CHAPTER 3

LIQUID PHASE HYDRATION OF PROPYLENE AND ETHERIFICATION OF ISOPROPANOL OVER SOLID ACID CATALYSTS

3.1 INTRODUCTION

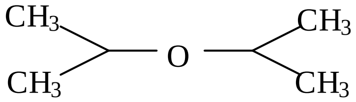
Hydration of propylene to 2-propanol followed by its etherification to DIPE is an important process for the industrial production of diisopropyl ether (DIPE). These two processes have been extensively studied either separately or in combination a single step. Solid acid catalysts such as zeolites, heteropolyacids, resins and nafions are frequently employed for the hydration of propylene, whereas clay, zeolites and heteropolyacids are employed for the etherification of isopropanol. Acid-catalyzed direct hydration of propylene to IPA is reversible and exothermic. Propylene is a non polar gas and hence its solubility in water is low. In order to increase the solubility of propylene, inert solvent like dioxane has been employed. H-zeolite-β catalyst, however, is extensively employed for the etherification reactions due to its higher selectivity and moderate acidity. Modified H-zeolite-β has also been employed for the etherification reaction. The etherification reaction which involves condensation of two molecules of IPA to form DIPE is known to follow the LH mechanism. Alternatively, DIPE can be formed by addition of IPA to propylene. The propylene formed during the dehydration of IPA or externally added, is known to increase the yield of DIPE from IPA. The reaction scheme for the DIPE production is indicated below.

Hydration:

$$CH_3CH = CH_2 + H_2O \rightleftharpoons (CH_3)_2\ CHOH \tag{3.1}$$

Etherification:

$$2(CH_3)_2CHOH \rightleftharpoons$$



(3.2)

Bezman *et al,* (1982) have developed a process for the production of isopropanol by reversing the byproduct which is formed along with the IPA (step 3.2) at a temperature range of 416 K - 452 K and pressure of 50-500 psig. The conversion obtained in this process is 67 % and the catalyst employed for the reaction is E-372 and H-ZSM-5, co-gel (Silica 65 % + 35 % Alumina) and alumina (Bezman *et al.*, 1982).

Carls *et al,* (1988) have developed hydration process from propene containing hydrocarbon mixture over the Amberlyst -15 catalyst. They have employed serially connected reactor in the temperature range of 403 K - 443 K with a pressure of 80-120 bar. The reactants were send to the reactor in opposite directions. They have obtained 98 % conversion with 99 % selectivity of DIPE for the above mentioned process (Carls *et al.*, 1988)

Latimer *et al,* (1990) have developed a process for the vapor phase hydration by employing serially connected reactor in which IPA is removed in between the reactor. These authors have employed the nafion catalyst in the temperature range of 493 K - 508 K and pressure of 1000 psig. They have used a mixture of ethylene and propylene as feed and obtained conversion of ethylene and propylene as 22 wt % and 25 wt % respectively (Latimer *et al.*, 1990).

Chang *et al,* (1980) have studied the hydration of propylene over H-ZSM-5 in the temperature range of 423 K - 473 K and a pressure of 100-250 psig which selectively produced only IPA as product (Chang *et al.,* 1980). Kim *et al,* (1989) have developed numerical simulation of fixed-bed catalytic reactor for isopropyl alcohol synthesis (Kim *et al.*, 1989). Marker *et al,* (1989) developed a process for the hydration of propylene with 1:1 mole ratio of water and propylene over H-ZSM-35 and alumina-bound ferrierite at 439 K and 70 bar. These authors observed a conversion of 55.1% with a selectivity of 99.5% for H-ZSM-5 and conversion of 8.7 for alumina-bound ferrierite catalysts. Bell *et al,*(1989) have developed a process for the production of isopropanol over H-zeolite-β (SiO_2:Al_2O_3 ratio>7; constraint index £2) in liquid phase a temperature range of 373K - 500 K and a pressure of 5-300 atm with a water: propylene ratio of 0.99. These authors observed the yield of isopropanol at 445.7 g/h/l (Bell *et al.,* 1989). Child *et al,* (1991*)* have developed a process for the hydration reaction over H-zeolite-β at 428 K and a pressure of 1000 psig in liquid phase. They observed the yield of isopropanol as 28 wt % and diisopropyl ether as 30 wt % (Child *et al.*, 1991*)*. Le *et al,* (1993) have developed a process for hydration in the presence of MCM-36 in the temperature of 603 K - 653 K and at a pressure of 1000 psig. They have observed the conversion of propylene as 17 wt % with selectivity of 89 wt % (Le *et al.*, 1993). Baker *et al,* (2002) have investigated the process for the manufacturing isopropanol by the hydration of propylene. They have employed a membrane to separate propylene from propane in the feed. Using the process, these authors achieved a very high propylene conversion of about 98-99 wt %. The reactor conditions are 308 K- 343 K and pressure of 75-225 psig. In this process sulfonated ion-exchange resin was employed as catalyst (Baker *et al.,* 2002). Brown *et al,* (1996) have developed a process for the hydration of propylene over zeolites such as H-ZSM-5 and H-ZSM-35 in the temperature range of 423 K and 473 K and a pressure of 2800 kPa and 7000 kpa. These authors have demonstrated the stability of the H-ZSM-5 catalysts for 70 to 170 h on stream (Brown *et al.*, 1996).

Tomita and Oshima (2004) have investigated the mechanism of hydration of propylene in terms of the H^+ concentration in the bulk phase and the activity of protonic acid sites on the catalytic surface. They have carried out the reaction in the presence of super critical water. Based on the theoretical studies these authors clearly showed that the acidity of the catalyst surface is strongly influenced by the change of the ionic product in the bulk phase water. These authors also carried out the reaction over TiO_2 and proposed the kinetic rate expression as a function of both reaction temperature and ion product of water (Tomita and Oshima, 2004).

Tomita *et al*, (2002) have studied the catalytic hydration of propylene over MoO_3/Al_2O_3 in the temperature range of 373 K- 693 K and a pressure of 21.6-31.4 MPa and propylene concentration of 3.6×10^{-3} to 3×10^{-2} mol/lit. They have observed that the conversion increases with respect to pressure and lower temperature affords high conversion than that of higher temperature and these authors have developed LH and ER type model for the reaction (Tomita *et al.*, 2004).

Mahajani *et al*, (2002) have studied liquid phase hydration of propylene by employing H-ZSM-5, Amberlyst -15 and H-mordenite in the temperature range of 373 K - 393 K. They have made comparison between all the catalysts and found that A-15 shows higher activity. IPA yield increases with temperature and pressure influences to increase the yield up to the supercritical pressure. These authors have calculated the activation energy as 20 kCal/g mol for hydration (Mahajani *et al.,* 2002). Ivanov *et al*, (2003) have studied the catalytic activities of H-ZSM-5, bulk HPW, 10 wt % HPW/SiO_2 and 70 wt % HPW/SiO_2 for hydration of propylene in the temperature range of 343 K - 423 K and pressure of 10-50 kPa. The authors observed high activity for 70 % wt HPW/SiO_2 among all examined catalysts (Ivanov *et al.,* 2003).

3.2 RESULTS AND DISCUSSION

3.2.1 Liquid phase hydration of propylene over solid acid catalysts:

Hydration of propylene was carried out in liquid phase using a Parr reactor at 393 K and a pressure of 60 bar with a mixture of 16 % propylene and 84 % of high pure nitrogen. The reaction was carried out for 4 h. The feedstock of water / propylene and the ratio is maintained at 7.2. The catalysts employed are zeolites like H-ZSM-5, H-zeolite-β and H-zeolite-Y, Amberlyst-15 and phosphotungstic acid. The isopropanol formed in terms of mole percentage are reported in Table 3.1. Preliminary results in liquid phase hydration of propylene suggest that phosphotungstic acid is more active for the preparation of isopropanol compared to zeolite and resin catalysts. The higher activity of the phosphotungstic acid is attributed to the higher acidity of the catalysts compared to other solid acids.

Table 3.1 Comparison of catalytic activities for the hydration of propylene

Catalyst	IPA (mol %)
H-ZSM-5	3.6
Amberlyst – 15	1.7
Phosphotungstic acid	8.7
H-zeolite-β	1.0
H-zeolite-Y	0.5

3.2.2. Effect of solvents on hydration of propylene

The influence of solvents on the catalytic activity was studied by employing Amberlyst-15 and H-ZSM-5 as catalysts. Isooctane, dioxane and THF are the solvents employed for the reaction with Amberlyst-15 as catalyst. Isooctane and dioxane were the solvents employed for H-ZSM-5 catalyst. The reaction was carried out at 393 K and a pressure of 60 bar with a mixture of 16 % propylene and 84 % of high pure nitrogen and employing water/propylene ratio of 7.2. 20 ml of solvent was used for the reaction. The influence of solvent on catalytic activity over H-ZSM-5 is given in Table 3.2. Among isooctane and dioxane, isooctane was found to promote the yield of isopropanol compared to dioxane and neat reaction system. Isooctane adsorbs to a lesser extent on H-ZSM-5 compared to dioxane. Hence the surface acidic sites of H-ZSM-5 are relatively more available to the dissolved propylene under high pressures. The presence of isooctane also helps to increase the solubility of propylene in water.

Table 3.2 Effect of solvent on hydration of propylene over H-ZSM-5 at 393 K, 60 bar and water/propylene ratio of 7.2.

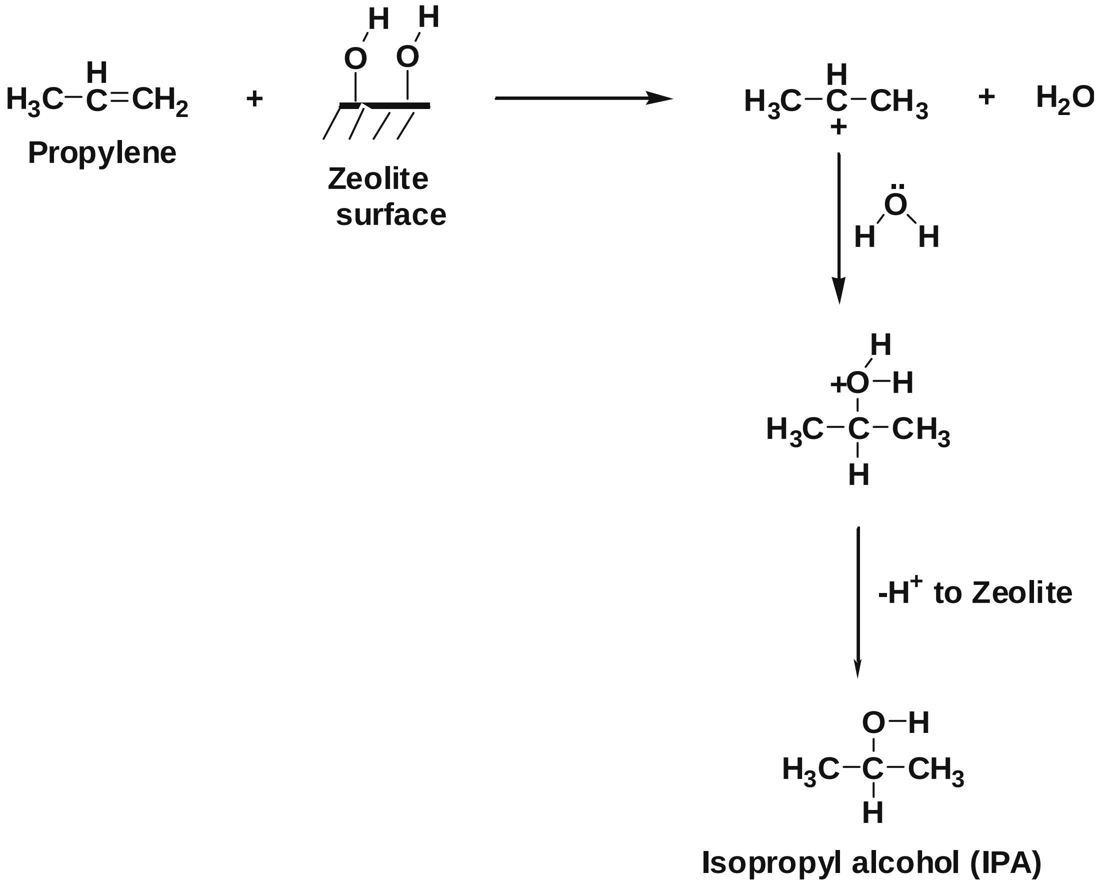
Solvent	IPA (mol %)
Neat	3.6
Isooctane	7.1
Dioxane	2.1

The influence of solvent on catalytic activity over Amberlyst-15 is given in Table 3.3. Dioxane influences to increase the formation of isopropanol compared to isooctane and THF in accordance with the earlier reports in literature. The higher activity of the dioxane is attributed to the high polar nature of the dioxane which is capable of increasing the solubility of the propylene.

Table 3.3 Effect of solvent on hydration of propylene over Amberlyst-15 at 393 K

Solvent	IPA (mol %)
Neat	1.8
Isooctane	1.5
Dioxane	14.2
THF	2.2

Mechanistically, propylene adsorbed on the surface acidic sites of the catalyst gets converted to propyleneium cation. In the next step, a water molecule is added to the carbocation to form oxonium ions. Finally, removal of H^+ ion by zeolite, results in the formation of iospropanol as shown in Scheme 3.1



Scheme 3.1 Mechanism of propylene hydration over solid acid catalyst

3.2.3 Vapor phase synthesis of DIPE from isopropanol over zeolites

Production of diisopropyl ether from isopropanol was carried out over H-zeolite-β in the vapour phase by employing high pressure reactor. The reaction was performed at 423 K and a pressure of 10 bar with high pure nitrogen. The contact time was varied from 4-33 sec and product was collected at a time interval of 30 mins. The mol % of DIPE obtained is tabulated with contact time in Table 3.4. The yield of

DIPE increases with the contact time and a maximum yield of 25.8 mol % was obtained at contact time of 29 Sec.

Table 3.4 Vapor phase synthesis of DIPE from isopropanol over H-zeolite-b at 423K and 10 bar

Contact time (Sec)	DIPE (mol %)
14	18.2
15	18.2
16	19.9
21	21.5
23	22.7
26	24.5
29	25.8
33	24.0

The preparation of DIPE from IPA was carried out over H-ZSM-5 with varying pressure of 10 - 20 bar. The yield of DIPE in terms of mol % is given in Table 3.5. The DIPE yield increases with pressure. This may be due to the increase in the adsorption of reactant on the surface of the catalyst at higher pressures which leads to higher activity. In the vapor phase, H-zeolite-ß 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.

Table 3.5 DIPE production using H-ZSM-5 as catalyst in the vapour phase Temperature: 443 K

Pressure (bar)	DIPE (mol %)
10	5.8
15	6.8
20	9.2

3.2.4. Liquid phase synthesis of DIPE from IPA over heteropolyacids

Liquid phase synthesis of DIPE from IPA by bimolecular dehydration was carried out in high pressure autoclave in the pressure range of 60-100 bar and a temperature range of 433 K - 453 K for a time period of 24 h with stirring. Heteropolyacids namely HSiW, HPW and HPMo were employed for the reaction. The data on catalytic activity of these catalysts are given in Tables 3.6 and 3.7 along with the experimental conditions. The phosphotungstic acid catalyst was found to be more active for DIPE formation compared to other heteropolyacid catalysts.

Table 3.6 Catalytic activity of HPAs for the production of DIPE in liquid phase

Catalyst	HSiW		HPW		(HPMo)
IPA Volume (ml)	50	50	50	100	50
Pressure (bar)	60	60	60	100	60
Temperature (K)	433	453	453	433	443
Stirring rate(rpm)	100	100	100	100	100
DIPE yield (% mole)	19.4	29.6	32.0	17.5	28.4

Catalyst amount = 2.5 g

Table 3.7. Comparison of catalytic activity of heteropolyacids at 453 K

Catalyst	DIPE (mol %)
Silicotungstic acid (HSiW)	29.6
Phosphotungstic acid (HPW)	32.0

3.2.5. Liquid phase synthesis of DIPE from IPA over zeolites

Liquid phase synthesis of DIPE from IPA by etherification was carried out in a high pressure autoclave in the pressure range of 20 - 100 bar at 433 K for a time period of 24 h with stirring. Zeolites such as H-zeolite-β and H-ZSM-5 were employed as catalysts. Both H-ZSM-5 and H-zeolite-β are inactive for DIPE production upto reaction pressure of 80 bar at 433 K. Only at 80 bar or higher pressures these catalysts are active for the DIPE formation from IPA. Comparison of catalytic activity at a particular temperature of 433 K is given in Table 3.8. As shown in the Table 3.8 H-ZSM-5 is as active as H-zeolite-β, when the reaction was carried out at 100 bar in the case of H-ZSM-5 and 80 bar in the case of H-zeolite-β. The comparable activity of H-ZSM-5 is due to increase in the adsorption of IPA on the catalyst surface of H-ZSM-5 at high pressure.

Table 3.8 Catalytic activity of zeolites for the production of DIPE in liquid phase

Catalyst	**H-zeolite-**b **(5.0 g)**	**H-ZSM-5 (5.0 g)**
IPA volume(ml)	100	100
Pressure(bar)	80	100
Temperature(K)	433	433
Stirring rate(rpm)	100	100
DIPE yield (mol %)	12.3	12.3

3.2.6. Synthesis of DIPE from isopropanol in the presence of propylene

Liquid phase production of DIPE from isopropanol was carried out 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 the other case a mixture of propylene and high pure nitrogen were used. It had been observed that in the presence of propylene, the DIPE production was facilitated irrespective of the solid acid catalysts used. The effect of propylene on DIPE formation under three different catalysts is given in Table 3.9.

Table 3.9 Catalytic activity for DIPE formation on various catalysts in presence and absence of propylene

Catalyst	**DIPE (% mol)**	
	Without propylene	**With propylene**
Phosphotungstic acid	18.0	26.9
H-zeolite-ß	21.0	29.0
H-ZSM-5	22.5	23.0

It is apparent that two different reaction pathways can take place in the presence of propylene. In the case of pure isopropanol bimolecular dehydration, the carbocations generated on the surface of the catalyst, can condense with another isopropanol molecule to give DIPE. Whereas in the presence of propylene, carbocation formed from propylene reacts with isopropanol in an alternate reaction path. Moreover, the kinetics of reaction can also vary considerably in the presence of propylene. In the case of pure isopropanol, the reaction is most probably governed by Langmuir-Hinshelwood type of mechanism. However isopropanol along with the presence of propylene both Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) mechanisms are operating.

3.3 CONCLUSION

Phosphotungstic acid is more active for the preparation of isopropanol compared to other zeolite and resin catalysts. In the hydration of propylene solvent increases 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. H-zeolite-ß catalyst was found to be more active than that of H-ZSM-5 catalyst for the poduction of DIPE from IPA in the vapour phase and DIPE formtion increases with increase in contact time and pressure. Zeolite catalysts (H-ZSM-5 and H-zeolite-β) were found to be less active than the heteropolyacid catalysts for liquid phase DIPE production. Among the zeolite catalysts H-zeolite-ß catalyst is more active than H-ZSM-5. The higher activity of H-zeolite-ß in comparison with H-ZSM-5 can be attributed to the larger pore size and milder acidic properties. Heteropolyacids namely, phosphotungstic, silicotungstic and phosphomolybdic acids were evaluated for DIPE production in liquid phase from isopropanol and phosphotungstic acid catalyst was found to be more active for DIPE formation compared to other heteropolyacid catalysts. Isopropanol containing propylene enhances the yield of DIPE compared to isopropanol without propylene over H-zeolite-β and phosphotunstic acid as catalyst.