SYNOPSIS OF

EVALUATION OF CATALYTIC ROUTES FOR THE PRODUCTION OF OXYGENATES FROM REFINERY FEED STOCKS

A THESIS
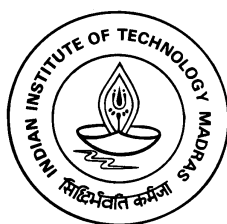
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INTRODUCTION

The increase in energy consumption world wide has spurred the need to find new energy sources as well as to use the existing sources to maximum efficiency. Till now, fossil fuels have been the main source of energy for transportation sector. With the world wide reserve of the fossil fuel dwindling, it is essential to use them economically to derive maximum efficiency. Similarly, new energy sources with cleaner technology like fuel cells have also to be evaluated to meet the future demand for energy. To increase the combustion efficiency of gasoline, several additives such as antioxidants, oxygenates and other functionalities have been added. Most prominent additives among them are oxygenates, which are a class of oxygen containing compounds used as blending components to improve the combustion efficiency of the fuel. Blending of oxygenates with the gasoline results in complete combustion, thereby reducing the CO and hydrocarbon (HC) emissions to a large extent under full load operating conditions (Randy et al, 1996). The three primary functions of oxygenates in blended gasoline are extending the gasoline pool, boosting the octane values and providing refiners with additional blending flexibility to meet ever increasing product demands with maximum efficiency (Lang and Palmer, 1989). Several oxygen containing compounds such as alcohols and tertiary ethers have been explored to improve the performance of gasoline. Alcohols such as ethanol and methanol were recognized as octane boosters in 1920. But the usage of alcohols as oxygenates are limited due to their high water solubility and unfavourable vapour pressure (Krchstetter et al, 1996). Tertiary alkyl ether based oxygenates such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl ethyl ether (TAEE), tertiary amyl methyl ether (TAME), isopropyl tertiary butyl ether (IPTBE) and diisopropyl ether (DIPE) are other possible candidates for gasoline blending (Frey et al, 1998). Among the above mentioned oxygenates, DIPE is the most preferred oxygenate because of its compatible blending properties, ready availability of

feed stock and very low water solubility (Huang et al, 1990). Catalytic production of DIPE from propylene feed stock is a widely adopted process in petroleum industry. Several types of acidic catalysts such as heteropoly acids (Haining et al, 1999), ion exchange resins (Marker and Kempf, 1994), nafion (Olah, 1989), clays and zeolites have been used for DIPE production. Zeolites were exploited extensively compared to other solid acid catalysts due to their uniform pore size, high thermal stability and desired product selectivity. Alternately, DIPE can be prepared from crude acetone, which is a by- product in propylene oxide industry and this alternative route is extensively studied using bifunctional catalysts in vapour phase under high pressure conditions (Taylor et al, 2000). Supported bimetallic systems such as Ni-Cu/alumina, Ni-Cu/H-zeolite-β and Ni-Cu/H-ZSM-5 are some of the catalysts employed for this process (Knifton and Dai, 1995).

MOTIVATION

The search for a commercially viable oxygenates having compatible characteristics with gasoline is the primary focus of current research in the field of petroleum chemistry. DIPE is known to possess favorable Reid vapour pressure, easy miscibility with gasoline and low water solubility which makes it an attractive alternate as oxygenate. DIPE can be prepared from acetone and propylene which are by-products in propylene oxide industries and is available in refineries (in fluid catalytic cracking unit) respectively. This has motivated to prepare DIPE from propylene, isopropanol and acetone using different zeolites, heteropoly acids and ion exchanged resins based solid acid catalysts as well as supported bimetallic particles. The reaction parameters such as temperature, pressure, metal loading and amount of catalyst have been studied in detail to obtain necessary information on DIPE formation.

Methyl isobutyl ketone (MIBK) is an industrially important solvent used in paint and ink industries. The conventional method of preparation of MIBK, multi step processes involving basic, acidic and metallic catalysts. In the present work, the use of Ni-Cu-Mg/zeolite as catalyst has been investigated for the single step production of MIBK from acetone.

The H-zeolite-β supported trimetallic catalyst has been identified to show maximum activity and selectivity for MIBK production.

OBJECTIVES AND SCOPE

The main objectives of this thesis include (i) Catalytic production of isopropyl alcohol (IPA) and DIPE by employing solid acids such as heteropoly acids, ion exchange resins and zeolites, (ii) Preparation and catalytic studies on zeolite supported Ni, Ni-Cu and Ni-Cu-Cr metallic particles for DIPE production from acetone, (iii) To evaluate the effect of reaction parameters such as metal loading, temperature and pressure for optimum DIPE production using the supported metallic catalysts, (iv) Production of MIBK from acetone using Ni-Cu-Mg/zeolite and Ni-Cu-Cr/zeolite catalysts and (v) In the appendix, the related work carried out by the candidate relating to preparation of Pt/CDX-975 supported catalysts with varying metal loading for application as anode electro-catalyst for methanol oxidation in DMFC application is given.

MATERIALS AND METHODS

1.   Preparation of H-zeolite-β supported Ni and Ni-Cu catalysts

The H-zeolite-β supported Ni and Ni-Cu catalysts with varying metal loadings were prepared using wet impregnation procedure.   Two different H-zeolite-β samples with SiO_2/Al_2O_3 ratio of 30 and 40 were used as supports.   Before the preparation of the catalysts, the Na form of zeolite-β samples were converted to their H^+ form by exchange with NH_4^+ ions and subsequent heat treatment at 823 K.   The required amount of copper and nickel nitrate were added to an aqueous suspension of the H-zeolite-β in distilled water.   The mixture was stirred for 24 h at room temperature and then evaporated to dryness.   The resulting material was then calcined at 823 K for 12 h in air and subsequently reduced at 623 K for 24 h in hydrogen atmosphere to obtain the supported metallic catalyst.

2.   Preparation of Ni-Cu-M (M = Cr, Mn, Fe)/ H-zeolite-β catalysts

The Ni-Cu-M/H-zeolite-β catalysts were also prepared to study the effect of the third metallic component on the activity of the Ni-Cu supported catalysts.   The supported trimetallic

catalysts were prepared by wet impregnation procedure as described in the previous section. The total metal content is 25 wt % with respect to the H-zeolite-β support and the amount of the third metal is 1 atom % with respect to the total metal content. The supported metallic catalysts were reduced in hydrogen atmosphere at 623K for 24 h prior to their use in catalytic reactions.

3. *Preparation of Ni-Cu-Mg/zeolite catalysts (H-ZSM-5, H-zeolite-β and H-mordenite)*

The 5 wt % Ni-Cu doped Mg catalysts loaded on various zeolites such as H-ZSM-5, H-zeolite-β and H-mordenite were prepared to study their catalytic activity for production of MIBK in a single step from acetone. The catalysts were prepared by adding required amount of nickel, copper and magnesium nitrate into an aqueous suspension of the protonic form of the zeolites. The mixture was stirred for 24 h at room temperature and heated under stirring to evaporate the water to dryness. This material was then calcined at 823 K for 8 h and reduced under hydrogen atmosphere at 623 K for 24 h prior to the catalytic studies.

4. *Preparation of catalyst with Pt loaded on CDX-975 carbon*

The Pt/CDX-975 catalyst for electrode applications was prepared using reduction by formaldehyde. Appropriate amount of carbon was dispersed in distilled water and required amount of 5% H_2PtCl_6 was added to it. The pH of the mixture was adjusted to 10-11 using 0.1 M NaOH and required amount of 20% formaldehyde solution was added. The above mixture was heated at 343 K for 1h under constant stirring. It was then washed thoroughly with distilled water, filtered and dried in hot air oven at 393 K for 4 h. The percentage loading of Pt on carbon was varied between 5- 40 wt %.

5. *Characterization of the catalysts*

The zeolitic and supported metallic catalysts were characterized by XRD, ESR, TGA, DSC, SEM-EDAX, CV and Sorptometric techniques.

### 6.	Catalytic studies

High pressure vapour phase production of DIPE from IPA was studied using a SOTELEM reactor.   The liquid phase hydration, etherification and production of DIPE from acetone were carried out in a Parr autoclave pressurized with high pure nitrogen gas.   The effect of various reaction parameters such as pressure, temperature and concentration of the reactants were studied in detail.   The products were analyzed by gas chromatography using a 2 mr length carbowax column in isothermal mode at 323 K.

RESULTS AND DISCUSSION

1. Catalytic production of IPA and DIPE using solid acid catalysts

The production of IPA and DIPE has been carried out using various solid acid catalysts such as zeolites, heteropoly acids and ion exchanged resins.   The hydration of propylene to isopropanol was carried out in both vapour and liquid phase.   Preliminary results in vapour phase hydration of propylene suggest that the phosphotungstic acid is more active for preparation of isopropanol compared to other zeolite and resin catalysts.   Under liquid phase conditions for hydration of propylene, different solvents were used to study the hydration activity of the solid acid catalysts. It has been observed that the solvent helps in the solubility of propylene in the aqueous phase and hence accelerates the hydration rate.   The polarity of the solvent is also found to be important for the observed hydration activity.   In the subsequent stage of the investigation, DIPE was prepared from isopropanol under vapour phase and liquid phase conditions.   In the vapour phase the H-zeolite-β catalyst was found to be more active than that of H-ZSM-5 catalyst. The catalytic activity was evaluated at different contact times and pressures at 423 K.   It has been observed that the DIPE formation increases with increase in contact time and pressure.   Under liquid phase conditions, zeolite catalysts (H-ZSM-5 and H-zeolite-β) were found to be less active than the heteropoly acid catalysts. Among the zeolite catalysts H-zeolite-β catalyst is more active than H-ZSM-5. The higher activity of H-zeolite-β in comparison with H-ZSM-5 can be attributed to the larger pore size and milder acidic properties.   Three different types of heteropoly acids

namely, phosphotungstic, silicotungstic and phosphomolybdic acids were evaluated for DIPE production in liquid phase from isopropanol. The silicotungstic acid catalyst was found to be more active for DIPE formation compared to other heteropoly acid catalysts. Production of DIPE from isopropanol was also carried out in liquid phase in presence of propylene. Two different experimental strategies were adopted for the reaction. In one case, the Parr batch reactor was pressurized with high pure nitrogen, whereas in other case a mixture of propylene and high pure nitrogen was used. It had been observed that in presence of propylene, the DIPE production was facilitated irrespective of the solid acid catalyst used. The effect of propylene in DIPE conversion for three different catalysts is seen from the values given in Table 1.

Table 1. Catalytic activity for DIPE formation on various catalysts in presence and absence of propylene

Catalyst	DIPE (mole %)	
	Without propylene	With propylene
Phosphotungstic Acid	18.0	26.9
H-zeolite-β	21.0	29.0
H-ZSM-5	22.5	23.0

It is presented that two different reaction pathways are operative, in presence of propylene. In the case of isopropanol bimolecular dehydration, the carbocations generated on the surface of the catalyst, can condense with another isopropanol molecule to give DIPE. Whereas in presence of propylene, carbocation formed from propylene reacts with isopropanol and results in an alternate reaction path. Moreover, the kinetics of reactions can also vary considerably in presence of propylene. In the case of only isopropanol the reaction is being governed by Langmuir-Hinselwood type of mechanism. Whereas in presence of propylene both Langmuir-Hinselwood and Eley-Rideal mechanisms may have to be involved to account for the higher observed activity.

2.   *Catalytic production DIPE from acetone over Ni based catalysts*

The single step production of DIPE from acetone via hydrogenation and bimolecular dehydration using supported Ni-Cu catalysts has been investigated. The H-zeolite-β

(SiO_2/Al_2O_3 = 30 and 40) supported Ni, Ni-Cu and Ni-Cu-M (M = Cr, Mn and Fe) catalysts were prepared by wet impregnation method. The DIPE production from acetone was carried out at different pressures and temperatures under hydrogen atmosphere. Prior to the reaction the catalyst and corresponding metal oxide precursors were characterized using XRD, TGA, EPR, SEM and EDAX techniques. The TG analysis of the nitrate precursors on zeolite matrix indicates complete decomposition to the oxide form at 723 K. The TG analysis of the reduced catalysts do not show any appreciable weight loss indicating complete transformation of the nitrate salts to metallic particles through the intermediate oxide phases. XRD analysis of the supported catalysts before and after reduction exhibits the characteristic peaks of the zeolite matrix. The zeolite matrix remains unchanged during the preparation steps and is stable under the preparation conditions. The mixed oxides of the type Ni-Cu-O are detected on the zeolite matrix from the XRD analysis of the unreduced samples. XRD results also indicate complete reduction of the oxidic samples to the corresponding metals which is accomplished by reduction at 723 K. The ESR spectra of the oxidic precursors in zeolite matrix show a symmetrical peak at $g_\perp$ value of 2.07 whereas hyperfine splitting pattern of Cu^{2+}(I = 3/2) was observed at lower magnetic filed with $g_\parallel$ value of 2.37. These values are typical of Cu^{2+} ions in an octahedral symmetry in the form of CuO clusters. SEM analysis of the supported metallic catalysts reveals that there was

in homogeneous growth of particles with various shapes and sizes. The presence of the supported metallic particles and their composition was further confirmed from sorptometric and EDAX analysis of the supported metallic catalysts. The pore volume and surface area are found to decrease linearly with increase in the metal loading due to partial blocking of the zeolite pores with metal particles. EDAX analysis indicates homogeneous distribution of the metallic particles on the surface. However, in case of Ni-Cu bimetallic catalysts there is surface enrichment of copper metal that has been attributed to the lower surface energy of copper compared to that of metallic nickel. The Ni-Cu bimetallic catalysts were tested for acetone transformation to DIPE under hydrogen atmosphere at 433 K. The effect of

reduction temperature, amount of metal loading, presence of third metal component, pressure and temperature were studied in detail. It has been observed that the etherification activity exhibits a volcano type curve with the amount of metal loading. The optimum metal loading for DIPE formation was identified to be 25 wt % with respect to the zeolite support. This strengthened the fact that a balance between the surface exposure of metallic site as well as the acidic sites of the support is critical for higher conversion. The effect of reduction of the metallic components studied over a temperature range of 573-773 K indicates that reduction of the oxide precursors to metal particles was facilitated even at 573 K. The activity of DIPE formation remains unchanged in the temperature range of reduction without any particle sintering up to 773 K. The DIPE yield is found to increase linearly in the pressure range of 20 to 80 bars. Effect of temperature studied over the 25 wt % Ni-Cu/H-zeolite-β catalyst in the range of 403-453 K indicates that in general the acetone conversion increases with temperatures up to 443 K. Lower temperatures (403-423 K) favour the IPA formation whereas at higher temperatures DIPE is formed at the expense of IPA. These results establish the fact that acetone is hydrogenated to isopropanol which is subsequently converted to DIPE by bimolecular dehydration on the acidic sites of the H-zeolite-β support. The effect of third metal component on the activity of Ni-Cu catalysts was studied by doping 1 atom % of Cr, Fe and Mn into the supported metallic catalyst. It has been observed that Fe doped metallic catalysts shows higher catalytic activity and selectivity for DIPE compared to the Cr and Mn doped samples. The catalytic studies involving various reaction parameters clearly demonstrate the potential of the supported Ni-Cu/ H-zeolite-β catalysts for the production of DIPE from acetone in a single step.

3. *Preparation of MIBK from acetone by employing Ni-Cu-Mg /zeolites*

The single step preparation of methyl isobutyl ketone (MIBK) from acetone has been studied using Ni-Cu-Mg/zeolite catalysts. MIBK is an industrially important reagent used as solvent in paint industries and for dewaxing of minerals. Preparation of MIBK by conventional route involves multistep process requiring basic, acidic and metallic sites.

Acetone is converted to diacetone alcohol using basic sites, which undergo intramolecular dehydration on acidic sites producing mesityl oxides. Mesityl oxide is subsequently hydrogenated in presence metallic catalysts to produce MIBK. In this study, the Ni-Cu-Mg/zeolite catalysts used for single step preparation of the MIBK are prepared by wet impregnation procedure using nitrate and acetylacetonate precursors of the corresponding metal ions. Four different types of zeolites (H-Y, H-mordenite, H-ZSM-5 and H-zeolite-β) with varying pore size and pore volumes were used as support. The total metal loading was 5 wt % with respect to the zeolite support. Catalytic studies conducted over these catalysts indicate that H-zeolite-β is a better support for MIBK production compared to other zeolites. The effect of support on the activity of Ni-Cu-Mg metallic catalyst at 40 bar and 433 K is seen from the data given in Table 2. It has been observed that larger pore size and moderate acidity of the support are beneficial for MIBK production. The Ni-Cu-Cr catalysts prepared by the decomposition of the acetylacetonate complexes show higher activity compared to the materials prepared from nitrate precursor.

Table 2.   Catalytic activity of Ni-Cu-Mg catalysts supported on various zeolites.

Catalyst	Conversion (wt %)	Product (wt %)		MIBK selectivity (%)
		IPA	MIBK	
5 wt % Ni-Cu-Mg/H-Y	27.5	25.8	1.6	5.8
5 wt % Ni-Cu-Mg/H-mordenite	22.7	16.3	5.0	23.5
5 wt % Ni-Cu-Mg/H-ZSM-5	25.3	12.8	12.5	49.4
5 wt % Ni-Cu-Mg/H-zeolite-β	55.0	12.0	24.2	66.8

The reaction time is also found to be an important factor for acetone conversion and MIBK selectivity. For all the catalysts, the acetone conversion was found to increase with time up to 15 hours of the reaction. In case of H-Y and H-ZSM-5 zeolite supports, the selectivity for MIBK remains unchanged throughout the reaction period whereas H-mordenite support displays a mild increase in selectivity with reaction time. However, the behavior of the Ni-Cu-Cr/ H-zeolite-β catalyst is interesting. It has been observed that the selectivity of MIBK

increases with reaction time with maximum selectivity of 85.7 was obtained after 15 h of reaction. Since a drastic increase in selectivity of MIBK was observed for Cr doped Ni-Cu catalysts, it is proposed that the presence of Cr induces basic character into the supported catalyst which helps in the aldol condensation of acetone to produce diacetone alcohol. The diacetone alcohol reacts further on the acidic sites of the zeolite support leading to intramolecular dehydration to produce mesityl oxide. The mesityl oxide is hydrogenated on the Ni-Cu site to produce MIBK.

Appendix.   Carbon supported Pt catalysts for electrode applications in direct methanol   fuel cells (DMFC)

Direct methanol fuel cell (DMFC) has received considerable attention in recent years as a leading candidate for portable power source of the future due to its high energy-conversion efficiency, easy storage of the liquid fuel, ambient operating temperature and simple construction (Dyer, 2002). The development of active anode is of primary importance in DMFC. Platinum based catalysts are promising candidates for anode electro-catalyst for direct methanol fuel cell. The presence of Pt appears to be necessary in the DMFC anode due to its excellent dehydrogenation properties at low temperatures. The electro-oxidation process of methanol to CO_2 occurs through an initial dehydrogenation step (Aricò et al, 2001). Various attempts have been made to reduce the Pt content in the DMFC anode electrode. Ultra-low Pt loading electrodes (0.1 mg/cm^2) have been developed for DMFC application (Aricò et al, 2004). Various reducing agents such as hydrazine, formic acid, sodium formate and formaldehyde have been used to prepare Pt loaded carbon catalysts (Ramesh et al, 1987; Lizcano-Valbuena et al, 2002). The method using formaldehyde for reduction is widely employed to prepare noble metal electrodes for application in fuel cells and this method has the advantages of preparing Pt particles of uniform size without introducing impurity (Neto et al, 2001). The main reason for using this method is that the reduction potentials of the various metal ions (namely, Ru^{2+} to Ru is 0.455 V, Rh^{2+} to Rh is 0.6 V, Pd^{2+} to Pd is 0.951 V and Pt^{2+} to Pt is 1.188 V) are appropriate for reduction by formaldehyde. Formaldehyde oxidation results in various species, which can reduce the

different metal ions of the same valence state, or metal ions of different oxidation states. Among the available supports, carbon based materials such as Vulcan XC-72 (cabot) and polymers such as polyaniline, polypyrrole, poly-3-methylthiophene and poly-3-ethylenedioxythiophene have been extensively used (Qi and Pickup, 1998; Rajesh et al, 2002).

There has been extensive effort in recent years to prepare electrode materials with good activity and stability for application in direct methanol fuel cells (DMFC). Pt and Pt based alloy materials supported on various forms of carbon and polymer are known to possess superior activity for methanol oxidation. The presence of sulfur and other metal impurities in the carbon support has a detrimental effect on the activity of the Pt catalysts. This has motivated the present work to look for new carbon support with suitable properties for application in electrode materials along with preparation methods, which can generate nanosize Pt particles with good dispersion. In this study CDX-975, a relatively impurity free carbon has been used as support for nanosize Pt particles prepared by reduction using formaldehyde.

The use of formaldehyde as a reducing agent and CDX-975 (a carbon material marketed by Ms. Columbian Chemicals Company) as catalyst support for the preparation of Pt/CDX-975 as anode catalyst systems for possible application in DMFC were investigated. The Pt loading was varied between 5 wt % and 40 wt % by weight in the catalyst. The Pt/CDX-975 catalysts were examined for Pt content, phase and crystallinity using UV-Vis spectrometry and XRD techniques. The electrochemical measurements were carried out over a Pt/CDX-975 on Glassy Carbon electrode. XRD patterns of the 20 wt % Pt/CDX-975 and 40 wt % Pt/CDX-975 samples exhibit characteristic peaks for the fcc structure of platinum. However, at lower loadings such as 5 wt % Pt/CDX-975, the characteristic peaks of Pt were completely absent. The average particle size calculated for these catalysts by Sherrer's equation is in the range of 2-11 nm. The lowest particle size of 2 nm was observed for 10 wt % Pt/CDX-975 sample. Cyclic voltametry was employed to obtain electro-active surface area of the Pt/CDX-975 electrode materials. The electro-active surface area was calculated using the expression,

$$EAS = Q_H/ [Pt] \times 0.21 \qquad (1)$$

where [Pt] represents the platinum loading (mg/cm^2) on the electrode, Q_H the charge for hydrogen desorption (mC cm^{-2}) and 0.21 represent the charge required to oxidize a monolayer of hydrogen on Pt. The value of Q_H was calculated as the mean value between the amounts of charge exchanged during the electro adsorption (Q′) and desorption (Q″) of hydrogen on Pt sites. Higher value of electro-active surface area was obtained for 10 wt % Pt /CDX-975 compared to other loadings such as 5 wt %, 20 wt % and 40 wt % which is due to the lower particle size of the Pt observed from XRD data. To evaluate methanol oxidation activity, cyclic voltametry was carried out in 1 M sulfuric acid and 1 M methanol solution between – 0.2 and 1.2 V at the scan rate of 25 mV/sec Vs Ag/AgCl (saturated KCl). Highest peak current of 11.7 mA was observed at 0.788 V for 10 wt % catalyst which is higher than other catalysts with the same geometry in the anodic sweep. The percentage loading of platinum above 10 wt % strongly influences potential for methanol oxidation. As the platinum loading increases, the peak potential shifted towards anodic direction. The possible reason for higher current in the case of 10 wt % Pt/CDX-975 is due to the higher electro-active surface area and smaller particle size of the metallic particles. The cyclic voltammograms for methanol oxidations are deconvoluted into three peaks and are shown in Figure 1.

- Experimental Voltammogram
—— Deconvoluted Voltammogram
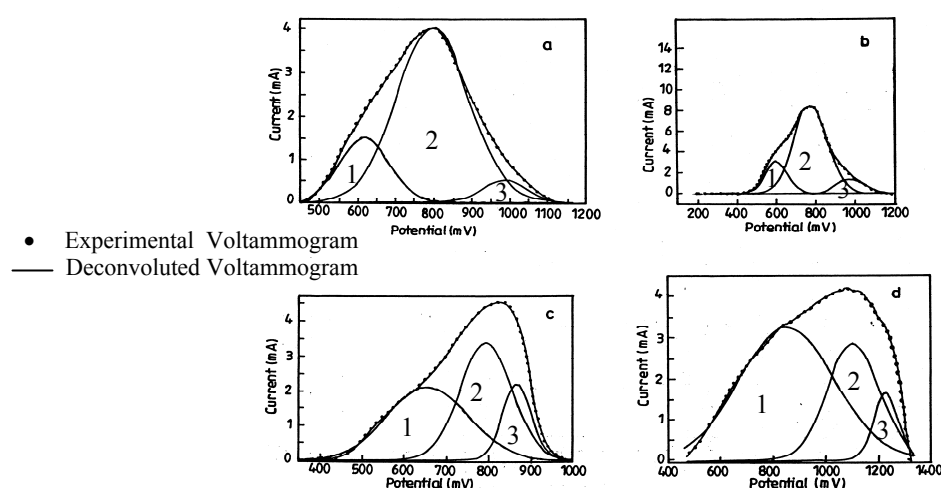
Figure 1. Deconvulated Cyclic Voltammogram of Pt/CDX-975 catalysts, a) 5 wt % Pt/CDX-975 b) 10 wt % Pt/CDX-975 c) 20 wt % Pt/CDX-975 d) 40 wt % Pt/CDX-975

Three well resolved components were observed in Figure.1 which have been attributed to oxidized form of Pt ions (peak 1), Pt in the zero valent state (peak 2) and some Pt complex species (peak 3) generated from oxidation products of formaldehyde used for the reduction of Pt ions from H_2PtCl_6.   All these species are found to be present in the electro catalysts obtained and are active for the oxidation of methanol.   It is therefore deduced that formaldehyde reduction method is appropriate for the preparation of Pt electro catalysts with low Pt loadings.   Stability of the electrode under potentiostatic conditions was evaluated for time period of 3 h.   It is seen that there is constant decay in the current with respect to time possibly suggesting the poisoning of the electrode by CO.   For 10 wt % Pt/CDX-975, though there is a gradual decay of current for a period of 4000 sec, the current appears to be stable afterwards, suggesting the better tolerance of 10 wt % Pt/CDX-975 electrode compared to other catalysts.   In conclusion it may be stated that CDX-975 is a suitable carbon support for electrode applications and an optimum amount of Pt loading is required for use of this material as anode in DMFC.

CONCLUSION

In this thesis an attempt has been made to evaluate different solid acids, supported metallic catalysts and various catalytic routes for the production of DIPE and IPA.   It has been observed that hydration of propylene to IPA is facilitated in presence of zeolites, heteropoly acids and ion exchange resins.   The solvent used for propylene hydration also plays an important role in the IPA formation.   For DIPE production from IPA in liquid phase, heteropoly acids have been identified as good catalysts compared to zeolites.   The dehydration activity of IPA to DIPE is influenced by the presence of propylene under high pressure conditions.   Formation of DIPE by acetone route was also evaluated using Ni-Cu based supported bimetallic systems.   The reaction parameters such as temperature, pressure, amount of catalyst, metal loading, reaction time and the effect of a third metallic component is described in detail.   The Ni-Cu/H-zeolite-β catalyst has been found to be composed of

finely dispersed metallic components with uniform composition. The presence of Fe and Cr as a third metallic component has been found to be beneficial for DIPE production.

The synthesis of MIBK in a single step from acetone has been accomplished using Ni-Cu-Mg/zeolite catalysts. H-zeolite-β has been identified as better support for MIBK production compared to other zeolitic supports. It has been observed that larger pore size and moderate acidity of the support are beneficial for production of MIBK. The Ni-Cu-Cr metallic catalyst prepared by decomposition of acetylacetonate precursor has been found to be more active and selective to MIBK.

Pt loaded carbon (CDX-975) catalysts were prepared by reduction by formaldehyde and examined for methanol oxidation activity. The reduction by formaldehyde method generates nanosize Pt particles with good electro-active surface area. The 10 wt % Pt/CDX-975 is found to possess sufficient electro-active surface area with finely dispersed nanosize Pt particles of < 2 nm, which correlates well with the observed methanol oxidation activity and stability under potentiostatic conditions. The methanol oxidation activity has been attributed to several types of Pt species generated during reduction by formaldehyde.

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