

MEETING REPORT

SEVENTH NATIONAL SYMPOSIUM OF THE CATALYSIS SOCIETY OF INDIA
Baroda, India, 6th-8th february, 1985

This meeting, held at the R & D centre of IPLC, Baroda, was attended by about 300 participants from India and more than 30 from various other countries.

Opening the meeting, the Financial Director of IPLC, Mr. Bakshi, outlined the importance of that organisation with respect to the catalytic processes used in India, for instance in the new petrochemical complex due to start operation in Maharashtra. He appealed for a self-reliance in the production of the requisite catalysts and pointed out that the Catalysis Society of India can play an active role in optimising the utilisation of national resources. Prof. Kuriacose, President of the Society, outlined its growth since its inception in 1973 and thanked IPLC for making their facilities available for the meeting. He also paid tribute to the late Professors Schwab and Boreskov who had contributed so much to Catalysis.

Prof. Haber of Kracow, Poland, gave an illuminating key-note address in which he considered the catalytic oxidation of hydrocarbons on oxide-catalysts. He classified all catalytic oxidation reactions in two simple categories, based on the participation of either electrophilic or nucleophilic oxygen species. In his attempt to rationalise the extensive data available on oxidation reactions, he stressed the need to understand the dynamics of the surface during reaction as well the necessity to treat the surface processes as three phase systems involving gas, bidimensional surface region and bulk solid. The published form of this systematic is recommended for study by those who wish to have a better understanding of oxidation catalysis.

Prof. Guzzi, Head of the Catalyst Research Group at the Institute of Isotopes of the Hungarian Academy of Sciences, gave a plenary lecture entitled "CO Hydrogenation on Fe-Ru Catalysts". He concentrated on the factors controlling the population of various surface species and the possibilities of inter-converting them so as to optimise the hydrocarbon yields. The structures of catalysts and the possibilities of interaction in bimetallic systems were also outlined.

Dr. Ballard of ICI, U.K., spoke on the use of model systems in comprehending the role of catalysts in synthesising polyolefins. He traced the evolution of organometallic chemistry and the production of polyethylene at low pressures, with exhaustive coverage of transition and non-transition metal alkyl catalysts used for this reaction; he also discussed aspects of copolymerisation and the control of crystallinity in polycrystalline materials. Dr. Menon of Chalmers University, Sweden, then delivered a plenary lecture entitled "Some Contributions to the Surface Chemistry of Platinum Reforming Catalysts", this being a review of the work of the speaker over the last fifteen years on methods for the estimation of metal dispersions in bimetallic (Pt-Re) reforming catalysts, the controversy surrounding the stoichiometry used for determining metal dispersions by gas titration and the effect of reduction treatment on the properties of the catalysts especially in the context of SMSI effects.

Prof. Chakrabarty of the Indian Institute of Technology, Bombay, reviewed in his plenary lecture the use of the XPS technique in catalysis research, cautioning about those areas where its application can lead to ambiguous and sometimes erroneous conclusions. Prof. Delmon of the Catholic University of Louvain, Belgium, focussed in his plenary lecture entitled "Approaches to the Study of Catalyst Deactivation" on three vital topics: the need to characterise deactivation; the type of information needed; and how to proceed to achieve this characterisation. This was a well-organised lecture and could form the basis for further studies in this field. Prof. Kuriakose of the Indian Institute of Technology then spoke on a topic of current interest, catalytic reactions on illuminated semiconductor solids, clearly bringing home the differences between photocatalytic and photoassisted processes and showing how catalytic and photo-electrochemical processes can be used advantageously to harness solar energy.

In addition to these six plenary lectures, 38 papers and more than fifty

posters were presented during the symposium. The posters were presented in two sessions and covered:

- (i) preparation and characterisation of catalysts, especially mixed oxides and supported metals used for Fischer-Tropsch and reforming reactions;
- (ii) evaluation of activity and selectivity of catalysts such as charcoal, FeTi, perovskite oxides, and CO-conversion catalysts;
- (iii) theoretical aspects of cluster systems and for treatment of reactions in industrial fluid-bed reactors;
- (iv) catalysis in organic synthesis, for example the conversion of isophorone to 3,5-xyleneol, bromination of phthalic and sulphobenzoic acids, etc.;
- (v) zeolites in catalysis, including synthesis and characterisation of high-silica pentasil, toluene disproportionation, methanol dehydration and reforming of n-hexane over $\text{Pt-Al}_2\text{O}_3$ -zeolite catalysts;
- and (vi) homogeneous catalysis.

The papers presented during the orals sessions could also be divided into broad groups. In the first session on "Catalysis, Principles to Practice", Pakhamov and Buyanov of the USSR Institute of Catalysis reported on the interrelation between the crystallographic properties of Pt-Sn and Pt-Zn alloys supported on ZnAl_2O_4 and their properties for the dehydrogenation of light paraffins. Sivasankar and coworkers of NCL, Puna, reported catalytic hydrodewaxing studies of oils from Bombay high crude using various bifunctional catalysts made up of a metal component (Pt or Ni) and a shape-selective ferrisilicate zeolite; a catalyst obtained by an anion-exchange procedure was found to be the most active. Imai and coworkers of UOP, USA, reported on the development of an improved paraffin dehydrogenation catalyst and also showed how the use of this active material could result in significant savings in operating costs. Viswanathan of IIT, Madras, outlined the use of the cluster model to treat catalysts exhibiting the SMSI effect, a subject also covered in four papers in the session: "Theories, Models and Concepts in Catalysis". In the first of these, Giordano and his colleagues of the University of Messina, Italy, introduced the concept of electronegativity in zeolite catalysis and showed the relationship between this parameter and the catalytic activity in complex reactions such as the conversion of methanol to hydrocarbons, dehydration of isopropyl alcohol and the isomerisation of xylenes. Gunasekaran and colleagues from IIT, Madras, considered the kinetics and mechanism of the oxidation of CO on $\text{Co}_{1-x}\text{Zn}_x\text{Mn}_{2-x}\text{O}_4$ spinels through conventional kinetics and in-situ IR measurements. Gross of BASF, FRG, considered the dynamics of the structure of the catalysts, especially in the context of added alkali metals. In the next session on "Synthesis, Characterisation and Evaluation of Catalysts", five papers were presented and discussed. Mayadevi and his coauthors from NCL, Pune, considered the effect of the addition of Ba and alkali metals (K and Cs) and of pretreatment temperature on the size and morphology of silver catalysts and the chemisorption of oxygen at 523 K. Pichat et al. of CNRS, France, considered the preparation, characterisation and use of Pt/TiO_2 photo-catalysts for a number of reactions including the dehydrogenation of alcohols. Narisimhan and colleagues of IIT, Bombay, reported on the synthesis and characterisation of $\text{LaCo}_{1-x}\text{Fe}_x\text{O}_3$ and LaMnO_3 perovskite oxides for CO oxidation and the NO-CO reaction. Gupta et al. of BARC, Bombay, considered the hydrogen and oxygen reactivity of carbonaceous species deposited from ethylene on a $\text{Ru/Al}_2\text{O}_3$ catalyst using a pulse injection method, inferring the presence of both mono- and di-carbon species whose concentrations depended on catalyst temperature. Lahari and Nindi of the University of Calcutta, in studies of the hydrodesulphurisation reaction, identified a material containing 0-3% Co, 1% Fe_2O_3 , 16% MoO_3 and the balance alumina as being most suitable for the HDS of thiophene in heptane.

In the session on "Heterogeneous Catalysis in Organic Synthesis", Pillai et al. of IIT, Madras, reported a novel catalytic transformation of dibenzyl ketone or its precursor, phenyl acetic acid, over alumina to give 2-phenylindine, 1,3-diphenylallene being an intermediate. Rajadhyaksha et al. then presented the results of studies on the amination of phenol and anisole over various types of zeolites and the correlations of catalytic activity with acidity and other properties of the cations involved. Narisimhan and coworkers from Alchemie Research Centre considered the oxidation of ethanol over V_2O_5 -based catalysts and showed that the concentration of the V^{4+} species controlled the activity towards

partial oxidation while the acid-base properties of the catalysts were also found to influence the course of the reaction. Kasumov, of the Gas Research Institute of the USSR, considered the potentialities of titanium and tin oxide solid solutions as catalysts in the selective oxidation of H_2S and hydrocarbons. Roy et al. of CFRI reported results for the catalytic synthesis of pyridine bases; catalysts with a silica:alumina ratio of 88.2:11.8 promoted by oxides and fluorides, particularly of Zn or Cd, showed highest activity for the production of alpha and gamma picolines from aldehydes and ammonia by dehydrocyclisation.

The fifth oral session concerned "Spectroscopy in Catalysis". Kochubei and Zamaraev, Novosibirsk, USSR, reported on the use of the EXAFS technique for the study of the structure of metal species in supported metal catalysts, the systems considered including Pt-alumina, Pt-silica, (Pt+Re)/silica, Rh/alumina, Rh/silica, Rh/lanthana and Pd clusters with bipyridine or acetate as ligands. Chary and coworkers of RRL, Hyderabad, and the University of Hyderabad reported on XRD and ESR studies of vanadia-titania catalysts, their results concerning the anatase-rutile and V^{4+} concentrations as a function of vanadia content. Guzzi reported an interesting study, using Mossbauer, IR, TPD, TPR and TPO techniques, of the characterisation of mono- and bi-metallic catalysts derived from molecular carbonyl clusters, comparing the catalysts with those prepared by conventional methods. Chakrabarty et al. of IIT, Bombay, studied the formation of supported ruthenium catalysts prepared by the decomposition of $\text{Ru}_3(\text{CO})_{12}$ and attempted to identify the various Ru species present on the catalyst. Ione and his colleagues of the Institute of Catalysis, USSR, reported that crystalline silicates with cations in octahedral oxygen environments promote reactions of methanol decomposition, reporting also the effects on this reaction of isomorphic substitution of cations in the zeolite structure.

In the session on catalyst deactivation and regeneration, Franck et al. of IFP, France, dealt with ageing of reforming catalysts. Chabra et al. of PDIL described a method for reprocessing a copper catalyst used in the manufacture of acetaldehyde. Chidambaram of IIT, Bombay, presented a theoretical modelling study of the effect of deactivation on the steady-state behaviour of cocurrent bubble column slurry reactors and Gour et al. of PDIL described a procedure for the regeneration of a spent Comox catalyst.

Five interesting papers were presented in the session on "Zeolite Catalysts". Hegde and Kulkarni of NCL described work on the textural characterisation and sorptive properties of ultrastable zeolite-Y systems while Matthews and Rees of Imperial College, London, presented interesting results for the exchange properties of Na-ZSM5, rationalising the exchange capacities with the thermodynamic parameters of the exchange and attempting to characterise the sites for exchange, especially for Fe^{2+} . Bawa and Bhattacharyya of IIP considered the trans-alkylation of di-isopropyl benzene with benzene in the liquid phase on various zeolite-based catalysts and established a correlation between activity and the concentration of strong acid sites. Halgeri et al. of IPCL reported the results of their study of the selective formation of p-xylene by alkylation of toluene with methanol over chromo-silicate zeolites; enhanced para-selectivity was also observed when Cr ZSM5 was modified with B, Mg or P compounds. Cursetji et al. of ACC reported the results of their study of higher silica-alumina ratio zeolites as well as zeolites containing iron for the production of ethylene from ethanol, showing that these systems are better than conventional catalysts because of their lower temperatures of operation and higher throughputs.

In the penultimate session, on "Process Optimisation", Nat of Ketjen, The Netherlands, described the objectives and limitations of equipment in catcracking, focussing attention on recent developments in catalysts for the Indian context. Daftary and colleagues of GSFC presented the results of a pilot-plant study of an indigenous benzene hydrogenation catalyst, showing that it compared favourably with an imported material. Satyanarayana et al. of RRL, Hyderabad, studied the hydrogenation of CO over multimetallic catalysts such as Fe-Mn and Fe-Mn-Ti supported on molecular sieves. Murthy et al. of IPCL studied the quality of naphtha with boiling range 110-140°C on the catalytic reforming of xylene production over commercial Pt-Re/alumina catalysts under simulated industrial operating conditions and obtained correlations between feed parameters and reformer performance.

The final session, "Homogeneous Catalysis", included a paper by Kelker et al. of NCL who showed that $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ is the most active and selective catalyst for the homogeneous reaction of CO , H_2 and methyl acetate to form diacetate. Ravi Kumar et al. of RRL, Hyderabad,² reported on the synthesis of a novel heterogenised $\text{Pd}(\text{II})$ montmorillonite catalyst useful for the hydrogenation of olefins and acetylenes. Bukatov et al. of the Institute of Catalysis, USSR, studied the composition and formation of highly active titanium-magnesium catalysts for polymerisation and Satish et al. of IPCL considered the effect of the structure of metal Schiff-base complexes on the oxidation of 2,6 di-tert-butylphenol.

The organisational efforts of the staff of IPLC were greatly appreciated by the participants at the symposium. The success of the meeting and the encouragement given to the participants will be some reward to them for the considerable work which it all involved.

The papers of the symposium have been published in a book, edited by Dr. T. S.R. Prasada Rao, by Wiley Eastern Ltd.

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