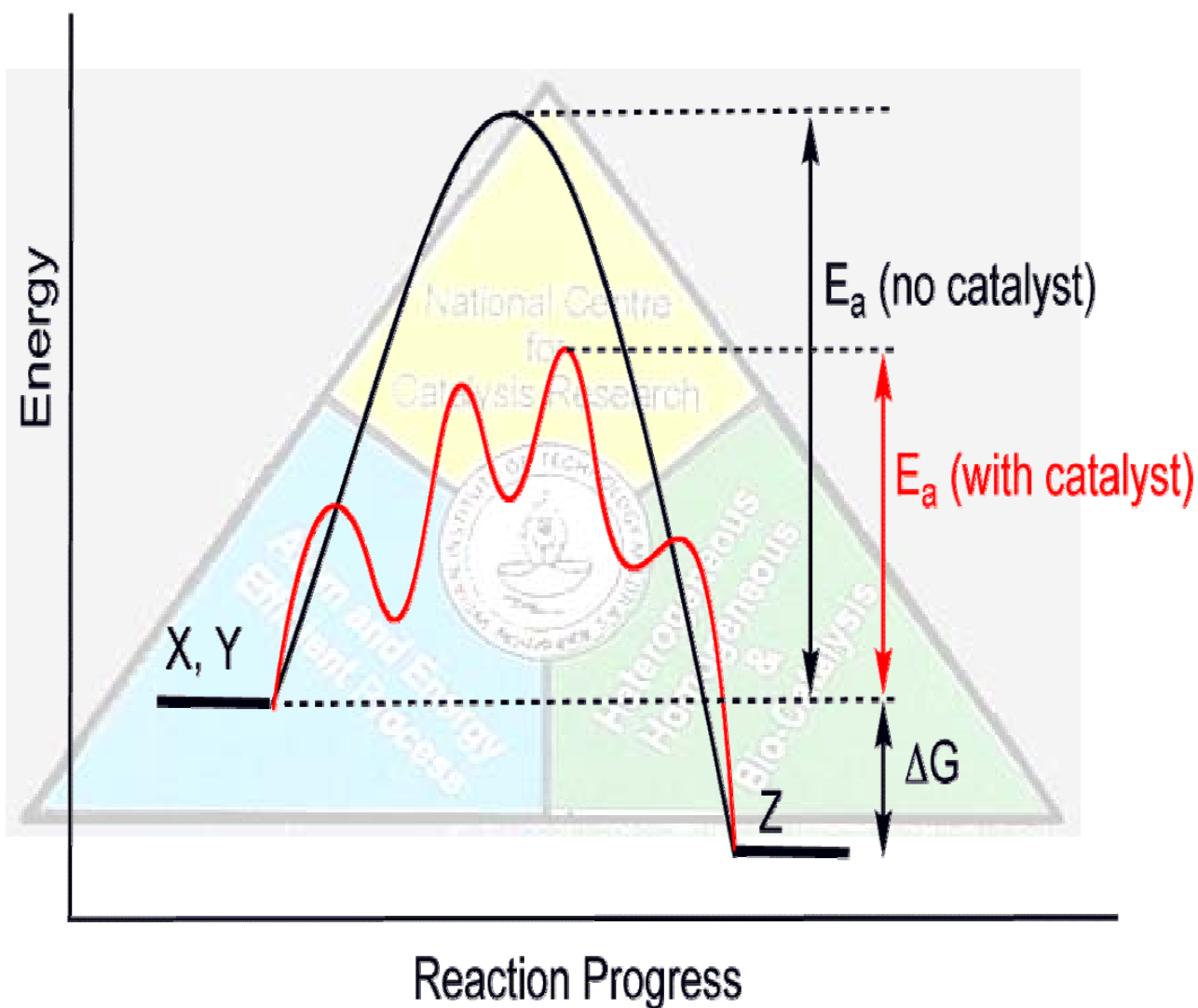*JOINT RESEARFELLOWS' WORKSHOP*
ON AUGUST 2, 2008
NATIONAL CENTRE FOR CATALYSIS RESEARCH
&
DEPARTMENT OF CHEMISTRY, ANNA UNIVERSITY
ABSTRACTS OF THE PRESENTATIONS
Venue: IC and SR Hall 3

Programme

Joint Research Fellows' Workshop

on Saturday, August 2, 2008

in the IC & SR Hall 3

9.30 -9.40a.m.	Introduction	The motivation for this workshop
9.40- 10.00	Presentation 1 -	**Mr Navaladian -** Role of Nanomaterials in Catalysis
10.00-10.20	Presentation II	**Mr. P. Vijayan -** Effect of method of synthesis and different metal doping on the photo-catalytic activity of Titania
10.20-10.40	Presentation III –	**Mr.B.Kuppan –** Meso-porous Architecture in Solids
10.40-11.00:	Break	Informal discussion and poster presentation
11.00-11.20	Presentation IV	**S.Vishnupriya -** Lewis acid metal ion-exchanged MAPO-36: Characterisation and catalytic performance
11.20-11.40	Presentation V	**Ms Helen –** Membranes and Catalysis
11.40-12.00	Presentation VI	**G. Karthikeyan**, HPWA supported MCM-41: An efficient solid acid catalyst for the green synthesis of xanthenedione derivatives under liquid phase conditions
12.00 - 12.20	Presentation VII	**D.Nedumaran** ,Phosphoric acid grafted MCM-41 is a novel Bronsted acid catalyst for transesterification of diethyl oxalate with n-Butanol.
12.20-01.00	Presentation	**Prof K Shanthi -**An overview of new approaches for removing sulfur from refinery systems"
01.00-01.10	Concluding remarks	Few remarks by participants and feedback and the desirability of such workshops in future
1.15-1.30	Poster presentation	
1.30	LUNCH	**At Tifanys in IIT Campus**

NATIONAL CENTRE FOR CATALYSIS RESEARCH

The National Centre for Catalysis Research at the Indian Institute of Technology, Madras is a Department of Science and Technology, Government of India sponsored research centre with the following objectives:

1. To create appropriate human resources in this technological area
2. To carry out research on some frontier areas of energy, materials and theory.

The Centre was established after approval of the Board of Governors of Indian Institute of Technology, Madras in July 2006. The centre will have a unique status of a National Centre within a national institution. The centre in this short period of two years has been growing into an internationally recognized centre for education and research. The centre has been recognized by various multinationals. The centre has won sponsored projects from famous multinationals like Shell, P and G, IOC, CPCL, and GM and have been in various stages of discussion with few others like BASF, W R Grace, Dow Chemicals and Tata Chemicals.

The centre conducts various educational programmes. The famous and popular one is the orientation for the research scholars of this country. Eight such programmes have already been conducted. The success of this programme is already visible since the scientific and research out put of this country in this high technology area has shown considerable improvement in terms of the impact it had in the scientific community. The scholars who have attended this programme have greatly appreciated this programme and have been advocating for this programme among their juniors.

The centre has already been equipped with state of art facilities for research in this area and it is conceived that in the formation period this will evolve into a full fledged international centre for research in this area.

International collaboration has already taken shape in bilateral programmes being evolved between NCCR and Hungary, Australia, Korea and Taiwan. Many more such international cooperation is expected to evolve soon.

The centre has attracted young and dynamic researchers and it has three young scientist (DST) awardees working in the centre with 8 PDFs and 20 research fellows working on various research projects in the centre.

The centre focuses on fundamental aspects of problems and the development of processes is mainly reflecting the needs of this country like adsorptive desulphurization, a process without any down stream processing of crude for obtaining directly diesel.

The centre it is hoped will evolve as one of the leading Centres in the world in the area of catalysis. It is heartening to note that the work carried out in this centre has already been recognized in various international forums, like the International Congress on Catalysis and are also selected for special highlights in Nature India and other media.

Extended Abstract Template, 2nd Annual day of NCCR, 2nd August 2008

The title of the presentation will be typed here at 14 point Times Roman

Name of the person presenting and his/her affiliation in single line spacing.

Abstract: Give a brief abstract of the talk in about 150-200 words in single line spacing.

Key words: Provide three or four key words.

1. **Introduction**
2. **Experimental section or theoretical models**
3. **Results and Discussion with figures and tables**
4. **Conclusion**
5. **References**

All these five subsections can be typed either single line or 1.5 line spacing and see to it that the whole thing does not exceed two pages. Kindly indicate the references within square brackets [1] and assemble all of them in the standard format at the end of the extended abstract.

Important information

Kindly note all presentation material must be previewed atleast two hours before the start of the programme. Please contact or send soft copies to NCCR accordingly. The presentations cannot be uploaded at the time of the presentation as we have to attach certain features before itself. The email on which the presentation power points can be sent is catalysisindia@yahoo.com . Please note this email and accordingly forward your material for presentation.

All those who wish to have an abstract copy are requested to print one from this soft copy emailed to all the participants. Those receive this email may forward to all others who may not be included in our mailing list especially the participants from Anna university since we do not have their email addresses.

Role of Nanomaterials in Catalysis

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Indian Institute of Technology Madras, Chennai- 600 03. India.

Key words: Nanoparticles, gold catalysis, band structure, density of states, morphology

Nanomaterials have vital role in catalysis due to the fact that their physical and chemical properties are different from that of their bulk counterpart. Though the crystallite size effect in catalysis has been understood in the beginning of the last century, the hype was given only at the end. This is mainly due to the advancement in the characterization techniques such as electron microscopes, in specific, transmission electron microscope (TEM). Supported gold nanoparticles of size below 5 nm have been reported to be active for CO oxidation even below 0 °C while the bulk Au is not active[1]. Since then, the importance of Au nanoparticles in catalysis has been realized and exploited for reactions such as peroxide synthesis, hydrogenation, dehydrogenation etc. Upon reduction in crystallite size, density of states is altered in solids. The redox potentials are getting changed due to the alteration of HOMO and LUMO in the case of semiconductors. In other words, band gap increases when the crystallite size is reduced[2,3]. In the case of Au catalysis, the catalytic activity is also accounted by low co-ordination number of Au atoms (in metal clusters), metal-support interactions and defect on surface of the supports.[4,5]

Apart from size, morphology of catalytically-active particles also have a role in catalysis. In the case of semiconductors, band structure varies with respect to the morphology (Fig. 3).[3] This is the reason why much importance is being given to size as well as morphology of the particles in these days. This presentation mainly deals with the effect of size and morphology of the nanomatererials in catalysis with the recent reports and observations.
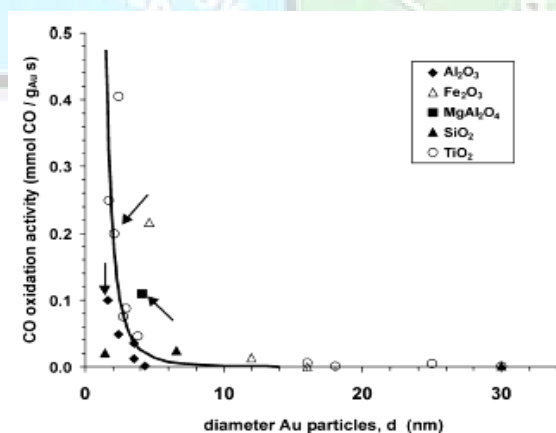

Fig1. CO oxidation activity of Au nanoparticles on various metal oxides at 0 °C. (Ref: 4)
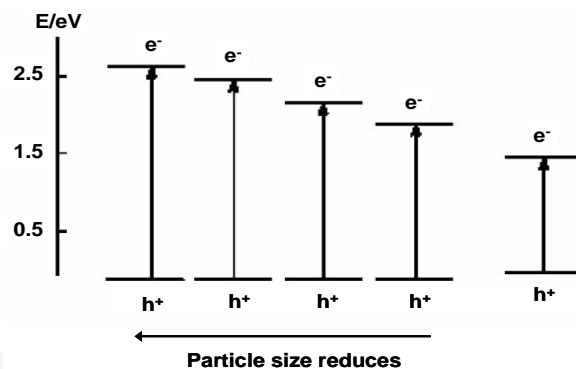
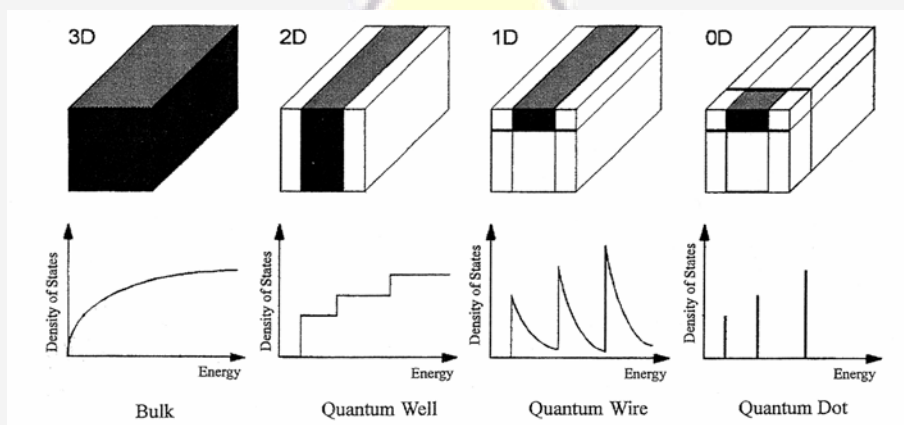Fig 2. Band diagram of CdTe nanocrystals with various particle sizes (Ref: 2)

Fig 3. Structure of the density of states of nanoparticles with different morphology (Ref:3)

References

1. M. Haruta, T. Kobayashi, H. Sano and N.Yamada, *Chem. Lett*. **4** (1987) 405.
2. R. F. Khairutdinov, *Russ. Chem. Rev*., **67** (1998) 109.
3. A. P. Alivisatos, *J. Phys. Chem.* **100** (1996) 13226
4. N. Lopez, T.V.W. Janssens, B.S. Clausen, Y. Xu, M. Mavrikakis, T. Bligaard, and J.K. Nørskov, *J. Catal*., **223** (2004) 232.
5. M.Sankaran and B.Viswanathan, *Bulletin of the Catalysis Society of Indi*a **5**(2006) 26.
6. B. Hvolbæka, T. V.W. Janssens, B. S. Clausen, H. Falsigc, C. H. Christensen and K. Nørskov, *Nanotoday*, **2** (2007) 14.

Effect of method of synthesis and different metal doping on the photo catalytic activity of Titania

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Pure and transition metals such as Fe, Cr, Co and Zr doped Titania were synthesized by sol-gel, hydrothermal and combination of these two methods. Various parameters affecting the structural and textural properties of Titania such as Water: Ethanol ratio, hydrothermal temperature, duration of hydrothermal treatment and calcinations temperature were optimized. Doping of the transition metals was performed with the above optimized conditions. The synthesized catalysts were characterized by XRD, DRS UV, EPR, FTIR, ICP-AES and TEM. Titania synthesized by combination of sol-gel and hydrothermal methods was found to be the optimum method to synthesize titania with required particle size and catalytically active phase. The synthesized pure and doped titania were used for the photo-catalytic oxidative degradation of 2, 4, 6-trichlorophenol in aqueous suspension. Among the different metal doped catalysts, cobalt doped titania showed higher photo-catalytic activity.

Mesoporous-Architecture in Solids

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Technical advances in various fields, such as adsorption, separation, catalysis, drug delivery, sensors, photonics and nanodevices, require the development of ordered porous materials with controllable structures and systematic tailoring pore architecture [1]. The architectural modulations in solid systems have been a research fantasy in recent years, ever since; the mobile group came up with mesoporous silicates in the early 90s using micellar templates [2-3]. Template assisted synthesis of porous materials has seen considerable developments in the last 15 years. In fact, this area has become a continuing endeavor in material science research, that new mesoporous materials are designed and prepared at regular intervals exploiting all kinds of micells and also other possible synthetic strategies. Among the various possible systems, silicates and carbon materials have attracted considerable attention in recent years due to the possibility of exploiting them for various applications.
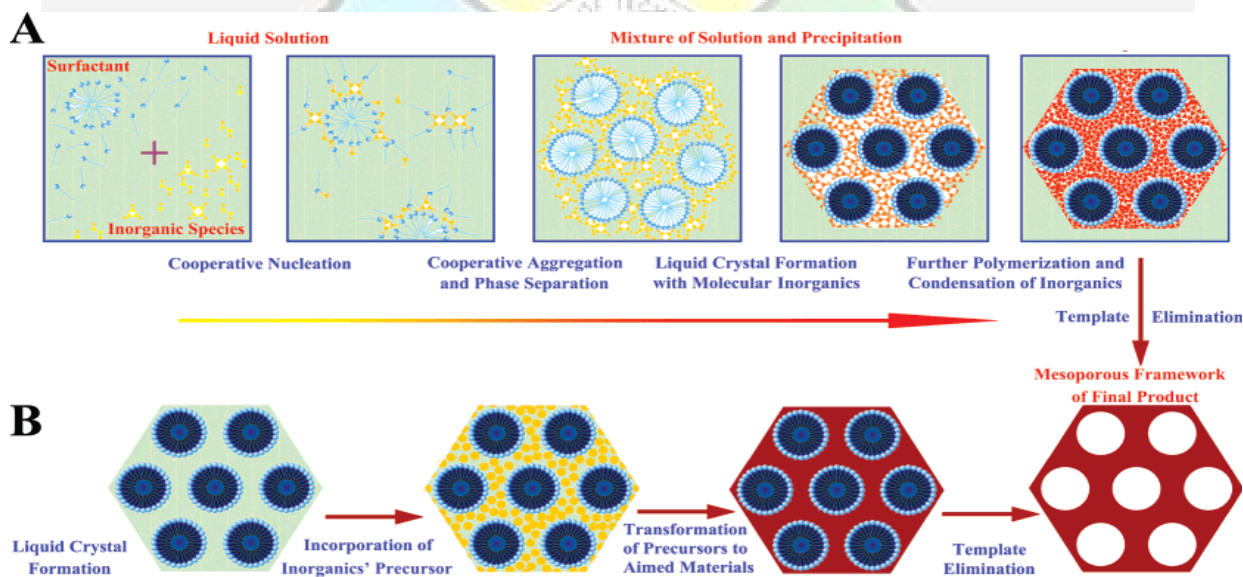

Figure 1: Two synthetic strategies of mesoporous materials: (A) Cooperative self assembly; (B) "true" liquid crystal templating process.

Among the silicate materials, the research endeavor is focused to exploit new templates and new bonding schemes so that the properties of the resulting mesoporous solids can be tailored. Mesoporous materials followed two main pathways, that is, cooperative self-assembly and "true" liquid-crystal templating process [4-5]. Carbon materials are prepared by nanocasting method.

This presentation therefore attempts to highlight some of the salient aspects on these materials as follows:
- (i) The possible synthesis strategies for these materials and the logic and science behind the procedures adopted.
- (ii) The physico-chemical characterization of these materials and the generalities that are possible.
- (iii) The application of mesoporous silicates and carbon materials
- (iv) Mesoporous transition metal oxides

Key words: Mesoporous, Templates, Liquid crystal, Nanocasting.

References:

1. Y. Wan, D. Zhao, Chem. Rev. 107 (2007) 2821.
2. C.T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli J. S. Beck, Nature. 359 (1992) 710.
3. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowiez, C. T. kresge, K. D. Schmitt, C. Chu, D. H. Oison, E. W. Sheppard. S. B. McCullen, J. L. Schlenker, J. Am. Chem. Soc., 114 (1992) 10834.
4. J. Y. Ying, C. P. Mehnert, M. S. Wong, Angew. Chem., Int. Ed. 38 (1999) 56.
5. F. Schuth, Chem. Mater. 13 (2001) 3184.
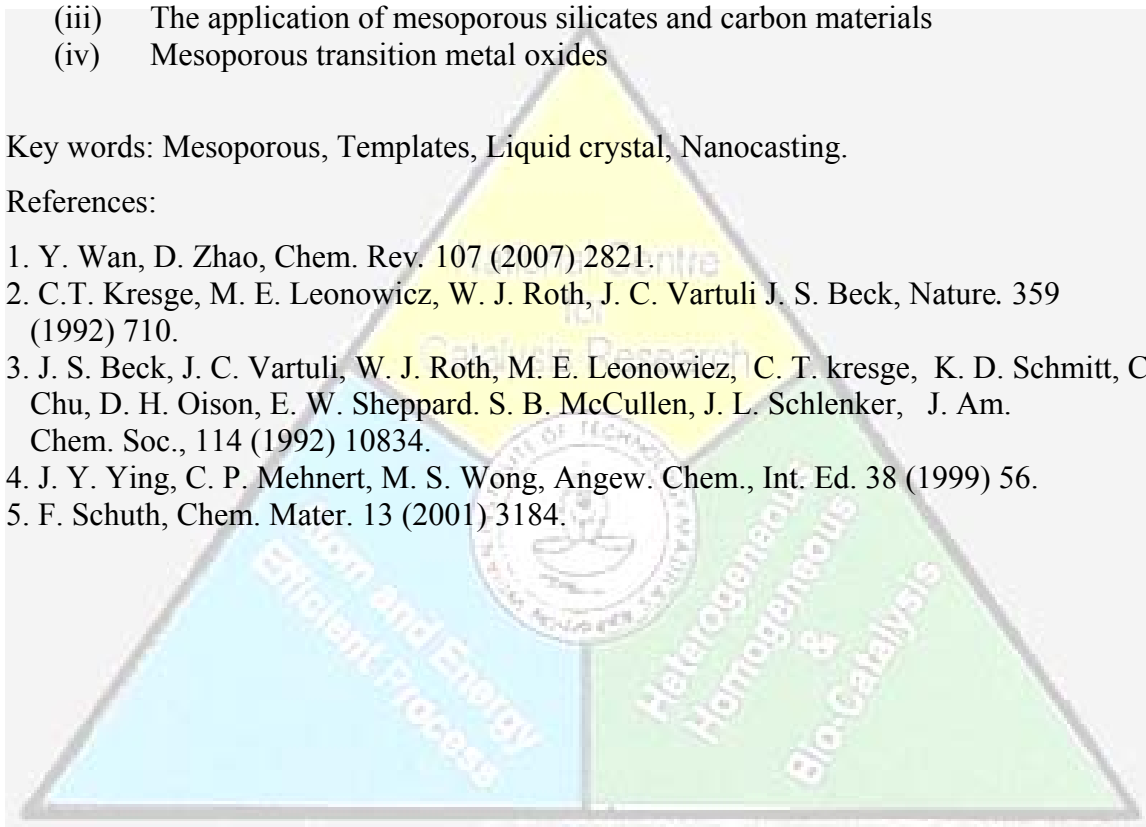
Lewis acid metal ion-exchanged MAPO-36: Characterisation and catalytic performance

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Aluminophosphate molecular sieves possess neutral framework which limits its application in catalysis and adsorption. In order to enhance their catalytic applications, it is necessary to modify the nature of framework walls of aluminophosphates by incorporation of heteroatoms. Isomorphous substitution of Al or P by foreign elements in AlPO-n family opened new fields of interest. The isomorphously substituted metal AlPOs are shown to possess both strong and weak Bronsted acid sites. Though there are many reports on their catalytic activity, there are only scanty references about Lewis acid ion-exchanged AlPOs. Hence, hydrothermal synthesis of MAPO-36, its wet ion-exchange with Zn^{2+}, Fe^{3+}, La^{3+} and Ce^{3+} ions, characterisation and catalytic evaluation of these catalysts are presented in this talk.

XRD patterns of calcined MAPO-36 and Fe^{3+}, Zn^{2+}, La^{3+} and Ce^{3+} ion-exchanged MAPO-36 revealed absence of both structural degradation and non-framework metal oxide. The thermogram of as-synthesised MAPO-36 coincides with the one already reported in the literature. The thermograms of Fe^{3+}, La^{3+} and Ce^{3+} ion-exchanged MAPO-36 showed three weight loss stages. The third weight loss is unique in the case of FeMAPO-36, LaMAPO-36 and CeMAPO-36 which is absent in the case of ZnMAPO-36. It is presumed that this weight loss is due to conversion of $M(OH)_2^+$ to MO^+ during calcination. The actual ion-exchanged species during ion-exchange is $M(OH)_2^+$ rather than M^{3+} according to the Plank-Hirschler mechanism. Acidity of ion-exchanged catalysts is also differ from that of calcined MAPO-36. Calcined MAPO-36 showed the presence of both weak and strong acid sites but the number and nature of acid sites is different in the case of ion-exchanged MAPO-36. The complete absence of strong acid sites was observed in LaMAPO-36 and CeMAPO-36. This kind of selective ion-exchange could be useful for specific chemical transformations which require only weak acid sites. *tert*-Butylation of phenol with *tert*-butyl alcohol was investigated over these catalysts in the vapour phase as model reaction. *tert*-Butylation of phenol occurs through dissociative chemisorption of phenol on MO^+ and the resulting phenolic proton is transferred to its neighbouring bridging oxygen. The other important observation of this study is 90% selectivity of 4-TBP. The minimal coke formation over these catalysts is an added advantage.

Membranes and Catalysis

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Membrane-based reactive separation processes (membrane reactor processes) are attracting attention in catalytic reactor applications, as two functions, namely catalytic reaction and membrane separation processes are coupled in a single unit. The separation function often results in enhanced reaction rate, selectivity and/or yield.   Though the study of catalytic membrane is a vibrant multidisciplinary activity dates back to 1860s [1], it can still be considered as an emerging technology.   Membrane reactor application use either porous or nonporous membranes based on inorganic materials (metals, ceramics, carbon or glass) or organic polymers. Considerable effort has been put in the development of inorganic membranes due to its high operating temperature (up to 1000 °C) and superior chemical stability relative to polymeric materials. At low temperatures (RT - 150 °C) the use of polymeric membranes has some advantages over the expensive inorganic membranes.   The three main configurations in a membrane reactor related to the role of membranes, designed to improve yield and selectivity is shown in Fig. 1. Membrane can act as i) an *extractor,* that is to selectively remove a reaction product from an equilibrium restricted reaction in order to increase the yield, ii) a *distributor,* that is to dose a reactant(s) by controlled manner thereby limiting side reactions, and iii) as an *active contactor,* by controlling diffusion of reactants to the catalyst leading to an engineered catalytic reaction zone.
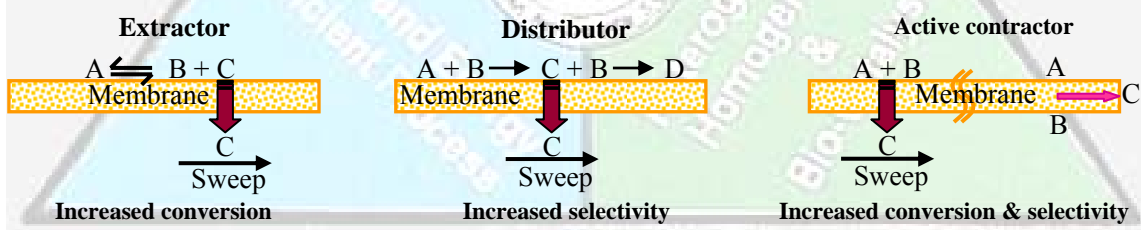

Fig. 1. Three main membrane functions to increase yield and selectivity

Catalytic membranes with increased permeability and high selectivity are the key requirements. The conceptual feasibility and the potential of catalytically active membranes investigated for a broad variety of reactions like dehydrogenation, hydrogenation, total and partial oxidation, NO reduction and others were investigated (Table 1). The motivation of this presentation is to elaborate on how far the field has developed and what challenges remain.

Table 1. Selected catalytic membranes and catalytic reactions performed

Catalyst–membrane material	Reaction
Pd & Pd alloy membrane [2]	Dehydrogenation reaction
Pd alloy membrane [3-5]	Hydrogenation of cyclooctadiene, nitrobenzene & Oxidation of Hydrogen to H_2O_2
Solid polymer electrolyte membranes [6-8]	Liquid phase hydrogenation of methanol, benzene & benzaldehyde
PVP–Pd/CA, PVP–Pd/PAN, EC–Pd/CA & AR–Pd/CA [9]	Hydrogenation of cyclopentadiene
PVP–Pd, EC–Pd or AR–Pd & PVP–Pd–0.5Co(Aca)$_2$ [10]	Hydrogenation of butadiene in 1-butene
Pd, Ag/PAIs, Pd/Ag [11]	Reduction of nitrous oxide
$H_3PW_{12}O_{40}$/PPO/Al_2O_3 [12]	MTBE decomposition
Nafion SAC-13/Teflon/PDMS [13]	Dimerisation of isobutene
HPA-PVA [14]	Dehydration of ethanol
PAN-PSSA, PVA-PSSA [15]	Pervaporation aided esterifications

Keywords: Catalytic membrane, polymeric membranes, catalysis

References
[1]   T. Graham, Phil. Trans. Roy. Soc. London, **156** (1866) 399.
[2]   V.M. Gryaznov, US Patent 3,950,447 (1971).
[3]   M.M. Ermilova, N.V. Orekhova, L.S. Morozova, E.V. Skakunova, Membr. Katal., (1985) 70.
[4]   A.P. Mischenko, V.M. Gryaznov, V.S. Smirnov, E.D. Senina, I.L. Parbuzina, N.R. Roshan, V.P. Polyakova, E.M. Savitsky, U.S. Pat., 4 179 470 (1979)
[5]   V.R. Choudhary, A.G. Gaikwad, S.S. Sansare, Angew. Chem. Int. Ed. **40** (2001) 1776.
[6]   D.G. Bessarabov, Membr. Technol. **93** (1998) 8.
[7]   N. Itoh, W.C. Xu, S. Hara, K. Sakaki, Catal. Today **56** (2000) 307.
[8]   Y.L. Chen, T.C. Chou, Ind. Eng. Chem. Res. **33** (1994) 676.
[9]   H. Gao, Y. Xu, S. Liao, R. Liu, J. Liu, D. Li, D. Yu, Y. Zhao, Y. Fan, J. Membr. Sci. **106** (1995) 213.
[10]   C. Liu, Y. Xu, S. Liao, D. Yu, Appl. Catal. A: Gen. **172** (1998) 23.
[11]   D. Fritch, K.V. Peinemann, Catal. Today **25** (1995) 277.
[12]   J.S. Choi, I.K. Song, W.Y. Lee, Catal. Today **67** (2001) 237.
[13]   D. Fritsch, I. Randjelovic, F. Keil, Catal. Today **98** (2004) 295.
[14]   I.K. Song, W.Y. Lee, J. Kim, J. Catal. Lett. **9** (1991), 339.
[15]   M.-O David, Q.T. Nguyen, J. Neel, J. Membr. Sci. **73** (1992) 129.
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HPWA supported MCM-41: An efficient solid acid catalyst for the green synthesis of xanthenedione derivatives under liquid phase conditions

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HPWA/MCM-41 mesoporous molecular sieves of appropriate ratios were prepared by loading HPWA on siliceous MCM-41 by wet impregnation method. The prepared HPWA/MCM-41 materials were characterized by X-ray Diffraction analysis (XRD), BET surface area method, FT-IR measurements. The morphology of mesoporous materials was studied by TEM technique. The catalytic activity of the above materials was tested over the condensation of dimedone (active methylene carbonyl compound) and various aromatic aldehydes under liquid phase conditions at 90°C. The products were confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR studies. With respect to the catalysts used, HPWA supported MCM-41 catalysts catalyses efficiently the condensation of dimedone and aromatic aldehydes in ethanol and other solvents under liquid phase conditions to afford the corresponding xanthenedione derivatives. Activities of the catalysts follow the order: HPWA/MCM-41(20wt%) > HPWA/MCM-41(30wt%) > $H_3PW_{12}O_{40}.nH_2O$ > HPWA/MCM-41(10wt%) > HM (12) > Hβ (8) > Al-MCM-41 (50). Various advantages associated with these protocols include, simple work-up procedure, short reaction times, high product yields and easy recovery and reusability of the catalyst.

Key words: Dimedone, Aromatic aldehyde, Condensation, HPWA/MCM-41, Xanthenedione

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Phosphoric acid grafted MCM-41 is a novel Bronsted acid catalyst for transesterification of diethyl oxalate with n-Butanol

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The transesterification reaction of diethyl oxalate with n-Butanol was performed over Phosphoric acid grafted MCM-41 (PAM). The mesoporous material Si -MCM-41 is synthesized by hydrothermal method. The various normal solution of phosphoric acid (0.2N, 0.4N, 0.6N and 0.8N) were loaded on MCM-41.The synthesized catalyst was labeled as 0.2PAM, 0.4PAM, 0.6PAM and 0.8PAM.and these catalysts were characterized by X-ray diffraction. The effect of various parameters like temperature, mole ratio, and reaction time, catalyst amount on the formation of transesterification product were optimized. The catalytic activity increases in the following order 0.2PAM, 0.4PAM, 0.6PAM, and 0.8PAM.

Key words: Si-MCM-41, Transesterification

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Tel : +044 2220 3518, Fax: 044-22352642
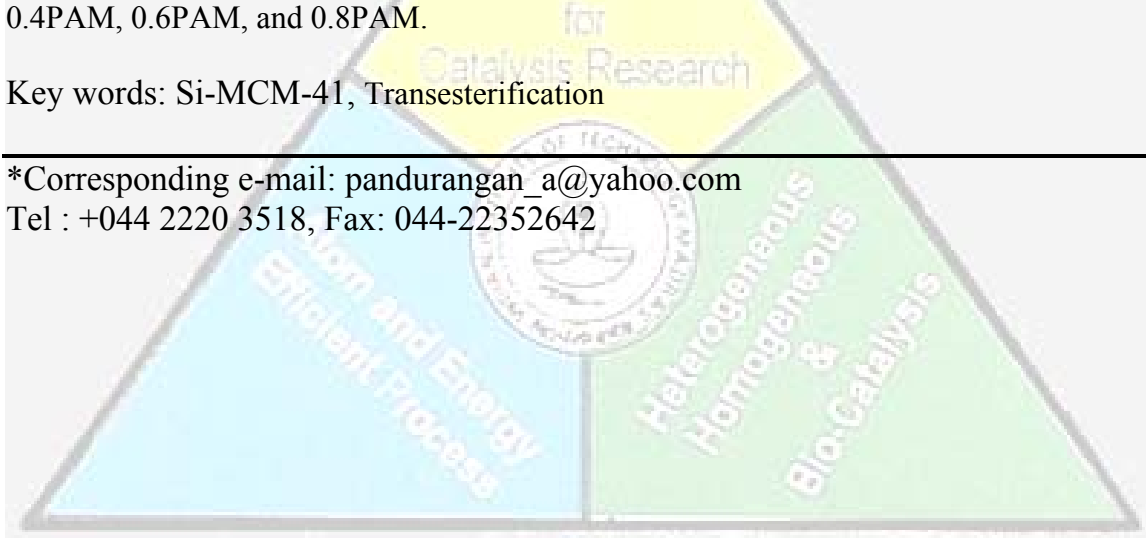
An overview of new approaches for removing sulfur from refinery systems

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Hydrotreating targets the elimination of sulfur and other heteroatoms involving drodesulfurization, Hydrodenitrogenation Hydrodearomatization. Industrial hydrotreating catalysts typically consist of γ-Al$_2$O$_3$ supported molybdenum promoted with either Co or Ni and the catalysts are sulfided prior to use. The increasing abundance of lower quality feedstock in the refinery, together with stricter environmental regulations has motivated an intensive research on new hydrotreating catalysts. As the lower quality feedstock becomes more abundant, additional challenges arise such as more severe operation conditions (T, P), higher corrosion of the refinery installations, catalyst deactivation and poisoning. Therefore, one way to face these challenges is to develop catalysts that can better withstand the severe operation conditions prevailing in the hydrotreating of heavier gas oils.

A modern refinery is a highly integrated industrial plant, the main task of which is to efficiently produce high yields of valuable products from a crude oil feed of variable composition. Oil refinery related catalysis, particularly hydrodesulfurization (HDS) processes, is viewed as a mature technology and it is often stated that break-through are not to be expected. The applicability and perspectives of various desulfurization technologies are evaluated taking into account the requirements of the produced fuels. The progress achieved during recent years is in catalysis-based HDS technologies (synthesis of improved catalysts, advanced reactor design, combination of distillation and HDS). The external and internal factors which influence strongly the modern refineries are depicted in the Fig.1
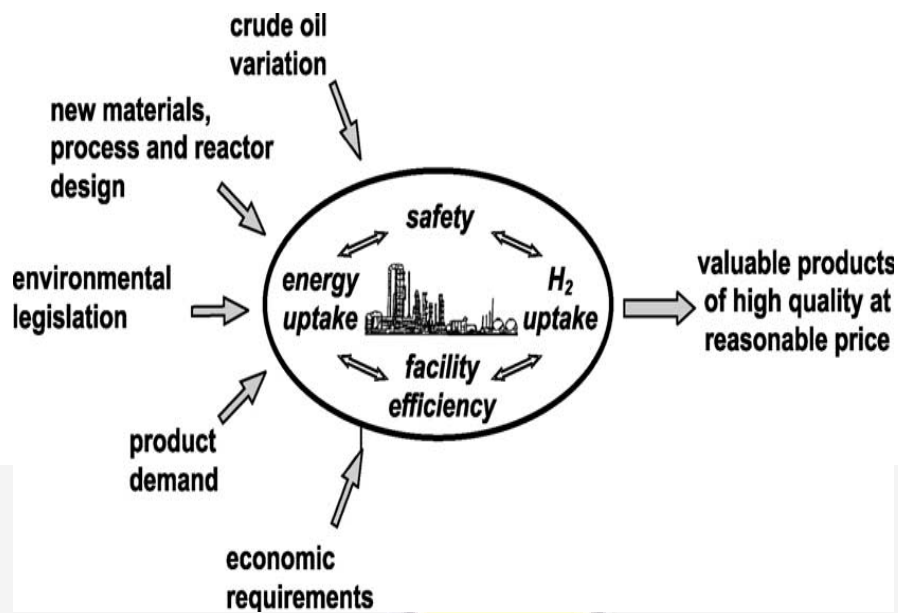
Fig.1 External and internal factors influencing modern refineries

The deep HDS problem of diesel streams is exacerbated by the inhibiting effects of co-existing polyaromatics and nitrogen compounds in the feed as well as H_2S in the product. The approaches to deep desulfurization include catalysts and process developments for hydrodesulfurization (HDS). Recent developments in environmental legislation are moving us to a world of zero-sulphur, i.e., in this respect spectroscopically pure, transportation fuels. For the time being, ''zero-sulphur'' means <10 ppmw Sulphur, but it is not excluded that the upper limit will in time come down even further.

Overall, new and more effective approaches and continuing catalysis and processing research are needed for producing affordable ultra-clean (ultra-low-sulfur and low-aromatics) transportation fuels and non-road fuels, because meeting the new government sulfur regulations in 2006–2010 (15 ppm sulfur in highway diesel fuels by 2006 and non-road diesel fuels by 2010; 30 ppm sulfur in gasoline by 2006) is only a milestone. The society at large is stepping on the road to zero sulfur fuel, so researchers begin with the end in mind and try to develop long-term solutions. The latest developments in hydrotreating processes will be discussed with a special focus to Hydrodesulphurisation catalysis.

POSTER PRESENTATIONS

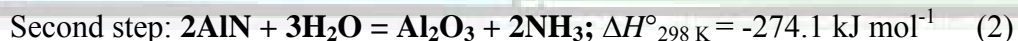| S.No	Name of the author	Title of the presentation
1	**Ms.C.M.Janet**	A novel cyclic process for atmospheric pressure ammonia formation: From Fantasy to Realization.
2	Ms.S.Chandravathanam	Role of Citrate anions in the activity and stability of Pt/C catalysts for the electro-oxidation of methanol
3	Ms. R Mahalakshmy	Electronic and geometrical effects of anchoring bio-mimetic catalyst onto oxidized carbon support – A Density Functional Theory approach
4	Dr Vidya Krishna	Synthesis and Characterization of Vanadium and Chromium incoporated SBA-15: Potential Photocatalysts for the Reduction of NO
5	Mr.Sankaranarayanan et al	Zeolite catalysts for end point reduction of a straight run diesel fraction
6	Mr.P.Indra Neel	The production and activation of carbon materials from natural sources

A Novel Cyclic Process for Atmospheric Pressure Ammonia Formation: From Fantasy to Realization.

C. M. Janet, B.Viswanathan, T.K.Varadarajan and R.P.Viswanath
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Department of Chemistry, Indian Institute of Technology Madras,
Chennai- 600 036. India.

Key words: *Alumina, cyclic process, ammonia formation*

***Preface*:**

Alumina has been used, so far either as a support or as a structural promoter in ammonia synthesis. It was assumed that alumina has a mere function of dispersing the active component and preventing its sintering or agglomeration. When the primary source for ammonia, the Chile saltpetre was depleting, the search for an alternative source was in demand. Destructive distillation of animal parts such as hoofs and horns and mineral deposits of metallic nitrides such as MgN_2, AlN were proved to be much reliable sources. But the availability of such sources was limited. Synthesis of mineral nitrides required high pressures and high temperatures and hence, it was not practiced. But the possibility of such metallic nitrides as a source for ammonia remained an attractive solution provided the synthetic methodology should be simple. Few reports are available in the literature where AlN was synthesized by the carbothermal reduction of alumina[1] (Chen and Lin, 1994). But in general AlN is synthesized by the reaction of Al wafer with ammonia[2] (Di Lello et al., 2001). Very recently Galvez *et al.*, (2008) have reported the production of ammonia from AlN synthesized by carbothermal reduction of α-alumina[3]. Their method involves a cyclic process involving two thermochemical steps[4] (Galvez *et al.*, 2007). The first, high-temperature, endothermic step is the production of AlN by carbothermal reduction of Al_2O_3 in a N_2 atmosphere. The second step is the hydrolysis of AlN to form NH_3 and Al_2O_3; the latter is in turn recycled to the first step. The reaction steps can be represented by,

$$\text{First step: } \mathbf{Al_2O_3 + 3C + N_2 = 2AlN + 3CO}; \Delta H°_{298\,K} = 708.1 \text{ kJ mol}^{-1} \quad (1)$$

$$\text{Second step: } \mathbf{2AlN + 3H_2O = Al_2O_3 + 2NH_3}; \Delta H°_{298\,K} = -274.1 \text{ kJ mol}^{-1} \quad (2)$$

They have used concentrated solar energy to supply heat for the first step and the CO formed has been methanated. They claimed that this method has advantages such as (1) it eliminates the need for high pressure, minimizing costs and safety concerns; (2) it eliminates the need for catalysts, minimizing costs associated with their production and recycling; (3) it eliminates the need for hydrogen as feedstock, reducing energy consumption. The first step (equation 1) is highly endothermic and thermodynamically favorable above 1300 °C. The second step (equation 2) is exothermal and thermodynamically favorable below 375 °C; above this temperature Al_2O_3, N_2, and H_2 are the stable products[5,6,7]. However, the presence of metastable NH_3 is possible in the absence of catalysts[8]. AlN can be hydrolyzed to Al_2O_3 in contact with water or in the presence of moisture even at ambient temperature, [9,10,11] but at low reaction rates. Even

though the pressure component has been eliminated, temperature still remained as high as 1500 °C. The presented work bridges the gap between the fantasy of formation of AlN from Al_2O_3 at lower temperatures and atmospheric pressure and the realization of NH_3 being formed from the intermediate AlN via a cyclic process.

References

1. H. K.Chen and C. I. Lin, *Journal of Materials Science*, **29** (1994) 1352-1357.
2. B.C. Di Lello, F.J. Moura and I.G. Solorzano, *Materials Science and Engineering C*, **15** (2001) 67–69.
3. M. E. Galvez, I. Hischier, A. Frei, and A. Steinfeld, *Industrial & Engineering Chemistry Research*, (2008) (In press).
4. M. E. Galvez, M. Halmann and A. Steinfeld, *Industrial & Engineering Chemistry Research*, **46** (2007) 2042- 2046.
5. Bowen, P., J.G. Highfield, A. Mocellin and T.A. Ring, *Journal of the American Ceramic Society*, **73** (1990) 724-728.
6. A. A.Gromov, A.P. llyin, E.M. Popenko, T.A. Khabas and V.I. Vereshchagin. *Modern Technique and Technologies: Section VI: Electrical Material Science*, (2000)168-170.
7. J. Li, M. Nakamura, T. Shirai, K. Matsumaru, C. Ishizaki and K. Ishizaki *Journal of Materials*, **1** (2005) 1-10.
8. M. E.Galvez, A. Frei, M. Halmann and A. Steinfeld, *Industrial & Engineering Chemistry Research*, **46** (2007) 2047-2053.
9. J. Li, M. Nakamura, T. Shirai, K. Matsumaru, C. Ishizaki and K. Ishizaki *Journal of American Ceramic Society*, **89** (2006) 937-943.
10. J. G. Highfield and P. Bowen, *Analytical Chemistry*, **61** (1989) 2399- 2402.
11. K. Kernel, G. Drazic and T. Kosmac, *Journal of Material Research*, **19,** (2004)1157-1163.

Role of Citrate anions in the activity and stability of Pt/C catalysts for the electrooxidation of methanol

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Direct methanol fuel cells (DMFCs) have been the subject of great interest in recent years due to their potential applications in electric vehicles and as portable power sources. Although several electrocatalysts have been employed for the oxidation of methanol, Pt and Pt based alloys are the preferred anode catalysts due to their high electrocatalytic activity [1]. Pt is often dispersed as nanoparticles on a suitable support to increase the surface to mass ratio for increased metal utilization. The simplest method for preparing a supported Pt electrocatalyst is to impregnate the support (usually carbon) with a platinum precursor [2] followed by thermal or chemical reduction methods. However, with these conventional methods, achieving desired sizes of Pt nanoparticles (2 - 5 nm) with homogeneous dispersion on the carbon support appears to be difficult. Hence, in order to produce desired sizes of Pt nanoparticles with uniform dispersion on the carbon support, some kind of stabilizing agents, such as surfactants, ligands or polymers, are usually employed during the preparative process [3]. But the heat treatment applied to remove the polymer or surfactant stabilizers results in the agglomeration of metal particles. Therefore, electrostatic stabilization by different anionic species has been evolved such as citrate [2-5], glycolate [6] or acetate [1]. The excess anionic stabilizer can be easily removed by washing with distilled water at room temperature itself.
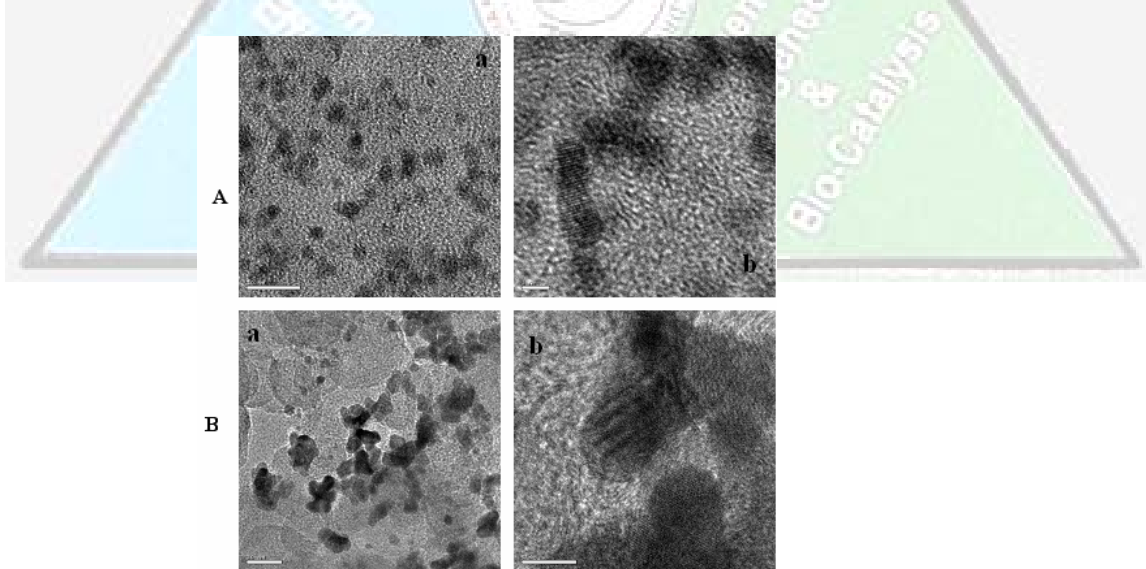
a)TEM and b)HRTEM images of 10% Pt/CDX975 catalyst A) with citrate and B) without citrate

The present study has shown that the citrate anion has not only enhanced the dispersion of the Pt nanoparticles, but also has better stabilized the metal particles (from the chronoampherometric studies) along with the enhanced methanol oxidation activity.
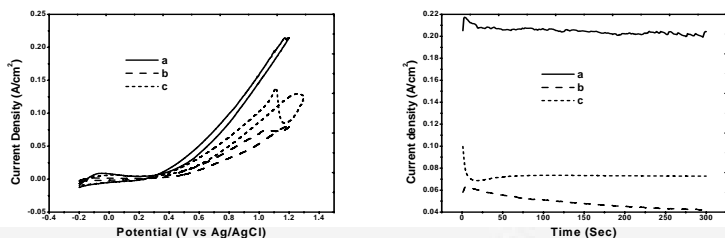
A) Cyclic Voltammetry at a scan rate of 25 mV/sec and B) Amperometric i – t plot at 1.0 V, of 10% Pt/CDX975 a) with b) without citrate and c) 10% Pt/Vulcan ETEK catalyst in 1M H_2SO_4 and 1M Methanol

References

1. Jie Zhao, Peng Wang, Weixiang Chen, Run Liu, Xiang Li, Qiulin Nie, Journal of Power Sources **160** (2006) 563–569.
2. Jianhuang Zeng, Jim Yang Lee, Weijiang Zhou, Applied Catalysis A: General **308** (2006) 99–104.
3. J.W. Guo, T.S. Zhao, J. Prabhuram, C.W. Wong, Electrochimica Acta **50** (2005) 1973–1983.
4. A. Henglein and M. Giersig, J. Phys. Chem. B **104** (2000) 6767- 6772.
5. Yuzuru Shimazaki, Yoshio Kobayashi, Shinji Yamada, Takao Miwa, Mikio Konno, Journal of Colloid and Interface Science **292** (2005) 122–126.
6. C. Bock, C. Paquet, M. Couillard, G.A. Botton, B.R. Macdougall, J. Am. Chem. Soc. **126** (2004) 8028-8037.

Electronic and geometrical effects of anchoring bio-mimetic catalyst onto oxidized carbon support – A Density Functional Theory approach

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A great challenge in the field of catalysis is the development of catalysts which possess the major advantages of both homogeneous (e.g. high activity, high selectivity, and mild reaction conditions) and heterogeneous (e.g. ease of catalyst recovery, high turnover numbers) catalysis. One way of bridging this 'gap' between homogeneous and heterogeneous catalysis is heterogenization of homogeneous catalysts. Heterogenization is achieved via either physisorption or through covalent grafting of a ligand or transition metal complex onto a solid support [1] (e.g., Alumina, silica, MCM, carbon). Generally the activity and selectivity of the homogeneous catalysts are changed (either it increases or decreases) after heterogenization. This may be due to the changes in geometry and electronic properties of the catalytic active site. In order to study these changes in advance, prior to carring out the reaction in the laboratory; a theoretical study has been carried out. Moreover, these properties of a catalyst can be obtained computationally more easily [2] than by experimental means. In this paper, the electronic and geometrical effect of anchoring biomimetic galactose oxidase catalyst [3] onto oxidized carbon supports has been studied by Density Functional Theory.
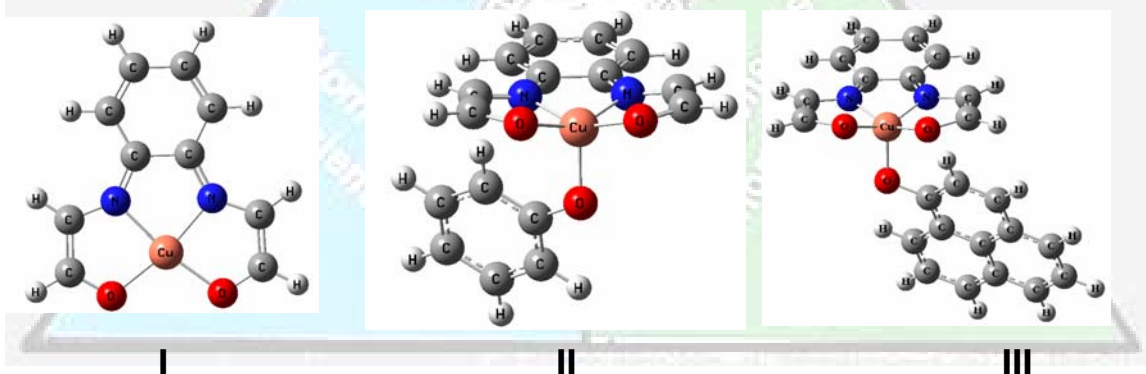

Fig. 1. Truncated models used for computational study

The molecular geometries of all the truncated model structures I, II and III (Fig.1) studied in this work were fully optimized at Density Functional Theory using the Gaussian 03 suite of program on IBM p- series machine server. Gauss view 3.0 was used as a graphical user interface. The effects of electron correlation on the geometry optimization were taken into account intensively by using B3LYP exchange correlational functional [4] in conjunction with the 6-31G(d) basis set for C, H, N and O atoms and LANL2DZ basis set for Copper atom.

As a result of anchoring, there is a change in bond lengths and bond angles in the active site of catalyst. The HOMO-LUMO energy gap (Table 1) also decreases. The percentage orbital contribution of ligand p orbitals to HOMO and LUMO energy level is more compared to metal orbitals. The HOMO and LUMO orbitals of model-II is shown in figure 2.

Table 1. Comparison of HOMO-LUMO energy gap of the models I, II and III

	HOMO (eV)	LUMO (eV)	ΔE (eV)
Model-I	-4.35 (α) -4.76(β)	-2.83 (α) -2.86 (β)	1.52 1.90
Model-II	-4.43	-3.57	0.86
Model-III	-3.85 (α) -4.57 (β)	-2.72(α) -2.72 (β)	1.13 1.85

Fig. 2. HOMO-LUMO molecular orbitals Of model-II

HOMO   LUMO
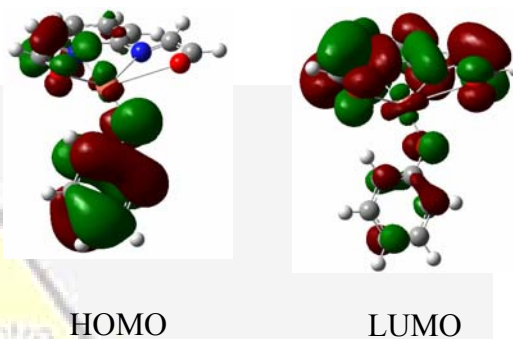
Thus in this study, an initial theoretical attempt has been made to study the electronic and geometrical effects of anchoring the biomimetic galactose oxidase catalyst onto oxidized carbon support. The influence of these parameters towards the selective oxidation of polyol will be analyzed in near future.

Keywords: Biomimetic catalyst, Density Functional Theory, Anchoring, HOMO-LUMO

References

1. T. Luts, W. Suprun , D. Hofmann, O. Klepel, H. Papp, J. Mol.Catal.A: Chemical, **261** (2007) 16.

2. K. Malek, Can Li, R.A. Van Santen J.Mol.Catal.A**:** Chemical, **271**(2007)98.

3. P. Chaudhuri, M. Hess, J. Mu1ller, K. Hildenbrand, E. Bill, T. Weyhermu1ller and K. Wieghardt, J. Am. Chem. Soc.**, 121** (1999) 9599.

4. A.D.Becke In: Exchange-Correlation Approximation in Density-Functional Theory,Yarkony DR, Ed, Singapore: World Scientific, 1995.

Synthesis and Characterization of Vanadium and Chromium Incoporated SBA-15: Potential Photocatalysts for the Reduction of NO

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The role of zeolites/molecular sieves as a support/anchor for transition metal oxides is to increase the lifetime of the photocatalytically excited $(M^{n+}–O^-)^*$ group of tetrahedrally coordinated metal oxides (MO_4) by distortion of the M=O bond, thus increasing its ability towards the reduction of innocuous gases such as nitric oxide (NO). In this regard, we have synthesized vanadium and chromium incorporated mesoporous SBA-15 by a direct hydrothermal route. We have chosen SBA-15 owing to its high surface area, uniform pore size distribution, large pore size, and high thermal and hydrothermal stability.[1] The role of vanadium and chromium tetrahedrally coordinated metal oxides within the framework of the mesoporous support is to explore its photocatalytic activity towards the reduction of NO. Further, the absorption of chromium (VI) in the visible region of the solar spectrum (> 380 nm) makes it feasible for its use under ambient sunlight conditions.

The incorporation of transition metal ions into the framework of mesoporous silicate, SBA-15 is difficult, owing to the facile dissociation of M—O—Si bonds under strongly acidic conditions. In the present study, an attempt has been made to introduce vanadium and chromium ions into SBA-15 under mildly acidic conditions.[2] A molar ratio of 0.039 TEOS: 0.00039-0.0039 V_2O_5: 0.00021 P123: 0.0021 HCl: 1.67 H_2O and 0.039 TEOS: 0.00039-0.0039 Cr_2O_3: 0.00021 P123: 0.00564 HCl: 1.67 H_2O was employed for VSBA-15 and CrSBA-15, respectively. The resulting gels were stirred for 24 h at 313 K and were subsequently aged in an autoclave for 24 h at 373 K. The as-synthesized VSBA-15 and CrSBA-15 were synthesized at varying ratios of Si/V and Si/Cr = 100, 50, 25, 10. Calcination of the as-synthesized samples was carried out in air at 773 K for 6 h.

Powder X-ray diffraction of calcined VSBA-15 and CrSBA-15 exhibit reflections characteristic of hexagonal SBA-15.[2] Table 1 shows an increase in the unit cell parameter (a_o) of calcined VSBA-15 and CrSBA-15 as compared to parent SBA-15, owing to the greater ionic radius of r_V^{5+} = 0.59 Å, and r_{Cr}^{6+} = 0.52 Å than r_{Si}^{4+} = 0.40 Å, thus indicating a possible incorporation in the SBA-15 framework. Diffuse reflectance UV-VIS spectra of calcined VSBA-15 show bands at ~ 210, ~260, and ~340 nm, characteristic of tetracoordinated V^V.[3] Absence of bands > 375, indicates absence of square pyramidal and octahedral coordination to V^V.[2] Calcined CrSBA-15 exhibited bands at ~ 250, ~ 360, and ~450 nm, characteristic of tetrahedral Cr^{VI}.[4] Absence of bands between 500-700 indicates that Cr^{III} is not present. XRD and DRUV-VIS studies indicate that tetracoordinated V^V and Cr^{VI} ions are incorporated within the mesoporous framework and are well-dispersed and isolated. Studies to check the photocatalytic activity of the VSBA-15 and CrSBA-15 samples towards the reduction of NO is underway.

Table 1. Unit cell parameters for VSBA-15 and CrSBA-15.

Sample	d_{110} (Å)	a_o (Å)*
Cal SBA-15	50.7305	101.461
Cal CrSBA-15 (100)	59.6420	119.284
Cal CrSBA-15 (50)	58.8468	117.693
Cal CrSBA-15 (25)	58.0726	116.154
Cal CrSBA-15 (10)	55.8674	111.735
Cal VSBA-15 (100)	63.0499	126.099
Cal VSBA-15 (50)	63.9636	127.927
Cal VSBA-15 (25)	63.0499	126.099
Cal VSBA-15 (10)	-	-

*a_o lattice parameter calculated from XRD using formula $a = 2d_{110}$

References

1. D. Zhao, Q. Huo, J. Feng, B.F. Chmelka and G.D. Stucky, *J. Am. Chem. Soc.* **120** (1998) 6024.
2. P. Shah, A.V. Ramaswamy, K. Lazar, and V. Ramaswamy, *Micropor. Mesopor. Mater.* **100** (2007) 210.
3. S. Dzwigaj, M. Matsuoka, R. Franck, M. Anpo, and M. Che, *J. Phys. Chem. B.* **102** (1998) 6309.
4. H. Yamashita, K. Yoshizawa, M. Ariyuki, S. Higashimoto, M. Che and M. Anpo, *Chem. Commun.* (2001) 435.

Zeolite catalysts for end point reduction of a straight run diesel fraction

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Over the years, for environmental reasons, the diesel end point (T$_{95}$) is being lowered in order to decrease soot production. Lowering of the end point reduces the overall availability of diesel and the profitability of the refiner. One solution for the refiner will be to cut the diesel fraction at a higher temperature and then reduce its end point to the desired level by catalytic treatment without much yield loss. As the major components in the heavier end of diesel are the alkyl di- and poly-nuclear aromatics and long chain n-paraffins, it is possible to bring down the end point of heavier diesel fractions (T$_{95}$ ≥ 380°C) by dealkylation and ring hydrogenation of the aromatics, mild isomerization and cracking of the n-paraffins and ring opening of the naphthenes. As feed S and N are poisons for hydrogenation and isomerization reactions, in commercial end point reduction processes, the catalyst is loaded in the last reactor in a DHDS train so that it encounters a clean feed [1].

We now report our studies on the endpoint reduction of a straight run diesel feedstock containing a large amount of S (17,600 ppm), N (140 ppm) and paraffins (58 wt %) over different supported Ni-Mo catalysts. As the S and N content of the feed is large, the only reactions that can successfully reduce the end point of this feed at ≤40 bar (desired operating pressures) are isomerization and cracking of n-paraffins. We, therefore, decided to study the application of zeolite based catalysts for this reaction. Four different zeolites, viz., HY, H-Mordenite (MOR), H-ZSM-5 (MFI) and H-beta (BEA) were blended with alumina monohydrate (Sasol), extruded and calcined (500°C, 6h) to make four supports. The zeolite content of the suppots was 50 – 60 wt%. The supports were then loaded with Mo (10 wt% as oxide) and Ni (3 wt% as oxide) by standard impregnation methods.
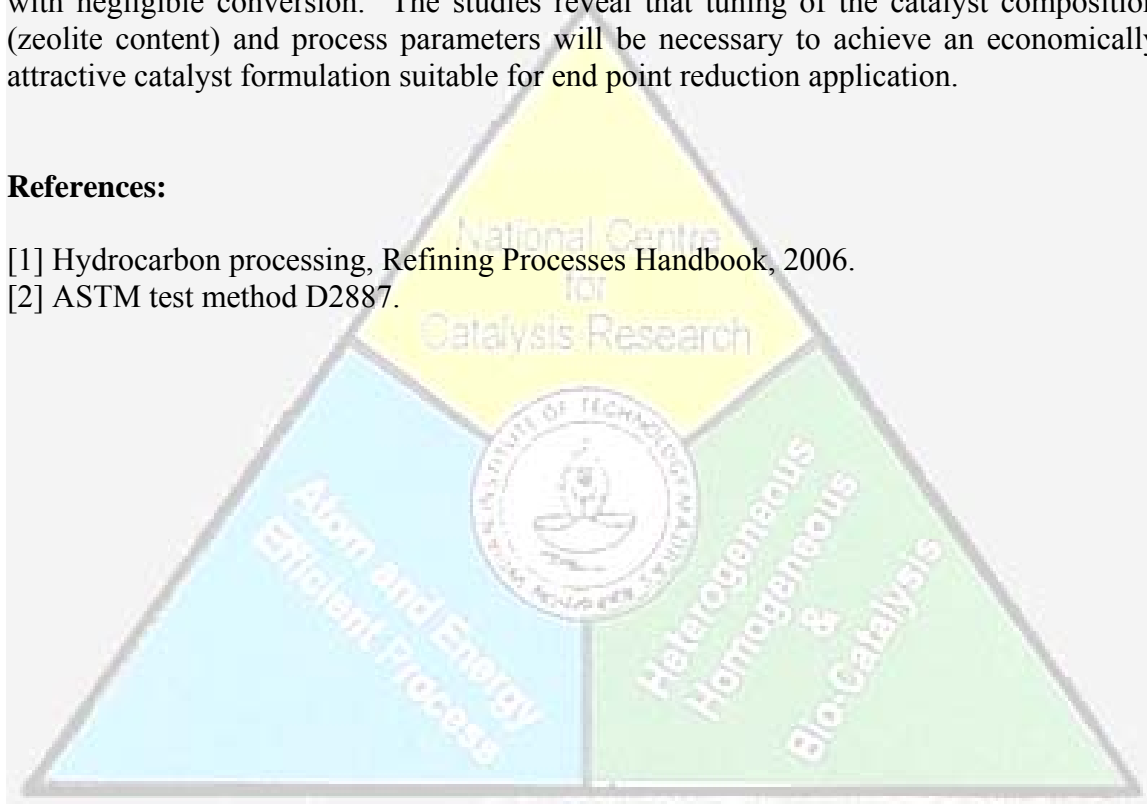
The different zeolites and supports were characterized by XRD, surface area (S$_{BET}$), pore-size distribution and acidity measurement by temperature programmed desorption of NH$_3$. The TPD profiles of the supports were deconvoluted into three or more individual peaks and based on the peak-maximum-temperature of these peaks, the acidity distribution in these supports was profiled as weak, medium and strong. Further characterization of the zeolites (loaded with 0.1 wt% Pt) was done by a model reaction (transformation of n-hexane) at atmospheric pressure at different temperatures (280 - 340°C). The studies were used to understand the relative isomerization to cracking activities of the zeolites. The order of activity (based on conversion) of the zeolites was: ZSM-5 > H-Y > BEA > MOR, while the isomerization to cracking selectivity decreased in the order: HY > BEA > ZSM-5 > MOR.

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The end point reduction studies were carried out in a high pressure bench-scale reactor using about 25g catalyst. The products were analyzed by a Simulated Distillation procedure [2] using a Varian GC. The catalysts were sulfided in-situ using a diesel feed spiked with 2 wt% S as DMDS. The reactions were generally carried out at temperatures in the range of 330 - 350°C, pressures between 40 – 60 bar, weight hourly space velocity (WHSV) of 1 - 2 h^{-1} and H_2/ oil ratios of 400 v/v. The studies revealed that substantial end-point (T_{95}) reduction (>25°C) of the feed could be achieved over the catalysts. The best catalyst was HY-Ni-Mo-alumina. An end point decrease of about 25°C at 86% diesel was observed over this catalyst. Simulated distillation GC chromatograms of the products revealed some interesting features of the catalysts: 1) ZSM-5 converted mainly the n-paraffins, 2) HY transformed mainly the non-n-paraffinic fractions, 3) BEA converted both n-paraffins and the other compounds and 4) MOR deactivated rapidly with negligible conversion. The studies reveal that tuning of the catalyst composition (zeolite content) and process parameters will be necessary to achieve an economically attractive catalyst formulation suitable for end point reduction application.

References:

[1] Hydrocarbon processing, Refining Processes Handbook, 2006.
[2] ASTM test method D2887.

NOTES

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Heterogeneous
Homogeneous
&
Bio-Catalysis