CATALYTIC PRODUCTION OF DIPE FROM ACETONE OVER NICKEL BASED CATALYSTS

1 INTRODUCTION

In recent years, there is a growing interest in the production of DIPE as a possible oxygenate for gasoline blending. Favorable blending properties, ready availability of feedstocks and lower water solubility of DIPE makes it an efficient alternative to MTBE (Huang *et al.*, 1990). Catalytic production of DIPE from propylene feed stock is a widely used process for DIPE production in petroleum refinery. Several types of acidic catalysts such as heteropoly acids (John *et al.*, 1999), ion exchange resins (Marker, 1994), nafion (Olah, 1989), clays and zeolites have been employed as catalysts 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. H-ZSM-5, H-ZSM-12, H-ZSM-35, H-zeolite-ß, H-zeolite-Y and H-mordenite (Harandi *et al.*, 1992; Bell *et al.*, 1996; Harandi *et al.*, 1993) are examples of zeolites, which are utilized for the production of DIPE. Apart from propylene feedstock, crude acetone which is obtained as a byproduct in propylene oxide industry is used as an alternate feedstock for the preparation of DIPE. This alternative route is extensively studied using bifunctional catalysts under high pressure vapor phase conditions (Taylor *et al.*, 2000). The process involves hydrogenation of acetone to isopropanol followed by etherification to DIPE in a single or two step process. Supported bimetallic systems such as Ni-Cu/alumina, Ni-Cu/H-zeolite-ß, Ni-Cu/H-ZSM-5, PW/SiO_2 and Pd/H-zeolite-ß are various catalysts employed for this process (Knifton and Dai, 1995). Different types of reactors such as two and three zone reactors have been utilized for the single step production of DIPE from acetone (Dai *et al.*, 1995; Taylor *et al.*, 1997). Supported multimetallic systems such as Fe-Cr-Mn/H-zeolite-β, Ni-Cu/H-zeolite-β (zone-I; Hydrogenation) and dealuminated H-zeolite-Y (zone-II; Etherification) were used as catalysts to evaluate the effect of temperature on the DIPE formation (Knifton and Dai, 1999).

In this chapter, catalytic activity of Ni-Cu and Ni-Cu-Cr metallic catalysts supported on H-zeolite was evaluated for single step liquid phase production of DIPE from acetone feedstock. The supported metallic catalysts were characterized by XRD, EPR, SEM, EDAX and sorptometric measurements. The influence of experimental parameters such as pressure, temperature, catalyst amount and percentage loading of Ni-Cu on DIPE production were studied in detail.

1.2 RESULTS

1.2.1 TG Analysis of the Nickel based catalyst precursor

TGA analysis of nickel based catalysts supported on H-zeolite-β like Ni/H-zeolite-β, Ni-Cu/H-zeolite-β and Ni-Cu-M (M = Cr, Mn and Fe)/H-zeolite-β were carried out from 423 K to 1073 K in order to confirm the complete decomposition of metal salts. All the catalysts were calcined under oxygen atmosphere to decompose the metal salts and the calcination temperature (723 K) was ascertained from the thermogram of the assynthesised catalyst (Fig. 4.1 a). The thermograms of the calcined catalyst precursors did not show any observable sharp weight loss up to 1073 K (Fig. 4.1 b and 4.2) indicating the complete decomposition of metal salts.

1.2.2 X-ray diffraction patterns of catalyst precursors

The XRD pattern of the H-zeolite-ß exhibits two intense reflections at d values of 11.4 Å and 3.99 Å as presented in Fig. 4.3 a. These values agree with those reported in literature and indicate crystalline nature. Fig. 4.3 b-e and Fig. 4.4 depicts the XRD patterns of nickel based bimetallic and trimetallic catalysts supported on H-zeolite-β. In addition to the peak of parent zeolite, additional peaks were observed at d values of 2.41, 2.08, 1.46, 1.25 and 1.19 Å. These d values correspond to the reflections from the (200), (111), (220), (311) and (222) planes of the supported NiO and (Ni, Cu) O phases (47-1949 and 25-1049). The X-ray reflections of pure CuO were not observed because of lower amount of Cu loading with respect to Ni. Similarly, the reflections of pure chromium oxides were not observed in case of trimetallic systems. The existence of the zeolite peaks at 11.4 Å and 4.0 Å in the supported metallic catalyst indicates that the crystalline nature of the zeolite is retained in the catalyst.

1.2.3 ESR spectroscopic study

Electron spin resonance spectroscopic study was carried out to obtain information on the presence and chemical state of copper in the Ni-Cu/H-zeolite-ß catalyst precursors. The ESR spectra of the catalysts are shown in Fig. 4.5. The signal observed at higher magnetic field corresponds to a $g_{\perp}$ value of 2.07, while hyperfine splitting pattern of Cu^{2+} (I=3/2) was observed at lower magnetic field with a $g_{?}$ value of 2.37. These values are typical of CuO particles and have been observed for well dispersed supported systems (Kucherov and Slinkin, 1994).

1.2.4 SURFACE AREA AND SEM ANALYSIS

Nitrogen adsorption studies were carried out to measure the surface area and pore volumes of the catalyst precursors. The surface area and pore volume of the Ni-Cu and Ni-Cu-Cr metals supported on H-zeolite-ß are given in Table 4.1. It has been observed that with an increase in the metal loading on H-zeolite-ß catalyst, the surface area and pore volume were found to decrease. $\mathrm{T}^{\text{35wt\% Ni-Cu/H-zeolite-}\beta}$ blocking of the pores in the zeolite matrix by the supported metallic particles. The 45 wt % Ni-Cu supported on H-zeolite-ß show minimum pore volume and surface area. The surface compositions of the bimetallic particles as determined by EDAX analysis are also presented in Table 4.1.

In general, a good agreement was observed between the amount of metal used and the data obtained from EDAX analysis. However, the Ni to Cu ratio is found to be different form the original value of 5:1. This is ascribed to the lower surface energy of copper (1850 mJm^{-2}) compared to nickel (2450 mJm^{-2}) which results in surface segregation of copper metal on the surface of the Ni-Cu particles. Scanning electron microscopic pictures were taken to study the morphology of the catalysts. The SEM pictures of the supported metal systems are shown in Fig. 4.6 and 4.7. The supported catalyst particles are of irregular shape and are non - homogeneous. The surfaces of the supported metal catalysts are generally rough without growth of small particles. The surface morphology of the catalyst is little affected by the variation in the amount of metal loading.

4.2.5 Diisopropyl ether production from acetone using bimetallic Ni-Cu/H-zeolite-ß catalyst

Single step production of DIPE involving hydrogenation of acetone followed by dehydration to DIPE was carried out with the supported bimetallic catalyst system namely Ni-Cu/H-zeolite-β in the temperature range of 403 K – 453 K and a pressure range of 20 - 80 bar. The H-zeolite-ß support used for this study has a Si/Al ratio of 40.

4.2.5.1 Effect of amount of (Ni-Cu) loading on H-zeolite-b for the production of DIPE

The effect of amount of metal loading on the yield of DIPE for a series of catalysts in the range of 5 - 45 wt % was studied and the results are presented in Table 4. 2 and Fig. 4.8. The DIPE yield is found to increase with an increase in the metal loading up to 25 wt % and further increase in loading leads to decrease in DIPE yield. The optimum metal loading was found to be 25 wt % for the maximum yield of DIPE. It has been observed that a considerable amount of MIBK was formed with 5 wt % Ni-Cu/H-zeolite-ß catalyst.

4.2.5.2 Effect of Ni:Cu ratio on H-zeolite-b on the production of DIPE

Catalytic activity of 25 wt % Ni/H-zeolite-β, 25 wt % Ni-Cu (3:1)/H-zeolite-β and 25 wt % Ni-Cu (5:1)/H-zeolite-β was studied for the production of DIPE from acetone at 433 K and a pressure of 60 bar for a time period of 5 h to evaluate the role of copper on the DIPE yield (Table 4.3). Isopropanol and DIPE are the products obtained in all the catalysts. Isoproanol formation is more in the case of Ni/H-zeolite-β and Ni-Cu (3:1)/H-zeolite-β. However, 25 wt % Ni-Cu (5:1)/H-zeolite-β catalyzed reaction results in the formation of higher amount of DIPE compared to other two catalysts.

4.2.5.3 Effect of reduction temperature on catalytic activity of 25 wt % Ni-Cu/H-zeolite-ß catalyst ($SiO_2/Al_2O_3 = 40$).

The catalyst precursors (oxide form) were reduced in an atmosphere of hydrogen at higher temperature to generate the active metallic catalyst. The effect of the reduction temperature on catalytic activity was studied for the 25 wt % Ni-Cu/H-zeolite-ß catalyst by varying the reduction temperature of the catalyst precursor in the temperature range of 573 K - 773 K. The reduction temperature has little effect on the activity of the catalyst in the range of temperature studied as given in Table 4.4 and the DIPE yield is also found to remain unchanged in this temperature range. This indicates that the reduction of the oxide precursor to the corresponding metal is accomplished at 573 K and facilitates DIPE formation.

4.2.5.4 Influence of reaction temperature on the catalytic activity of 25 wt % Ni-Cu/H-zeolite-ß catalyst ($SiO_2/Al_2O_3 = 40$)

The catalytic activity of 25 wt % Ni-Cu/H-zeolite-β for DIPE production was evaluated at different temperatures (403 K - 453 K) for a reaction time period of 10 h

(Fig. 4.9). Acetone conversion was found to increase with reaction time and attain a saturation value around 5-7 h in the temperature range studied (Fig. 4.9 a). Isopropanol and DIPE were obtained as major products along with minor amount of methyl isobutyl ketone. The effect of temperature on the yield of isopropanol and DIPE in the range of 403 K - 453 K is shown in Fig 4.9 b and c and Table 4.5. High reaction temperature conditions favour DIPE formation while isopropanol is formed as a major product under low reaction temperatures. At low temperatures (403 K - 423 K) the hydrogenation of acetone is favored leading to the formation of isoproponol. However, the subsequent bimolecular dehydration of isopropanol to DIPE is not efficient. On the other hand, DIPE yield increases in the temperature range of 433 K - 453 K indicating that the acidic sites of the H-zeolite-ß is active towards etherification at higher temperatures. Taylor *et al,* (1999*)* have studied the single step formation of DIPE from acetone in vapor phase using different reactor configurations and Ni-Cu/H-zeolite-ß as catalyst in order to evaluate the influence of temperature on DIPE formation and obtained results indicated that temperature influence to increase the yield of DIPE in the temperature range of 433 K- 453 K (Taylor and Dai, 1999; Taylor and Dai, 1999).

Ni-Cu/H-zeolite-ß catalyst (SiO_2/Al_2O_3 = 40)

Liquid phase production of DIPE over zeolite supported metallic catalysts was generally carried out under an atmosphere of hydrogen. The effect of pressure of hydrogen on the DIPE yield with 25 wt % Ni-Cu/H-zeolite-β is studied in the range of 20 - 80 bar at 433 K and the results are given in Table 4.6. It is observed that the DIPE yield increases with increase in pressure before it saturates around 60 bar.

4.2.5.6 Catalytic activity of 35 % Ni-Cu/H-zeolite-b for DIPE production

Under identical reaction conditions, Table 4.2 shows that 35 wt % loading of Ni-Cu on H-zeolite-β produces higher yield of DIPE (26.1 %) next to 25 % Ni-Cu/H-zeolite-β (30.5 %). Catalytic activity of 35 % Ni-Cu/H-zeolite-β for the preparation of DIPE from acetone at 60 bar was studied in the range of 393 K - 443 K in order to evaluate the influence of temperature on the catalytic activity. The acetone conversion, IPA and DIPE yield at different reaction temperatures are given in Table 4.7 and Fig. 4.10 shows the variation in the yield of DIPE at various temperatures screened (393 K - 443 K). The temperature response of 35 wt % Ni-Cu/H-zeolite-β is found to be identical to that of 25 wt % Ni-Cu/H-zeolite-β and aggress with the literature report (Taylor and Dai, 1999) where the yield of DIPE increases with increase in temperature.

4.2.5.7 Recyclablity of 25 wt % Ni-Cu (5:1)/ H-zeolite-b

The recovery and reusability of 25 wt % Ni-Cu/H-zeolite-β was studied. After the completion of the reaction, the catalyst was filtered, washed with acetone and regenerated in oxygen atmosphere at 823 K for 12 h followed by hydrogen reduction at 623 K for 24 h. The recovered catalyst was employed for further runs and the whole process was repeated for three times (Table 4.8). The activity of the recycled catalyst gradually decreased upon successive use possibly due to agglomeration of the catalyst at higher temperature activation.

4.2.6 Diisopropyl ether production from acetone using trimetallic Ni-Cu-Cr/H-zeolite-ß catalyst

4.2.6.1 Effect of zeolite support on the catalytic activity of Ni-Cu-Cr/H-zeolite

Influence of the type of zeolite as supports for Ni-Cu-Cr on the production of DIPE from acetone was studied by employing H-ZSM-5, H-mordenite and H-zeolite-β. Acetone transformation was studied at a temperature of 433 K and 60 bar pressure and the results obtained are given in Table 4.9. HZSM-5 showed complete conversion of acetone into IPA without further transformation to DIPE. H-mordenite afforded around 60 % of IPA along with trace amount of DIPE and even though conversion of acetone over H-zeolite-β was lower, it gave rise to considerable amount of DIPE (8.4 mol %) along with the formation of IPA.

4.2.6.2 Diisopropyl ether production from acetone using 15 wt % Ni-Cu-Cr/H-zeolite-ß catalyst (SiO_2/Al_2O_3 = 30)

The acetone hydrogenation reaction followed by its dehydration to DIPE was carried out on 15 wt % Ni-Cu-Cr/H-zeolite-ß catalyst with SiO_2/Al_2O_3 ratio of 30 in liquid phase in the temperature range of 413 K - 453 K. The catalytic activity data generated are presented in Table 4.10 It has been observed that acetone conversion is found to increase with an increase in temperature up to 443 K. Further increase in the temperature results in decrease in acetone conversion. The products such as DIPE and IPA which are obtained by acetone transformation at different temperatures are shown in Fig. 4.11. It can be seen from the Fig. 4.11 that yield of DIPE increases in the temperature range 413 K - 453 K which is favorable for etherification reaction over acidic H-zeolite-ß support.

4.2.6.3 Catalytic activity of 25 wt% Ni-Cu-Cr/H-zeolite-b for the production of DIPE

The optimum loading of Ni-Cu was found to be 25 wt % on H-zeolite-β for the DIPE production from acetone in liquid phase in the section 4.2.5.1. 25 wt % Ni-Cu-Cr/H-zeolite-β was employed as catalyst to study the activity for DIPE formation in the temperature range of 403 K- 443 K and pressure of 60 bar. The results obtained were given in Table 4.11. The DIPE formation of DIPE at different time interval and in the temperature range 403 K - 443 K are shown in Fig. 4.12. It can be inferred from data in this figure that DIPE yield increases with the temperature as in the case of all other catalysts studied in this chapter and this temperature range (423 K - 443 K) is appropriate for bimolecular dehydration reaction over acidic etherification catalyst namely H-zeolite-β.

4.2.6.4 Evaluation of influence of amount catalyst for the production of DIPE

In order to get information on the effect of amount of catalyst on DIPE formation, the catalyst amount was varied from 0.5 to 2.5 g keeping other parameters constant and the results are tabulated in Table 4.12. When the amount of catalyst used is 0.5 g, there is no formation of DIPE, whereas the formation of IPA is observed during the course of the reaction. This implies that when less amount of catalyst is used, the metallic component is still promoting acetone transformation to IPA. However, amount of acidic sites are not enough to promote the etherification of IPA to DIPE. Considerable amount (5-10.7 mol %) of DIPE formation was observed when the catalyst amount is 1.0 g, 1.5 g and 2.5 g. The DIPE yield and the selectivity towards DIPE were found to be maximum at a catalyst loading of 1.0 g. Apart from DIPE, minimum amount of MIBK was observed in the case of 0.5 g, 1.5 g and 2.5 g of loadings.

4.2.6.5 Effect of hydrogen pressure on the catalytic activity for the production of DIPE

The effect of hydrogen pressure on the DIPE yield is studied in the range of 40-80 bar at two different temperatures (423 K and 433 K) and the results are given in Table 4.13 and 4.14. The influence of pressure on the acetone conversion, IPA and DIPE yield are shown in Fig. 4.13. The DIPE yield is found to increase with increase in pressure at both temperatures. The hydrogen pressure also increased the yield of isopropanol and acetone conversion as can be seen from the Fig. 4.14. The initial rate of reaction was calculated from the plot of DIPE yield vs time and plotted against respective hydrogen pressures. The initial rate increases linearly with pressure, which is shown in Fig. 4.15.

4.2.6.6 Effect of acetone concentration on the catalytic activity for the production of DIPE

The influence of acetone concentration in terms of volume on the catalytic production of DIPE was evaluated by varying the volume of acetone from 20 ml to 80 ml and keeping other parameters constant. The results obtained are given in Table 4.15 where DIPE and IPA yields are found to be decreasing with increase in volume of acetone. The lowering of the activity may be due to the saturation or flooding of the catalysts surface by acetone, which results in the lower catalytic activity.

4.2.6.7 Diisopropyl ether production from acetone using other trimetallic Ni-Cu-M (M = Mn and Fe)/H-zeolite-ß catalyst

The influence of Fe and Mn as third metallic component in comparison with Cr on the catalytic production of DIPE was studied by employing Ni-Cu-Fe/H-zeolite-ß and Ni-Cu-Mn/H-zeolite-ß as catalysts in liquid phase. The results are given in Table 4.16 and compared with that of Ni-Cu-Cr/H-zeolite-ß. Apart from Cr as third metal, Fe and Mn were also found to be active for the production of DIPE. It has been found that, under identical reaction conditions, the Fe doped sample shows higher catalytic activity and DIPE yield compared to the Cr and Mn containing samples. In the case of the Mn containing catalyst although the conversion is higher compared to Cr catalyst, the selectivity towards DIPE is rather poor favoring large amount of isopropanol formation. The catalytic activity of trimetallic catalysts namely Ni-Cu-M (Mn, Fe and Cr)/H-zeolite-ß were lower than that of bimetallic Ni-Cu/ H-zeolite-ß as given in the Table 4.16 and Fig. 4.16.

4.3 DISCUSSION

It is necessary that the results reported in this chapter are discussed in the light of the existing patent and open literature because of the commercial as well as other academic interest. Knifton and Dai (Knifton and Dai, 1999) investigated this reaction employing crude acetone streams and have shown that three different acidic catalysts namely H-zeolite-ß modified with (Ni,Cu), (Fe-Cr-Mn) and dealuminated H-zeolite-Y. They have shown that there is an increase in the ether yield (especially that of DIPE, MIPE and DME) with an increase in temperature in the range of 393 K - 453 K. In addition, they have established that the etherification is controlled by kinetic factors and the yield of various ethers depends on the competition for the etherification sites. Their studies thus showed that Ni-Cu on H-zeolite-ß system showed more etherification sites as compared to other catalyst systems investigated by them. The results of the present study not only supports this observation but also shows that even in the pure acetone stream (that has been employed in the present work) that Ni-Cu on H-zeolite-ß promotes effectively the IPA formation as well as its subsequent etherification to DIPE. In this sense, the present system is comparable to the bimetallic catalysts systems normally employed in the reforming reactions. One of the metallic components promotes the hydrogenation activity and the other metallic component not only moderates the hydrogenation activity of the first metallic component but also facilitates the etherification sites suitably. This is one aspect that needs to be examined in closer detail in future.

Taylor and coworkers (Knifton and Dai, 1995; Dai, *et al.*, 1995; Taylor *et al.*, 1996; Taylor 1996) have shown that an integrated two reactor concept either with gradient functions or use of two distinct catalyst systems with nearly 32 wt % Ni-Cu on metal zeolite –alumina gave nearly 30 mole % of DIPE yield with least amount of undesirable gas. In the present study the optimum catalyst composition (Fig 4.8) is 25 wt % of Ni-Cu on H-zeolite-ß and the DIPE yield is also around 30 mole % which are in agreement with the results reported by Taylor and coworkers (Taylor *et al.*, 1996). However the striking difference is that the present study eliminates the two reactor concept and shows that a single catalyst system itself is capable of promoting both hydrogenation as well as etherification reaction.

In a series of patents (Dai, *et al.*, 1995; Taylor *et al.*, 1997; Taylor *et al.*, 1996) Texaco Chemical Inc., has shown that an integrated catalysts reactor system for the conversion of crude acetone to DIPE while in another series of patents (Olah, 1989; Harandi *et al.*, 1992; Harandi and Owen, 1993) the same reaction is achieved using propylene as the feed. The present study demonstrates that one can not only eliminate the use of two reactor concept (though the chemical identity is the same, the compositions were different) but also shows a catalysts of a single composition is capable of promoting acetone to DIPE reaction effectively in consecutive fashion. The optimum composition of the single catalyst and the temperature range (403 K - 443 K) of operation are also established for optimum conversion to oxygenates especially DIPE.

The preferential segregation of copper over nickel not only modulates the hydrogenation activity of acetone to IPA but also modulates the etherification activity of the H-zeolite-ß. The addition of the third element especially, Fe, Cr and Mn favours hydrogenation activity over the etherification reaction and hence the choice of the third component should be based on increasing the surface acidity of the catalyst and inhibiting or reducing the hydrogenating activity. Therefore, the choice of the third component has to be found elsewhere and not in the transition metal series as has been reported in the literature. The results presented in this study is based on pure acetone feed as compared to the crude acetone feed or refinery based propylene feed and in this sense the results of these studies have to be contrasted with the results reported in literature and have to be evaluated for its worth.

4.4 CONCLUSIONS

In this study, an attempt has been made towards the synthesis of DIPE from acetone in a single step under liquid phase conditions for the first time. Ni-Cu bimetallic catalysts supported on H-zeolite-ß are found to be active for DIPE production. The amount of metal loading, temperature and hydrogen pressure are crucial factors for higher yields of DIPE. 25 wt % Ni-Cu metal supported on H-zeolite-ß catalyst shows higher activity and DIPE yield compared to other metal loadings studied. The reduction temperature of the catalyst precursor is found to be less significant when it is higher than 573 K. Ni-Cu-Cr trimetallic catalysts supported on H-zeolite-ß are also found to be active for the production of DIPE from acetone reaction. The effect of amount of catalyst loading, hydrogen pressure, volume of acetone and temperature on DIPE formation are studied. A moderate reaction temperature in the range of 433 K - 453 K and catalyst amount of 1 g (wt %) are found to be favorable for higher DIPE yields. Hydrogen pressure (30 - 80 bar) increases the yield of DIPE. The effect of addition of a third metallic component (Mn and Fe) apart from Cr is also studied for the supported Ni-Cu system. Among Fe, Mn and Cr metals, the incorporation of Fe along with Ni-Cu exhibit better activity compared to Mn and Cr.