehydrogenation of alkanes, selective oxidation of alcohols and H₂S, and CO oxidation, and these kinds of presentation were noticeable by their number.

Session 4 “Oxidation engineering” covering the topics 6-“Combinatorial catalyst screening”, 7-“Characterization and in situ analyses of catalysts”

Kohji Omata, *Department of Applied Chemistry, Tohoku University, 6-6-04, Aramaki Aza Aoba, Aoba-ku, Sendai, Miyagi 980-8579, Japan*

This session dealt with various oxidation reactions: total oxidation, combustion, partial oxidation, oxidative dehydrogenation, and so on. It was aimed at discussing a novel utilization of catalyst, catalytic process evaluation, and the catalyst development method rather than the catalysis itself. Distinctive topics at this conference were combinatorial catalysis, membrane reactor, microreactor and wall type reactor. Above all, there was a lot of emphasis on combinatorial catalysis. Combinatorial catalysis usually consists of high-speed library synthesis, high throughput screening, and informatics. All these topics were covered by the plenary lecture, keynote lectures, and morning lectures of this session, and reported from leading research groups.

Although there are not so many groups studying combinatorial catalysis in Japan, a variety of researches in combinatorial catalysis in EU and USA were reported in a special issue of *Catalysis Today* in 2002. In the reports the importance of “descriptors” in a general format to build a catalyst databank was pointed out. This unfamiliar concept was unveiled in oral contributions, and such a database is partially realized using mark-up language. Furthermore, the importance of implementation of chemical “common sense” into the database was also emphasized. An example of database to predict chemically impossible catalyst was impressive. While such topics on database are hardly recognized in the research of combinatorial catalysis in Japan, the collaborative project on the reference catalysts organized by Catalysis Society of Japan that evaluated catalytic properties of common reference catalysts and the pioneering work on “CHEMOGRAM” by Professor Yoneda, were presumed to have made important breakthroughs. Anyway, the usefulness of these combinatorial catalysis techniques will be recognized if a new truly excellent catalyst is developed by them.

As for a membrane reactor, partial oxidation of methane using a novel oxygen permeating oxide membrane was introduced in the featured lecture. Development of new materials will promote the industrialization of the highly selective process. There are a moderate number of presentations in the field of microreactor research, considering the activities of this research area. Stimulating results, from fundamental to commercial levels, were presented. The microreactor technology has been recognized to cause a ripple effect to a membrane reactor, the HTS reactor for combinatorial catalysis, etc.

Whereas the selectivity improvement of a partial oxidation reaction could be an eternal subject, it seems that reaction engineering is indispensable as a judicious approach.

Session 5 “Environmental oxidation” covering the topics 12-“Photochemical and electrochemical oxidation, including fuel cells”, 13-“Catalytic combustion and VOC removal”

Koichi Eguchi, *Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan*

The Environmental oxidation session consisted of 2 keynote lectures, 1 featured lecture, 3 OM-type oral presentations (morning) and 9 OA-type oral presentations (afternoon), and 31 poster presentations. The session covered a wide variety of oxidation catalysis related to the environment, e.g., desulfurization, deNO_x, particulate oxidation, VOC removal, oxidation of dioxin-related compounds, oxidation with ozone, catalytic combustion of hydrocarbons, photocatalytic oxidation, hydrogen production by partial oxidation-reforming, electrocatalytic oxidation of hydrocarbons, preferential oxidation of CO, environmentally friendly catalytic processes in vapor and liquid phases, etc. Attractive three presentations for keynote and featured presentations will be briefly introduced hereinafter.

The keynote presentation by Prof. Forzatti et al. (Politecnico di Milano, Italy) was entitled, “NO_x Removal Catalysis under Lean Conditions”. The principal operating mechanism of NO_x storage–reduction catalysts has been clarified for the application to automotive engine exhaust. The two governing routes, i.e., the nitrate route via formation of NO₂ and the nitrite route via direct oxidation and adsorption near Pt, were proposed. Catalytic oxidation of nitrogen oxide species should play a key role in the NO_x storage–reduction catalysts.

Prof. Wachs et al. from Lehigh University, U.S. proposed a novel process of “oxidesulfurization (ODS) of organosulfur compounds”. Although hydrodesulfurization accompanies consumption of valuable hydrogen, the proposed ODS is effective in converting organosulfur compounds into valuable chemical intermediates such as maleic anhydride and concentrated SO₂. Vanadia on titania has been reported as being active for this reaction.

Dr. Tanaka from Daihatsu Motor, Japan presented his novel findings in intelligent catalysts for automotive exhaust having a self-regenerative function. Palladium species on Co-based perovskite is reversibly incorporated in and excluded from the oxide lattice with the cyclic reduction–oxidation treatment of the catalysts. Thus, the coarsened precious metals particles could be dispersed with this treatment cycle to maintain high activity usable for super ultra low emission vehicles.

The active discussion has been made throughout the session in addition to these three prominent presentations, suggesting the importance of oxidation catalysis for environmental protection.