Indo-Hungarian Workshop on

Future Frontiers in Catalysis

February, 16 - 18, 2010
National Centre for Catalysis Research
Indian Institute of Technology Madras
IC SR Hall III

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Influence of chain length of carboxylic acid on the esterification activity of TPA/Nb_2O_5 catalyst

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Low molecular weight carboxylic acids have been widely used to correlate their chemical structure and reactivity in esterification due to their simplicity, availability and ease of product analysis. The Hammett equation for aromatic systems and the Taft equation for aliphatic systems were the first models proposed that attempted to quantify polar, resonance and steric effects of substituents in carboxylic acid esterification [1, 2]. These models were improved [3], modified [4] and expanded to other reactions [5]. However, such studies are mostly carried out using homogeneous catalysts. Studies on understanding the probable structural effects of large carboxylic acids, particularly on the activity of heterogeneous catalysts are scarce [6-8]. The present work reports on the esterification reactivity of long chain fatty acids present in different oils, which is more relevant to the synthesis of biodiesel. The objective of the work is to study the reactivity of individual fatty acids of chain length varying from C_8 to C_{18} and to compare their reactivity when they are in the combined form in selected oils. Correlating the degree of saturation with the reactivity is yet another objective. These studies were carried out using 12-tungstophosphoric acid supported niobia catalysts.

Results and Discussion:

Esterification of different individual carboxylic acids (C_8 to C_{18}) with methanol was carried out on 25% TPA/Nb_2O_5 catalyst at reflux temperature (65 ^oC) with an acid to alcohol molar ratio of 1: 15. It was found that increasing chain length of acid had a retarding effect on the reaction rate. The study was extended to different mixtures of fatty acids present in oils. Coconut fatty acid was taken for this study as it contained essentially saturated fatty acids of varying carbon chain length. The results on esterification activity are shown in Fig. 1. The decreasing trend in carboxylic acid reactivity with increasing alkyl chain length can be seen. In order to understand the influence of unsaturation on the reactivity of fatty acids, the esterification was carried out on different vegetable fatty acids at different temperatures and reaction times and the results are given in Fig. 2. It is evident that the unsaturation content of the fatty acid also retards the esterification reactivity.

Conclusions: As the chain length increases the reactivity of fatty acids decreases. The esterification reactivity of fatty acids in oils decreases with the increase in the unsaturation.

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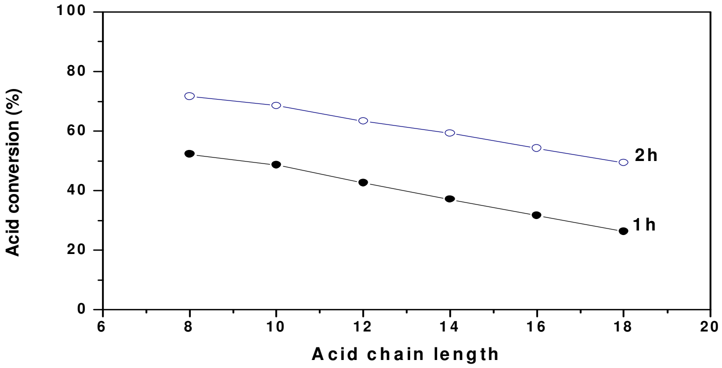

Figure 1. Reactivity of fatty acids present in coconut oil (catalyst = 25% TPA/Nb_2O_5)
(Reaction conditions: Temperature = 65 °C; catalyst amount = 15 wt% of acid)

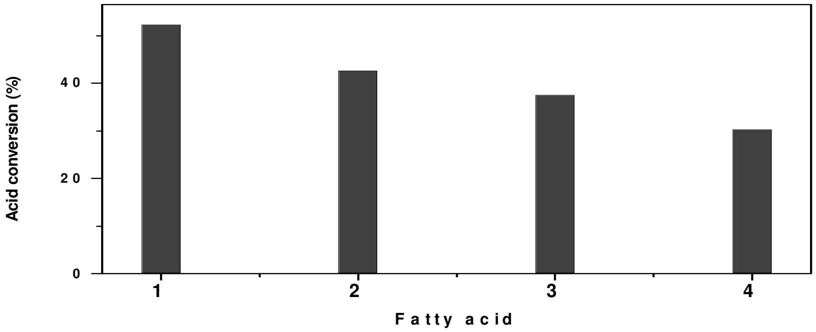

Figure 2. Reactivity of edible oil fatty acids (catalyst = 25% TPA/Nb_2O_5) (Reaction conditions: Temperature = 65 °C; catalyst amount = 15 wt% of acid): 1-Coconut fatty acid; 2-Ground nut fatty acid; 3-Olive fatty acid and 4-Soybean fatty acid.

Mesoporous silica anchored palladium and gold Schiff base complexes and their catalytic activity in C-C coupling reactions.

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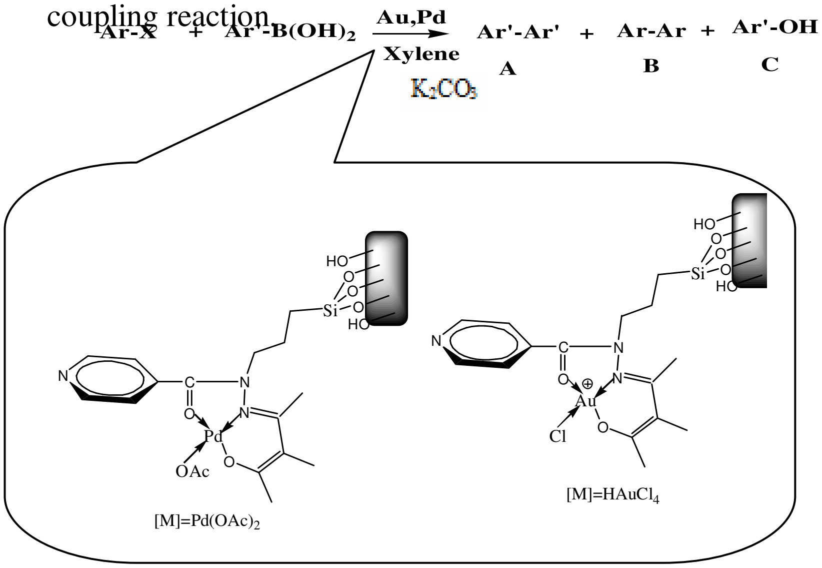
The Suzuki reaction is by far the most versatile synthetic method available for the generation of unsymmetrical biaryl compounds which are important building blocks in natural products and in materials sciences. The Schiff base palladium (II) and gold (III) complexes were prepared and immobilized on chloropropyl modified MCM-41. Characterization of the heterogeneous catalyst was done by powder X-ray diffraction (XRD), N_2 adsorption-desorption, CP MAS NMR spectroscopy (^{13}C and ^{29}Si), Fourier transform infrared spectroscopy (FT-IR), diffuse reflectance UV–Vis spectroscopy. The immobilized palladium complex exhibits high activity towards cross coupling of aryl boronic acid and aryl halide while the corresponding gold complex shows high activity for homo coupling of aryl boronic acid. The heterogeneous catalysts were reusable and stable to allow easy to use. We are also studying the application of the catalyst in Heck coupling reaction.



$$\text{Ar-X} + \text{Ar'-B(OH)}_2 \xrightarrow[\text{Xylene}\ K_2CO_3]{\text{Au,Pd}} \underset{\text{A}}{\text{Ar'-Ar'}} + \underset{\text{B}}{\text{Ar-Ar}} + \underset{\text{C}}{\text{Ar'-OH}}$$

Promising catalytic and hybrid materials of Keggin type polyoxometalates

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In heterogeneous catalysts with polyoxometalates (POMs), the chemical interaction and bonding, dispersion, stability and catalytic activity of POMs depend strongly on the amount loaded and the nature of the solid support employed. POMs (heteropoly acids) are normally dispersed on acidic or neutral substances such as SiO_2, ZrO_2, TiO_2, carbon, acidic organic resins, MCM-41, Y-zeolite, layered double hydroxides, clays and SBA-15. As a new approach in this direction, reducible oxides such as $Ce_xZr_{1-x}O_2$ solid solutions with mild acid-base and strong redox properties have been proved to be promising supports to develop heterogeneous catalysts with POMs. In our study, the Keggin ions of 12-tungstophosphoric acid (PWA) dispersed on solid solutions are elusive to PXRD at all loadings. However, Keggin ions present in the initial layers of PWA on $Ce_xZr_{1-x}O_2$ support show intrinsic IR bands at 1080 cm$_{-1}$ ($\nu_{P\text{-}O}$) and 982 cm^{-1} ($\nu_{W=O,\ \mathrm{terminal}}$) due to the unperturbed Keggin ions, and non-intrinsic bands at 1051 cm^{-1} ($\nu_{P\ O)}^{-}$ and 957 cm^{-1} (ν, $_{W=O,\ \mathrm{terminal}}$) from the perturbed Keggin ions present on $Ce_xZr_{1-x}O_2$ surface. At higher coverages of PWA, the non- intrinsic IR bands disappear due to the formation of bulk-like PWA phase. The Raman spectra show O^{2-}—Ce^{4+}-O^{2-} stretch (468 c$\tilde{m}_{1}$) and the bands attributable to Ce^{4+} ...O_{terminal} =W and $_{4+\ \delta\text{-}\ \mathrm{terminal}}$ Zr^{4+} ...O_{terminal} =W bonds formed between surface metal ions and $H_3\ PW_{12}\ O_{4\text{-}0}{}^{n-3}$ (n = 0 to 3) species. The ^{31}P MAS NMR spectra show uniquely broad peaks between 13 ppm to 18 ppm indicating stronger interaction of Keggin species with $Ce_xZr_{1-x}O_2$ solid solutions. The Keggin ions are packed as molecular layers on $Ce_xZr_{1-x}O_2$ and their H_2-TPR behaviour is quite different from that of the bulk PWA. The NH_3-TPD study indicates various adsorption sites on bare $Ce_xZr_{1-x}O_2$ support and Keggin molecular layers. TEM analysis suggests that the Keggin units are spread in the form of molecular patches (~ 5 nm size) on $Ce_{0.5}Zr_{0.5}O_2$ support. The activity of 20wt% HPW/$Ce_{0.5}Zr_{0.5}O_2$ support is tested for vapour phase conversion of acetophenone to styrene which occurs via the formation of cyclic intermediate involving Ce_{4+}/Zr_{4+} and possibly the oxygen defect Lewis sites. In summary, the Keggin ions of PWA show strong interaction with $Ce_xZr_{1-x}O_2$ support and spread as molecular layers. The perturbed Keggin units are characterized by nonintrinsic IR bands and ^{31}P MAS NMR. The PWA molecular layers are catalytically active. Organic-inorganic hybrid materials have also been synthesized which show hydrophobic nature. Details will be discussed in the Indo-Hungarian workshop at NCCR.

Platinum and Gold supported Mesoporous Carbon Molecular Sieves

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Mesoporous carbons and nitrogen containing carbons having very high surface areas are of great technological interest for the development of catalytic, electrocatalytic and hydrogen-storage systems. Ordered mesoporous carbons and nitrogen containing carbons with various structures, e.g., NCCR-1, CMK-1, CMK-3, etc., have been synthesized by carbonization of sucrose, furfuryl alcohol and other suitable carbon and nitrogen containing precursors within the pores of mesoporous silicate molecular sieves. The inorganic templates were then removed by etching with HF, followed by filtration, washing and heat treatment to obtain the nanoporous carbons and nitrogen containing carbons. Subsequently, platinum was loaded on these mesoporous carbons and nitrogen containing carbons. Electrochemical oxidation of methanol over the platinum supported carbons and nitrogen containing carbons were studied by cyclic voltammetry at room temperature. The high dispersion of platinum on these nanoporous carbons gives rise to promising electrocatalytic activity for methanol oxidation. In addition, the catalysts exhibit better carbon monoxide tolerance thus showing promise as electrode material for the methanol fuel cell application. In addition, the structured carbons were also used as support for gold nanocatalysts which show promise for the oxidation of glycerol.

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ON THE SEARCH FOR EFFICIENT CATALYSTS FOR OXYGEN REDUCTION REACTION

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Cathodic oxygen reduction reaction (ORR) has technological importance in the development of electrochemical devices such as fuel cells, zinc-air batteries and many industrial electrolytic processes. The sluggish kinetics of oxygen reduction reaction under experimental conditions causes the deterioration of performance of the devices. In order to improve the performance with enhanced kinetics, a better electrocatalyst is necessary. Though various compositions and configurations of the electrocatalysts have been proposed, the search for an efficient electrocatalyst has always been continuing. Even though, one tends to believe that the basic principle of oxygen reduction reaction is known, the formulation of a compositional electrode, satisfying the basic requirements of the components of the overall reaction has not yet been successful. This could be due to various factors inherent in extrapolation as well as the gap existing between theoretical formulation and experimental realization. Conventional carbon supported platinum is the best catalyst for oxygen reduction reaction. However, it is associated with several drawbacks besides the high cost. Even though it is commercially exploited, the overpotential is found to be around 300-400 mV and the kinetics is not fast enough. In addition, Pt is expensive and less abundant. The main objective of the present work is to develop both Pt and non-Pt based oxygen reduction electrocatalysts for exploitation in electrochemical devices. Conventional metals and metal alloys, chalcogenide and macrocycle based systems have been prepared in nano-size range and examined for the oxygen reduction reaction in this study. The prepared materials are characterized by using variety of techniques such as X-ray diffraction (XRD), Transmission electron spectroscopy (TEM), Scanning electron spectroscopy (SEM), Energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS), Ultraviolet-Visible (UV-Vis) spectroscopy. The electrochemical measurements are carried out in aqueous media at room temperature using cyclic voltammetry. The ORR activity of the electrocatalyst was evaluated from the steady-state cyclic voltammograms and the evaluation of the performance in kinetically controlled region was measured by chronoamperometry. In the present work, carbon supported Pt nanoparticles of different sizes were synthesized by polyol reduction method. The optimum size of Pt for maximum ORR activity is determined. To improve the ORR activity and reduce Pt loading, carbon supported Pt-M (M = Fe, Co and Cr) alloys were synthesized by polyol reduction method and the role of alloying element towards enhanced ORR activity was studied. As an alternative to Pt, carbon supported Pd, Pd-Co-M (M = Mo and Au) alloys, Ru and RuxSey (x = 1 and y = 0-1) were synthesized by reverse microemulsion (RME) method and the ORR activity was investigated. Density functional calculations were performed to study the facile reduction of oxygen on MN4 (M = Fe and Co) clusters. MNxCx (M = Fe and Co) clusters were prepared by pyrolyzing the corresponding metal macrocycles supported on carbon and the ORR activity was investigated

The author is thankful to Dr Venkateswara Rao for carrying out most of the experimental work reported in this communication.

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Selective liquid phase oxidation of p-cresol using solid catalysts

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Among various catalytic processes, oxidation of organic substances is one of the most important methods for producing diverse chemicals from oil derivatives and vegetable raw materials. In the production of fine chemicals it is imperative that the reactions are selective. The traditional oxidation methods often involve the use of stoichiometric amounts of inorganic oxidants, such as chromates, which clearly cause serious effluent problems. In addition, these reactions usually require high temperatures and pressures, which consume a lot of energy and cause lower selectivities. These drawbacks can be overcome by developing catalytic processes for oxidation. From an industrial point of view oxidation catalysis poses three challenges: a) activation of molecular oxygen, b) avoid over oxidation of the substrate, and c) overcome the lack of functionality in the feedstock.

Oxidation of various phenol substituted derivatives such as *o*-cresol, *p*-cresol, *m*-cresol, 3,4-dimethoxy toluene, *p*-cresyl isobutyrate, *p*-cresyl acetate, *p*-phenoxy toluene, *p*-cresyl methyl ether, *p*-cresidine, 2-nitro-*p*-cresol etc. leads to the variety of chemical products. The resulting oxidation products viz. hydroxy-substituted aromatic alcohols, aldehydes or ketones and acids are important intermediates in the manufacture of pharmaceuticals, agrochemicals, polymeric resins and artificial flavours. One such example is the oxidation of *p*-cresol which gives *p*-hydroxy benzyl alcohol and *p*-hydroxybenzaldehyde. Derivatives of *p*-hydroxy benzyl alcohol and *p*-hydroxybenzaldehyde (PHB) are important intermediates for the manufacture of vanillin, a widely used flavoring agent, trimethoxybenzaldehyde, various agrochemicals and pharmaceuticals such as semi synthetic penicillin, amoxicillin, antiemetic drug trimethobenzamide. *p*-Hydroxybenzaldehyde is also used as an additive for metal plating brighteners, electroplating, in perfumes and in liquid crystals. Hence, developing/designing new stable solid catalysts for liquid phase oxidation of *p*-cresol and similar derivatives is still a challenge in the area of oxidation catalysis. In our laboratory, we have successfully developed variety of novel solid catalysts involving metal-Schiff complexes intercalated into montmorillonite clay, Co-saponite catalyst and nano structured cobalt oxide catalyst for selective liquid phase oxidation of *p*-cresol derivatives.

In our study, two-dimensional montmorillonite and saponite clay were chosen as a host framework for intercalation of Co-salen type complexes. The intercalated heterogenized catalysts were thoroughly characterized by Fourier−transform infrared (FT−IR) spectrum, ultraviolet−visible (UV−vis) spectrum, X-ray diffraction (XRD), thermogravimetry analysis (TGA), scanning electron microscope (SEM), X-ray photoelectron spectroscopy(XPS), atomic absorption spectroscopy (AAS), and extended X-ray absorption fine structure (EXAFS). This heterogeneous catalyst was found to give a five fold higher TON than the homogeneous cobalt salen complex for liquid phase air oxidation of *p*-cresol.

We also designed the cobalt saponite catalyst which is an example of trioctahedral smectite in which the charge imbalance due to isomorphic substitutions in the structure layers is compensated by cations placed in interlamellar position. Therefore, Co-saponite obtained can be viewed as a nanocomposite (100nm) of Co phases over aluminosilicate support as a catalyst for oxidation reactions.

The third type of oxidation catalyst developed was the spinel nano structured cobalt oxide catalyst by simultaneous co-precipitation and digestion method. The colloidal form of cobalt oxide was also synthesized by precipitation method. Both types of nano size cobalt catalysts were synthesized without a template and any stabilizer. These nanoparticles were found to be highly active for air oxidation of *p*-cresol under mild conditions while the selectivity to the oxidation products could be altered by changing the digestion time during the preparation of the catalyst. The catalysts were characterized by TEM, XPS, XRD and BET surface area. The surface area of cobalt oxide nano particles was found to be $95m^2/g$ while that of bulk cobalt oxide was only $9m^2/g$.

In summary, this presentation demonstrates the approach of designing heterogeneous catalysts for liquid phase oxidation reactions of industrial importance.

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Oxidative degradation of lignin model phenolic compounds over mesoporous catalysts

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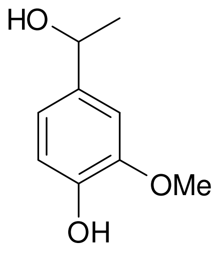
Lignin occurs as an integral cell wall constituent of all vascular plants including the herbaceous varieties. It is a polymer of phenyl propanoids and largest abundant aromatic biomass available on earth. Conventionally it has been used as fuel, adhesive and animal feed etc. Increasing demand of biomass utilization as a source of chemical feedstock has further broadened the application of this under used biomass. The structure of lignin suggests that under controlled degradation it can yield a spectrum of low molecular weight aromatic compounds, i.e., it can serve as a renewable resource of chemical feedstock. Long term opportunities that arise from lignin utilization involve aromatics and miscellaneous chemicals can be obtained. However, the structural complexity of lignin in wood tissues seriously hinders studies of its degradation mechanism.

The common ways for elucidation of lignin reaction pathways is to use oligomeric (mostly dimeric) phenyl propane structures as lignin models. The current pathways available for the lignin degradation are by use of photochemical energy, gamma irradiation, photo-catalysis and homogeneous catalysis using metal complexes or polyoxometalates. However, these processes are non-selective and often cannot be recycled. Development of robust and selective catalytic system to selectively break or make a bond will be and interesting area of technology development. In this regard, heterogeneous catalytic systems based on molecular sieves appear to be a promising alternative for selective degradation of lignin structure.

In the present study we have chosen two lignin model molecules, i.e., the monomer [1-(4-hydroxy-3-methoxyphenoxy)-ethanol, apocynol **1**] and dimer [1-(4-hydroxy-3-methoxyphenoxy)-2-(2-methoxyphenoxy)-propane-1,3-diol **2**].



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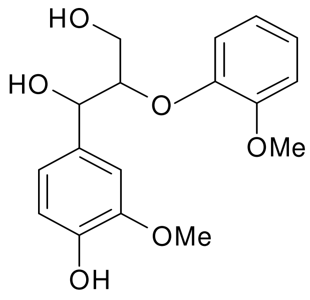

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Microwave assisted oxidation of **1** was carried out over mesoporous SBA-15 catalyst using H_2O_2 as oxidant to produce acetovanillone, vanillin and 2-methoxybenzoquinone. Reaction conditions were optimized in order to obtain acetovanillone selectively, which serves as a raw material for 3,4-dimethoxybenzoic acid, a building block for synthesis of the smooth muscle relaxant mebeverin [1]. Under conventional heating reactions were sluggish and gave poor yields of a mixture of products. Further, we studied the microwave assisted oxidation of apocynol catalysed by Co(salen)/SBA-15 catalayst. The catalyst was prepared by immobilizing [N,N′-bis(salicylidene)ethane-1,2-diaminato]Cobalt(II), Co(salen) complex on to the periodic mesopore channels of siliceous SBA-15 and characterized by appropriate spectroscopic and analytic techniques. The activity of the Co(salen)/SBA-15 was investigated for the oxidation of **1** in the presence of hydrogen peroxide as oxidant. Complete degradation of **1** was obtained after 40 min of reaction under microwave irradiation, compared to a poor 57% degradation after 24 h under conventional heating [2]. We have also attempted the oxidation of **2** over Co(salen)/SBA-15 and 2-methoxy phenol was obtained with very high selectivity.

The use of increased amount of catalyst, reusability the catalyst, role of different solvents and use of other mesoporous catalysts have also been investigated [3].

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Discrimination of acidic sites in anion modified metal oxides – An experimental and DFT study

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Mixed iron and titanium oxides with different quantities of sulphate were prepared by sulphation of ilmenite, followed calcination at 500 and 700 ^{o}C. The structures of pyridine adsorbed sulphated Fe_2O_3-TiO_2 is essential for understanding of how these materials would perform as catalysts. The sulphated Fe_2O_3-TiO_2 samples were characterized by XRD, TG-DTA, XRF, and DRIFT spectroscopy. The structures of pyridine adsorbed sulphated Fe_2O_3-TiO_2 were studied with a combined approach using DFT / B3LYP / Lanl2DZ and DRIFT spectroscopy. The infrared absorptions, Mulliken charges and bond lengths are investigated by DFT for the various possible pyridine adsorbed sulphated Fe_2O_3-TiO_2 structures. The covalent character of S=O was found to decrease with the adsorption of pyridine on sulphated Fe_2O_3-TiO_2. The DFT studies demonstrated the strong affinity of adsorption of water for sulphated Fe_2O_3-TiO_2 samples. The evaluation of IR absorptions obtained by DFT and DRIFT spectra reveal the presence of Bronsted and Lewis acid sites on the surface of sulphated Fe_2O_3-TiO_2 samples.

Density Functional Theory Studies on Base and Zeolite Supported Nanoclusters of Gold and Palladium

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We have investigated the structures, properties and reactivity of small gas phase clusters of gold (Au_n, n=1-13)[1i] and palladium (Pd_n, n=1-13)[2] using density functional theory (DFT). From these studies, different parameters namely bond length, binding energy, stability function, fragmentation energy, bond dissociation energy, ionization potential, electron affinity, HOMO-LUMO gap, global hardness and dipole moment have been calculated for the clusters. On the basis of these data, we have predicted the stability of small gold and palladium clusters. We also studied the adsorption of CO on some of the stable clusters. Adsorption of CO over zeolite supported Au c monomer has been studies using both quantum cluster approach as well as QM/MM method. Further, from the study of CO interaction with bare and oxidized Pd clusters, the intermediates of CO oxidation reaction catalyzed by small palladium clusters have been identified.[3] The reaction energy profiles indicate the effect of charge state of Pd cluster on CO oxidation. Structural, energetics and reverse hydrogen spillover have also been investigated zeolite supported Au_6 and Pd_4 clusters.[4,5]

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Use of Whole Cells of *Candida parapsilosis* ATCC 7330 for the Synthesis of Optically Pure Secondary Alcohols

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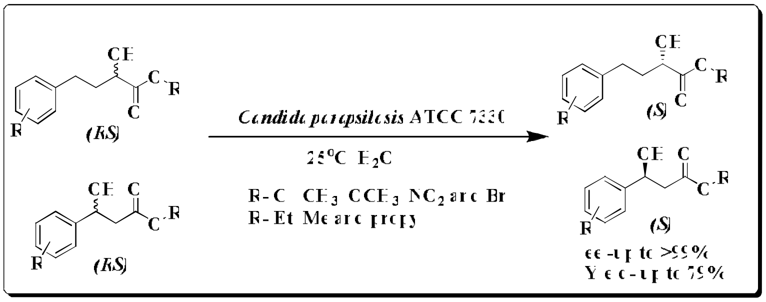
Optically pure secondary alcohols are important chiral precursors for the synthesis of many bioactive molecules[1]. They can be synthesized by both, chemical[2] and biocatalytic methods[3]. Biocatalytic methods include asymmetric reduction of the corresponding prochiral ketones[4], resolution[5] and deracemisation of the racemic hydroxy compounds[6]. Deracemisation, unlike resolution (which gives maximum yield of 50% for each enantiomer) has the distinct advantage of giving only one enantiomer in high chemical and optical yields[7]. *Candida parapsilosis* ATCC 7330 is efficient in deracemisation of α- and β-hydroxy aryl esters as reported by us earlier[8]. The steric bulk of the substrates though, seem to influence the outcome of deracemisation and it was seen that substrates like disubstituted (dichloro and dimethoxy) benzene ring, naphthalene ring and benzyl ester as side chain gave less ee of the product enantiomer. Futhermore, deracemisation of racemic α- propargylic esters gave optically pure α- propargylic esters in high ee and yield[9]. In addition to hydroxy esters, *Candida parapsilosis* ATCC 7330 was used to synthesize optically pure aryl/heteroaryl but-3en-2ols[10.]



Scheme 1. Deracemisation of α-and β-hydroxy aryl esters

In addition to deracemisation, asymmetric reduction of prochiral ketones and imines by *Candida parapsilosis* ATCC 7330 yields optically pure alcohols and amines e.g. α-hydroxy aryl esters and secondary amines[9b]. In the case of aliphatic secondary alcohols both (*R*) and (*S*)- enantiomers of ethyl 4-chloro-3-hydroxy butanoate were synthesized in high yield and ee by *Candida parapsilsosis* ATCC 7330 mediated asymmetric reduction[11].

Mechanism of *Candida parapsilosis* mediated deracemisation revealed atleast two reactions – an *R*-specific oxidation and an *S*-specific reduction **(Fig 1).** In order to understand the deracemisation mechanism and to increase the substrate loading for deracemisation reaction, purification of the enzymes involved is currently in progress. Initial results in this direction[12] and our attempts to understand the molecular mechanism using enzyme docking [simulation] studies with our experimental data[13] will be presented.

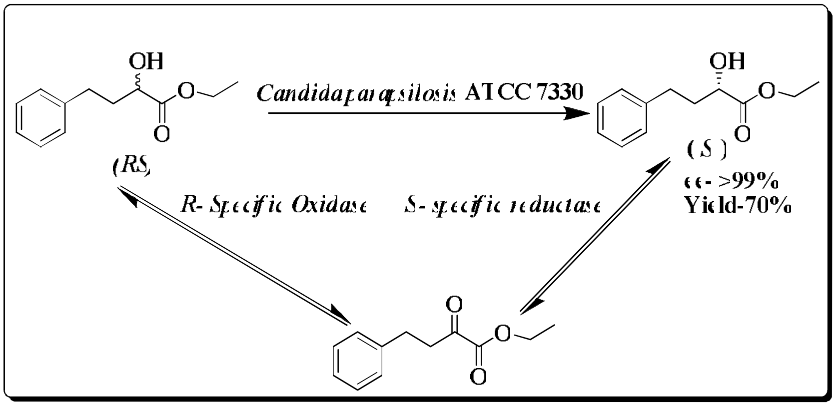


Fig 1. Mechanism of deracemisation reaction

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Phosphoric Acid Modified ZSM-5 and Its Application towards Shape Selective Alkylation

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Alkylation of alkyl aromatics are carried out over various zeolites such as Y, Beta, Mordenite and ZSM-5 and their modified forms. Pore size modification is the one of the versatile method to achieve high selectivity. Alkylation of toluene with methanol was investigated over ZSM-5 with silicon isomorphously substituted by trivalent cations like Al, Fe and B. It was also observed that enhanced para-selectivity for the alkylation of toluene with methanol on phosphorus-modified H-ZSM-5 zeolites and suggested that the phosphorus reagent interacted with the acid sites of the zeolite and attached to the zeolite via framework oxygen atoms, which partially blocked the pore openings and restricted the diffusion of m- and o-xylenes [1]. In this study, we have reported phosphoric acid modified ZSM-5 for the t-butylation of ethylbenzene with t-butyl alcohol in the vapour phase.

10% Phosphoric acid modified-ZSM-5 was prepared by treating appropriate amount of H-ZSM-5 with phosphoric acid and water at 60 ºC for 6 h by wet incipient method. The resulting material was dried at 100 ºC and calcined at 750 ºC. The same procedure was adopted for different percentage loadings.

All the P-modified samples exhibit similar XRD patterns to that of H-ZSM-5. Hence, there is no structural degradation as a consequence of phosphoric acid modification. The thermogram of 8% P-ZSM-5 exhibits a weight loss below 200 °C due to desorption of water in addition to the weight loss between 200 and 300 °C which is assigned to condensation of defective O-H groupings. There is an additional weight loss between 550 and 700 °C which is assigned to conversion of phosphate into metaphosphate.

The temperature programmed desorption (TPD) of ammonia showed the consumption of strong acid sites during phosphoric acid modification. The peak due to weak acid sites appear below 300 °C in all the samples, is due to Lewis acid sites and defective sites, as the P^+ site is a Lewis acid site. These results also confirm conversion of Si-OH-Al bridges into metaphosphate bridges.

t-Butylation of ethyl benzene over H-ZSM-5, 8, 10, 12% P-ZSM-5 was carried out at 200, 250, 300, 350 and 400 ºC with feed ratio 1:1 and WHSV 2.46 h^{-1}. The major product was found to be 4-t-butylethylbenzene (4-t-BEB) and 2-t-butylethylbenzene (2-t-BEB) was found to be formed in small amount. In addition, diethyl benzene and benzene in smaller amounts were also observed. The ethylbenzene conversion was nearly equal to zero at lower temperatures. But at 350 and 400 ºC, it was significant and higher than 40%. Lower conversions at low temperatures is attributed to difficulty in chemisorption of t-butylalcohol. The three methyl groups attached to carbon bearing the -OH group is suggested to cause steric hindrance for chemisorption which was also reported already [2]. Coke formation was also noted at 350 and 400 ºC which is due to the formation of polybutenes. The major product was found to be 4-t-BEB and its selectivity was found to be more than 80% where as 2-t-BEB was formed with lower selectivity.

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DESIGN OF NOVEL NANOSIZED CERIA-BASED SOLID SOLUTIONS FOR CATALYTIC APPLICATIONS

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Being a unique functional rare earth material, ceria (CeO_2) has been widely used in different fields such as catalysis, sensors, electronics, optics, and so on [1-2]. The ability of ceria to cycle between 3+ and 4+ oxidation states is the key factor for these applications. Ceria has been extensively used as an active component in three-way catalysts (TWC) where pollutant emissions from internal combustion engines are effectively reduced. The reason for extensive use is acknowledged from the nature of outstanding redox behavior being amenable for absorbing and giving off the oxygen from the atmosphere, which is known as oxygen storage/release capacity (OSC) [1]. This unique property of ceria has been triggered off many salient applications of industrial significance. However, despite its wide applicability, pure ceria is associated with some disadvantages like thermal sintering and deactivation of the redox couple, which result in the decline of OSC and catalytic activity. Hence, several efforts have been directed towards eliminating the disadvantages of ceria by doping it with other isovalent/aliovalent cations [2-7]. In many cases, the redox properties and chemical reactivity of pure ceria could be enhanced by introducing dopant cations into the oxide lattice. As reported, small ionic size and low valence states of dopants have shown strong influence on the physicochemical properties such as the number of vacancies and defect reaction energies. Recently, considerable attention has also been paid to introducing variable valence ions into the ceria lattice to recognize their role in the defect chemistry. The oxygen ions/vacancies attached to reducible elements are mobile, which could contribute to the OSC of the mixed oxides. Among various elements, zirconium, hafnium, terbium, praseodymium and lanthanum are particularly suitable for making solid solutions with ceria. The present investigation was undertaken against the aforesaid background. In the present study, we have investigated the influence of non-reducible and reducible (Zr^{4+}, Hf^{4+}, La^{3+}, $Tb^{3+/4+}$ and $Pr^{4+/3+}$) cations on the structural, redox and acid-base properties of ceria. Accordingly, nanosized ceria-zirconia, ceria-hafnia, ceria-terbia, ceria-lanthana and ceria-praseodymia solid solutions were synthesized by a soft chemical method from ultrahigh dilute solutions and subjected to thermal treatments at various temperatures [3-7]. The structural, redox and surface acid-base properties were characterized by BET surface area, XRD, Raman, TEM, XPS, TPR, TPD and OSC measurements, and evaluated for soot and CO oxidation reactions. From this comprehensive study it was established that introduction of both non-reducible and reducible cations enhance reducibility and OSC of ceria by creating more number of oxygen vacancies. Further, these doped catalysts also exhibited better CO and soot oxidation activity than Zr^{4+} incorporated ceria solid solutions. Some of these solid solutions when supported on silica and alumina also showed better conversion and selectivity towards dehydration of 4-methylpentan-2-ol to 4-methylpent-1-ene. A high specific surface area, textural strength, moderate reduction temperature and high OSC appear to make these new solid solutions as promising materials for low temperature CO oxidation, soot oxidation and alcohol dehydration reactions. The combined use of different sophisticated techniques provided interesting key information pertaining to enhanced catalytic efficiency and high thermal stability of the synthesized solid solutions [4-7]. More details on these studies will be elaborated in this presentation.

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Synthesis and functioning of catalytic materials: A better insight using first principle methods

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A molecular level understanding of the catalytic systems and their activity is a basic thrust for a catalytic researcher so that focused improvements can be brought in by designed modifications. Though experimental spectroscopic techniques help in this direction, inherent technical limitations bring in hurdles while probing at molecular level. Quantum chemistry based computational studies provide better insight in such situation and also bridges the gap to perceive a complete picture. Our group at NCL is working on such approaches in all three major areas of catalysis viz., synthesis, characterization and application of catalytic systems such as molecular sieves, metal oxides and nano- and subnano- level metal particles. The present talk would exhibit various salient understandings during a few case studies in our work.

Influence of alkali elements on the pre-nucleation species of zeolite synthesis.

The interactions of the most basic building block of zeolite synthesis, namely the ortho-silicic acid [Si(OH)4] (also known as Q0) species with the reaction mixture and with in themselves are key factors to drive a zeolite synthesis on a specific route to form different microporous silicate structures. A zeolite based on their structure and pore architecture entitles to be some of the best industrially known catalyst for complex reactions. It is well known that the alkali element's presence in the reaction mixtures brings a substantial difference in the crystallization time. However, its role on the kinetics of the synthesis is not completely understood as the Q0 species are highly challenging to be studied using experimental spectroscopic techniques viz., NMR etc. Quantum mechanics (Density Functional Theory - DFT) based computational studies carried out in our laboratory, has brought a significant insight into this crucial problem.

Ab initio theoretical calculations were carried out over a wide range of optimized models of Q0 species with different alkali cations such as Na+, K+, Ca2+ etc., at DFT level with the HF self-interaction corrected, hybrid B3LYP functional with split valence basis set along with polarization and diffuse parameters viz., 6- 311G+(2d,p). Their 29Si NMR chemical shifts were also calculated using GIAO method. Natural Bonding Orbital (NBO) and Perturbation Theory based energy analysis were used to understand various interactions between different alkali ions with Q0 species. NMR chemical shift variations as a function of geometrical parameters indicated a possibility of different modes of interactions with different alkali elements substituted Q0 species which was also confirmed by the NBO occupancy analysis. The electron density iso-surfaces (Fig. 2) showed that few alkali cations have characteristic non-bonded interactions that significantly modify electron density around the central Si atom which is reflected in the NMR chemical shift values. On the use of more than one alkali elements for eg., Na+ and K+ in the synthesis, the calculations shows that the kinetics of zeolite crystallisation would alter as the polarization of the Q0 species changes drastically.

Proviso criteria for noble bimetallic nano and sub-nano clusters for catalysts in Fuel-Cell (DMFC) applications

Although a lot of progress has been made in the development of direct methanol fuel cell (DMFC), its performance is still limited by the poor kinetics of the anode reaction and the crossover of methanol from the anode to the cathode side through the proton exchange membrane. The half cell reactions and their mechanism are complex to understand. Noble metals are the most active catalysts for dissociative adsorption of methanol, but, as it is well-known, at room or moderate temperatures they are readily poisoned by carbon monoxide, a byproduct of methanol oxidation. Developing a sufficiently selective and active electrocatalyst for the DMFC remains one of the key tasks for further progress of this technology. When non-noble metals are added with the noble metals, the combinations improve selectivity and efficiency. However, very little has been understood about the know-how of these enhancements and assortments. First principle based studies being carried out in our laboratory to understand such links to bring effective modifications of the preparation of electrodes. We have used *deMon2k,* a DFT supporting code to study the structure, stability aspects of various compositions of noble bimetallic subnano- clusters, viz., Aum, Ptn, and [Au/Pt]m+n where m+n = 2-8.

Half cell reactions at each electrode is complex and involve several reactants and intermediates. For instance, a part of the studies provide clear proof for the stabilization effects of one metal on the other and the compositional effects on methanol oxidation capabilities of the clusters. Another example of conspicuous evidence for the fine tuning of oxidation capabilities of the bimetallic cluster may be demonstrated using a detailed analysis of CH3OH interactions with bimetallic clusters. In the Figure (Not shown in this abstract)it has been provided the structure details of the methanol adsorbed Au, Pt and Au/Pt dimer clusters of the most stable spin state and their energies of methanol adsorption on them. Pure Au cluster known to normally exist in singlet state shows a CH3OH adsorption energy of 0.41eV while the Pt dimer shows about 0.17 eV. However, the bimetallic effect drastically brings down to just 0.06 eV. A significant charge transfer from Pt to Au is observed to stabilize the structure and alters the cluster's redox capabilities. Studies carried out on dimer and higher order clusters provide significant clues on the catalyst modification for enhanced selectivity. These results will be highly useful to predict the effective metal compositions and their redox capabilities that in turn help to selectively coat the electrode with preferred bimetallic pairs of noble metals and their ratios.

Selected publications

· *Micropor. Mesopor. Mater.,* 122, 105, **2009**

· *J. Phys. Chem A.* **2009** *(communicated)*

· *Theo. Chem.* ***2010*** *(communicated)*

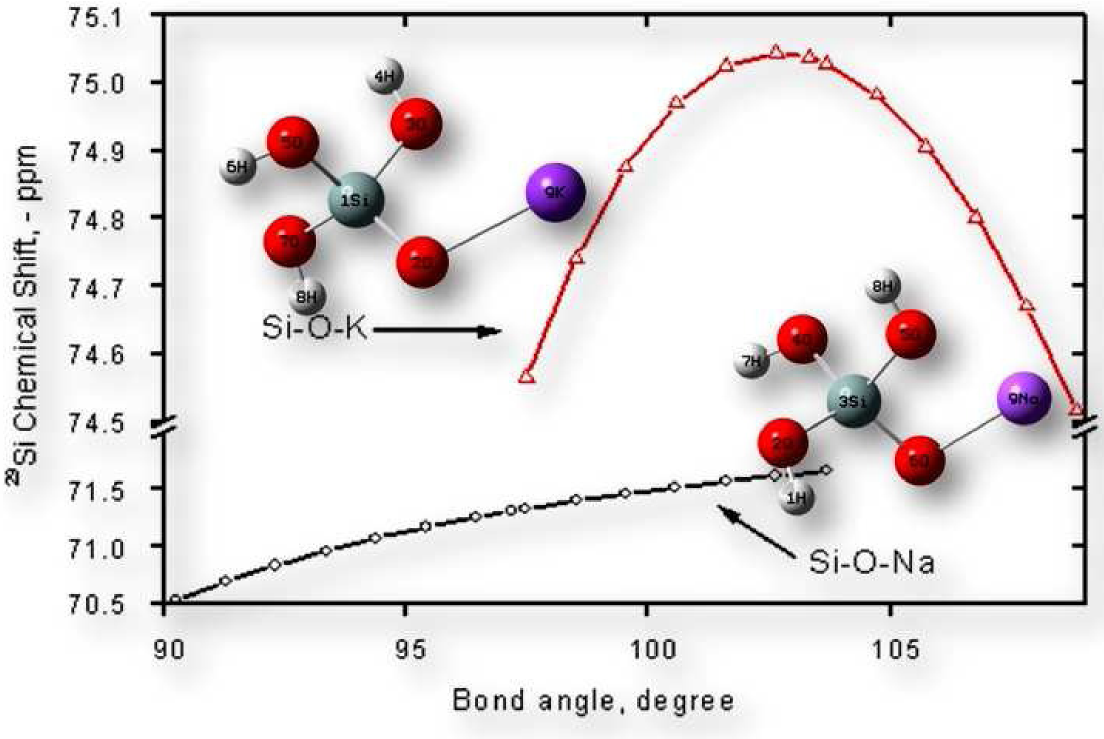

Figure 1. Distinct trends in the 29Si NMR chemical shifts as a function of changing Si-O-M+ bond angle of different alkali-Q0 species.

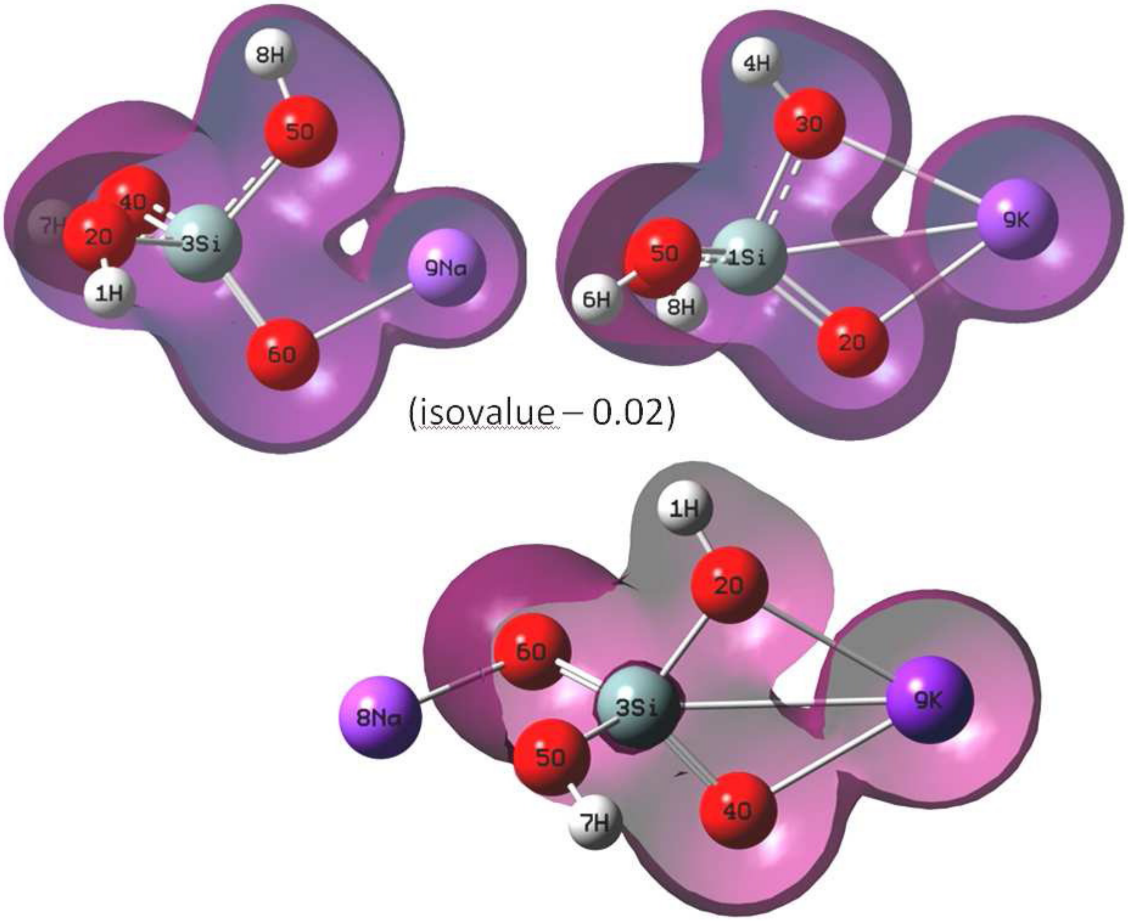

Figure 2. Sliced electron density iso-surfaces for different alkali-Q0 species shows distinct interaction between the alkali and the non-bonded bridging oxygen.

Strategy to Stabilize Pd Nanoparticles by Polyamine based Hybrid materials for Catalytic Applications

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Abstract: The strategy adopted to entrap metallic Pd nanoparticles involves combined functions of polyamines for stabilizing Pd (0) that can enhance catalytic activity, and the magnetic nanoparticles to render easy recovery of the catalyst from the reaction mixture. The synthesized catalysts exhibit efficient catalytic activity in various hydrogenation and ligand free Suzuki–Miyaura reactions. The catalyst was completely recoverable and the separated catalyst could be reused with similar catalytic efficiency indicating well stabilization of Pd nanoparticles and there is no apparent change in the Pd content after the reuse.

Introduction:

Palladium particles are among the most popular transition metals, and known to present a very high catalytic activity toward a wide range of applications. Stabilized clusters and colloids of Pd with nanometer-scale dimensions are of particular interest as catalysts for organic and inorganic reactions. However, there are issues associated with the separation of palladium from the desired product, stability to retain its activity and reusability. Due to the increasing environmental requirements for green processes, it is therefore, important for development of new catalytic systems composed of nanoparticles that are not only stable and active, but also easy to separate and reuse. One promising solution to this problem consists in immobilizing the particles on a solid support. The most generally utilized methods for immobilization of catalyst are physical adsorption of palladium onto a support such as charcoal, silica, or alumina. However, though it may result in high catalytic activities, the stability against metal leaching is not satisfactory. Alternatively, encapsulation of the metal particles by polymers or dendrimers has been reported, but the catalysts further require mechanical stability against breakage of the host or leaching of the metallic particles. Moreover, being a soft material the polymer may not provide enough robustness either against metal leaching or for recyclability. So, our approach is to uniquely combine both inorganic nanoparticles and polymeric components in such way that while the polymer stabilizes the palladium nanoparticles, the inorganic particles can provide the required mechanical stability. Further, addition of nanoparticles amenable for magnetic separation to these structures can be of advantage. A key challenge is to surface functionalize these magnetic nanoparticles such that it allows immobilization of catalytically active metal on its surface while preventing their agglomeration.

Here in we discuss on our strategy to immobilize Pd on Fe_3O_4 nanoparticles. The catalyst is designed with an aim to combine the property of highly branched polyethylenimine (PEI) to effectively immobilize and stabilize Pd nanoparticles with the magnetic property of Fe_3O_4 nanoparticles for easy catalyst separation (Figure 1).[1] The methodology was further extended to use microcapsule (MC) structures formed by self-assembly silica nanoparticles and polyamines, for encapsulation of palladium nanoparticles. Ionically cross-linked polyamine aggregates act as templates for the silica nanoparticle to assemble and thereby creating pores for the Pd ions to penetrate and get reduced by external reducing agent inside these microcapsules.[2] The utility of the Pd containing catalysts was examined in reductive reactions such as hydrogenation reaction and Suzuki-Miyaura reactions. Suzuki-Miyaura coupling reactions is one of the most useful methods for selective C-C bond formation during the construction of biaryl skeletons, which are often included as partial structures in pharmaceuticals, natural products and functional materials. Recent work has been focused on new catalyst systems that efficiently process challenging substrates such as aryl chlorides while still using relatively mild conditions and low catalyst loading (Scheme 1). Our catalyst is capable of taking care of the above-mentioned inadequacy besides the common problems associated with dispersion and leaching of Pd. In case of MC, the combination of nanoparticles, polyamines and porous structure show synergistic effects to enhance the activity and durability of the catalyst in addition to their easy separability.

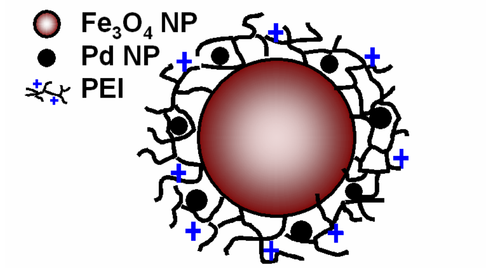
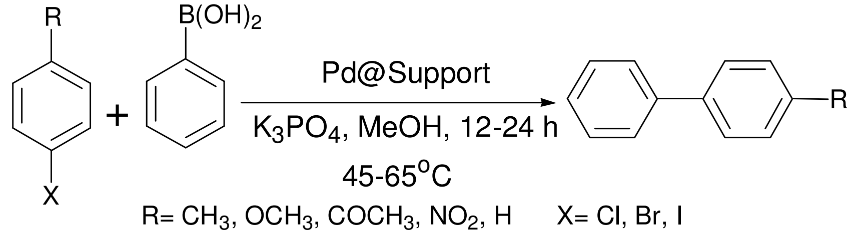


Figure 1. Pd nanoparticles immobilized on PEI functionalized Fe3O4



Scheme 1.Schematic illustration of Suzuki-Miyaura Coupling Reactions

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PHOTOCATALYTIC DEGRADATION OF POLLUTANTS BY VISIBLE LIGHT RESPONSIVE N, S CO-DOPED TITANIA

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Titania is a well-known photocatalyst for the removal or degradation of organic pollutants. It can be activated only under UV light irradiation due to its wide band gap of 3.2 eV, (anatase). Many attempts were reported by various research groups to bring the activity of titania into visible region such as doping with metals, non-metals, coupling with other semiconductors, sensitizing with colorful inorganic or organic compounds. However the anionic dopant species were found to be better than others with respect to the stability of the doped materials, photocatalytic efficiency, and ease of the doping process etcPhotocatalytic activity mainly depends on its method of preparation, surface area, phase purity, crystallinity, shift in band gap, presence of other impurities etc. Now-a-days double non-metal doped system become hot research topic in photocatlysis by titania. There are a few reports on, N-S codoped titania by sol-gel, hydrothermal, C-N codoped titania by mechano-chemical, N-P by sol-gel, F-N by low temperature chemical method C-F codoped by hydrothermal, F-N by pyrolysis etc with varying degree of photo-catalytic activity.

Here we are prepared highly visible light responsive anatase N-S co-doped titania through sol-gel precipitation method using titanium tetraisopropoxide and aqueous solutions of thiourea as the dopant source. The catalyst was characterized by various techniques - XRD, UV-Vis.DRS, BET surface area, TEM, XPS, Raman spectra etc. The photocatalytic efficiency of the catalyst was evaluated by the degradation of herbicide monolinuron [3-(4-Chlorophenyl)-1-methoxy-1-methylurea.] and 2,4,5-trichlorophenoxyacetic acid (245-T) [using uniform illuminator of 100W Xe ozone free lamp] and the ability of catalyst was reported as percentage of degradation of the pollutants in aqueous medium my measuring its change in concentration with respect to initial concentration, using HPLC [on a Luna ODS-2 C-18 column of 25cm, 5μm, with UV detector]. Studies involve the change in amount of catalyst, different amount of dopant loading, comparison of percent degradation in visible and UV region, adsorption and kinetics studies etc. We also compare the results with undoped titania and one of the anatase commercial titania.

The phase composition, crystallinity of catalysts are obtained from XRD and Raman, the chemical nature of the dopants from XPS, the particle size and shapes from TEM, shift in band gap from UV-Vis..DRS and surface area from

Nitrogen adsorption measurements. Results showed that more than 80% of the herbicides were degraded within one hour irradiation in visible region and is attributed to the synergetic effect of both dopant N and S by lowering its band gap by mixing their p states with o 2p states of titiania

Acknowledgements

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'Novel catalysts in bio-based products'

Prof G D Yadav

Director, University Institute of Chemical Technology, Matunga, Mumbai

[Abstract expected]

CATALYTIC ISOMERIZATION TO PERFUMERY CHEMICALS BY LAYERED DOUBLE HYDROXIDES AND THEIR MODIFIED FORMS AS SOLID BASES

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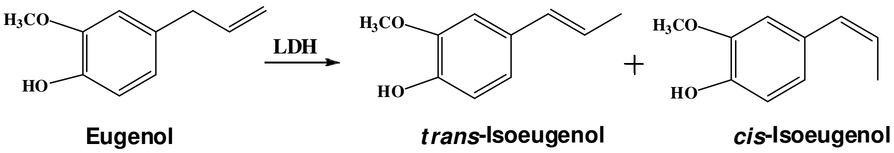
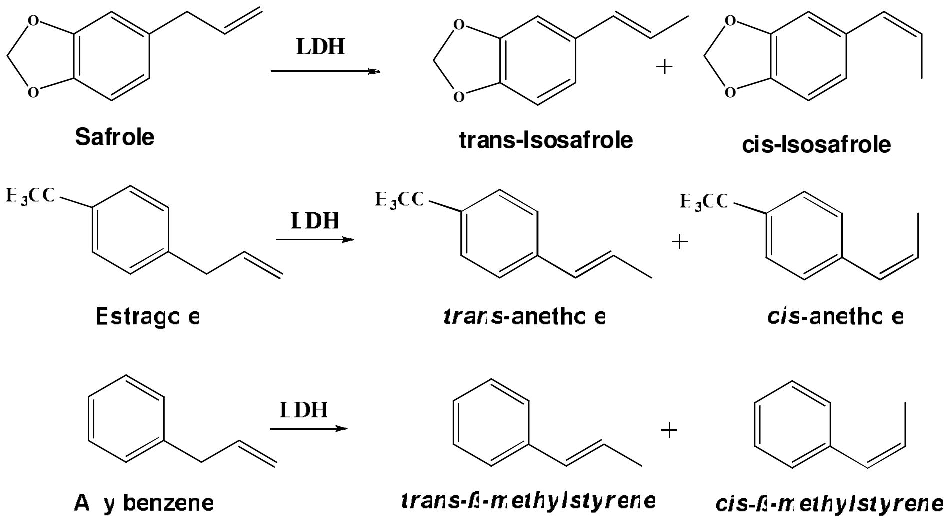
Isomerisation of alkenyl aromatics to the thermodynamically stable *iso*-compounds is an important reaction in the field of "closely guarded" perfumery chemicals. These compounds find an important role in fragrance and pharmaceutical industries. Traditionally, they are produced using conventional caustic alkali based homogeneous catalysts leading to large effluent streams and posing considerable environmental concern. Substituting such liquid bases by solid reusable catalysts is one of the research topics being pursued strongly by the researchers across the world. Some of the excellent reviews corroborate this necessity [1-3].

Layered double hydroxides (LDHs), otherwise referred as hydrotalcite-like (HT-like) compounds or sometimes referred as anionic clays are one of such solid base catalysts being studied extensively in the recent years. They possess brucite-like $[Mg(OH)_2]$ network wherein an isomorphous substitution of Mg^{2+} ion by a trivalent cation M^{3+} occurs and the excess positive charge is compensated by gallery anions which are located in the interlayer along with water molecules [4-6]. They are represented by the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+} [A_{x/n}^{n-}]^{x-}.mH_2O$ where M(II) and M(III) are various divalent and trivalent metal ions, A is the interlayer anion, x can have the values between 0.20 to 0.40 and m can generally have the value four [7].

The wide maneuverability of bivalent ions, trivalent ions, anions in interlayers with varied compositions assist in the design of large class of isostructural materials with varied physicochemical characteristics and thereby offer tunable catalytic properties. In this presentation, we would be discussing the results of catalytic applications of as-synthesized LDHs and their derived forms for the isomerization of alkenyl aromatics, in particular for the compounds namely eugenol, safrole, estragole and allylbenzene (See Scheme 1) [8-14].





Scheme 1 Isomerisation of akenyl aromatics

Some of the main findings of our study are:

- MgAl-LDHs and NiAl-LDHs are excellent catalysts for all these reactions. All other metal ions are not active or poorly active.
- Activity of as-synthesized LDHs is higher than their corresponding calcined forms.
- Measurable conversion is noticed above 120 ^{o}C and nearly stoichiometric conversion (> 98 %) was achieved between 160-200 ^{o}C depending on the substrate. Among the substrates, at 160 ^{o}C, isomerisation activity of eugenol is lowest while allylbenzene is highest. In all cases, thermodynamically stable *trans*-isomer is the preferred product.
- Solvents with higher polarity favoured the reaction.
- No necessity to carry the reaction under inert conditions, which is in general for most of the solid base catalyzed reactions, a beneficial feature for scale up.
- Very subtle substitution of active metal ions by inactive ones (for example Ni by Cu) significantly quenches the activity while synergism was found when highly active metal ions (Mg and Ni) were present together.
- Under our reaction conditions, LDHs based catalysts were superior to the conventional liquid base catalysts and also reusable.
- Various physicochemical measurements were done to derive activity-basicity correlation/relationship.
- Active centres are deduced and the reaction pathway over LDHs is proposed.
- Scale up studies indicated the promise of taking up these materials to the next level.

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Catalytic hydroconversion of tricaprylin and caprylic acid as model reaction for biofuel production from triglycerides

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Introduction

The aim of the present work was to learn more about the mechanism of the direct hydroconversion of vegetable oil into hydrocarbons over non-sulfide catalysts.

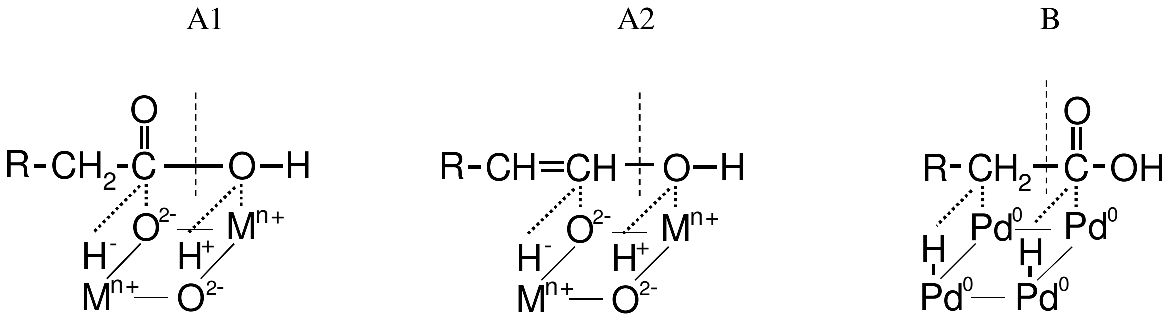
Experimental

Alumina-supported Ni,Mo-oxide hydrofining and carbon-supported Pd hydrogenation catalysts were used. Catalysts were characterized by temperature-programmed reduction and decomposition, DRIFTS and FT-IR spectroscopy. Tricaprylin (TC = octanoic acid triglyceride) and caprylic acid (CA = octanoic acid) were applied as model reactants. Catalytic hydrodeoxygenation (HDO) of TC and CA were carried out in a high-pressure flow-through reactor. The reactions were carried out using a flow of (TC or CA)/ H_2/He mixture. WHSV for the TC or CA was always 6 h^{-1}. Helium was admixed to the reactants to maintain the total pressure, usually at 21 bar, while the partial pressures of reactants could be changed. H_2/CA molar ratio and reaction temperature were varied in the range of about 1 to 20 and 300 - 400 ^{o}C, respectively.

Results

Results obtained in this study suggest that the hydroconversion of triglycerides to hydrocarbons proceeds in a series of consecutive reactions. It was found that the first step is the hydrogenolysis (HYS) of the ester to fatty acids and propane. The HYS reaction is followed by HDO. Relative to the HDO the HYS reaction is quite facile. As a result the concentration of the fatty acid intermediate can be quite high in the product mixture if the reaction conditions do not favor the HDO step.

The chain length of the product hydrocarbon depends on the type of the catalyst, suggesting that HDO proceeds by different mechanisms over supported oxide and metal type catalysts. Over the Pd/C catalyst the main hydrocarbon product was C_7 alkane, i.e., the alkane was one carbon atom shorter than the carboxylic acid. The activity and selectivity of the carbon supported Pd metal catalyst were virtually independent of the hydrogen partial pressure, but passed through a maximum as a function of the carboxylic acid partial pressure. The results are in accordance with the direct catalytic hydrogenolysis of the carboxylic acid to alkane and formic acid, followed by the rapid decomposition of the acid to CO and H_2.



Scheme 1. Transition states of the HDO reaction of carboxylic acid over supported oxide (A1, A2) and (B) metal type catalyst. The transition state relaxes by forming chemical bonds with the hydrogen atoms and splitting the bond at the vertical dashed line. The square with metal (M^{n+}, Pd^{o}) and oxide ions (O^{2-}) at the corners represent two active centers on the catalyst surface.

The HDO over the Ni,Mo/γ-Al_2O_3 catalysts proceeded in consecutive H_2 addition and dehydration steps giving predominantly $C_8^{=}$ alkenes, C_8 alkanes and water. Water and some alcohol were also formed and aldehyde was also detected. These products suggest that the dominating HDO reaction is the reduction of the acid to alkane in consecutive steps. The application of higher hydrogen and lower fatty acid pressures resulted in higher conversion. Products of hydrodecarbonylation (C_7 alkane) were also obtained, indicating that the oxide type Ni,Mo/γ-Al_2O_3 catalyst also presents some metal type catalytic activity.

The substantiated transition states of fatty acid HDO reactions over oxide and metal type catalyst are shown in Scheme 1.

STUDY OF 2D MODEL SYSTEMS AND ITS CONTRIBUTION TO CATALYTIC RESEARCH

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The mechanism of the formation of metal nanoparticles on oxide surfaces not only is an important theoretical issue, but also represents a key process in the fabrication of nanostructured ultrathin films. The study of 2D (planar) model catalysts prepared by deposition of metal (bottom-up techniques) provided an excellent example of how the complexity of the material systems can be increased step-by-step in order to investigate crucial issues related to the chemical reactivity of nanoparticles. It has been demonstrated in a number of cases that the activity and the selectivity of policrystalline supported transition metal catalysts depend sensitively on the morphology (size and shape) and the local enviroment (particle –support interface) of the metal particles.

In this work, we will show, how to prepare noble metal (Au, Rh, Pt) nanoparticles of different surface distribution, average size and shape, simply by variation of the deposition conditions, like temperature and pretreatment of the supporting oxide. Most of the work is performed on $TiO_2(110)$ surface and the main experimental method is the scanning tunneling microscopy (STM). By tailoring the morphology, it is possible to address several important questions emerging in the heterogeneous catalysis, like the change of the particle mean size in ambient gas atmospheres or the variation of the activity and selectivity in different catalytic reactions. Special emphasis will be given to the CO- and NO-induced disruption and agglomerization of metal nanoparticles. It will be also presented that it is possible to follow some atomic level processes like (1) the decoration of metal nanoparticles by reduced phase of the support (strong metal-support inteaction, SMSI), (2) in situ formation of core-shell bimetallic nanoparticles or (3) evolution of carbon deposits around the metal particles in the decomposition of C-containing molecules. These examples indicate clearly the capabilities of the two-dimensional systems where the full arsenal of the surface science techniques can be very efficiently applied.

Steam reforming of ethanol

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The increasing demand for alternative energy sources drew a great attention to the steam reforming of ethanol to produce H_2. From environmental point of view the use of ethanol is preferred because it can be readily produced from renewable biomass and ethanol could be a raw material for chemical industry.

Recently it has been found that supported noble metals are active catalysts of H_2 production in the ethanol reforming. It was found that while the selectivity of hydrogen decreased in time, the formation of ethylene increased parallel to it on all alumina supported noble metals at 723 K. This trend was less prominent by increasing the water concentration, the metal loading and the reaction temperature. By means of infrared spectroscopy and TPD measurements it was found that after the ethanol adsorption not only different types of ethoxy species but significant amount of adsorbed CO and acetate group were present on the surface. The latter species were stable even above 700 K. During the reaction at 723 K not only acetate but adsorbed CO was found. It is surprising to detect CO well above its desorption temperature. It means that the formation rate of the CO is higher than its desorption or further reaction rate. It was presumed that the surface acetate species bonded mainly to the support. In spite of the location of these species we stated that the surface acetate hindered the reaction to hydrogen on the metal.

After addition of K to the alumina supported catalyst or using mixed oxide as a support the stability of surface acetate decreased and the hydrogen selectivity in the steady state increased. When the support contains easily reducibly oxide such as CeO_2 or TiO_2 significant amount of acetaldehyde and acetone were also formed. The acetaldehyde and the acetone formation occurred on the clean oxide, too.

The mechanism of the hydrogen and acetone formation will be also discussed.

Gold and silver catalysts for abatement of environmentally harmful materials: modelling the structure dependency

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Introduction

the Automotive exhaust gas contains high concentrations of NO_x, CO, and hydrocarbons, which are harmful to human health. Although these components can be reduced drastically by the use of a three-way catalyst, nitrous oxide, N_2O, which has a strong greenhouse effect, is produced during the catalytic reaction. Since catalysts produce unexpected by-products like N_2O, not only human health effects but also environmental aspects must be considered in an automotive exhaust emission control strategy.

All commercial Three Way Catalysts (TWCs) in use at present are based on platinum, palladium, and rhodium (PGM) on a support comprised of zirconia-stabilized ceria, zirconia and α-alumina. Additives include barium oxide and zinc oxide. The present work is aimed at developing a novel family of catalysts, based on gold and silver, to replace more expensive platinum and rhodium metals.

Experimental

In the Institute of Isotopes during the years starting from 2000 a wide range of research activities have been developed to demonstrate the interactions creating synergism at the Au/metal oxide perimeter. The question was addressed of how the components modify each other's own catalytic properties. Namely, how gold affects the activity of iron oxide itself? The model catalysts were prepared by evaporation of gold onto native SiO_2 covered Si(100) wafers producing gold film of 10 and 80 nm thickness. The 10 nm $Au/SiO_2/Si(100)$ sample was implanted by Ar^+ ions creating nanosize gold particles on the support surface. Interface between gold and different oxides was created by pulse laser deposition (PLD) of TiO_2, FeO_x or CeO_2 over gold. The electron properties of the model systems were characterised by UV-photoelectron spectroscopy (UPS), the oxidation state and surface composition of the samples were studied by X-ray photoelectron-spectroscopy (XPS). The catalytic activity of the samples was tested in the CO oxidation using an all-glass circulation reactor connected to a quadrupole mass spectrometer (QMS).

Comparatively much less information is currently available on the performance of Ag-supported catalysts in the same reaction. Ag/TiO_2 catalysts with different Ag loadings (2, 4, 7 and 10% (w/w)) have been prepared by means of co-precipitation of Ag- and TiO-oxalates followed by temperature programmed oxidation (TPO). The catalysts were subjected to CO oxidation in a flow reactor at atmospheric pressure and temperatures up to 573 K.

Results and discussion

The formation of Au nanoparticles by Ar^+ ion implantation of the 10 nm Au film/SiO_2/Si(100) sample was established. The nanoparticle character was proved by the rearrangement of the Au 5d valence band, namely the decrease of the bands at 2-3 eV and at 6-7 eV, and by the 1eV shifts of the Au 4f core level binding energies to the higher values. [1]

The catalytic activity of the Au nanoparticles/SiO_2/Si(100) sample is significantly higher than that of the 80 nm Au film/SiO_2/Si(100) having Au with bulk character and higher surface area (Fig. 1.a). The activity decrease of Au nanoparticle containing samples in the repeated reaction was explained by the agglomeration of gold particles demonstrated by Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) measurements, accompanied by the reformation of the characteristic bulk XPS spectrum of gold. [2]

An increased activity measured on the 10 nm FeO_x/Au/SiO_2/Si(100) sample as compared to the corresponding FeO_x/SiO_2/Si(100) was demonstrated, and this is regarded as the promotion effect of gold not exposed to the gas phase, on the contacting iron oxide. The promoting effect of Au depends on the Au particle size, in the case of nanoparticles it is significantly higher than in the case of the bulk type Au film. The promoting effect of Au depends on the thickness of the iron oxide: it could not be observed on the surface of a 40 nm thick FeO_x overlayer. [3]

TiO_2 layer was deposited by PLD technique onto either 8- or 60-nm thick Au films supported by SiO_2/Si(100). The initial activity of TiO_2/Au/SiO_2/Si(100) turned out to be significantly lower than that of TiO_2/SiO_2/Si(100), while the Au/SiO_2/Si(100) was the least active (Fig. 1.b). The catalytic activity of the TiO_2/Au/SiO_2/Si(100) samples must be attributed to active sites located on the TiO_2 overlayer modified by gold underneath. [4]

In similar model system CeO_2 overlayer is under study whether the promotion of gold is existing for also CeO_2 or not.

Fig. 1.a

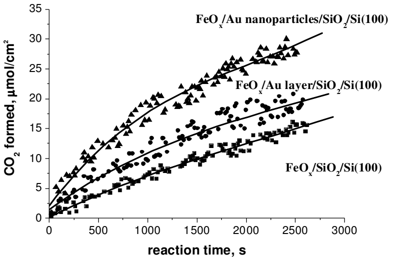


Fig. 1. b

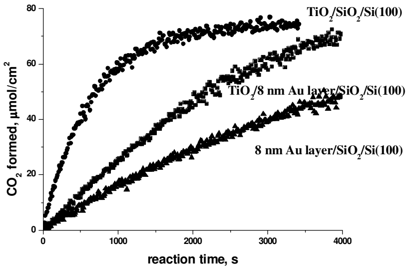
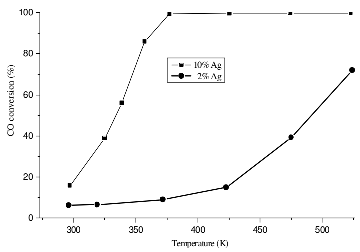


Fig. 1.c



In the case of Ag/TiO_2 catalysts with different Ag loadings (2, 4, 7 and 10% (w/w)) the best conversion performance was obtained in a CO/O_2=1:1 mixture over 10% Ag/TiO_2 for which the temperature of 50% CO conversion was T_{50}=333 K (Fig. 1.c). The initial reaction rates were determined in a circulation reactor at low conversions and apparent activation energies between 13 and 25 kJ/mol were found for all catalysts. TEM microscopy showed a broad range of nano-sized Ag particles on TiO_2 (nearly pure anatase). [5]

Conclusions

Decreasing the size of Au islands on a SiO_2/Si(100) substrate induces the redistribution of the Au 5d valence band structure and is accompanied by increased catalytic activity. Creation of interface of gold film and Au nanoparticles having bulk and size dependent electronic structure, respectively, with different oxides like TiO_2, FeO_x and CeO_2 changes the catalytic activity of oxide overlayers of the samples in the CO oxidation. The promotion effect of Au nanoparticles is significantly higher than that of a bulk-type Au layer beneath FeO_x of about 5–10 nm thickness. Catalysts containing between 4 and 10% (w/w) Ag have demonstrated low-temperature CO oxidation activity whereby T_{50} = 333 K has been obtained for the 10% Ag/TiO_2 sample.

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CO oxidation on Au/MgO and modified Au/MgO catalysts

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1. Introduction

In the last decades the interest and the number of investigations for supported gold catalysts increased in large extent, mainly due to their high activity in low temperature CO oxidation [1,2]. Many authors have stated that the basic condition for high activity of supported Au catalysts is the stabilization of gold nano-particles in the range of 1-5 nm. In this study we present that although the stability of gold particles of small sise under the range of 5 nm is very important, however the change of the properties of the support, namely the environment of the gold also strongly affect the activity (and selectivity) of gold catalyst. The supports for gold catalysts used in the low temperature CO oxidation are distingueshed as (i) active support (Fe_2O_3 [3], MnO_2 [4]) – these are mainly transition metals and (ii) inactive support (Al_2O_3 [5], MgO [6]) materials. Consequently, modifying the support of gold with transition metals (redox metals) that is metal oxides, a new type of active gold catalyst form.

Fe and Mn modified MgO supported Au catalysts were prepared and tested in temperature programmed CO oxidation (TPO) reaction and in continuous, time on stream (TOS) experiments. The influence of the gas atmophere used for the pretreatment of the base Au/MgO catlyst was also studied. The catalysts were characterized by temperature prog-rammed reduction (TPR), FTIR and TEM. FTIR studies indicate that the modification of MgO (with Fe and Mn) results in ”metal ion – matal” ensemble sites. These sites are involved in the activation of CO oxidation.

2. Experimental

The supported gold catalysts were prepared by precipitation – deposition method and $HAuCl_4.4H_2O$ was used as Au precursor. The modification of catalysts was performed in the slurry of MgO with Mn^{2+} and Fe^{3+} salts. TPR, TPO and TOS experiments were performed in quartz reactor at atmospheric pressure. The reaction gas mixture diluted with He. The FTIR spectra were taken at room temperature on pressed catalyst sample disks and those were pretreated before the IR measurement. The TEM images were obtained by JEOL electron microscope.The catalyst preparation, testing and characterization measurements are written detailed elsewhere [7].

3. Results and Discussion

The influence of the pretreating gas atmosphere on the activity of Au/MgO catlyst can be seen in Fig. 1. The conversion curve of CO oxidation shows an U shape after pretreating the catalyst in H_2 and Ar. After pretreatment in O_2 pregnant activity decrease occured. The decrease of activity is more significant under 50°C. The highest activity increase is surprizing after treatment at 500°C in Ar following the treatment in H_2 at 350°C. The modification Au/MgO catalyst with MnO_x – in Fig. 2. - resulted in a significant increase of the activity above room temperature. The modification with FeO_x gave similar results. TOS experiments also show higher activity, selectivity and stability mainly in the presence of H_2 (in preferential oxidation) than the base Au/MgO catalyst.

From the experiments and IR results we suppose that the high activity of Au /MgO catalyst can be attributed to the formation of “$Au^{\delta+}$ - Au^{0}” ensemble sites and they lose activity at higher temperature and pretreating in O_2. The modification with transition (or redox) metal (M) forms a new type of ”Mn+ - Au^{0}” ensemble site that has high activity above 50°C.

The results of the repeated runs of the TPO reaction for CO indicate continuous rearrangement of the structure of Au/MgO catalyst.

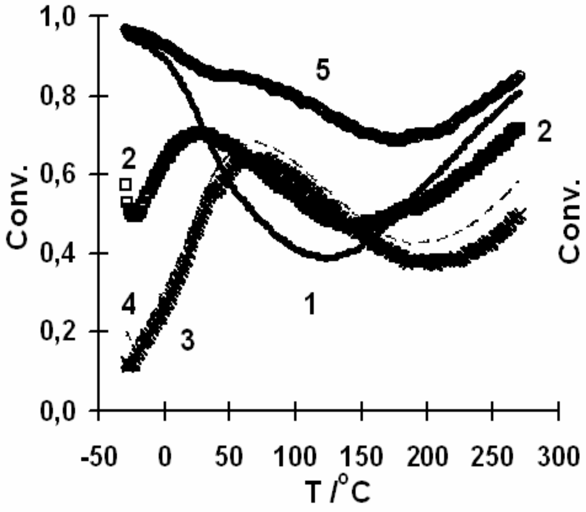

Figure 1

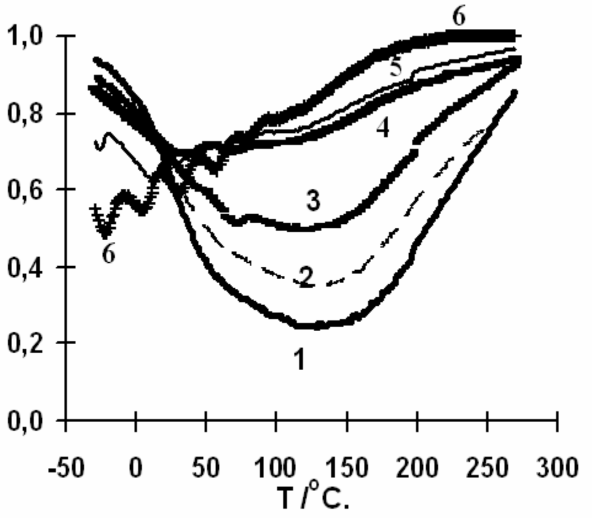

Figure 2

Figure 1. TPO oxidation of CO on Au/MgO catalyst after different treatment procedures. 1: H_2 at 350°C, 2:O_2 at 350°C, 3: O_2 at 500°C, 4: after 1 and O_2 at 500°C, 5: after 1 and Ar at 500°C.

Figure 2. TPO oxidation on Mn modified catalysts - Au/MgOMnO_x. 1: unmodified Au/MgO; Au/Mn ratio: 2=0.08, 3=0.2, 4=0.4, 5=0.8, 6=1.6

4. Conclusion

MgO supported Au catalyst was prepared and modified with transition (redox) metal oxides.The results indicate that the pretreating temperature and gas atmosphere has unambiguous influence on the activity in CO oxidation and addition of modifiers strongly increases the activity. Beside the particle size [8] the nano environment of Au has a significant contribution to the activity control.

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Metal Nanoparticles over Mesoporous Carbon as Catalysts: Synthesis, Characterization and Catalytic Properties

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Introduction

Carbon nanotubes (CNTs) have high thermal stability and are resistive against various corrosive chemicals. Their hollow interior is spacious and allows the free mobility of various reactant molecules. Carbon nanotubes appeared as prosperous supports for catalysts in various catalytic processes such as catalytic electrodes in fuel cells. When comparing the catalytic activity of metal catalysts on various carbonaceous materials, carbon nanotubes have often proved to be the best support. This was the case for the multi-wall carbon nanotube (MWNT) supported platinum catalyst in (i) the catalytic wet air oxidation of nitrogen containing compound, (ii) the oxidation of environmentally harmful organic compounds to CO_2 , (iii) hydrogen generation from ammonia and (iv) isopropanol dehydrogenation. Similar results were found for potassium doped ruthenium supported on MWNT in ammonia synthesis. Guczi and coworkers investigated a series of other Fe/CNT catalysts in Fischer-Tropsch synthesis. Single wall carbon nanotubes have been investigated as support material for transition metal catalysts in the production of carbon nanotubes by CCVD. Nickel and cobalt metals were anchored on MWNTs to investigate the influence of the particle size.

Recently, a new trend appeared for the preparation of mesoporous carbon material with regular pore system. In these process silica sol particles are used as template. Several papers were published in the last decade on the synthesis of mesoporous carbon using mesoporous silicates as template. The mesopores of MCM-48 or SBA-15 type materials were filled with carbohydrates, phenol-formaldehyde resins or styrene and these carbon sources were carbonized at high temperature while excluding oxygen and moisture.

Experimental

Synthesis of MWNTs

MWNTs were produced by catalytic chemical vapor deposition (CCVD) of acetylene over alumnia-supported iron-cobalt bimetallic catalyst. The catalyst was placed onto a quartz boat positioned in the heating part of the quartz reactor tube, and nitrogen was introduced into the reactor while the temperature was increased up to 1000 K. At this temperature, 30 cm^3 / min acetylene was mixed into the nitrogen stream (270 cm^3 /min). The catalytic chemical decomposition of acetylene took place under these conditions. After 30 min, the generation of MWNTs was completed; the acetylene stream was shut off, and the reactor was cooled in nitrogen flow. The raw product was suspended in NaOH solution to remove the alumina, followed by washing with distilled water. The metal catalyst particles formed at the beginning of the synthesis procedure were dissolved in diluted acid solution.

Synthesis of Mesoporous Carbon

Generally 30 g of Ludox® SM30, AS40 or HS40 colloid silica was used for the synthesis. We applied these materials both separately and as bi-component mixtures with 1:3, 1:1 and 3:1 ratios. The solvent was evaporated in a rotary evaporator at 363-423 K. The evaporation took 1-1.5 h. After evaporation the solid matter was dried at 423 K in air in order to remove the rest of moisture. A portion of this dried silica was weighed and placed in a quartz boat into a tubular quartz reactor. The reactor was purged with 300 cm^3 min^{-1} nitrogen flow for 10 min in order to remove air and traces of moisture. Then the reactor was pushed into a preheated (973 K) furnace and acetylene with a flow rate of 60 cm^3 min^{-1} was introduced. After 60 min reaction time, the acetylene flow was stopped and the reactor temperature was raised to 1170 K in 8 min. The carbonization procedure was continued for 60 min. The reactor was removed from the furnace and allowed to cool room temperature. The weight of the product was measured and the material was characterized by physical-chemical techniques.

Synthesis of catalysts

Two types of catalysts were prepared using MWNT s as support. Fort he first group of samples, a simple impregnation method was used to deposit the metal precursors (nickel chloride, iron and cobalt acetates) onto the MWNT support. The second family of the MWNT-supported metal catalysts was prepared in two steps. Metal chloride is transformed to metal oleate in a reaction with sodium oleate. Metal oleate is decomposed in a high-boiling point solvent such as 1-octadecene. After the metal oxide nanoparticles are separated and redispersed in ethanol, they are deposited onto the MWNT support from the suspension. Cobalt and iron oxide nanoparticles were prepared in this way.

A portion of SM30 silica and 1 cm^3 5.5 $mgcm^{-3}$ rhodium or platinum sol were combined. The solvent was evaporated using a rotary evaporator. The carbonization was performed as described above. The silica template was removed and the final product was characterized.

Sample characterization

The samples were investigated by different physico-chemical methods. The morphology of samples was characterized by transmission electron microscopy (TEM). For investigation of surface characteristics BET measurements were carried out. The structure of supported metal samples, including the state of metal was studied by XRD. Relatively simple reactions were used for characterization of the catalytic activity of catalyst samples prepared.

Summary of results

In CO hydrogenation Co and Fe catalysts supported on MWNTs the following activity order was found: salt impregnated iron > salt impregnated cobalt > prepared iron nanoparticles > prepared cobalt nanoparticles.

A new type of noble metal supported carbon catalyst was synthesized that has specific surface area over 1800 m^2g^{-1}. In cyclohexene hydrogenation rhodium nanoparticles containing mesoporous carbon proved to be more stable in time than the platinum loaded derivative.

For nickel loaded MWNT samples irreversible destruction of carbon nanotube structure was found. From this follows that the pretreatment of metal salt loaded catalysts has a great influence on the structure of support material.

Acknowledgement

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Synthesis, structural characterisation and catalytic testing of bioinspired electron transfer catalysts

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In recent years we have prepared various catalysts having electron transfer catalytic properties. In order to approach the activities and selectivities of enzymes their active sites were mimicked in these materials. Mainly versions of the superoxide dismutase enzyme provided with the inspiration. To enhance durability these bioinspired catalysts were immobilised on or in various supports using ionic or covalent bonding or secondary forces, mainly hydrogen bonds. The anchored materials were various mono- or heterobimetallic complexes having transition or early transition metal ions as central ions and amino acids, their derivatives or various N-containing organic molecules as ligands. The central ions were Cu(II), Ni(II), Co(II), Fe(III) or the Cu(II)-Zn(II) pair. The amino acid ligands were unprotected and N- or C-protected histidine, tyrosine, cysteine, or cystine. At the beginning only a single amino acid was used for ligation, later mixed amino acid complexes were also prepared. The solid supports were silica gel, montmorillonite or the Merrifield's resin.). When the Cu(II)-Zn(II) pair was used, an imidazolate-bridged complex was made and immobilised on silica gel or in montmorillonite. Various synthetic conditions were tried and the resulting substances were thoroughly characterised by a variety of instrumental (FT-IR, Raman, EPR [electron paramagnetic resonance] and atomic absorption spectroscopies, thermogravimetry) classical analytical (titrimetry) as well as computational methods. Their superoxide dismutase, catecholase and catalase activities were tested with appropriately chosen test reactions. Some of the thus prepared materials were found to be promising candidates as durable electron-transfer catalysts being close to the efficiency of the mimicking enzymes. One of the promising materials was the Cu(II)-Zn(II) imidazolate-bridged complex immobilised on silica gel *via* hydrogen bonding, but many covalently anchored monometallic amino acid complexes also performed well. It was found that complexes having protected amino acids as ligands were more active than those ligated by deprotected amino acids. Those containing only surface-grafted amino acids were more active than the ones synthesised under ligand-excess conditions. These facts indicated that a strained geometric environment around the central ion was a necessary prerequisite for obtaining an efficient catalyst. We have also found that the mixed-ligand complexes performed better than the ones having a single amino acid as ligand. It also became clear that (protected) histidine was a key player it should always be one of the ligands. These two latter observations called our attention to the importance of accurately copying the environment of the metal ion cofactor in the enzyme. Originally, we thought that Merrifield's resin would be the best choice for support, since the polymer due to its ability of conformation changing resembled the proteomic skeleton of the enzyme. It turned out that it was not better than the more rigid silica gel. Moreover, the vibrational characterisation of the silica gel anchored materials is easier, since the spectrum of the support is simpler. In addition, handling of these substances in the catalytic test reactions was also proved to be much easier.

Hydrogen production by means of steam reforming of bioethanol over $MgAl_2O_4$ supported catalysts

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Design of multicomponent $MgAl_2O_4$ supported catalysts have been done by means of combinatorial tools and high-throughput equipments. Our informatic platform consists of (i) a self developed optimization algorithm, the so called Holographic Research Strategy (HRS) [1,2], and (ii) chemometric tools, such as Artificial Neural Networks (ANNs) and, Partial Least Square (PLS) regression [3].

Four catalysts generations have been designed by means of HRS. Additionally, after HRS optimization small factorial designs have been performed as well. In this phase of our work only the five most promising components were varied on two-three levels. Finally, the sample size was 393.

Catalytic data have been processed by means of ANNs and PLS in order to establish quantitative composition-activity relationships. Both statistical tools have been proved to be a robust technique; the model parameters were not sensitive to the experimental error.

In PLS regression, applying the first 6 principal components the correlation between measured and predicted hydrogen production is plotted on Figure 1. Marten's uncertainty (jackknife) test showed that simultaneous addition of Ni and Co has crucial effect on the hydrogen production. The catalyst containing both Ni and Co provided remarkable hydrogen production at 450 °C. At lower temperature addition of Ce and La as modifiers to the bimetallic NiCo catalyst has high importance. In presence of Ce and La the resulted hydrogen concentration has been doubled at 350 °C. Addition of Pt had only little effect on the product distribution.

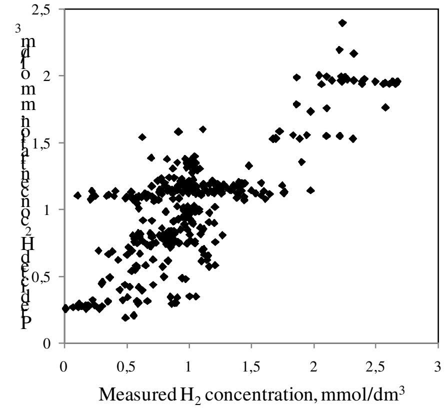

Figure 1. Predictive ability of PLS on the example of H_2 evolution

Ni-based catalysts suffer from coke formation that may lead to considerable performance degradation during long-term operation. The addition of modifiers such as Co and Ce to Ni leads to higher hydrogen yield but also higher amount of carbon deposits. Addition of Mo, as fourth component to the NiCoCe catalyst, could reduce significantly the extent of carbon deposition. It can be concluded that Ni catalysts modified with Co, Ce and Mo can be used in long term tests without significant loss in reforming activity.

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Brønsted acidity and catalytic activity of zeolites

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Introduction

Solid acid zeolites are widely used as active catalysts or catalyst components in different oil refinery technologies of high importance such as fluid catalytic cracking (FCC) or paraffin isomerization. The most often used zeolites in the industrial practice are Y-type zeolite, mordenite, and ZSM-5.

The activation of paraffinic hydrocarbons was proved to proceed on Brønsted acid sites, therefore catalytic activity is often related to the Brønsted acidity of the zeolites. Evaluation of the acidity-activity relation is a key to understand the mechanism of the above mentioned reactions. Problems arise from the difficulty to bridge the gap between the composite kinetic concept of catalytic activity and the equilibrium thermodynamic concept of acidity, the latter is being manifested in acid-base interactions. On one hand, only the so called apparent rate constant of the reaction can be determined directly from kinetic measurements, which – even for the paraffin reactions described with the simplest Langmuir-Hinshelwood kinetics – is the product of the intrinsic rate constant and the adsorption equilibrium constant. On the other hand, it is difficult to learn about the acid strength of the Brønsted acid sites from equilibrium adsorption measurements because the adsorbate base interacts not only with the acidic OH groups but also with their conjugate base, i.e. with the zeolite lattice. The strength of the acid-base interaction reflects the intrinsic acid strength of the Brønsted acidic sites only, if any interaction of the adsorbate base is negligible relative to the interaction of the base and the acid sites. It follows that the established acidity-activity correlation is meaningful only, if connected parameters are related to each other, namely, intrinsic activities are correlated with intrinsic acidities or relationship is established between corresponding apparent parameters.

Present work aimed the evaluation of the relation between the acidity of H-ZSM-5, H-mordenite and H-Y zeolites and their activity in the catalytic conversion of hexane (cracking and isomerization)

Experimental

DRIFT spectroscopy was used to determine $\Delta\nu_{OH}$ shifts, induced by adsorption of N_2 and hexane for zeolite H-ZSM-5 (Si/Al=15 – 26), H-mordenite (Si/Al= 6.8 – 10) and H-Y (Si/Al=2.5 – 10.4) samples. Catalysts were activated in O_2 flow at 773 K *in situ* in the DRIFTS cell and contacted than with N_2 at pressures up to 9 bar at 298 K or with 6.1% hexane/He mixture at 553 K, i.e., under reaction conditions. Catalytic activities of the solids were measured in a flow-through microreactor and k_{app} was obtained as slope of $-\ln(1-X_0)$ vs. W/F plots. The concentration of Brønsted acid sites was determined by measuring the NH_4^+ ion-exchange capacity of the zeolite. The site specific apparent rate constant, $TOF_{B,app}$, was obtained as the ratio of k_{app} and the concentration of Brønsted acid sites.

Results and discussion

The intrinsic acidities of zeolite samples are correlated with the $\Delta\nu_{OH}$ values induced by adsorption of N_2 ($\Delta\nu_{OH, N2}$), which can be determined by subtracting the frequency of the shifted OH-band from the frequency of the unperturbed OH-band. One shifted OH-band was observed for the ZSM-5 and mordenite samples, while two shifted bands appeared for the α- and β-cage protonic sites, respectively in zeolite Y samples. Results suggest that acid sites of H-mordenite and H-ZSM-5 samples have about the same intrinsic acid strength ($\Delta\nu_{OH, N2}$ = 81-85 cm^{-1}), while the bridged OH groups of the H-Y zeolites are much weaker acids ($\Delta\nu_{OH, N2}$ = 39-45 cm^{-1}).

The apparent acidities of zeolite catalysts are characterized by $\Delta\nu_{OH}$ values induced by adsorption of hexane ($\Delta\nu_{OH, C6}$) under the same conditions than those applied during separate catalytic experiments. The $\Delta\nu_{OH, C6}$ values suggest that the apparent acidity of the ZSM-5 and mordenite samples is distinctly different (111-116 and 85-94 cm^{-1} shifts, respectively) and significantly higher than that of the zeolite Y samples (41-52 cm^{-1}).

The $TOF_{B,app}$ is two order of magnitude higher over the ZSM-5 and mordenite than over the zeolite Y catalysts, suggesting that former zeolites are significantly stronger Brønsted acids. Indeed, Brønsted acid sites with significantly higher intrinsic acid strength were detected in ZSM-5 and mordenite than in zeolite Y. The H-ZSM-5 catalysts were found to be 2 to 4 times more active than H-mordenites. This finding is in conflict with intrinsic acid strengths. However, satisfactory activity-acidity correlation was found between the $TOF_{B,app}$ and the band shift $\Delta\nu_{OH, C6}$ induced under reaction conditions by the reactant itself. These results suggest that the apparent activity ($TOF_{B,app}$) of the active sites is related rather to the apparent than to the intrinsic acidity of the Brønsted acid sites. In order to better understand the activity-acidity relationship, it should be emphasized that intrinsic acidity (characterized here by the $\Delta\nu_{OH, N2}$ values) reflects the interaction of the weak base N_2 with the acidic protons of the solid, while all the other interactions, usually referred to as solvating and medium effects, are negligible. Conversely, the $\Delta\nu_{OH, C6}$ and the $TOF_{B,app}$ values, determined by all the hexane interactions within the zeolite pores, characterize the apparent acidity of the solid against the reactant hexane. Accordingly, the observed good correlation between the apparent acidity and activity suggests that Brønsted acid sites together with their oxide ion environment represent the active centers that are able to activate alkanes for transformations.

Operando DRIFTS measurements suggest that bridged hydroxyl groups are in extensive interaction with hexane molecules during the reaction even at 553 K. However adsorbed alkene or surface alkoxide could not be detected. These findings questions, whether the Haag-Dessau mechanism gives true description of the alkane activation process over zeolite catalysts.

Conclusions

Brønsted acid sites together with their oxide ion environment represent the active centers that are able to activate alkanes for transformations. Full proton transfer to the alkane molecule probably does not occur. During reaction adsorbed alkene or carbenium ion cannot be detected on the active catalyst.

POSTER PRESENTATIONS

STRUCTURAL AND CATALYTIC PROPERTIES OF V-SBA-15 FOR VAPOUR PHASE OXIDATION OF DIPHENYLMETHANE

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Catalytic oxidation of hydrocarbons in general is employed for the manufacture of fine chemicals. More than 60% of products synthesized by catalytic routes in the chemical industry are obtained by oxidation reaction [1]. The development of efficient mesoporous redox catalysts for the selective oxidation reaction by utilizing oxygen from air is of growing importance for the modern chemical industry [2]. In this regard, SBA-15 is a new type of mesoporous silica with tunable pore diameter, thicker walls and much higher hydrothermal stability than MCM type materials [3, 4]. The incorporation of metals into the framework of SBA-15 is of great interest to increase its application in the field of catalysis [5]. However, the attempt to incorporate metals into the framework of SBA-15 is seldom because of its acidic synthesis condition. Hence, it was aimed to synthesis metal incorporated SBA-15 by adopting direct hydrothermal method.

In this context, mesoporous V-SBA-15 (Si/V=25, 50, 75 and 100), molecular sieves were synthesized by direct hydrothermal method. The synthesized catalysts were characterized by various physico-chemical techniques such as XRD, BET, DRUV-Vis spectroscopy, ESR, ICP-OES, Cyclic voltammetry, Photoluminescence, SEM-EDAX and TEM techniques.

The efficiency of synthesized catalysts was tested for the vapour phase oxidation of Diphenylmethane using CO_2 free air as an oxidant. In order to achieve the better activity and selectivity the effect of temperature, time on stream, molar feed ratio of air to DPM and vanadium content were studied. The catalytic activity was correlated with reference to their physico-chemical properties.

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tert-BUTYLATION OF ETHYLBENZENE OVER ZSM-5 ZEOLITES, SYNTHESIZED IN FLUORIDE MEDIA

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Production of dialkyl-substituted benzene compounds via alkylation, trans-alkylation or disproportionation of aromatic hydrocarbons is an important step in a number of commercial chemical manufacturing processes [1]. Many di-alkyl substituted aromatics are commercially important, for example, *p*-xylene is used to produce terephthalic acid, a monomer for terylene [2], *p*-ethyltoluene to produce *p*-methylstyrene, a monomer for poly-*p*-methylstyrene [3], and *p*-diethylbenzene to produce divinylbenzene, a monomer to cross-link polystyrene [4].

ZSM-5 zeolites (Si/Al = 25, 50 and 75) were synthesized hydrothermally in fluoride media with phosphate as a co-complexant. They were characterized by XRD, SEM, EDAX, BET and TPD (ammonia). The XRD patterns indicated that the synthesized samples were more crystalline than the commercial sample. Hence, fluoride mediated synthesis was proved to provide a better crystallization route for ZSM-5 than the alkaline media [5]. The SEM pictures showed crystals with sharp edged and prismatic morphology. TPD (NH_3) showed the presence of only weak and medium acid sites without strong acid sites. As such zeolites are good to suppress dealkylation and isomerization of alkyl aromatics but to promote para-selective alkylation of the same. Their catalytic activity was tested for vapour phase tert-butylation of ethylbenzene. In contrast to commercial ZSM-5 catalyst these catalysts showed reduced de-alkylation of ethylbenzene and isomerization of 4-tert-butyl ethylbenzene (4-t-BEB). Hence, presence of only weak and medium acid sites without strong acid sites in them is suggested to be beneficial rather than detrimental in the alkylation of alkyl aromatics. The order of the activity of catalysts was ZSM-5 (25)>ZSM-5 (50)>ZSM-5 (75). Time on stream study indicated slow deactivation of the catalysts with a gradual increase in the selectivity to 4-t-BEB. An important observation is the influence of external surface acid sites on the isomerisation of 4-t-BEB was not severe, as the selectivity of the isomerized product 3-tert-butyl ethylbenzene (3-t-BEB) was found to be very much less.

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Transition metal impregnated SBA-15 for effective synthesis of carbon nanotubes by chemical vapor deposition (CVD) method

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Mesoporous SBA-15 molecular sieves were synthesized by hydrothermal method. Transition metals were loaded on SBA-15 by wet impregnation method and it was characterized by various physicochemical techniques such as X-ray diffraction (XRD), N_2 adsorption-desorption studies and DRS UV–visible Spectroscopy. The catalytic activity of molecular sieves was tested on growth of carbon nanotubes (CNTs) through the acetylene decomposition at atmospheric pressure utilizing chemical vapour deposition (CVD) technique. In order to achieve the high carbon yield, the decomposition of hydrocarbon was carried out in the temperature range of 700-900°C with different flow rate of acetylene. The effect of transition metal loaded SBA-15 was also investigated. The as-synthesized carbon nanotubes were characterized by TGA analysis. The carbon yield was calculated and then it was purified by acid treatment followed by air oxidation. The purified samples were characterized by SEM, HRTEM, XRD and Raman spectroscopy. The diameter of the CNTs was found to be in the range of 10-15 nm and the maximum carbon yield under the selected condition. Furthermore, it is observed that the purity of the as-synthesized CNTs is over 96.40%. The TEM analysis reveals that CNTs are free from amorphous carbon, where as Raman spectra shows two prominent peaks at 1409.2 cm^{-1} and 1630.7cm^{-1} as the tangential modes of CNTs. Our results indicated that these transition metal loaded SBA-15 mesoporous molecular sieves presented a good catalytic activity for the potential growth of high quality CNTs.

Key words: Chemical vapor deposition; Carbon nanotubes, SBA-15

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Synthesis and extrusion of mesoporous catalysts for alkylation of tertiary butyl benzene over AlSBA-1

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The powder form of mesoporous aluminosilicates molecular sieves (AlSBA-1) were synthesized by hydrothermal method. The powder form of the materials was characterized using XRD, FT-IR, TPD, BET, SEM, TGA and DTA techniques. The phase purity and structural order of the catalysts were obtained from XRD patterns**.** The hydrothermal synthesis of these materials is powder in nature, which could not be used directly for industrial application. As the mesoporous crystalline powders are in the particle size 1 to 10 µm, they need to be shaped into bodies such as granules, spheres, monoliths and extrudates prior to their use as catalysts and adsorbents in commercial tubular fixed bed reactors in order to avoid extreme high pressure drop and achieve to high mechanical strength [1, 2]. The characterized powder materials of the samples compounded with different inorganic binders (montmorillonite, bentonite, and kaolin) and organic binders (polyethylene glycol, starch, methyl-cellulose) and made into paste with addition of water. The paste was shaped into catalysts bodies with different geometries (spheres, hollow cylinders, extrudates). The extrude form of the materials was characterized using XRD, FT-IR, TPD, BET, SEM, TGA and DTA techniques. Vapor phase alkylation of tert-butyl benzene with ethyl acetate was carried out over mesoporous catalysts (extrusion) with different nSi/nAl ratios. *m*-ethyl-tert-butylbenzene was obtained as a major product with high selectivity. Mesoporous catalyst was found to be the most active catalyst in this study.

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Methanol electro oxidation on activated carbon supported Pt catalysts in alkaline medium

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Fuel cells are alternate, clean and noise free energy sources that can electrically power unmanned air vehicle systems used in space and military operations, mobile electronic devices and homes. Among several types of fuel cells, the Direct Methanol Fuel Cells (DMFCs) are expected to approach commercialization sooner owing to the possibility of adopting the existing and well developed infrastructure for the distribution of petroleum products for the distribution of the fuel (methanol) for DMFCs. More over DMFCs need no fuel processor to reform hydrocarbon fuel. The drawback with DMFCs preventing the commercialization is their inherent low power density. Research efforts are focused on improving the performance of the electro catalysts and also the electrolyte membrane as they are the two key components that have direct relevance to power density derivable for the fuel cell [1]. Nature of electrolyte also affects the fuel cell performance. In the acidic medium, during the electro oxidation of CH_3OH, poisoning species bind strongly to the active centers and impose limitation on the kinetics of the reaction and lead to polarization losses [2]. Parsons and Van der Noot have suggested for the first time the possibility of using alkaline medium for the fuel cell reactions [3]. There are only limited studies on the electro oxidation of methanol in alkaline medium [2, 4-10] unlike the acidic medium where in extensive research has been carried out. Operation of direct alcohol fuel cells (DAFCs) in an alkaline electrolyte instead of an acidic electrolyte is known to improve the kinetics of the oxidation process significantly [4]. Carrying out methanol oxidation reaction in alkaline medium is favourable owing to the reduction of electrode poisoning and also due to the corrosion resistance property of the carbon material which is a promising catalyst support [2]. The effect of the catalyst support material on the catalytic activity of the electro catalyst for the alcohol oxidation is of continued interest. A variety of carbon materials like activated carbon, carbon nanotubes, carbon nanocoils, carbon nanofibers, hollow graphitic nanoparticles, graphite powder, carbon black, carbon micro spheres and ordered nanoporous carbons have been used as catalyst supports for DMFC applications [4]. So far PtRu/C has beenthe prominent anode electro catalyst for the Direct Alcohol Fuel Cells (DAFCs) [4].

The objective of the current study is to develop an anode electro catalyst with improved performance compared to the state-of-the-art PtRu/C catalyst. In the present work, activated carbon (C_{WA}) was prepared from the shells of *Limonea acidissima* (wood apple) by chemical activation (KOH) and was employed as support for Pt. The Pt/CWA catalysts with different amounts of active component (5, 10 and 20 wt.%) were employed as electro catalysts for the oxidation of methanol in KOH medium. The electro chemical experiments (cyclic voltammetry and chronoamperometry) were carried out in a conventional three electrode glass cell using modified glassy carbon as the working electrode, Hg/HgO as the reference electrode and a platinum foil (1.5 cm^2) as an auxiliary electrode. 1.0 M KOH was employed as the supporting electrolyte. The CH_3OH oxidation reaction was carried out with 1.0 M CH_3OH in alkaline medium. The electro catalytic activity and stability of Pt/C_{WA} catalysts (5 wt.% Pt/C_{WA}, 10 wt.% Pt/C_{WA} and 20 wt.% Pt/C_{WA}) evaluated from cyclic voltammetric and chronoamperometric studies were compared with the commercial 20 wt.% Pt 10 wt.% Ru/Vulcan carbon (Johnson Matthey) catalyst. The cyclic voltammograms recorded with the fabricated electrodes (Pt/C_{WA}) and that of the commercial electro catalyst (PtRu/Vulcan carbon) were shown in Fig. 1.

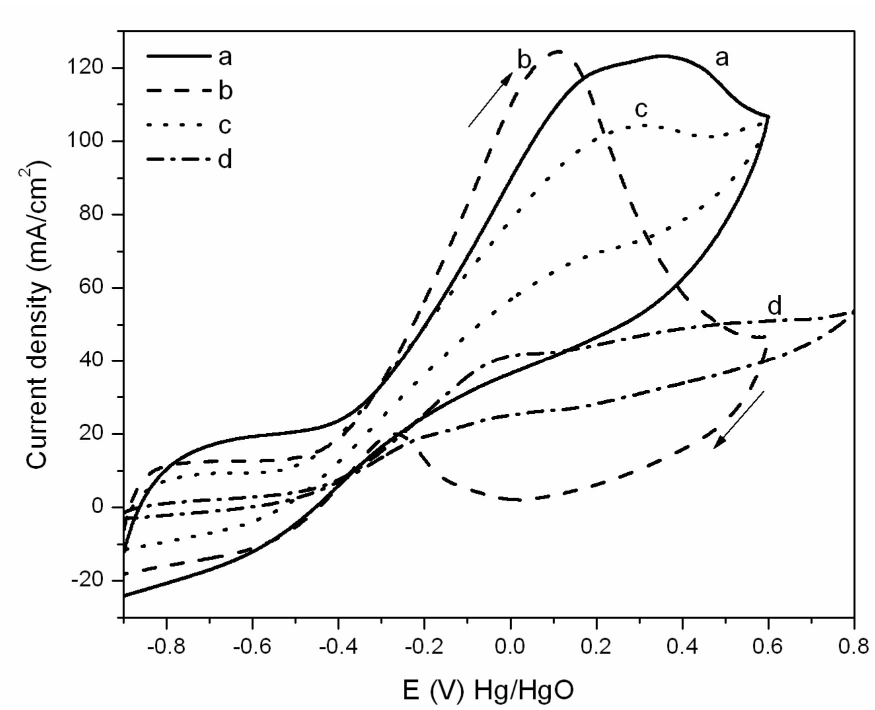

Fig. 1. Cyclic Voltammetric response of (a) GC/C_{WA} - 5 wt.% Pt - Nafion electrode (b) GC/C_{WA} - 10 wt.% Pt - Nafion electrode (c) GC/C_{WA} - 20 wt.% Pt - Nafion electrode and (d) GC/Vulcan carbon - 20 wt.% Pt 10 wt.% Ru (JM) - Nafion electrode in 1.0 M KOH and 1 M CH_3OH, at a scan rate of 25 mV/sec between -0.9 to 0.8 V Vs Hg/HgO

Same features typical of methanol electro oxidation in acidic medium are also observed in the alkaline medium but at more favourable (lower) potential values. The anodic peak in the forward (anodic) scan and another anodic peak in the reverse (cathodic) scan were attributed to the oxidation of methanol (step wise dehydrogenation of methanol) and to the removal of incompletely oxidized carbonaceous species respectively. The onset potential values, deduced from the cyclic voltammograms, along with the anodic peak potential and current values corresponding to the methanol oxidation were summarized in Table 1. It is observed that Pt/CWA catalysts (at all Pt loadings) showed higher activity (current) at relatively lower potential values compared to the commercial (PtRu/C) catalyst.

Table 1. Effect of Pt loading and the nature of the carbon support on the electro catalytic activity of MeOH Electrooxidation of Pt/C_{WA} and PtRu/Vulcan carbon

S. No.	Electrode	Onset Potential, V	Activity*	
			Forward sweep	
			I (mA/cm^2)	E (V)
1	GC/C_{WA}-5 % Pt-Nafion	- 0.42	123	0.35
2	GC/C_{WA}-10 % Pt-Nafion	- 0.52	124	0.15
3	GC/C_{WA}-20 % Pt-Nafion	- 0.54	104	0.27
4	GC/Vulcan carbon – 20 % Pt 10 % Ru - Nafion	- 0.52	50.9	0.57

*Activity evaluated in 1.0 M KOH and 1 M CH_3OH, at a scan rate of 25 mV/sec between -0.9 to 0.8 V Vs Hg/HgO

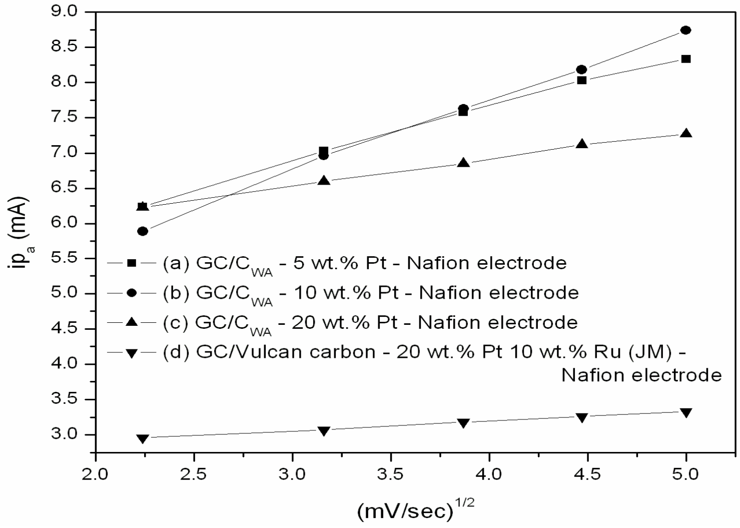

Fig. 2. Dependence of peak currents on the square roots of scan rates for (a) GC/C_{WA} - 5 wt.% Pt - Nafion electrode (b) GC/C_{WA} - 10 wt.% Pt - Nafion electrode (c) GC/C_{WA} - 20 wt.% Pt - Nafion electrode and (d) GC/Vulcan carbon - 20 wt.% Pt 10 wt.% Ru (JM) -

Nafion electrode in 1.0 M KOH and 1.0 M CH_3OH, at different scan rates (5, 10, 15, 20 and 25 mV/sec), between - 0.9 to 0.8 V Vs Hg/HgO

The effect of scan rate on the current out put on different electrodes is evaluated and the peak currents were found to be linearly proportional to the square root of scan rates as shown in Fig. 2. In all cases indicating that the process of the methanol oxidation is controlled by diffusion

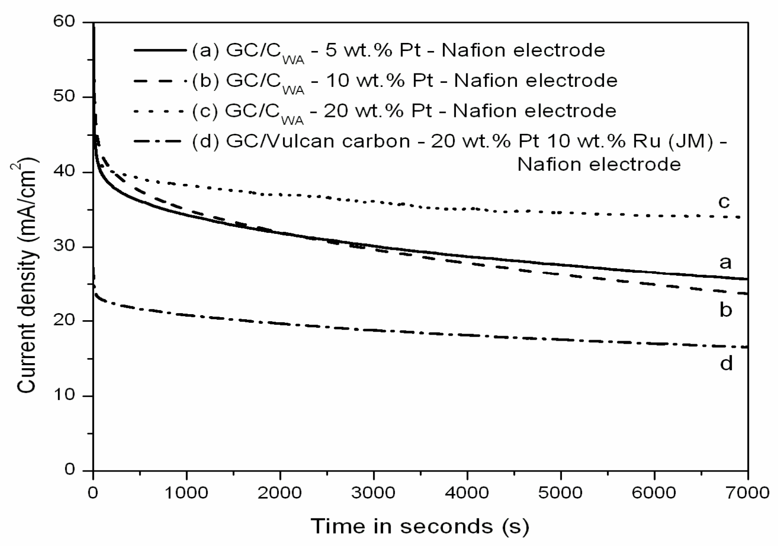

Fig. 3. Chronoamperometric response of (a) GC/C_{WA} - 5 wt.% Pt - Nafion electrode (b) GC/C_{WA} - 10 wt.% Pt - Nafion electrode (c) GC/C_{WA} - 20 wt.% Pt - Nafion electrode and (d) GC/Vulcan carbon - 20 wt.% Pt 10 wt.% Ru (JM) - Nafion electrode polarized at - 0.3 V Vs Hg/HgO in 1.0 M KOH/ 1.0 M CH_3OH for 3 hours

The long term stability of the fabricated electrodes and that of the commercial catalyst was evaluated by chronoamperometry and the current density Vs time plots derived for Pt/CWA and PtRu/C electrocatalysts were shown in Fig. 3. The Pt/CWA catalysts offered better long term stability compared to the commercial PtRu/C catalyst. Thus an electrocatalyst, based on activated carbon support, with improved activity and stability has been developed for the electro oxidation of methanol in alkaline (KOH) medium.

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Effect of grafting of methylsulfonic acid group on Pt supported carbon black catalyst for methanol electrooxidation

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The grafting of methylsulfonic acid group on Pt supported carbon black catalyst was carried out with sodium sulfite and formaldehyde. The sulfonated catalysts were characterized by FT-IR and XRD techniques. FT-IR spectrum shows the stretching vibrations for S-O at 1100 cm^{-1}, which evidences the incorporation of the sulfonic acid group on the carbon black support of the catalyst. It also shows an increased absorbance of the -OH vibration in the range of 3000-3600 cm^{-1} due to the increase of protonic acidity. X-ray diffraction pattern shows broadening of the XRD peaks for the sulfonic acid modified catalyst. The crystallite size determined with Debye-Scherrer equation shows a significant decrease in size upon sulfonation (from 13.5 nm of the unsulfonated to 4.4 nm of the sulfonated catalyst). This fact strongly evidences that the Pt nanoparticles are redistributed with better dispersion upon sulfonation. The effect of sulfonation of the catalysts was studied by methanol electrooxidation. The sulfonic acid modified catalyst has shown more than double the activity for methanol electrooxidation compared to the unsulfonated one. The increase in activity can be attributed to two factors: (i) Pt nanoparticle redistribution to smaller particles, thereby increasing the electrochemical active surface area of Pt and (ii) increased protonic conductivity inside the catalyst support.

Acetalization of heptanal over AlSBA-1

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AlSBA-1 (Si/Al = 40, 80, 120) and Al, Mg (40, 80) were synthesized hydrothermal method. The materials were characterized using XRD, FT-IR, TPD, BET surface area, SEM, TGA and DTA techniques. Isomorphic substitution of silicon by aluminium decreased the intensity of the XRD patterns and shifted them to slightly low 2θ values [1]. TPD ammonia showed the presence of both the strong and weak acid sites. The thermo-gram of AlSBA-1(40) was a major weight loss between 200 and 325 ºC due to degradation and desorption of template. The minute weight loss between 325 and 500 ºC was attributed to condensation of defective -OH groups. The percent weight loss due to template was close to about 45%, and is common for all mesoporous materials. The SEM picture of Al-SBA-1(40) is Most of the particles showed spherical morphology with different size. Such morphology was also reported reported by Balasubramanian et al [2]. Particles of irregular shape were also present. Acetalization of n-heptanal with methanol was studied under autogenous pressure over all the catalysts. Protonation of n-heptanal to hemiacetal is proposed to be slower than conversion of the latter to acetal. Nearly similar conversion was observed over all the catalysts irrespective of their acidity due to framework aluminium and magnesium content. Hence the effect of acidity is suggested to play only a minor role in acetalization and in differentiating the activity of the catalysts. But their hydrophilic and hydrophobic properties and free diffusion of reactants through the mesopores are suggested to be the major controlling factors for n-heptanal conversion.

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BIOFUEL PRODUCTION FROM JATROPHA OIL THROUGH CATALYTIC CRACKING TECHNOLOGY

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The rapid exhaustion of fossil fuels and alarming rate of pollution leading to green house gases are the two important factors which made US & Europe to make new energy legislations. As per the legislations (Energy independent & Security act 2007 USA) the country should use 36 billion gallon of renewable fuel by 2022 whereas Europe's modified legislation states that transport fuel should contain at least 10% of biofuels by the end of 2020. Similarly in India much of our money in the form of foreign exchange goes to gulf countries for importing oil. Therefore there is a quest for the alternative fuel from bioresources. The energy independent India can be developed by employing the numerous barren lands present in our country. Jatropha is the plant which can be grown on barren lands of our country and if successful technology to convert vegetable oil into OLP is derived, the energy rich India can be developed.

In the present work, the conversion of Jatropha oil into liquid hydrocarbons was carried on by cracking of oil in fixed bed catalytic reactor using solid acid catalysts like microporous and Mesoporous materials such as HY, Hβ & AlMCM41. Mechanical mixtures of mesoporous with microporous and Composite Catalyst in Core-Shell model HY/AlMCM41 & Hβ/AlMCM41 were also used for the study to obtain OLP.

Variables like a) Effect of Temperature ($250^{o}C$ – $450^{o}C$), b) Effect of time of reaction, c) Effect of contact time (2ml/hr -3.5ml/hr) and selectivity towards OLP were studied and optimized.

Keywords: Biofuel, Catalytic Cracking, OLP, composite catalyst.

Synthesis of ZSM-5 in fluoride media and characterization

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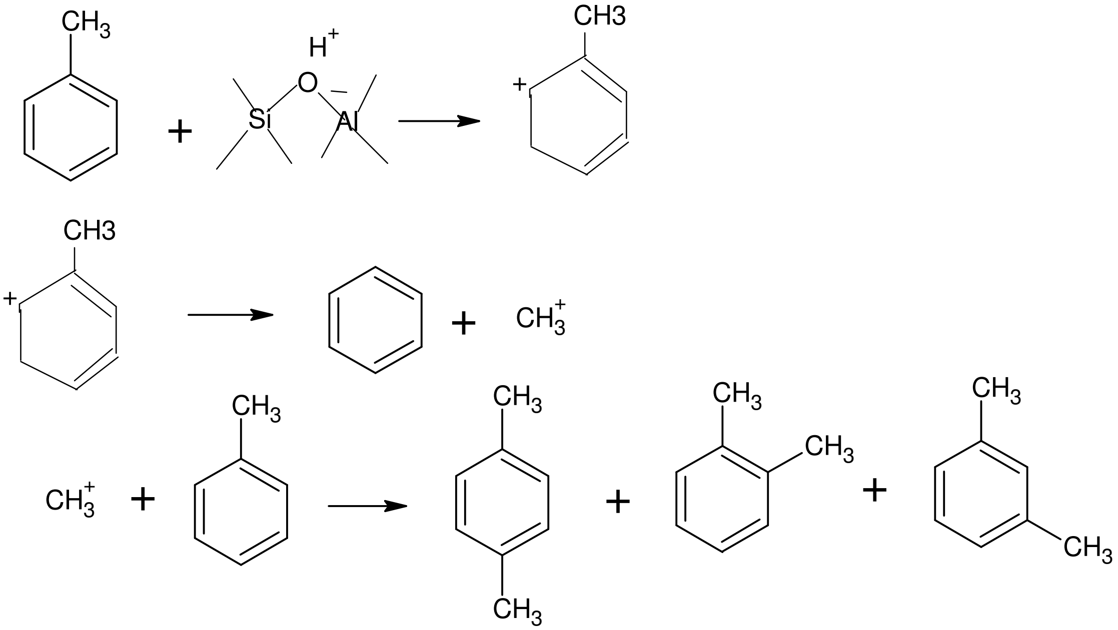
ZSM-5 zeolite is the mostly exploited zeolite for catalytic applications in industries. Alkylation, isomerization, cracking, disproportionation and trans-alkylation are some of the major reactions of petrochemical industries catalyzed by ZSM-5 zeolite. It is a medium pore zeolite with pore diameter of 5.5A°. It has been synthesized in alkaline media using silicon and aluminium sources without template. In such media hydroxide ions are the mineralizer of silica for the construction of ZSM-5. In 1994 synthesis of ZSM-5 in fluoride media was reported in which the fluoride ions are the mineralizer of silica. It was established that mineralization of silica by fluoride occurs in mild alkaline and in acidic media. Fluoride media is proved to be better than alkaline media, as it provides ZSM-5 with high crystallinity, high surface area, large crystal size and high bulk density. There are many groups of researchers working on this route to synthesize ZSM-5 in both acidic and alkaline media below pH 9.5 for catalytic applications. But there is a major problem of reduced supply of aluminium from the gel to the framework during the synthesis. Attempts have been made to circumvent this problem using alkali metals and ammonium salts, but the former was shown to be better than the latter. But the transport of aluminium was only partly complete. In our lab a new procedure was developed to transport aluminium completely from the gel to the framework during the synthesis. In the present study, applying the same procedure with slight modifications in the gel composition, ZSM- zeolite was synthesized in different Si/Al ratios 25, 50 100,150. They were characterized by XRD, FTIR, SEM, BET and TGA. The XRD showed intense patterns for all the four calcined samples compared to the as-prepared ones. Though calcination was done in air structural degradation was not observed. Presence of template in the as-prepared samples and their absence in the calcined samples were clearly evident from the analysis of their FTIR spectra. Their surface areas were in thee range 260 -400m^2/g. Smooth elongated prismatic crystals were seen in their SEM images. Further characterization and catalytic studies towards disproportionation of toluene are under progress. As per the following reaction scheme, three isomers of xylene are formed during disproportionation. But only the slim para isomer can diffuse out of the pore. It is expected that the large crystal size of ZSM-5 can facilitate better separation of the para isomer from the others.



Mesoporous materials an efficient catalyst for the synthesis of carbon nanotubes by chemical vapour deposition (CVD) method

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Mesoporous molecular sieves were synthesized by hydrothermal method. The synthesized mesoporous molecular sieves were calcined at 550 ºC for 6 h in air atmosphere. Appropriate weight percentage of transition metal was supported on calcined mesoporous molecular sieves by wet impregnation method. The impregnated materials were calcined at 500 ºC for 3 h in air atmosphere. Various physicochemical techniques such as X-ray diffraction (XRD), Thermo gravimetric analysis (TGA), DRS-UV spectroscopy, Scanning electron microscopy (SEM) and Transmission Electron Microscopy (TEM) were used to characterize the calcined materials. Metal impregnated mesoporous material was used as catalytic template for the growth of carbon nanotubes using acetylene as a carbon precursor by chemical vapor deposition technique at 700, 800, and 900 ºC. The reaction parameters such as flow rate and temperature were optimized for better formation of carbon nanotubes. The deposited carbon materials were purified by acid treatment and air oxidation. The purified materials were characterized by XRD, SEM, HRTEM and Raman spectroscopy techniques. Carbon nanotubes morphology was observed from HRTEM. The observation clearly depicts that the transition metal loaded mesoporous catalytic template influenced on the high yield of ordered carbon nanotubes.

Keywords: Mesoporus Materials, CNTs, CVD, Acetylene

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Catalytic mechanism of Glycerol oxidation by Galactose Oxidase mimic – A DFT study

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The metalloenzyme Galactose Oxidase(GOase) is a highly efficient catalyst for two-electron oxidation of a broad variety of primary alcohols. Even polyalcohols are converted in a highly regio and stereoselective way into the corresponding aldehydes. This elegant synthetic route stands out against the stoichiometric alternatives of the same reaction as performed by the traditional inorganic oxidants. Not surprisingly, GOase, thus constitutes a highly attractive target for the development of biomimetic strategies aimed at the design of eco-friendly catalysts for green oxidation . In the GOase radical chemistry, the metal ion serves as a one electron redox center whereas the second electron is provided by a protein radical site.

The glyceralehyde has versatile applications in various fields. The synthesis of glyceraldehyde from glycerol is one of the value added processes. The oxidation to get maximum yield is challenging since glycerol has two primary hydroxyl groups. To solve this problem and to find an alternative method to work out that process, Quantum Mechanical (QM) methods provide an opportunity to study the different possibilities of the reaction. Hence, QM was employed method to study the oxidation of glycerol molecule using the modified copper catalyst mimic of the (E)-2-((2-hydroxybenzylideneamino)methyl)phenol and pyridine as the active site of GOase enzyme. mimic of. This catalytic mechanism was studied using the Density Functional Theory (DFT) calculations, carried out with the GAUSSIAN 03 program. The complex was treated as an open-shell system using spin unrestricted DFT wave functions (UB3LYP). In the B3LYP method, Becke three-parameter exchange functional in combination with the LYP correlation functional of Lee, Yang and Parr and the Los

Alamos ECP plus DZ basis sets (Lanl2DZ) was used for the geometry optimization calculations.

The mechanism is shown in figure-1. includes the first step of substrate binding to the catalyst. The second step is proton transfer from the substrate hydroxyl group proton to the axial tyrosine unit. Step three consists of hydrogen atom transfer from of glycerol alpha carbon to the equatorial tyrosine unit. The single electron transfer to the central copper(II) ion then the breaking of Cu-O bonds leads to an unstable Cu(I) species. The oxygen molecules from air bind to the complex replace the aldehyde. Oxygen is reduced finally as a hydrogenperoxide by getting the two hydrogens from two tyrosine units then the catalyst is regenerated. The HOMO-LUMO gap of the pure catalytic complex is 0.197eV. The substrate bound complex has the correspondig value of 0.192 eV. Gap values of 0.154eV and 0.194eV were obtained for the proton transfer and the reduction of dioxygen respectively . The HOMO-LUMO values reveal the feasibility of oxidation and reduction process of the mechanism. The energy profile diagram of various steps involved in the above reaction is shown in figure-2. It reveals that the free energy of system yields negative values for the oxidation. The above findings predicts that the oxidation process will be spontaneous. Hence, the model compound can be a successfully used in place the GOase enzyme for the above reaction.

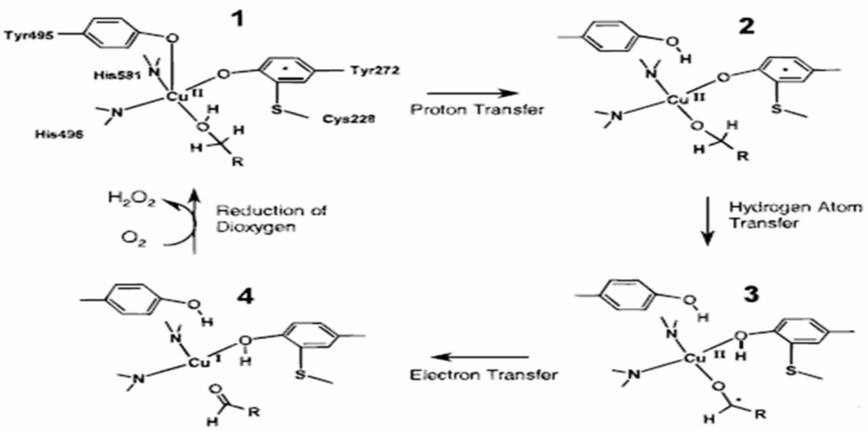

Figure 1

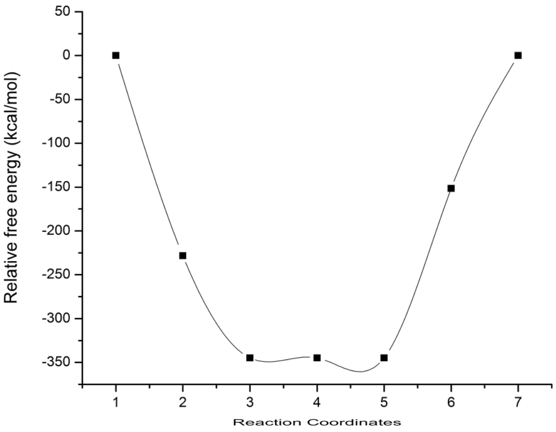

Figure - 2.

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Effective Synthesis of Boron Nitride Nanotube by catalytic Chemical Vapour Deposition

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Boron nitride nanotubes (BNNTs) found to be a novel material in high temperature applications, bio-sensors, nano-electronic devices and drug delivery systems. BNTs could be used in the fabrication of novel devices in which pure carbon nanotube do not perform very efficiency. Generally BNTs were synthesized by Arc discharge, laser ablation, ball milling and CVD method. Among these CVD method is best way to synthesis of boron nitride nanostructure, using a mixture of nickel oxide, molybdenum oxide and amorphous boron powder in flowing ammonia gas. The reaction temperature and the ratio of $Ni_2O_3/MoO_3/B$ are found to play an important role in determining the morphology of the product. The in situ generated boron oxide vapour is responsible for nanotube growth. The growth of BN nanotube is ascribed at a catalytic growth of a Vapour-Liquid-Solid mechanism. The samples were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), FT-IR and Transmission Electron Microscope (TEM). These results open up a new kind of synthesis method with low expense and important perspectives for use in large quantity production.

Keywords: Nickel oxide, Molybdenum oxide and Chemical Vapour Deposition

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Synthesis of Ce $AlPO_4$-5 molecular sieves in fluoride media: Characterization and catalytic application

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The aluminophosphate ($AlPO_4$) based molecular sieves are a landmark discovery in new generations of molecular sieves. Their number and scope provides a plethora of new materials for research investigation by present and future generations of molecular sieve scientists. The remarkable diversity in crystal structure and crystal chemistry offers a nearly unlimited number of design parameters to tailor adsorptive and catalytic properties [1]. They exhibit characteristics nearly similar to zeolites [2]. Here the framework is built with aluminium and phosphorus tetrahedra [3]. As the parent aluminophosphate does not keep any acidity for catalysis, isomorphic substitution of small amount of aluminium or phosphorus tetrahedra of the framework becomes a necessity in such materials. In this context many metal substituted AlPO's were synthesized and characterized.

Cerium substituted aluminophosphate molecular sieves, Ce $AlPO_4$-5, with Al/Ce ratios equal to 25, 50, 75, 100 and 125 were synthesized hydrothermally in fluoride media. Fluoride mediated synthesis is advantageous, as it reduces the crystallization period and increases crystallinity and surface area. The synthesized materials were characterized by XRD which showed the characteristic XRD pattern of $AlPO_4$-5 framework. The TGA results indicated loss of template starting from 200 ºC. The effect of dielectric constant of the medium on the crystallinity of the materials was examined using ethanol. The crystallinity of the materials increased with the increase in the dielectric constant of the medium upto 12.78% of alcohol and then decreased. In addition a gradual increase in weight was observed above 400 ºC, it is ascribed to chemisorption of oxygen. This property is important for examining the application of Ce $AlPO_4$-5 molecular sieves for selective oxidation of alkyl aromatics. The adsorption of oxygen was noted upto 800 ºC. Hence the material could be exploited for oxidation for a wide range of temperatures particularly above 400 ºC. SEM images of Ce $AlPO_4$-5 showed the characteristic hexagonal rod like shape similar to pure $AlPO_4$-5, synthesized in fluoride media. Their catalytic activity is under examination for the oxidation of ethylbenzene to acetophenone.

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Indium tin oxides, Sulfated tin and zirconia materials as super acid green catalysts for multi component organic synthesis

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Indium tin oxides (ITO) of various weight percentages were synthesized by co-precipitation method. Indium nitrate and tin chloride were dissolved in de-ionised water and stirred, precipitated by adding aqueous ammonia. The hydrated precipitate was filtered , dried and calcined at various temperatures. The sulfated tin oxide and sulfated zirconia were synthesized by tin tetrachloride and zirconium oxychloride as sources using sulfuric acid by impregnation method. The prepared materials were characterized by XRD, FT-IR, BET method, pyridine FT-IR spectra, ammonia TPD measurements and scanning electron microscopic technique. All the solid acid catalysts were tested over the multi component synthesis involving cyclo-condensation and addition mechanism to yield acridine, alkyl amido naphthols and quinoline derivatives. Various advantages associated with these protocols include, simple work-up procedure, solvent-free conditions, short reaction times, high product yields and easy recovery and reusability of the catalyst. The completion of the reaction was monitored by thin layer chromatography using appropriate eluents. The products were confirmed by ^{1}H NMR, ^{13}C NMR and FT-IR spectral studies.

Keywords : *Solid acid catalysts, Multi component reactions, Green chemistry*

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Synthesis, Characterization and Photocatalytic Application of Metal Doped Mesoporous TiO_2

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La^{3+}, Ce^{3+} and Zr^{4+} (0.5, 1.0, 2.0, 3.0 wt%) doped mesoporous TiO_2 was synthesized using non-ionic triblock co-polymer (Pluroinc P123) as the structure directing agent under sol-gel condition. The synthesized materials were characterized by XRD, N_2 sorption analysis, SEM, HR-TEM, XPS, UV-Vis DRS, FT-IR, Raman and TGA. The XRD patterns of the materials revealed that TiO_2 possesses ordered mesoporous structure with high crystalline anatase form. Their specific surface areas were in the range 125-170 m^2/g for doped mesoporous materials. In comparison to pure mesoporous TiO_2, metal doped TiO_2 showed high surface area and enhanced pore size. The TEM images showed aggregates of TiO_2 nanoparticles that constructed the wall of the mesoporous structure. The photocatalytic activity of the metal doped mesoporous TiO_2 was tested for the mineralization of alachlor using light of wavelength 254 nm and 365 nm. The successive progress of mineralization of alachlor was monitored by TOC analysis. Thus the doped mesoporous TiO_2 is found to be an effective catalyst for the mineralization of pollutants in general and pesticides in particular.

SYNTHESIS OF NEW MONO SITE PHASE TRASFER CATALTST FOR THE FREE RADICAL POLYMERIATION OF ALKYL METHACRYLATES

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Phase transfer is a technique for conducting heterogeneous reactions where the reagents are located in different phases. The scope of PTC technology is most appropriately applied to wide range of reactions. Various types of phase transfer catalyst includes quaternary ammonium salts, phosphonium salts, crown ethers, cryptands, polyethylene glycols and polymer supported ammonium or phosponium salts , among those various phase transfer catalysts, quaternary ammonium salts were the best of choice due to their easy availability, stability , convenient and easy preparation. This current research work is designed for the free radical polymerization of alkyl methacrylates is carried out under water soluble initiator instead of organic initiators under phase transfer conditions. The effect of monomer, PTC, initiator and variation in the aqueous phase is discussed. By performing the effect of temperature of the reaction the activation energy (Ea) is deduced and the randomness (ΔS), enthalpy (ΔH), free energy (ΔG) also derived. The obtained rate of polymerization on the effect of monomer and initiator shows a gradual increase by increasing the concentration. Rising in catalyst concentration indicates a gradual decrease in rate of polymerization. For this kinetic research a suitable mechanism is proposed. The formed polymers are characterized by FT- IR, NMR, TGA and DSC.

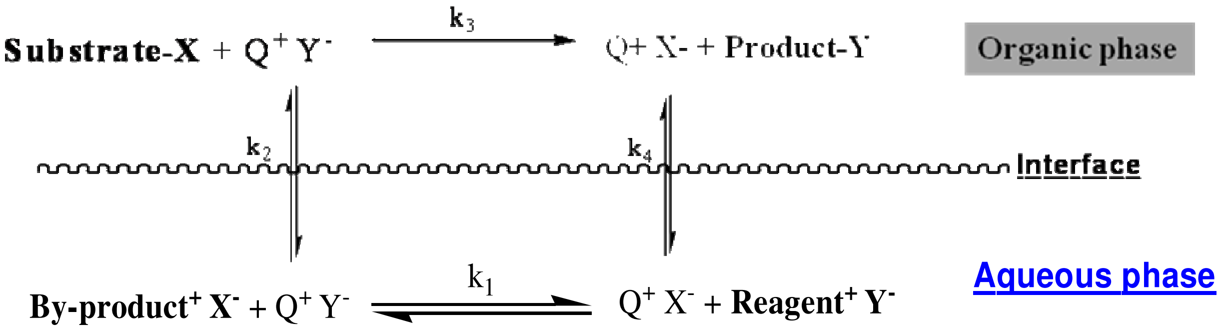

Figure 1 General Mechanism of PTC

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CATALYSIS BY IONIC SURFACTANTS IN THE OXIDATION OF BENZYL ALCOHOL

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The kinetics of oxidation of benzyl alcohol by acidified potassium dichromate in DMSO – water medium have been studied in the presence and absence of anionic (SLS) and cationic (CTAB) surfactants. At lower concentrations, the cationic surfactant increases the rate by about 10 times and reaches a maximum value but decreases the rate above its critical micelle concentration. Thus exhibits a sigmoidal profile. Though similar results are observed with the anionic surfactant also, the trend is not so well defined. The observed data are analysed on the basis of the pseudo-phase micellar model and the catalytic cooperativity index and a suitable mechanism is proposed .

Synthesis and Characterization of Carbon Nanomembranes using Catalytic Chemical Vapour Deposition Method

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Carbon mono membranes were synthesized using catalytic chemical vapour deposition method (CCVD). Sodium carbonate loaded with cobalt was used as the novel catalyst for the synthesis of carbon nano membranes. Various atomic weight percentage loading of the cobalt were done from 1-20%. The catalyst was characterized using X-ray diffraction, thermogravimetric analysis and Scanning Electron Microscopy. Acetylene was used as the carbon source. The flow rate was optimized from 10 to 100sccm. The operating temperature was optimized from600-800^{0}C. Amorphous carbon and the impurities were removed using acid treatment and air oxidation at 400^{0}C for 1 hr. The pure carbon nanotubes were characterized using X-ray Diffraction, Thermogravimetric Analysis, Scanning Electron microscopy, Tunneling Electron Microscopy and Raman Spectroscopy.

Keywords: Catalytic chemical vapour deposition, carbon nanomembrane

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