

6th annual day of the

NATIONAL CENTRE FOR CATALYSIS RESEARCH

**INDIAN INSTITUTE OF TECHNOLOGY MADRAS
CHENNAI 600 036**



Abstracts of the presentations

**Sunday, July 29, 2012
[9 a.m. to 12.45 p.m.]**

Program for the 6th Annual Day of NCCR

9.00 to 9.30 a.m.	Current trends in catalysis Report of ICC	Professor S Sivasanker
9.30 to 10.00 a.m.	Light weight Metal Hydrides for Hydrogen Storage	Dr L.Himakumar
10.00 to 10.20 am	Topic to be announced	A.Selvamani, Anna University
10.20 to 10.40 a.m.	Topic yet to be known	M.Selvaraj, Anna University
10.40 to 11.00 a.m.	Coffee break	S. Lalitha
11.00 to 11.20 a.m.	Activation of CO ₂ on ZnO:N surface	Mr. R. Shanmugam
11.20 to 11.40 a.m.	Fuel cell trends and challenges	Ms. S. Lalitha
11.40 to 12.00 noon.	Photo-catalytic Degradation of Monocrotophos in An Immobilized Bead Photo catalyst Using Factorial Design of Experiments	Ms.K.Sivagami Department of Chemical Engineering
12.00 noon to 12.30 p.m.	Facts and Fictions on Hydrogen Spill Over	Dr R C Arundhathi
12.30 to 12.35 p.m.	Conclusion	Dr K R Krishnamurthy

Preface

National Centre for Catalysis Research was established at Indian Institute of Technology, Madras by the Department of Science and Technology, Government of India in 2006 with the specific objectives for generation of **suitable manpower** in this area and also to carryout **research in frontier areas** of catalysis.

Accordingly the centre has been working on four main areas of research namely **Materials for Catalysis, Surface Science, Energy Conversion and Theoretical Studies** related to catalysis.

The centre has been associated with a number of industries for development of specific processes and also introduced a new master's degree program in catalysis Technology. NCCR has so far passed out **two batches of M Tech students** in this branch and also contributed in terms of publication and books the details of which are available in NCCR website.

The centre has been conducting the **orientation program** in catalysis continuously and this program is open to all the research students of this country. In addition to this orientation program the centre also conducts special programs on specific topics and the details of the special program conducted by the centre are also available in the website.

The centre has also placed more than **6 ebooks** for the teaching and learning process and these books are freely available for anyone who wants to download them.

The centre is maintaining a number of web sites among which the catalysis data base is widely used by the academic community all over the world and leading publishers are contemplating of making similar web sites on catalysis for commercial purposes. (<http://www.eprints.iitm.ac.in>)

The centre has its own web site at <http://www.nccr.iitm.ac.in>.

Readers are requested to refer to these websites for any information on the centre and its activities. One can also email us for any further information.

Light Weight Metal Hydride for Hydrogen Storage

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Hydrogen storage is one of the biggest hurdles to the implementation of hydrogen fuelled fuel cell vehicles. Though, metal hydrides have the advantages of the highest volumetric density, moderate temperature and pressure working conditions, they suffer from significant weight penalty. Metal alanates and borohydrides have among the highest gravimetric hydrogen storage capacities with the potential to meet the DOE gravimetric density targets and to offset the system weight penalties. However, high desorption temperature, reversibility and unwanted byproducts during dehydrogenation are challenging issues for these materials. Catalytic effect of nitrogen doped CNT and graphene on NaAlH_4 ; synthesis, characterization, hydrogen storage properties of Al, Mg, B and N based hydrides will be discussed during the presentation.

References

1. **H. K. Lingam**, B. Viswanathan and S. Srinivasa Murthy, "Dehydrating behavior of LiAlH_4 —the catalytic role of carbon nanofibers", *International Journal of Hydrogen Energy* 33, 2008, 366-373.
2. **H. K. Lingam**, X. Chen, T. Yisgedu, Z. Huang, J. -C. Zhao and S. G. Shore, Redetermination of Magnesium, di(μ -(tetrahydrido aluminium)) tetrakis(tetrahydrofuran), *Acta Crystallographica Section E66*, 2010, M575 .
3. X. Chen, **H. K. Lingam**, Z. Huang, T. Yisgedu, J. -C. Zhao, S. G. Shore, "Thermal decomposition behavior of hydrated magnesium dodecahydrododecaborates", *The Journal of Physical Chemistry Letters*, 1, 2010, 201.
4. **H. K. Lingam**, X. Chen, S. G. Shore, "A new Convenient Synthesis and NMR study of diammoniate of diborane" *Chemistry: A European Journal* 18, 2012, 3490.

Hydrogen Spill-over- Facts and Fiction

(Chem. Rev. 2012, 112, 2714–2738. Roel Prins*)

Racha Arundhathi

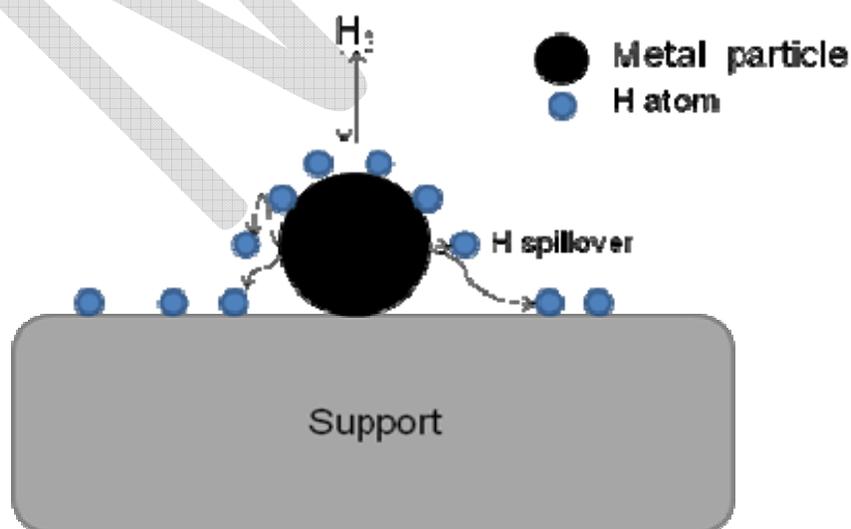
A detailed theoretical investigation has been carried out with experimental proof to support facts and fictions about hydrogen spill-over on various supports.

Hydrogen gas • metal-support • reducible support • non-reducible support

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1. Introduction

Boudart et al. coined the word “spillover”,¹ Hydrogen spillover arises in hydrogen catalyzed reactions on supported metal catalysts. Dihydrogen molecules dissociate on the metal part of the catalyst. Some hydrogen atoms remain attached to the metal whilst other H atoms migrate from the metal particles to the support and are said to *spillover* (Scheme 1). The starting point of spill over is first observed by Khoobiar in 1964 with Pt/WO₃ with hydrogen to give blue WO_{3-x}.² However, spill-over does not occur in all circumstances, caution must be exercised before suggesting that spill-over is the explanation of a scientific event. The role of hydrogen spill-over is important in the synthesis of methanol, hydro-isometization, and the hydrogenation of alkenes and aromatics, besides having the prominent application in the hydrogen storage. Spillover hydrogen has often been inferred from hydrogen adsorption and reactivity studies. Experimental proofs such as, energy correlation and H-D exchange on the support of a metal catalyst as a proof of no hydrogen spill-over.



Scheme 1. Spillover of a H atom on reducible supports

Here, we report a study on the review reported by *Roel Prins*³ that explains in detail the facts and fictions about hydrogen spill-over.

2. Experimental

The H-D exchange experiments on non-reducible supports show H-D exchange is not a proof of spill-over, H-D exchange, and hydrogenation are not correlated and do not support the spill-over. ESR, DFT, TPR, IR, or NMR investigation constitutes no proof of spilled-over hydrogen atoms on the non-reducible supports. Neither the ESR investigation of the solution of *N*-benzylidene-*t*-butylamine-*N*-oxide gives no strong evidence for the spilled-over hydrogen atoms on the support.

3. Results and Discussion

In scrutinising the facts and fictions of hydrogen spill-over on reducible and non-reducible supports. The review covers the major part and proves the fact about the spill-over of hydrogen on reducible supports and the fiction on the analogous spill-over over of hydrogen on non-reducible supports which is energetically impossible (Fig 1). The review also covers the experimental facts how a contamination in the non-reducible supports or with defects support spill-over. If metal cations are preferentially adsorbed on the surface defects during wet catalyst preparation, the metal particles that are created by reduction may well be positioned at or close to surface defects. In that case, an energetically easy migration path for H atoms from metal particle to surface defects may be possible.

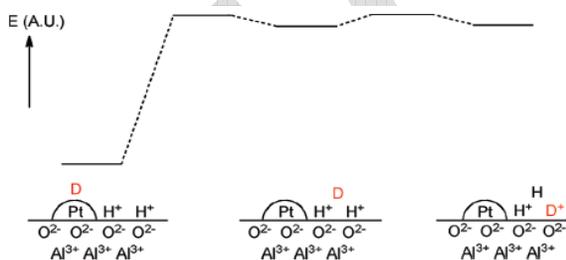


Fig. 1. Energy scheme of spill-over of a D atom from a metal particle to the support followed by H-D exchange on the support.

Acknowledgement

This study was partly supported from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

- 1) M. Boudart, M. A. Vannice, J. E. Z. Benson, *Z. Phys.Chem. NeueFolge*, **64**, 171 (1969).
- 2) S. Khoobiar, *J. Phys. Chem.* **68**, 411 (1964).
- 3) R. Prins, *Chem. Rev* **112**, 2714 (2012).

HYDRODEOXYGENATION OF METHOXYPHENOL USING Ni-Mo SUPPORTED NANOSTRUCTURED ALUMINOSILICATES

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DEPARTMENT OF CHEMISTRY, ANNA UNIVERSITY, CHENNAI-600025

The rate of requirement of fuel increases with decrease in current fossil fuel resources. Hence, the focus is to convert the easily available bio resources like lignin derived from wood by pyrolysis method, non-edible oil such as jatropha and all vegetable oils to fuels. The direct uses of all these sources are very difficult because of highly polymeric nature of wood and the presence of high oxygen content. Hence, the processing of bio-oils by various methods such as high temperature thermal cracking, hydrotreating and transesterification becomes essential. In transesterification, the presence of oxygen proportion was very high and it is not suitable to meet the current standards. In conventional hydrotreating method, Ni-Mo catalyst supported over Al_2O_3 was used to improve the fuel characteristic properties. The conventional process improves the quality of biofuels to the some extent of the current standards with high calorific value, chemical stability and economically viable fuel. However, the oxygen content in the bio-oil does not get reduced by the conventional hydrotreating catalyst. Hence, a new pioneering catalyst is essential for high conversion of bio resource to produce liquid hydrocarbons.

Recently mesoporous aluminosilicate nanoparticles have attracted attention as catalyst as well as support due to high surface to volume ratio compared to conventional catalysts. In the present work, the high surface area mesoporous aluminosilicate supported Ni-Mo catalysts is synthesized by varying the Si/Al ratio of the support at constant percentage of MoO_3 and NiO and used for removal of oxygen from a model oxygen compound, viz., methoxy phenol by HDO. The catalytic activity of the catalysts was measured for hydrodeoxygenation of methoxyphenol, a model compound for liquid hydrocarbon production using a fixed bed down flow reactor under different experimental conditions to achieve good conversion and selectivity of the products. The interaction between metal and support was studied by the TPR and dispersion of metal was measured by H_2 pulse titration. The catalytic activity was correlated with the surface area and metal dispersion over the support. The structure - activity relationship is discussed with reference to metal dispersion and surface area for HDO of methoxyphenol.

SELECTIVE OXIDATION OF CYCLOHEXANE USING MANGANESE LOADED CERIA NANOCATALYSTS

A.Selvamani and K. Shanthi*

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Cyclohexane oxidation is an important commercial reaction for the preparation of cyclohexanol and cyclohexanone, which are intermediates in the production of adipic acid and caprolactam, respectively. These two products are important in the manufacture of nylon-6 and nylon-6,6 polymers. Transition metal doped molecular sieves such as Ti-MCM-41, V-MCM-41, V-MCM-48, Bi/MCM-41, Au/MCM-41, Au/ZSM-5, Fe(III), Mn(III) and Fe-MCM-41 have been widely used for cyclohexane oxidation. However, these catalysts are capable of oxidizing cyclohexane only at higher temperatures. It has been reported that Ceria is a versatile catalyst for the oxidation of many organic substrates due to high oxygen storage capacity (OSC) and surface area. Hence, to achieve high conversion especially at low temperatures, it is proposed to use transition metal incorporated ceria nano-particle.

In this context, manganese is incorporated into ceria framework and catalytic activity is measured for the partial oxidation of cyclohexane into cyclohexanol and cyclohexanone at low temperature (180°C). In this part of work, attention is paid to manganese oxides which exhibit good oxidation ability due to various oxidation states of manganese species such as +2, +3, +4. In the present work, Mn/CeO₂ nanocatalysts with varying Ce/Mn ratio (25, 50 and 75) were prepared using cerium nitrate and manganese acetate as a precursor by precipitation method. The physicochemical properties of the synthesized materials were studied by X-ray diffraction method (XRD), N₂ adsorption/desorption, DRS-UV, SEM and TPR techniques. The selective vapour phase oxidation of cyclohexane was studied at various temperatures using a fixed bed reactor. The catalytic activity results are discussed in correlation with physico-chemical characterization data.

FUEL CELL TRENDS AND CHALLENGES

S. Lalitha

National Centre for Catalysis Research, IITM

“Energy can neither be created nor it is destroyed however energy can be converted from one form energy in to any other form of Energy” - law of conservation of energy.

Each generation is confronted with new challenges and opportunities. As chemists, one should contribute his research focus on these needs. In this century, energy is the most important one. Up to this century, fossil fuel is playing a vital role. But now everyone is focused to change fossil fuel due to pollution, green house effect and insufficient production of fossil fuels. Fuel cell is an advanced power system for the future that is sustainable, environmental friendly. The modern development of fuel cell and current status of national and international research has to be established. This review discusses the research and development issues that still need to be resolved before fuel cells are available for commercial application.

Activation of CO₂ on ZnO:N surface

R. Shanmugam

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Activation of CO₂ on nitrogen substituted zinc oxide has been examined theoretically with the DFT/B3LYP level of theory. Among the Different modes of CO₂ adsorption, the combination mode of adsorption via carbon and oxygen of carbon dioxide on to the surface nitrogen atom shows that the activation of CO₂ via the formation of CO+O species on the surface.

Photo-catalytic Degradation of Mono-crotophos in An Immobilized Bead Photo catalyst Using Factorial Design of Experiments

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The discharge of wastewaters containing pesticides from industries, agricultural applications and surface run off is a major cause for a variety of adverse environmental impacts. *Heterogeneous photo catalysis* has proved to be an effective treatment method for removal of toxic pollutants in to CO₂, H₂O and mineral acids. Although this field has experienced tremendous expansion in scientific research, its implementation in large scale has not been successful so far. The reason is the slow development of efficient and economic practical photo catalytic systems that can be used for the decontamination of water in large-scale application. New reactor was developed using light weight polymeric beads as immobilization base surface. The circulation of the immobilized surface allows the formation of a thin film of pesticide solution over the catalyst surface. This enables efficient penetration of UV radiation; good mixing and mass transfer rates and reaction within thin liquid film.

The performance of Immobilised Bead Photo catalyst was evaluated using photo catalytic degradation of Monocrotophos, an Organo Phosphate Pesticide using TiO₂ was investigated under UV irradiation. Batch recirculation experiments were carried out at initial concentrations ranging from 1 to 15 mg l⁻¹ at a pH ranging from 3.5 - 10.5 and at a catalyst loading of 2 –6 g. The study shows that about 50–80% degradation can be achieved depending on the initial pesticide concentration, pH and the amount of catalyst. Using a 2³ central composite factorial design of experiments a quadratic polynomial model was fitted to predict the removal efficiency. The statistical analysis revealed that the coefficients for the main effects are significant. High removal efficiency obtained in 1-15 mg l⁻¹ indicated effectiveness of this process and its potential for practical application.

Keywords: Photo catalysis; TiO₂; Im-mobilised bead photo catalyst, Mono-crotophos; Factorial design, ANOVA and Optimization

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Registration for the 6th annual day function on 29th July 2012

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