CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

In the past decade, oxygenates have attracted attention from refineries as blending component for gasoline. Gasoline or petrol is a mixture of hydrocarbons (paraffins, aromatics and olefins) which is used as energy source in internal combustion engines. The gasoline is produced from crude petroleum by fractional distillation catalytic reforming and cracking (Scherzer *et al.*, 1989). The intricate characteristics of internal combustion engine requires efficient fuel system which can fulfill engine performance such as easy start up in cold, rapid warm up with smooth running, deliver the adequate power without knocking, good fuel economy and generate low exhaust emissions. However, IC engines with gasoline alone as fuel are not able to meet the requirements and environmental regulations due to incomplete combustion and preignition, which leads to knocking. Consequently, compounds like unburnt hydrocarbons (HC), CO and NO are produced from the engines, which are needed to be controlled to meet environmental regulations. To improve the efficiency of the gasoline, lead (tetraethyl lead and tetramethyl lead) and manganese based additives have been added to gasoline to prevent knocking and increase the octane number of gasoline. The poisoning effect on human health forced these metal based additives to be phased out form the gasoline pool. During late 1970s and early 1980s, oxygenates were used to offset the octane loss due to lead removal. Chemically, oxygenates are organic compounds which contain an oxygen atom in their structure. These compounds are combustible in nature which allows gasoline to burn completely. Though, the blending of oxygenates to gasoline results in decrease in the energy content of gasoline blend it assists in complete combustion of gasoline, thereby reducing the CO and 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). Oxygenated gasoline also meets the required product specification of gasoline like Reid vapor pressure (RVP), distillation temperature, boiling point and high blend octane number. The volatility of oxygenated gasoline is characterized by RVP. RVP of blended gasoline is directly correlated to the ability of a gasoline to operate an engine under both cold and hot start conditions. The typical value of Reid vapour pressure varies depending on the season. These are 13 PSI RVP in winter and 2.5 PSI RVP in summer. The volume of oxygenates required to be added to gasoline for optimum performance depends on the oxygen content of the desired oxygenates.

1.2 TYPES OF OXYGENATES

Several options are available to choose the appropriate oxygenate for gasoline blending. Refiners can choose the preferred oxygenate according to their requirement and infrastructure to get blend of oxygenates and gasoline. These oxygenates are basically low molecular weight alcohols and ethers. The blending properties and physical characteristics of oxygenates are significant for optimum performance of the blend. Some of the widely used oxygenates and their physicochemical properties are presented in Tables 1.1 and 1.2 respectively.

Table 1.1 Alcohol and ether based oxygenates used for blending with gasoline.

Alcohols	**Ethers**
Methanol	Methyl *tert* butyl ether(MTBE)
Ethanol	Tertiary amyl methyl ether (TAME)
Isopropanol	Ethyl *tert* butyl ether(ETBE)
Isobutyl alcohol	Tertiary amyl ethyl ether (TAEE)
Tertiary butyl alcohol	Isopropyl *tert* butyl ether (IPTBE
Tertiary amyl alcohol	Diisopropyl ether (DIPE)
	Other higher carbon ethers

Table 1.2 Physical and chemical properties of some of the alcohol and ether based oxygenates.

Property	Alcohols			Methanol based ethers		Ethanol based ethers		Isopropanol based ethers		
	Ethanol	Methanol	TBA	MTBE	TAME	ETBE	TAEE	IPA	IPTBE	DIPE
Molecular weight	46.07	32	74.12	88.15	102.18	102.18	85.5	60.09	120	102.18
Molecular formula	C_2H_5OH	CH_3OH	$C_4H_{10}O$	$C_5H_{12}O$		$C_6H_{14}O$	$C_7H_{16}O$	C_3H_8O	$C_7H_{16}O$	$C_6H_{14}O$
Boiling point (^OC)	78 ^0C	65 ^0C	71 ^0C	55 ^0C	86 ^0C	72 ^0C	102 ^0C	82 ^0C	-	68^0C
Vapor pressure @25C.mmHg	49.565	121.58	40-42	245-256	68.3	152	-	45.76	-	149-151
Weight % oxygen	34.7	50.0	21.6	18.2	15.7	15.7	13.8	26.3	13.5	15.7
HenrysLaw Constant(atm-m^3/mol)	5.13×10^{-6}	$4.42X\ 10^4$	$1.19x10^5$	$4.4\ X\ 10^{-4}$	$1.27\ X\ 10^{-3}$	$2.66\ X\ 10^{-3}$	-	$7.9X10^6$	-	$4.77\ X\ 10^{-3}$- $9.97X10^{-3}$
Water solubility (mg/l)	Infinitely soluble	Infinitely soluble	infinitely soluble	48,000	20,000	26,000	4000	infinitely soluble	-	9000
Log Koc	1.57	0.44	1.57	1.049	1.27 - 2.2	0.95-2.2	-	1.4	-	1.46-1.82
Log K_{ow}	-0.31	- 0.75	6.35	1.20	-	1.74	-	0.05	-	-
Specific Gravity	0.794	0.796	0.791	0.744	0.77	0.744	0.75	0.790	-	0.725
MON	96	92	95	101	99	102	95	98	-	105
RON	130	125	105	118	109	118	105	118	-	
RVP (PSI)	18.0	50-60	9.0	8.0	2.5	4.0	1.0	14.0	-	5.0

MON- Motor octane number, RON- Research octane number and RVP- Reid vapor pressure

Log Koc	-	Organic carbon sorption coefficient; partition coefficient of a contaminant in the organic fraction of soil; potential for adsorption to non-aqueous aquifer materials.
Log Kow	-	Octanol-water partition coefficient; measure of the degree to which an organic substance will preferentially dissolve in water or an organic solvent; measure of hydrophobicity of a compound,
Henry's Law Constant	-	Partitioning of a compound between water and air; measure of the volatilization from water,
Water Solubility	-	Concentration of a saturated solution; amount dissolved in water to make a saturated solution

1.3 ALCOHOLS AS OXYGENATES

Alcohols such as ethanol and methanol were recognized as octane boosters in 1920. Among alcohols, ethanol is known to be a preferred oxygenate due to its high octane number (115) and complete miscibility with gasoline. Ethanol has been blended with gasoline in 10 % volume and it is commercially known as "gasohol". 100 % ethanol (E100) and blend of 85 % volume ethanol mixed with 15 % volume gasoline (E85) have also been used (Jose *et al.*, 1998). The ethanol molecule contains 34.8 percent oxygen by weight; thus, ethanol is expected to provide less dilution in the blend. In addition to the favorable blending properties, the advantage of using ethanol as oxygenates also lie in its wide availability and easy production. Ethanol is produced from plants that harness sunlight; ethanol is also considered as a renewable fuel. In India ethanol is made by the fermentation of sugars. Earlier method of ethanol synthesis includes fermentation of fruit juices and vegetable matter. Fermentation of carbohydrates also gives rise to ethanol in commercial scale. The other route to prepare ethanol involves the hydration of ethylene over acid catalyst such as heteropoyacids. Methanol, tertiary butyl alcohol, tertiary amyl alcohol and isopropanol are other possible alcohols for gasoline blending (Lang and Palmer, 1989).

1.4 DISADVANTAGES OF ALCOHOLS AS OXYGENATES

Even though alcohols are known to possess high octane rating and are easily produced from renewable energy source, alcohols possess certain disadvantages which prevent their usage as oxygenates. The primary disadvantage of alcohols is their high water solubility and generally forms a separate phase with water. The consequence of the phase separation is that alcohol blended gasoline cannot be transported through pipelines for large distance. As a result alcohols can be blended with gasoline only at the terminals. The other problem associated with the alcohols is high blend RVP which leads to vapor lock in the engine (Jose *et al.*, 1998).

Similarly, methanol blended gasoline is more corrosive towards metals and accelerators. Adding methanol to gasoline significantly increases the vapor pressure of the blend and causes environmental pollution. The use of methanol blended fuel in non-catalyst equipped vehicles results in higher formaldehyde emission. Alternatively, blending the gasoline with *tert*-butyl alcohol (TBA) increases the volatility of the gasoline and so TBA cannot be employed as oxygenate. The disadvantages associated with alcohols limits possibility of using alcohol as oxygenates and research in refinery was focused on the alternative oxygenates.

1.5 TERTIARY ETHERS AND DIPE AS OXYGENATES

In search of alternate oxygenates to alcohols, Diisopropyl ether (DIPE) and tertiary ethers attracted attention due to their low water solubility and favourable blending properties. 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) are the possible ether candidates for gasoline blending. DIPE is one of the promising oxygenate for gasoline blending apart from tertiary alkyl ethers. The production of ethers involves addition of alcohols to olefins over acid catalysts. Based on the alcohol feedstock used for the production, ethers are classified into methanol based ethers, ethanol based ethers and isopropanol based ethers as shown in Fig. 1.1. The tertiary ethers and DIPE were prepared by employing solid acid catalysts namely zeolites, amberlyst resins, nafion, heteropolyacids and clay and the preparation was carried out either in liquid phase or in vapour phase. The structure and properties of these solid acids are given in detail in section 1.6. The production of oxygenates including ethers and alcohols are presented in Scheme 1.1.

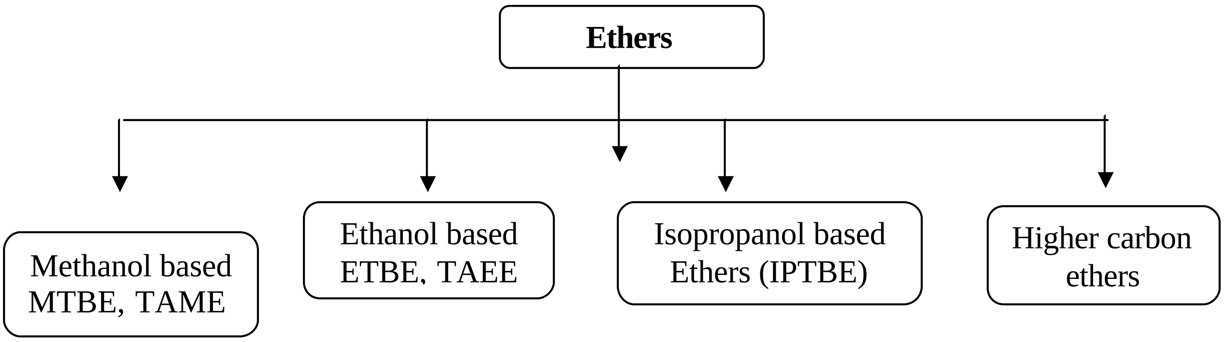
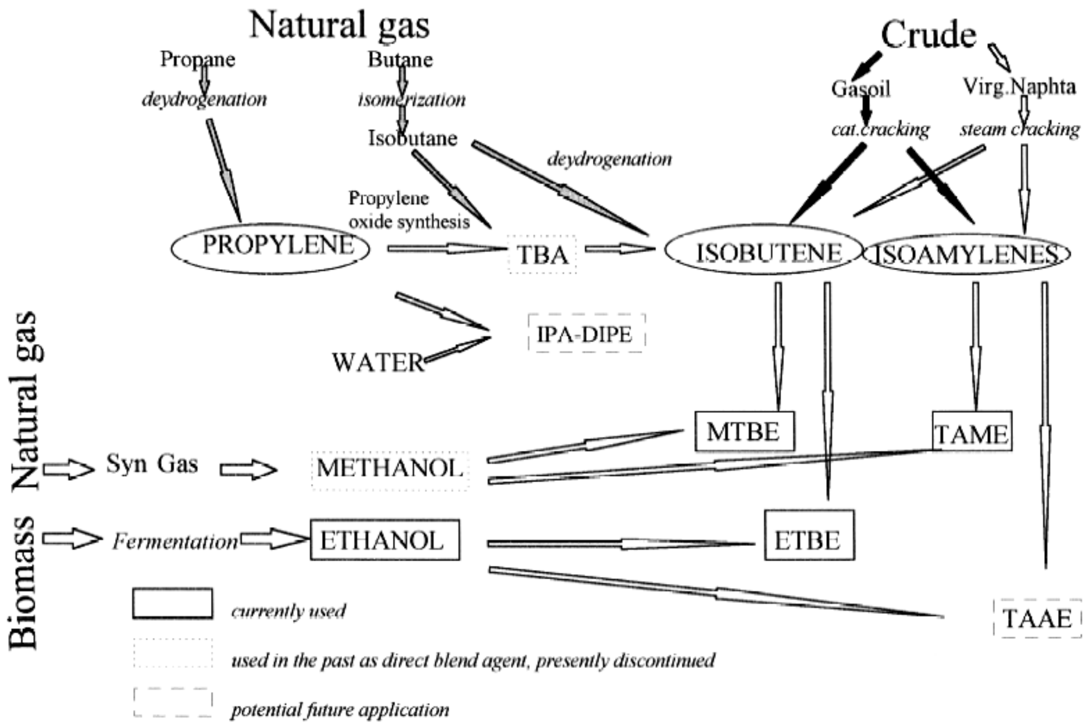


Fig. 1.1 Classification of ethers based on alcohol feed stocks



Scheme 1.1 Production of oxygenates

(Reproduced from *Fuel Processing Technology*, 57 (1998) 163)

1.6 CATALYTIC ASPECTS OF PRODUCTION OF TERTITARY ETHER AND DIISOPROPYL ETHER

Industrial production of ethers started as early as 1972 in Italy and the production increased remarkably. Tertiary alkyl ethers such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl ethyl ether (TAEE), tertiary amyl methyl ether (TAME) and isopropyl tertiary butyl ether (IPTBE) are generally prepared by the addition of alcohol to tertiary olefin, while diisopropyl ether (DIPE) can be prepared either from propylene feedstock or from acetone feedstock. Detailed investigations on the ether production were developed to understand the mechanism and the choice of the catalysts (Ancillotti and Fattore, 1998). Production of oxygenates over solid acid catalysts were investigated in detail due to their thermal stability, high catalytic activity and recyclability of solid acids.

Among solid acids, amberlyst resin was employed for commercial and industrial scale preparation; the other solid acids which were employed are zeolites and heteropolyacids. The physical and catalytic properties of amberlyst resin, zeolites and heteropolyacids are discussed in detail in consecutive sections.

1.6.1 Amberlyst resin as catalyst

Amberlyst resins are employed for the production of almost all the oxygenates in the industrial scale. Amberlyst resin is sulfonated polystyrene cross linked with divinyl benzene (DVB) and they are composed of gel like microsphere bonded at interface. The SO_3H groups attached to the polymer network are the active sites for catalytic activity (Dogu *et al.*, 2001). Polymerization route is preferred compared to poly condensation route for the preparation of ion exchange resin. The property of resin depends on the polymer backbone (styrene), bridging agents for cross linking (DVB) and type of active functional group (Marker *et al.*, 1994). The quantity of DVB can vary from 12 to 20 wt %, and it directly determines the degree of cross linking and the rigidness of the structure. More amount of DVB results in more rigidity and affords macroporous structure to the catalyst. The resins swell in polar solvents: those with less DVB swell more than the ones with more DVB. Alternatively, macroporous structures of resins were obtained by swelling the corresponding polymers in polar solvents during their synthesis (Marker *et al.*, 1995). The number of sulfonic acid group varied form 4.8 mmol/g (A-15) to 5.2 mmol/g (hypersulfonated A-35). The catalytic activity of the resins also correlated to the structure and polarity of the reaction medium (Corain *et al.*, 2001).

Other examples of resins are polymers from (i) DVB and acrylic acid, and (ii) phenol and formaldehyde. The properties of resins are varied by changing the ratios of monomers.

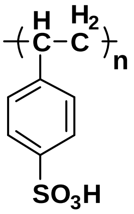
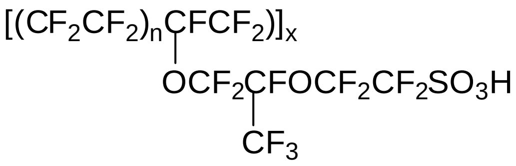


Fig.1.2 Structure of sulfonated polystyrene

Although ion exchange resins are good solid acid catalysts, their use as catalysts is limited by low thermal stability. The lower thermal stability of resins is overcome by chlorination of copolymer of styrene and DVB. The finished catalyst has high thermal stability compared to as prepared resins and the examples for the same are Amberlyst XN-1011, Amberlyst XE- 372 and Purolite CT-175.

1.6.2 Nafion as catalyst



$$[(CF_2CF_2)_n\underset{\substack{|\\ OCF_2\underset{\substack{|\\ CF_3}}{C}FOCF_2CF_2SO_3H}}{C}FCF_2)]_x$$

Fig. 1.3 Structure of nafion

Nafion is perfluorinated sulfonic acid resin obtained by copolymerization of tetrafluoroethylene and perfluoro-2-(fluorosulfonylethoxy)propylvinyl ether followed by hydrolysis with sulfonyl fluoride which yields the strongly acidic terminal –$CF_2CF_2SO_3H$ group as shown in Fig. 1.3. The equivalent weight of the polymer is typically about 1070. Unlike Amberlyst resins, nafion resin is both chemically and thermally stable up to 280 °C (Olah *et al.*, 1989). Nafion resins are stronger acids compared to amberlyst resin, but have five times less number of active sites compared to amberlyst resins.

1.6.3 Heteropolyacids as catalyst

Polyoxometallates are compounds of elements of groups 5 and 6 of the periodic table, mostly molybdenum, tungsten and vanadium, in their highest degree of oxidation. They are characterized by complex anions with composition schematically expressed as $[X_xM_mO_y]^{n-}$ (M = Mo, W, V; $m > x$). When x = 0, the species are isopolymetalates and for x > 0, they are heteropolymetalates. Almost all elements can be incorporated as heteroatom in their structure though P or Si is mostly employed for this purpose. Among various heteropoly anions (Table 1.3), Keggin type anion (Fig. 1.4) was investigated for most of the catalytic applications partly due to the easy synthesis over other structures.

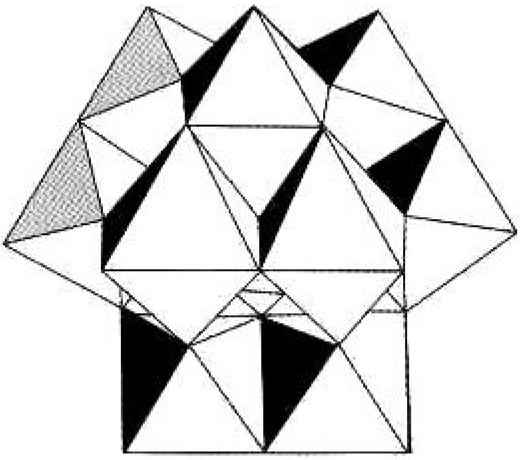


Fig. 1.4 Structure of Keggin anion

Heteropolyacids (HPA) are suitable materials for catalyst design, because of following features: (1) acidic and redox properties of HPA can be controlled by choosing the constituent elements of anions and counter anions, (2) the HPAs provide unique reaction fields such as pseudoliquid phase and have ability for complex formation to stabilize reaction intermediates, and (3) structures can be better defined at the molecular level to prepare tailor made catalysts (Mizuno and Misono, 1994).

Table 1.3 Various types of heteropolyanions

Structure	Formula	Negative charge	X^{n+}
Keggin	$XM_{12}O_{40}$	8-n	P^{5+}, As^{5}, Si^{4+}, Ge^{4+}, C^{4+}
Silverton	$XM_{12}O_{42}$	8	Ce^{4+}, Th^{4+}
Keggin-like (lacunary)	$XM_{11}O_{39}$	12-n	P^{5+}, As^{5+}, Ge^{4+}
Dawson	$X_2M_{18}O_{62}$	6	P^{5+}, As^{5+}
Waugh	XM_9O_{32}	6	Mn^{4+}, Ni^{4+}
Anderson (type A)	XM_6O_{24}	12-n	Te^{6+}, I^{7+}

Keggin-type heteropolyacids are essentially completely dissociated in aqueous solution and the dissociation is often stepwise in organic media. The acidity of HPA is higher than that of the oxoacids of constituent elements and mineral acids. The acidic properties of heteropoly compounds in the solid state are very sensitive to counter cations as well as constituent elements of polyanions. In the case of metal salts of HPAs, five mechanisms are possible for the origin of acidity: (1) protons in the acidic salts, (2) partial hydrolysis during the preparation process, (3) acidic dissociation of coordinated water, (4) Lewis acidity of metal ions, and (5) protons formed by the reduction of metal ions (Misono, 1987). Heteropolyacids are potential and promising catalysts in various acid catalyzed organic reactions because of their unique physicochemical properties. The acidic behavior of HPA catalyzed reactions depends mainly on the acidity of HPA, structure of heteropoly anion and type of reaction (nature of reagents). Bulk and supported HPAs are widely exploited for liquid- and gas-phase reactions. In heterogeneous as well as homogeneous conditions HPAs are more effective than conventional catalysts such as SiO_2–Al_2O_3 and zeolites. Bulk and supported $H_6P_2W_{18}O_{62}$, $H_6P_2W_{21}O_{71}$, $H_{21}B_3W_{39}O_{13}$ and keggin type of acids were employed as catalysts for the production of methyl *tert* butyl ether (MTBE) and alkylation of isobutene (Baronetti *et al.*, 1998; Shikata *et al.*, 1995). Hydration of nitriles, hydration of alkynes, and hydration of epoxides are the other reactions catalyzed by heteropolyacids (Izumi *et al.*, 1997).

Heteroployacids (Keggin, Dawson and Silvertone type of heteropolyacids) were employed as potential alternative to the Amberlyst resin catalysts for the production of oxygenates. In order to tune and increase the catalytic activity, these acids were dispersed on the matrices like MCM-41, silica, alumina, titania and SBA-15. The dispersion influences to increase the stability and activity of heteropolyacids.

Heteropolyacid catalysts were demonstrated mostly for MTBE production compared to other oxygenates.

1.6.4 Zeolites as catalyst

Zeolites belong to microporous material which display pore size with diameter less than 20 Å. They play a dominant role in heterogeneous catalysis besides ion-exchange applications, sorption and molecular sieve applications. Zeolites are classified on the basis of either pore opening size or Si/Al ratio. Based on the pore opening, zeolites are classified into four types namely small pore (8 member ring), medium pore (10 member ring), large pore (12 member ring), and ultra-large pore (14 or more member ring). According to Si/Al ratio zeolites are classified into three types such as low silica, high silica and all silica.

Two categories of zeolites namely, the intermediate and large pore zeolites are useful as catalysts for olefin conversion and etherification reactions. These zeolites are selected based on their constraint index. Constraint index is the ratio of cracking rate constant for n-hexane and 3-methyl pentane under identical conditions. To measure the constraint index, reactions are generally carried out in the temperature range of 288 K - 510 K and liquid hour space velocity (LHSV) of 1 to give an overall conversion in the range of 10 to 60 %. Constraint index for different zeolites catalyst varies in the range 1-12. For example H-ZSM-5, which possesses a constraint index of greater than 2 is suitable for olefin hydration. Similarly, large pore zeolites such as H-zeolite-Y and H-zeolite-β, with constraint index less than 2 are suitable for etherification reaction. Both varieties of zeolites contain a framework Si/Al ratio of greater than 7. Typical values of constraint index of various zeolites catalyst are given in Table 1.4.

Table 1.4 Constraint indexes of some of the zeolites

Zeolites	Constraint index	Zeolites	Constraint index
H-ZSM-5	8.3	TMA offretite	3.7
H-ZSM-11	8.7	H-zeolite-β	0.6
H-ZSM-11	2	H-ZSM-4	0.5
H-ZSM-38	2	Synthetic mordenite	0.5
H-ZSM-35	4.5	REY	0.4
Amorphous silica alumina	0.6	-	-

The other important property which is necessary for the etherification reaction is acidity. The acidity of zeolites is measured by alpha values. Alpha value is the relative rate constant for n-hexane cracking activity with reference to highly active conventional amorphous SiO_2-Al_2O_3 (surface area 420 m^2/g) which is assigned an α value of 1 (Weisz and Miale, 1965). Most of the zeolites possess an alpha value around 1. It has been observed that composite of zeolites, in which they are bound to catalytically active or inactive materials such as alumina or silica exhibit high stability under the olefin conversion conditions. Large pore acidic zeolites such as H-zeolite-β, X, L, Y, USY, REY, Deal-Y, H-ZSM-3, H-ZSM-4, H-ZSM-12, H-ZSM-20 and H-ZSM-50 are various examples of catalysts which have been used for etherification reactions.

1.7 ETHYL TERTIARY BUTYL ETHER (ETBE) AS OXYGENATE

In recent years, ethyl tertiary butyl ether (ETBE) has been identified as a potential alternate to MTBE. The main advantage of using ETBE as oxygenate is that it can be produced easily in the existing MTBE process plants. ETBE has a lower Blend Reid Vapor Pressure (BRVP) (4 psi) than MTBE (8-10 psi) and higher octane number.

One of the feedstocks for ETBE production is renewable source namely ethanol and hence ETBE production can create the additional market for grain based products and agricultural waste and this option is more viable for countries like India. Commercial production of ETBE has been carried out in liquid phase over ion exchange resin in the temperature range of 323 K - 343 K and pressure of 10-15 bar. It has been observed that at higher temperatures and above stochiometric amount of reactants, byproducts namely diisobutene and diethyl ether are formed. Water if present in the reaction medium promotes the formation of TBA, hence the ethanol which is used as feedstock should be highly pure and free from water. Production of ETBE in homogeneous phase from TBA and hot compressed ethanol was performed over sulfuric acid at 3 MPa and 433 K. Cation exchange resins in the form of pellets and particles were used as catalysts for the production of ETBE from TBA and ethanol. The results showed that pellets were less active than resin particles and the decrease in activity is attributed to the shielding of reactants by binder which was used during the preparation of resin. Comparison of catalytic activities of resins has been reported by employing A-15, S-54 and D-72 on the basis of activation energies (Christine *et al.*, 1997). The observed results concluded that D-72 has a higher level of activity and S-54 has a higher level of the selectivity and lower effect of water inhibition for the production of ETBE. A Comparison of catalytic activity of monolith supported H-zeolite-β with A-15 was studied in liquid phase. A lower activity was observed for H-zeolite-β catalyst compared to the resin, however, the H-zeolite-β catalyst showed higher selectivity towards ETBE than A-15 resin (Assabumrungrat *et al.*, 2002). Francoisse and Thyrion (1991) have studied the kinetics of ETBE formation in liquid phase over A-15 catalyst. The reaction was performed in the temperature range of 323 K - 363 K and pressure of 2 MPa (Francoisse and Thyrion, 1991). The experimental kinetic data were compared with theoretical calculations (UNIFAC method). The reaction mechanism and kinetic modeling have been proposed based on the results obtained. Iborra and coworkers (1989) have calculated the equilibrium constants for the vapor phase synthesis of ETBE over A-15 resin in the temperature range of 319 K - 373 K (Iborra *et al.*, 1989). Collignon and Poncelet (2001) have studied the catalytic activity for vapor phase synthesis of ETBE from isobutene and ethanol by employing zeolites such as H-zeolite-β, USY, H-ZSM-5, H-mordenite and A-15. The reaction yield was found to increase with temperature, passed through a maximum and decreased thereafter. They have observed that the order of reactivity among the zeolites is H-zeolite-β > USY≥ H-mordenite > H-ZSM-5 (Collignon and Poncelet, 2001). The higher activity of H-zeolite-β has been attributed to high hydroxyl content and a large external surface area of the catalyst. Knifton and Dai (1995) have employed H-zeolite-β and Fe-Cr-Mn/H-zeolite-β for the synthesis of ETBE from TBA and ethanol in the temperature range of 393 K - 433 K and 300 psi. They have observed that conversion of TBA increases with temperature whereas selectivity decreases due to byproduct formation. The yield of ETBE was found to remain constant for a period of 43 h (Knifton and Dai, 1995). Gas phase synthesis of ETBE over A-15, A-35, H-ZSM-5(60), and S-115 at pressure of 200 - 300 psi have been studied in the temperature range of 333 K - 373 K. Among the examined catalysts H-ZSM-5 was found to be more active and selective than A-15 and A-35. It was proposed that the reaction involves an Eley Rideal type mechanism where adsorbed carbocation reacts with gas phase ethanol. Pozniczek *et al*, (2005) have studied the catalytic activity of Dawson type heteropolyacids for the synthesis of ETBE in the temperatures range of 308 K - 353 K in vapour phase (Pozniczek *et al.*, 2005**)**. Conversion of ETBE was found to stabilize after 30 min with a conversion of

44 mol % which is maintained for a period of 9 h. An increase in temperature was found to increase the conversion up to 298 K whereas at higher temperatures conversion decreased due to the exothermic nature of the reaction. The influence of water on conversion has been studied by varying the water content of the medium at 0.25 %, 0.32 % and 4.4 %. The results show that feed containing 4.4 % water content gives higher conversion with high selectivity. Park *et al,* (2002) have attempted to study the catalytic properties of heteropolyacid-polymer composite for vapor phase synthesis of ETBE from isobutene and ethanol in comparison with pure heteropolyacids (Park *et al.,* 2002). The $H_3PMo_{12}O_{40}$/polysulfone and $H_3PMo_{12}O_{40}$/polyphenylene oxide composite film catalysts were examined for this purpose. An enhanced activity was observed for the composite catalyst compared to pure $H_3PMo_{12}O_{40}$. The enhancement in activity has been ascertained to the uniform dispersion of heteropolyacid on polymer matrix. New class of PMo-polymer composite catalysts namely PMo-PPO-EC and PMo-PSF-EC, formed from PSF (polysulfone) or PPO (polyphenylene oxide; poly-2,6-dimethyl-1,4-phenylene oxide) in a mixed solvent of ethanol(E)–chloroform(C) were employed as catalysts for the vapor phase synthesis of ETBE. The catalytic activity of these materials were in the following order; $H_3PMo_{12}O_{40}$-PPO-EC > $H_3PMo_{12}O_{40}$-PSF-EC > bulk $H_3PMo_{12}O_{40}$ (Lim *et al.*, 2002). It was revealed that the residual ethanol in the composite film played an important role to improve and maintain the catalytic activities of these composite film catalysts. Composite catalyst formed from PPO exhibited a higher activity compared to the PMo-PSF composite which is attributed to the high absorption capability of PPO ingredient for isobutene. Larsen investigated the catalytic activity of H-mordenite which is a large pore zeolite for gas phase synthesis of ETBE from isobutene and ethanol in the range of 313 K - 363 K and atmospheric

pressure. The order of the reaction was found to be 0.8 with respect to isobutene and - 0.8 with respect to ethanol. The activation energy was found to be 82 kJ/mol (Larsen *et al*., 1995).

1.8 TERTIARY AMYL ETHYL ETHER (TAEE) AS OXYGENATE

Tert-amyl ethyl ether (TAEE) is considered as a potential and attractive oxygenate for gasoline blending due its high octane number and low volatility. TAEE improves the burning characteristics of fuel which results in less CO and unburnt HC emissions. TAEE is produced by reacting C_5-isoolefins (isoamylene (IA)) such as 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B) with ethanol over acidic macro reticular resin catalysts such as A-15. Isomerisation of isoamylene and diethyl ether formation are other reactions possible in this process. Apart from these products, TAA is also formed in lower amount. Among the two isomers of IA namely 2M2B and 2M1B, the reactivity of 2M2B is higher compared to that of the other isomer. Alternatively TAEE is synthesized by acid catalysed reaction of TAA and ethanol which involves dehydration of TAA to isoamylene (IA) as the side reaction. The byproduct IA can undergo further etherification with ethanol to afford TAEE (Boz *et al.*, 2005). Kinetics and thermodynamic study of TAEE formation reveals that the reaction is limited by chemical equilibrium which is due the inhibiting effect of water and dehydration of isoamylene. Langmuir–Hinshelwood type rate model has been proposed for the formation of TAEE from isoolefin and alcohol over Amberlyst resins. The reaction takes place between adsorbed alcohols and isoolefins on the acidic sites of resins. Rideal–Eley type mechanisms involving adsorbed alcohol molecules and fluid phase isoolefins were also proposed for the formation of TAEE (Rihko and Krause, 1995). Dogu *et al*, (2001) and Boz et *al*, (2005) have studied the mechanism of the ether formation using DRIFT (diffuse reflectance FT-IR) spectroscopy. Their results support the Langmuir–Hinshelwood type rate models based on the IR characteristics of the adsorbed species. The reaction kinetics of etherification has also been studied in the temperature range of 323 K - 358 K in a CSTR with ethanol/olefin ratio of 0.3-3 at 0.8 MPa over A-16 (Dogu *et al.*, 2001; Boz *et al.*, 2005). The kinetic measurement shows that equilibrium constants for etherification decrease as a function of temperature. The calculated enthalpy and entropy of the reaction are 34.3 kJ/deg/mol and 81.8 kJ/deg/mol, respectively. The effect of ion exchange capacity on the production of TAEE in the temperature range of 333 K - 370 K has been studied for heattreated A-15, lab synthesized A-15 and commercial A-15. It has been observed that catalytic activity increases as a function of temperature and among the catalysts laboratory synthesized A-15 with the capacity of 2.8 meq H^+/g showed highest activity for TAEE synthesis. The conversion of 2M2B to TAEE linearly increases with the ion exchange capacity. Three reversible reactions that occur simultaneously in TAEE production are etherification of 2M1B to TAEE, etherification of 2M2B to TAEE and isomerisation between 2M1B and 2M2B. Thermodynamics of TAEE formation along with the isomerisation was studied by Kitchaiya and Data (1995). These authors have calculated the values of equilibrium constants as a function of temperature from which reaction parameters such as $-\Delta G^o$ and $-\Delta H^o$ are obtained. Their results suggest that at low temperatures, isoolefin /ethanol ratio along with less amount of an inert solvent enhance the yield of TAEE. Rihko *et al,* (1994) have calculated the value of equilibrium constant for liquid phase synthesis of TAEE from 2M1B and 2M2B over A-16 at 0.7 MPa in the temperature range of 323 K to 363 K and the equilibrium constant found to be 17.4 ± 1.1 for TAEE from ethanol and 2M1B and 1.7 ± 0.1 from ethanol and 2M2B (Rihko *et al.*, 1994). Equilibrium constant values obtained from experiment and theoretical calculation are found to be in good agreement with one another. Kinetics of the etherification from isoamylene and ethanol was also studied by Linnekoski in 1997 over A-16 W in the 323 K - 363 K range at 0.7 MPa. Kinetic experiments were done in solution at a stirring speed of 17 s^{-1} with average particle size range of 0.35- 0.65 µm to avoid external and internal mass transfer. The reaction data were analyzed by these authors by adopting three models namely pseudohomogeneous model, Eley - Rideal type model and Langmuir - Hinshelwood model to explain the formation of TAEE. Langmuir - Hinshelwood type model which describes the activation energy within the range of etherification reaction was found to be close to the values reported in literature and hence among various models studied, they proposed the LH model for this etherification reaction. The effect of sorption of reactants on the TAEE synthesis from TAA and ethanol has also been evaluated by employing A-15 catalyst in the batch reactor at 323 K - 353 K and a pressure of 0.8 MPa. In this study, sorption of reactants was carried out at non reactive conditions at a temperature of 278 K for 1 h. The experimental data show that the steady state reaches within 2 min. The water sorption is found to be strong in this catalyst and TAEE, IA sorption is very weak in nature while TAA, ethanol exhibit intermediate sorption. Theoretical calculation using UNIFAC reveals that water-polymer (A-15) interaction is more compared to other molecules. In case of ethanol, ethanol-polymer interaction is more and ethanol - TAA interaction is weak. Similarly polymer interacts with TAA more compared to TAEE and IA (Linnekoski *et al*., 1997).

1.9 TERTIARY AMYL METHYL ETHER (TAME) AS OXYGENATE

TAME is considered to a be a preferred oxygenate in gasoline pool because it behaves more like conventional hydrocarbons in terms of physical properties such as favorable vapor pressure, boiling point, energy density and phase separation when blended with gasoline pool. TAME contributes to meet three important requirements of reformulated gasoline namely high oxygen content, reduction in volatility and removal of highly volatile and photochemically reactive olefin which leads to complete combustion. Industrial synthesis of TAME involves a liquid phase reaction of methanol (MeOH) and isoamylene (IA) over sulfonated ion exchange resin (Amberlyst 15) in the temperature range of 313 K - 373 K (Kerry, 1992). IA used in this process is obtained from Fluid Catalytic Cracking unit (FCC) which is a mixture of 2-methyl-1-butene (2M1B), 2- methyl-2-butene (2M2B) and 3-methyl-1-butene (3M1B). Among these isoolefins, 2M2B, 2M1B are active and 3M1B is inactive for etherification. During formation of TAME, isomerisation among the isoolefins takes place simultaneously. TAME synthesis occurs by electrophilic addition of methanol to carbocation intermediate, the rate determining step being the protonation of isoamylene. This is well supported by kinetic and thermodynamic data. During the reaction MeOH acts as a protic solvent above the molar ratio of MeOH/Isoamylene =1.

Side products such as dimethyl ether (DME), dimers of isoolefin and *tert*-amyl alcohol (by hydration of isoamylene if water is present in the reactor system) are formed along with TAME at high temperatures. Various types of resins which differ in ion exchange capacity and surface area values have been employed for TAME synthesis. The catalysts used for etherification include A-15, A-16, A-35, Dowex, Lewatit SPC-118, Lewatit SPC-108 and nafion. Alternatively, TAME can also be prepared from methanol and *tert*-amyl alcohol (TAA) over solid acids. Recently, a new type of catalyst, namely UDCaT was developed which is prepared from HMS and chlorosulfonic acid at 393 K for this purpose. This investigation has demonstrated the influence of experimental parameters such as temperature, reactant partial pressure, space time and mass transfer in detail and the catalytic activity of the desired catalyst was compared with other industrial catalysts such as A-15, sulfated-zirconia, HMS and UDCaT-5. Comparison of catalytic activity in the rate of formation TAME has also been studied by employing ion-exchange resin beads (A-16, A-35 and XE-586) and fibrous catalysts. The temperature for these catalysts was varied in the range of 323 K - 353 K with stoichiometric amount of reactants in a continuous stirred tank reactor (CSTR) at a pressure of 0.7 MPa. Among the catalysts employed A-35 is found to be more active compared to other catalysts (Yadav and Murkute, 2004). Catalytic activity of bentonite has also been studied for the synthesis of TAME in the temperature range of 343 K - 373 K and at a pressure of 400 kPa. The activity of bentonite was found to be better than that of resins. Besides the heterogeneous synthesis (Fleitas *et al.*, 1991), Guttmann *et al*, *(*1981) have demonstrated TAME synthesis under homogeneous conditions from isoamylene with methanol (1:1) over 0.5 wt % $H_4SiMo_{12}O_{40}.XH_2O$ at 408 K (Guttmann *et al.*, 1981). They observed that the conversion of isoamylene and methanol were 34.4 % and 28.4% respectively and the yield of TAME as 28.2 % with selectivity of 80.2 %.

Synthesis of TAME is exothermic in nature and hence it is limited by thermodynamic equilibrium at higher temperatures. Investigation and measurement of reaction equlibria are important from which one can calculate equilibrium constant and enthalpy. Randriamahefa and coworkers in 1988 investigated the kinetics of TAME synthesis in the temperature range of 328 K - 363 K by calculating the equilibrium constants as a function of temperature, enthalpy of formation and activation energy. They observed that the equilibrium constant decreases as the temperature increases. The enthalpy and activation energy values were found to be - 41.17 kJ/mol and 81.09 kJ/mol respectively (Randriamahefa *et al.*, 1988). Rihko *et a,* (1994) investigated the reaction equlibria and measured the equilibrium constant and enthalpy of formation for liquid phase synthesis of TAME over Amberlyst-16. The experimental values of equilibrium constants are found to be higher than that calculated by these authors which is due to influence of enthalpy of formation on equilibrium (Rihko *et al.,* 1994*).* Oktar *et al* (1999) have calculated the adsorption equilibrium constants for TAME formation using A-15 catalyst from packed bed movement technique in the temperature range of 323 K - 373 K. These authors showed that equilibrium constants for adsorption of alcohols were two orders of magnitude higher than that of isoamylene and ethers and their heats of adsorption are lower than isoamylene. Among the two isoamylenes, heat of adsorption and reactivity of 2M2B are higher than those of 2M1B (Oktar *et al.*, 1999). Since the formation of TAME is limited by thermodynamic equilibrium, few investigations focused on the confirmation of thermodynamic equilibrium. In this regard Krause et al have verified the thermodynamic equilibrium as a function of temperature over Amberlyst-15. Rihko and Krause (1996) have studied the equilibrium limitations as a function of space velocity in the temperature range of 333 K - 353 K and they observed that there is no change in conversion above 333 K due to limitation by thermodynamic equilibrium (Rihko and Krause, 1996). Syed *et al,* (2000) investigated the equilibrium and equilibrium constant for TAME production in the temperature range of 298 K - 363

K. The equilibrium conversion decreased as temperature increased which are in agreement with the results reported earlier (Syed *et al*., 2000).

A detailed kinetic study of TAME formation has been investigated in which the effect of experimental variables such as pressure, temperature, internal and external mass transfer of reactants, reactant concentration and space time on TAME formation was studied. Kinetic equations derived for three different mechanisms were compared. In the forward reaction the adsorbed methanol reacts with isoamylene (2-methyl-1-butene or 2-methyl-2-butene) present in the bulk liquid phase. In the reverse reaction the adsorbed ether split to corresponding alcohol and isoamylene. Rihko *et al*, (1997) have investigated TAME formation from methanol and isoamylene in a batch reactor, using an ion-exchange resin (Amberlyst-16) as catalyst in order to derive kinetic modeling of the reaction in the temperature range of 333 K and 353 K. The experimental results were best described by kinetic equations. The investigators proposed a reaction mechanism where the alcohols and the ether adsorbed on the catalyst surface and the isoamylenes reacted from the bulk liquid phase which is in good agreement with modeling results (Rihko *et al.*,1997) Kiviranta *et al*, (1998) have proposed a mechanism along with kinetic modeling for the liquid phase synthesis of TAME at 322 K - 353 K and 0.8 MPa using UNIFAC method in which reaction between adsorbed alcohol and liquid phase olefin leads to the formation of TAME. A Langmuir-Hinshelwood-Hougen-Watson mechanism was also proposed for the TAME formation in which the rate controlling step is the surface reaction. Experimental results confirmed that methanol adsorbs strongly on the active sites, covering them completely and thus the reaction follows an apparent first-order with respect to methanol. Isoamylene, adsorbs simultaneously on the same single active center already occupied by methanol, migrating through the liquid layer formed by the alcohol around the catalyst to react in the acidic site (Kiviranta *et al.*,1998). Kinetic modeling for TAME formation and activation energy measurements have been carried over SMOPEX-101 as catalyst. TAME follows dual site L-H mechnaim at stoichiometric conditions which is confirmed from inversely related rate with respect of square root of acidity. For the catalyst the activation energy was found to be 93.7 kJ /mole which is higher than that of A-16 catalyst (Paakkoene and Krause, 2003)

1.10 METHYL *TERT*-BUTYL ETHER (MTBE) AS OXYGENATE

MTBE has been widely used as oxygenates for gasoline blending because of its good anti knocking properties and outstanding physical properties like volatility, miscibility with gasoline, storage stability and reduction in hazardous emission (Piel and Thomas, 1990). Since investment, operating cost and energy consumption are lower for MTBE synthesis, industrial production is more economical (Subramaniam and Bhatia, 1987).

Commercial production of MTBE involves the liquid phase reaction of methanol and isobutene over sulfonated ion exchange resin at low temperatures (303 K - 373 K) and moderately low pressures (up to 2.0 Mpa).

1.10.1 Resin as catalysts for MTBE synthesis

Amberlyst resins are very active for the production of MTBE. Ancillotti *et al*, (1977) investigated in detail the addition of alcohols to tertiary olefins catalyzed by a macroporous sulfonic acid resin. The initial rate calculated showed zero order with respect to methanol and first order with respect to isobutene. They have proposed an ionic mechanism based on experiments wherein the protonation of the olefin by the solvated proton is the rate determining step at stoichiometric or higher methanol/isobutene ratio. When the ratio of methanol/isobutene (R) decreases from 0.5- 0.1, it was observed that initial rate increased and reached the maximum at R = 0.1. At R< 0.1, the rate was zero order with respect to isobutene and first order with respect to methanol (Ancillotti *et al.*, 1977). Subramanian and Bhatia (1987) studied the influence of the experimental parameters such as catalyst loading, particle size and temperature on the reaction rate over A-15 resin in the temperature range of 313 K - 328 K in liquid phase. They observed that the conversion increases with catalyst loading and temperature with a maximum MTBE selectivity of 98 %. They also studied the kinetics of the reaction and developed both homogeneous and heterogeneous model and proposed LH mechanism for the reaction based on heterogeneous model (Subramanian and Bhatia, 1987). Ali and Bhatia (1990) have studied the kinetics and modeling of MTBE by employing A-15 as catalyst in the temperature range of 328 K - 348 K in a fixed bed reactor. However, they found that kinetic data well fitted with Langmuir-Hinselwood–Hougen-Watson (LHHW) rate model (Ali and Bhatia, 1990). Parra and coworkers (1998) have investigated kinetics of MTBE formation over Bayer catalyst K-2631 by employing differential reactor at 1.5 MPa. They proposed the Eley-Rideal mechanism for the formation of MTBE (Parra *et al.*, 1998)

Tejero *et al*, (1989) have studied the influence of the pressure and kinetics of the reaction in vapor phase over A-15 resin. They have studied rate in terms of reactant pressure and observed that rate increases with pressure of isobutene at constant pressure of methanol whereas the rate decreases with the methanol pressure at constant pressure of isobutene. They have proposed LHHW mechanisms for the MTBE formation (Tejero *et al.*, 1989). Gicquel and Torck (1983) have studied the influence of methanol concentration and temperature on MTBE formation over ion exchange resin in the temperature range of 323 K – 365 K and these authors proposed the LH model for MTBE synthesis over ion exchange resin and calculated the energy of activation as 82.0±6.7 kJ/mol (Gicquel and Torck, 1983). Anicillo *et al*, (1977) found negative order for methanol, first order for isobutene and third order for acidic group for the reaction with methanol concentration [CH_3OH] > 4mol/l. They have employed A-15 as catalyst in the temperature range of 333 K - 353 K and calculated activation energy as 71 kJ/mol (Anicillo *et al.*, 1977). Rehfinger and Hoffman (1990) have proposed the LH mechanism for MTBE production employing CSTR in the temperature range of 323 K - 363 K and a pressure of 2.0 MPa over A-15 and CVT resin catalyst and calculated Ea as 82.4 kJ/mol (Rehfinger and Hoffman, 1990). Zhang and Datta (1995) have investigated the kinetics of the liquid phase synthesis of MTBE in isothermal integral packed-bed reactor over a commercial ion exchange resin catalyst (Amberlyst-15). The intrinsic kinetics was determined under conditions which are free of diffusional influence. The activation energy of 85.4 kJ/mol, is found to be average of those reported in the literature (Zhang and Datta, 1995).

Tejero *et al*, (1996) have proposed two mechanisms namely LH and ER type for MTBE synthesis over Amberlyst resin catalyst. In the ER type mechanism, methanol bonded to the network of sulfonic acid group by hydrogen bonding react with isobutene in solution. Whereas in LH mechanisms methanol and isobutene are immobilized on the SO_3H group and reacts with each other. They have observed that the key step in both type of mechanism is the formation of cyclic intermediate in which three SO_3H groups enable concerted proton transfer. It was observed that ER mechanism operates at large excess of methanol and LH operates at lower methanol concentration. In intermediate concentrations of methanol, both the mechanisms coexist and cooperate to the reaction (Tejero *et al*., 1996).

Caetano and co-workers (1994) investigated the kinetics of liquid phase synthesis in batch mode over the A-18 catalyst in the temperature range of 323 K - 328 K and pressure of 0.8-1.0 MPa. They have proposed ER type mechanism to determine the kinetic parameter using homogeneous and heterogeneous model. In homogeneous model, reactant concentration was uniform throughout the system whereas non ideality was taken into the consideration in heterogeneous model. The comparison of both models does not show much difference. The activation energy calculated based on these models indicate that homogeneous model shows 25 % larger value of E_a compared to heterogeneous model(Caetano *et al*.,1994).

Tejero *et al*, (1988) have determined the equilibrium constant of MTBE formation experimentally over continuous flow atmospheric reactor by employing the A-15 as catalyst. They have also evaluated the thermodynamic parameters such as ΔH, ΔS and ΔG from equilibrium constant variation with respect to temperature in the range of 313-383 K (Tejero *et al*., 1988). Izquierdo *et al*, (1994) have calculated the equilibrium constant experimentally for MTBE formation in liquid phase using C4 olefin cut in the temperature range of 313 K - 353 K and at 1.6 MPa over the acidic resin K-2631 catalyst. They used the reactant ratio of methanol/isobutene in the range of 0.92-1.14 and also calculated standard enthalpy of formation both theoretically and experimentally which correlate with literature values (Izquierdo *et al*., 1994). Fite *et al*, (1998) have evaluated the influence of reaction medium and kinetics of the MTBE formation over Bayer K-2631 in the temperature range of 318 K - 363 K at 1.6 MPa. Rate of the reaction was found to increase with concentration of methanol and decrease with isobutene. The concentration of C4 olefin influences to decrease the rate of the reaction which is due to the fact that n-butene in feed collapses the structure of the catalyst. They also studied the influence of the polarity of the medium on reaction rate. When the reaction medium is highly polar it affects the catalytic behavior by breaking the hydrogen bond network. This makes the acid sites accessible to the reactant which results in the rate enhancement. At the same time polar molecules solvate the proton and decrease the acidity that results in the lower reaction rate (Fite *et al*., 1998).

Vila *et al*, (1994) studied the byproduct formation along with MTBE synthesis over Lewatit K - 2631 resins. The influence of dimethyl ether and diisobutene was studied over the temperature range of 323 K - 355 K in the methanol/isobutene ratio of 1-3.5. It has been observed that byproduct formation is predominant at high temperature. Methanol/isobutene ratio higher than stoichiometric amount favors the MTBE formation (Vila *et al*., 1994). Sundmacher and Hoffman (1992) developed microkinetic model for the liquid phase synthesis of MTBE in the temperature range of 333 K - 363 K at 2.1 MPa employing CVT resin. Based on the experimental results, LH mechanism was proposed (Sundmacher and Hoffman, 1992).

1.10.2 Zeolites as catalysts for MTBE synthesis

Low temperature requirement for higher conversion, sensitivity to methanol/isobutene ratio (stoichiometric amount), limited conversion and lifetime of 2 years are the major disadvantages when ion exchange resins are employed as catalyst. This motivated researcher to design an alternative catalyst for the MTBE production (Takezono and Fujiwara, 1980). Zeolites are a class of inorganic solid acids and considered as potential alternative to ion exchange resin. Zeolites have been employed as catalysts for MTBE synthesis both in liquid and gas phase. Mobil Oil Corporation in 1989 investigated the catalytic activity of zeolites namely H-zeolite-β, H-ZSM-5, H-ZSM-11, rare earth exchanged zeolite-Y and H-mordenite for the production of MTBE in vapor phase. H-ZSM-5 and H-ZSM-11 show higher conversion with high selectivity compared to other zeolites which is attributed to difference in diffusion rate of reactants within the zeolites (Harandi and Owen, 1989). Methanol diffuses rapidly than isobutene and slow diffusing isobutene reacts with excess methanol and give rise to high selectivity in H-ZSM-5 and H-ZSM-11. Large pore zeolites (H-zeolite-β and H-mordenite) suffered from lack of shape selectivity. Lower SiO_2/Al_2O_3 ratio of REY enhances the adsorption of methanol which results in high selectivity. Further studies on H-ZSM-5, H-ZSM-11 along with A-15 for the liquid phase synthesis of MTBE indicate that H-ZSM-5 is highly selective compared to A-15 over a wide range of methanol/isobutene ratio. Harandi and Owen (1989) of Mobil Oil Corporation developed combined process of methanol to gasoline and etherification for conversion of methanol to MTBE. In this integrated process, excess methanol was used over the zeolite catalyst H-ZSM-5 and etherification reaction is conducted without the need to recycle excess alcohol for the etherification reaction (Harandi and Owen, 1989).

The strength of acid sites in the zeolites can be increased by removing lattice Al from the network and this process is known as dealumination. The dealumination results in the high acid strength with decrease in number of acid sites. Dealumination can be done by various methods namely steam dealumination, acid leaching and coordinating Al with appropriate ligand. The effect of dealumination on the catalytic activity of acidic zeolites for MTBE production was evaluated by many investigators (Colligon *et al.,* 1997; Nikopolous *et al.,* 1994; Kogelbauer *et al.,* 1994). Nikolopoulos and coworkers (1994) have prepared dealuminated zeolites by employing three methods namely ammonium hexafluorosilicate (AHFS) dealumination at 348 K, mild steam dealumination at 773 K and a combination of both. It was found that the dealuminated zeolites showed significantly higher activity than the parent zeolites (Nikolopoulos *et al.*, 1994). However, the doubly dealuminated zeolite Y-62 (combined AHFS + steam dealuminated) showed lower activity than the parent zeolites. The activity was found to increase with the reduction in acid site concentration in the range of 4.2 – 2.2 mmol/g due to acid strength enhancement. Further increase in acid site concentration lead to a linear decrease in the activity. The formation of extra-lattice Al has been observed for the dealuminated zeolites during the process of dealumination. Interaction between extra-lattice Al and the acid sites connected with lattice Al appeared to cause acid strength enhancement, responsible for an increase in catalytic activity. Attempt was made to understand the effect of variation of acidity by dealumination of zeolite-Y on MTBE synthesis. For comparison, other catalysts were also chosen which include H-ZSM-5, silica-alumina and industrial catalyst A-15. Catalytic activity at 333 K of all zeolites is lower than that of A-15. Catalytic activities of zeolites such as H-zeolite-Y, H-zeolite-β, fluoride treated H-zeolite-β and H-ZSM-5 for the production of MTBE have been studied using in situ MAS-NMR in the temperature of 333 and 353K. Fluoride treatment decreases the number of OH groups and increases the strength of sites. Time on stream studies showed that the performance of H-zeolite-β and fluoride treated H-zeolite-β is was comparable to A-15, whereas H-zeolite-Y and H-ZSM-5 were less active than A-15. The MTBE is formed by the reaction between alkoxy species (tertiary carbocation) on the surface and physically adsorbed methanol on silanol group. Number of OH groups in H-zeolite-β is more compared to other zeolites and hence more number of alkoxy species and methanol are adsorbed on the surface of H-zeolite-β which results in the higher activity (Thomas *et al*., 2000).

Collignon *et al*, (1997) studied the effect of dealumination on zeolite activity using H-zeolite-Y, H-ZSM-5, zeolite omega and H-mordenite. The methods employed for dealumination include steam treatment and acid leaching with 6 M HNO_3. Catalytic activity enhancement was observed for zeolite omega upon dealumination. Gas phase synthesis over H-zeolite-Y(Si/Al ratio of 6, 8, 14 and 18) was also investigated by these authors (Collignon *et al.,* 1997). In gas phase synthesis of MTBE over H-zeolite-Y (Si/Al = 6,8,14 and 18) and the effect of extra frame work lattice Al(Al_E) on turnover frequency (TOF) was investigated and it was found that the TOF decreases with increase in $Al_E/(Al_L$(Lattice Al) + Al_E) ratio and Al/unit cell.

Catalytic activity of zeolites can be improved by treating with strong electron

withdrawing compounds namely ammonium fluoride, HF and triflic acid. The influence of ammonium fluoride treatment on the acidity and activity was demonstrated by Mao and coworkers (Mao *et al*., 1999). They have treated H-ZSM-5 with ammonium fluoride with varying concentrations and activated at various temperatures. Low concentration of ammonium fluoride in the range of $1.0\text{-}2.6 \times 10^{-3}$ mol along with stepwise activation results in catalytic activity enhancement of H-ZSM-5. The reason for higher activity has been attributed to the formation of new Bronsted acid sites along with increase in acid strength. Efficient and promising H-ZSM-5 was developed for the production of MTBE in gas phase by modifying the H-ZSM-5 with desilication and ammonium fluoride treatment. In this modification zeolites were desilicated by Na_2CO_3/NaOH followed by NH_4F (3.55 wt %) treatment. This catalyst shows higher activity compared to A-15 without oligomer formation.

The treatment results in the high density and high strength of acid sites affording an increased activity (Lee and Mao, 2000).

Catalytic activity of triflic acid treated zeolites namely H-ZSM-5 and H-zeolite-Y has been compared with that of A-15 for the gas phase synthesis of MTBE. Triflic acid modified H-zeolite-Y shows comparable activity as that of A-15 whereas H-ZSM-5 is less active. The lower activity of H-ZSM-5 is attributed to negative influence of triflic acid coating on diffusion of reactants and products (Nikolopoulos *et al.,* 1996). Nikolopoulos *et al,* (1994) have studied triflic acid treated zeolites such as H-zeolite-Y, H-mordenite and H-ZSM-5 for the production of MTBE in gas phase. The activity enhancement upon triflic acid modification was observed only for the large-pore H-zeolite-Y. The activity was maximized after adding 3 wt % triflicacid. This modification results in the formation of extra–lattice Al which is responsible for the higher activity. Higher loading of triflic acid above 3wt % decreases the activity due to blockage of the pores of the H-zeolite-Y. The lower activity of triflic acid modified zeolites such as H-ZSM-5 and H-mordenite is mainly due to pore blockage (Nikolopoulos *et al.,* 1994).

Alkali exchanged zeolites such as Li-Y, Na-Y and Rb-Y have been employed for the production of MTBE at 363 K in comparison with H-zeolite-Y. Rb- exchanged zeolite showed lower activity than other zeolites due to partial blockage of pores. All the catalysts are found to be stable for about 2 h under the reaction conditions. The time on stream studies on zeolites shows that initial activities of all ion exchanged zeolites are same. This has been attributed to the formation methanol clusters on proton site which dissipate charge on acid site and results in decrease in the activity (Kogelbauer *et al*., 1994).

1.10.3 Clays as catalysts for MTBE synthesis

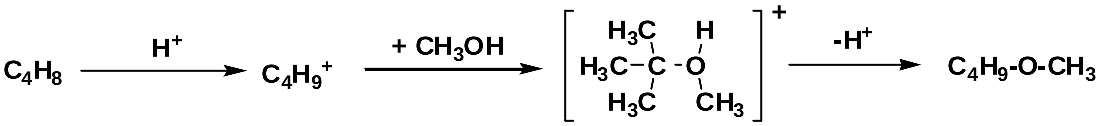
Adams *et al,* (1986) have employed cation exchanged smectite clay as catalyst for MTBE production wherein smectite clay was exchanged with Al^{3+}, Fe^{3+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Ca^{2+} and Na^{+} ions. Among these catalysts, they observed that 60 % yield of MTBE was obtained when Al^{3+}, Fe^{3+} or Cr^{3+} are the interlayer cations, whereas 8 % yield of MTBE was observed with Cu^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Ca^{2+} and Na^{+} cations. They have also studied the influence of solvent such as 1, 2-dimethoxyethane, n-pentane, THF and 1, 4- dioxane. 1,4- Dioxane was found to promote the reaction compared to other solvents (Adams *et al.*, 1986). Tetrahydrofuran give rise to 35 % yield of MTBE at 333 K with Fe^{3+}- or Cr^{3+}-smectites but approximately 4 % yield was observed with Al^{3+}-smectite. Acid treated montmorillonite clay has also been employed for the production of MTBE from methanol and tertiary butanol. Catalytic activity of montmorillonite based catalysts was compared with that of A-15 and the influence of the solvent has been studied. Al^{3+} exchanged monmorillonite catalyst shows lower activity compared to A-15 catalyst. Solvent influences to increase the rate of both resins and clay catalyst. The performance of clay based catalysts is increased by decreasing the water content

1.10.4 Heteropolyacids as catalyst for production of MTBE

Guttmann and Grasselli (1981) have developed a homogeneous liquid phase process for the production of MTBE from isobutene and methanol in the presence of heteropolyacid of molybdenum, tungsten and vanadium. At isobutene/methanol molar ratio of 0.25 and temperature of 408 K at 150 PSI, they have observed 68-88 % conversion with 90-100 % selectivity towards MTBE. Among examined HPAs, phosphotungstic acid shows higher activity with 83 % conversion and 100 %

selectivity (Guttmann and Grasselli, 1981). Gas phase synthesis of MTBE over heteropolyacids has been systematically investigated by employing Keggin and Wells–Dawson type HPAs. The catalysts employed include $H_6P_2W_{18}O_{62}$, $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_4GeW_{12}O_{40}$, $Na_2WO_4.2H_2O$, $H_5BW_{12}O_{40}$, $H_6CoW_{12}O_{40}$, SiO_2-Al_2O_3, SO_4/ZrO_2 and H-ZSM-5 in the temperature range of 303 K to 393 K (Shikata *et al.*, 1995). It has been observed that Dawson type HPAs shows higher activity compared to Keggin type HPAs and other catalysts. Unique dependence of reaction rate on methanol vapour pressure has been reported. Reaction rate was found to increase with increasing partial pressure of methanol upto a certain value depending on the kind of HPA. This unique behavior has been attributed to penetration of methanol to the bulk of HPA crystallites forming protonated oligomers which are not active for catalytic reactions. $H_6P_2W_{18}O_{62}$ catalyst was more active than $H_3PW_{12}O_{40}$ at temperatures below 323 K - 363 K, even though both the acid strength and BET surface area of $H_6P_2W_{18}O_{62}$ are lower than those of $H_3PW_{12}O_{40}$ catalyst. The unexpected catalytic behavior of Dawson type HPAs has been explained based on the pseudoliquid behavior which assumes that the reaction between methanol and isobutene occurs in the “pseudoliquid” state. Methanol is readily adsorbed in the bulk of heteropoly acids such as $H_4PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_6P_2W_{18}O_{62}$. It has been proposed that although isobutene is not absorbed by pure dehydrated $H_6P_2W_{18}O_{62}$, its sorption might be enhanced by the presorption of methanol, expanding the crystal lattice of HPA. The pseudoliquid phase behavior of these heteropolyacids, in which the protons are solvated by methanol, plays a key role in the high selectivity for MTBE suppressing the dimerization of isobutene. The adequate amount of methanol absorption by Dawson type heteropolyacid brings about its high catalytic activity. In order to understand the mechanism of the formation of

MTBE over HPA two different models have been proposed. Shikata *et al*, (1995) proposed that the presence of methanol in the bulk of HPA crystallites enables the penetration of non-polar isobutene and the reaction occurs in the pseudoliquid phase. Alternately, it was proposed that the isobutene is adsorbed at the HPA crystallites surface and methanol is supplied from the bulk of HPAs during MTBE formation (Shikata *et al.*, 1995). Bielanski *et al*, (1999) have studied the activity of polyaniline supported $H_4SiW_{12}O_{40}$ for the synthesis of MTBE in the temperature range of 313 K - 353 K. They observed that air activated sample shows higher activity than helium activated sample for the supported catalyst. These authors have proposed the scheme for the MTBE production wherein proton plays an essential role in MTBE formation. The porotonated form of isobutene reacts with methanol generating a cationic intermediate which subsequently leads to MTBE according to Scheme 1.2 (Bielanski *et al.*, 1999)



Scheme 1.2 Proposed mechanism for MTBE production (Taken from Bielanski *et al*., *Journal of Catalysis*, 185, 363-370, (1999).

Dawson-type heteropoly acids such as $H_6P_2W_{18}O_{62}$ have been employed for the production of MTBE. It has been observed that the activity is comparable to that of sulfonated polymer resin and Amberlyst 15, the selectivity being higher than that of Amberlyst-15. Keggin-type heteropolyacid $H_3PW_{12}O_{40}/SiO_2$, was also efficient for this reaction, while pure $H_3PW_{12}O_{40}$ (Keggin) was less active than pure $H_6P_2W_{18}O_{62}$ (Dawson). Calorimetry of NH_3 adsorption of catalyst revealed that the difference in acid strength between $H_6P_2W_{18}O_{62}$ and $H_3PW_{12}O_{40}$ was large; however the difference between the two became smaller when they were supported. By supporting

$H_6P_2W_{18}O_{62}$ on SiO_2, the MTBE selectivity on the basis of methanol increased, but the selectivity on the basis of isobutene decreased, which was explained by the decrease in the relative contribution of pseudoliquid phase reaction to the surface reaction as a result of supporting the catalyst. The pressure dependency on methanol for $H_6P_2W_{18}O_{62}/SiO_2$ was close to that of unsupported $H_6P_2W_{18}O_{62}$, but differed from those of solid acids like SO_4^{2-}/ZrO_2 and H-ZSM-5, indicating that MTBE synthesis proceeds in the pseudoliquid phase of $H_6P_2W_{18}O_{62}/SiO_2$. Shikata *et al,* (1997) have investigated the catalytic activity of silica supported heteropoly acids such as $H_6P_2W_{18}O_{62}$ and $H_nXW_{12}O_{40}$ (X = P, Si, Ge and Co) for the production of MTBE in comparison with H-ZSM-5, A-15, SiO_2-Al_2O_3, SO_4^{-2}/ZrO_2, and $CS_{2.5}H_{0.5}PW_{12}O_{40}$. They have observed that 20 % $H_6P_2W_{18}O_{62}$ loaded on SiO_2 shows high activity similar to A-15 and affords higher yield of MTBE than parent heteropolyacids. Other catalysts such as SO_4^{2-}/ZrO_2, H-ZSM-5, SiO_2-Al_2O_3 are inactive at 383 K (Shikata *et al.*, 1997). Baronetti *et al*, (1998) have investigated the catalytic activity of Dawson acid, $H_6P_2W_{18}O_{62}$ for MTBE synthesis at 373 K in gas phase. The pretreatment temperature of the catalyst is found to influence MTBE yield and conversion. The activity of the catalyst drops down to zero at a pretreatment temperature of 673 K (Baronetti *et al.,* 1998). Xia and coworkers (2002) have studied the influence of support on the activity of heteropoly acid catalysts for MTBE formation from MeOH and TBA. They have employed MCM-41 as support for active HPW with loading of 15, 30 and 50 %. The observed catalytic activity of HPW/MCM-41 was compared with pure HPW, Si-MCM-41, H_2SO_4-MCM-41, SO_4-ZrO_2/MCM-41, NaAl-MCM-41 and H-MCM-41. Among the examined catalysts 50% HPW/MCM-41 shows higher activity at lower temperatures compared to other catalysts. In comparison with A-15, 50 % HPW/MCM-41 showed comparable activity in the temperature range of 363 K -

373 K. The activity of the catalysts has also been correlated to the number of acid sites and all the catalysts were found to be stable for 100 h except H_2SO_4-MCM-41due to leaching of H_2SO_4. (Xia *et al.*, 2002).

The influence of structure and composition of heteropolyacids on the catalytic production of MTBE from methanol and TBA have been examined in detail (Maksimov and Kozhenikov, 1989). The different types of HPA such as Dawson, Keggin and Dexter-Silverton have been used for this reaction. Among these catalysts, Dawson type structure shows higher activity than other two structures. Cu, Pd, Hg and Ag salts of HPA have also been employed for MTBE synthesis. These show comparable activity with pure HPA (Kim *et al.*, 1988).

Single step synthesis of MTBE from methanol and TBA have been studied over K-10 clay supported HPW in liquid phase using dioxane as solvent (Yadav and Kirthivasan, 1995) in comparison with A-15 and H-ZSM-5 catalyst. Even though HPW/K-10 shows slightly lower conversion than H-ZSM-5 and A-15, it shows higher selectivity towards MTBE at 358 K. Recently, Manju and Sugunan (2005) have studied the catalytic activity of Fe-pillared montmorillonite, Co/Fe pillared montmorillonite and Fe/Al pillared montmorillonite for the MTBE production from TBA and methanol. Down flow fixed bed reactor was utilized for the reaction in the temperature range of 383 K - 463 K with methanol/TBA ratio of 10. Among examined catalysts, they observed higher activity for Co/Fe with 100 % selectivity towards MTBE (Manju and Sugunan, 2005). Molnar *et al,* (1999) have studied the catalytic activity of PW/SiO_2, SiW/SiO_2, $Cs_{2.5}H_{0.5}PW_{12}O_{40}/SiO_2$ and $Cs_{3.5}H_{0.5}SiW_{12}O_{40}/SiO_2$ for liquid phase synthesis of MTBE in presence of 1,4-dioxane as solvent. At autogeneous pressure PW/SiO_2, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and SiW/SiO_2 shows similar activity which is higher than other catalysts. When pressure was increased to 50 bar, the activity of PW/SiO_2 and SiW/SiO_2 increased appreciably (Molnar *et al.*, 1999). Kinfton and Edwards (1999) have studied supported heteropoly acids namely $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ on oxides such as titania, silica, and alumina along with HF treated montmorillonite and mineral acid treated clays. Catalytic activity of PW/TiO_2 shows 81 % conversion with 94 % selectivity of MTBE at 20 bar. Catalytic activity of HF treated clay increases up to 433 K as a function of temperature and decreases further at high temperatures due to byproduct formation (Kinfton and Edwards, 1999).

1.11 ISOPROPYL *TERT*-BUTYL ETHER (IPTBE) AS OXYGENATE

Isopropyl *tert*-butyl ether (IPTBE) is known to have high blending octane number, optimum oxygen content, lower blending vapor pressure for possible application as oxygenates. Production of IPTBE from refinery feed stocks such as isopropanol and isobutene makes it into a completely refinery based ether. Industrially IPTBE is produced by the acid-catalyzed addition of 2-propanol to isobutene at 1.4 - 1.8 Mpa and in the temperature range of 323 K - 363 K in the liquid phase. The formation of IPTBE is thermodynamically less favored which results in formation of significant amount of byproducts. Different byproducts such as *tert*-butyl alcohol (TBA) 2, 4, 4-trimethyl-1-pentene (TMP1), 2,4,4-trimethyl-2-pentene (TMP2) and diisopropyl ether (DIPE) are formed along with IPTBE and formation of these products increases with temperature. Amberlyst resins were extensively employed for the liquid-phase etherification of isobutene with alcohol in industrial scale. However, the Amberlyst resins are sensitive to the alcohol/isobutene ratio and this opens up the possibility of employing zeolite as catalysts. Zeolites have been frequently employed as catalysts for the synthesis of MTBE and ETBE and the results reveal that zeolites are more selective than amberlyst resin catalyst in a wide range of alcohol/alkene ratio. Based on the results of MTBE and ETBE production, zeolites have also been considered as possible alternative to amberlyst resin for the production of IPTBE. Iborra and co-workers (2005) made comparison of the catalytic activity of H-ZSM-5 (SiO_2/Al_2O_3 = 25), H-zeolite-β (SiO_2/Al_2O_3 = 28) and H-zeolite-Y for the liquid phase synthesis of IPTBE from 2-propanol and isobutene at 353 K and 1.6 MPa. They observed higher activity for H-zeolite-β compared to H-ZSM-5 and H-zeolite-Y. However, selectivity of H-zeolite-Y towards IPTBE is more than that of H-zeolite-β and H-ZSM-5 (Iborra *et al.*, 2005). Comparative studies on the activity of zeolites and ion exchange resins have shown that H-zeolite-β has similar activity as that of A-15. Zeolites are less selective towards IPTBE, however the distributions of by-products on H-zeolite-β and ion exchangers are similar. Since TMP1 (possible octane booster) is the main byproduct and its octane number is close to IPTBE, H-zeolite-β has been claimed as possible alternative to resins. The effect of various reaction parameters such as temperature, reactant ratio and catalyst loading have been studied for IPTBE production on H-zeolite-β catalyst. From the kinetic studies, the reaction mechanism has been proposed wherein 2-propanol and isobutene adsorbed on adjacent sites react to give the ether. It has been observed that the surface reaction is the rate-controlling step and adsorption of 2-propanol and IPTBE is significant. The activation energy has been found to be 92 kJ/mol. Tejero *et al*, (2001) studied the synthesis of IPTBE over H-ZSM-5 in comparison with A-15, A-35 and purolite CT-275 in liquid phase at 1.3 Mpa and in the temperature range of 343 K - 363 K. The influence of isopropanol/isobutene molar ratio ($R_{A/O}$) and temperature on isobutene conversion (X_{IB}), IPTBE yield ($Y_{IPTBE/IB}$) and selectivity towards IPTBE was examined in detail and the activation energy for IPTBE was determined. They observed that alcohol/olefin ratio influences to increase the conversion while temperature decreases the conversion in all type of resins (Tejero *et al.*, 2001**)**. All the resins have shown comparable activity for IPTBE synthesis. H-ZSM-5 (Z28) and H-ZSM-5 (Z55) have been used as catalysts for IPTBE synthesis and their activity were compared with various resins namely A-15 and A-35. Acidic resins are more active than H-ZSM-5 (Z28 and Z55) though higher catalyst loading was used in case of H-ZSM-5. The activity of the H-ZSM-5 decreases significantly as their aluminum content decreases and hence among the two zeolites, Z28 is more active than Z55. Based on the yield and by product formations during IPTBE synthesis, medium pore zeolites like H-ZSM-5 are found to be less active and selective than resins. Kinetics measurement indicates that the amberlyst resins are having lower values of activation energy compared to the H-ZSM-5. However, activation energy values are the same for all resins within the limits of experimental error.

Alternatively, IPTBE can be prepared from acetone and tertiary butanol (TBA), by selective hydrogenation of acetone followed by etherification with TBA. Kinfton *et al*, (1999) have prepared IPTBE from acetone for the first time by employing Ni-2715 as hydrogenation catalyst with H-zeolite-ß and Pd-zeolite-ß as etherification catalyst. IPA formed by the hydrogenation of acetone further reacts with TBA to afford 7-8 % IPTBE along with MTBE. They observed low selectivity towards IPTBE in the case of H-zeolite-ß. Pd-zeolite-ß catalyst is also active for this transformation and gives same product distribution like H-zeolite-ß (Knifton *et al.*, 1999). Knifton *et al,* (1999) have also developed a two step process for the production of IPTBE from crude acetone which consists of hydrogenation over nickel rich catalyst followed by etherification of isopropanol intermediate in presence of H-zeolite-ß, Pd-zeolite-ß and dealuminated zeolite-Y (Knifton *et al.*, 1999). Tejero *et al,* (1997) have studied the formation of byproducts such as TBA, DIPE, TMP1 and TMP2 as functions of temperature over Bayer K-2631 catalyst in the temperature range 303 K - 353 K (Tejero *et al.*, 1997). They have observed that high temperature and low alcohol/olefin ratio favor the dimerisation of isobutene to form TMP1 and TMP2. DIPE formation takes place at higher temperature and TBA is formed if water is present in the system. Sola *et al,* (1997) studied the kinetics and thermodynamics of the IPTBE formation over Lewatit K-2631 catalysts at P = 0.35 Mpa in the temperature range of 312 K - 340 K (Sola *et al.*, 1997). Activation energy calculated from kinetics measurement is found to be 78.4 kJ/mole. Linnekoski *et al,* (1997) have measured the equilibrium constants for the formation of IPTBE from 2-propanol and isobutene in a batch reactor at temperatures of 313 K - 353 K. The influence of olefin/alcohol ratio on the rate of etherification has been studied at 313 K and the rate increases with increasing mole ratio and reaches the maximum value (Linnekoski *et al.*, 1997).

1.12 DIISOPROPYL ETHER AS POTENTIAL ALTERNATIVE OXYGENATE TO MTBE

MTBE was mostly employed as oxygenate in gasoline pool to improve the combustion efficiency in many countries. However it was phased out from the gasoline pool (Goodwin *et al.*, 2002; Ahmed *et al.*, 2001). Carcinogenic nature of MTBE, causing nausea, headache and neurotoxic effect and polluting the ground water are the main disadvantages that forced to remove MTBE from the gasoline pool. The possibilities of using other ethers such as TAME, TAEE and ETBE are also limited because of unfavorable blending properties and difficulties in synthesis. Isopropyl based ethers such as IPTBE and DIPE are the other options for refiners to blend with gasoline for complete combustion. Synthesis of IPTBE is always associated with a large amount of by products, which results in the lower selectivity of IPTBE and hence industrial production of IPTBE is not economical. DIPE appears to be promising for gasoline blending with more compatibility. In recent years, there is a growing interest in the production of DIPE as a possible oxygenate for gasoline blending. Favorable blending and physical properties, ready availability of feedstock, lower water solubility, vapor pressure, complete miscibility with gasoline and initiation of combustion inducing consecutive combustion are the main advantages of the DIPE which makes it most promising alternative to MTBE in gasoline blending. Moreover DIPE is completely refinery-based ether that does not depend on the external supply of feedstock. Propylene and acetone are the two feedstocks, which are used to prepare DIPE. Industrially, DIPE is produced from propylene and water. Catalytic and mechanistic aspects of production of diisopropyl ether from two different feedstocks were treated separately and given in subsequent sections.

1.12.1 Catalytic production of DIPE from propylene feedstock

Catalytic production of DIPE from propylene feedstock is a widely used process in petroleum refinery. Typical preparation of diisopropyl ether consists of two steps, namely hydration of propylene to isopropanol and etherification of isopropanol to DIPE over acid catalysts. Several types of acidic catalysts such as heteropolyacids (John *et al.*, 1999), ion exchange resins (Marker *et al.*, 1994; Olah, 1989), mesoporous materials, clays and zeolites have been employed as catalysts for DIPE production. The reaction is reversible and exothermic in nature and hence it is thermodynamically limited reaction. Low temperatures and highpressures are favoured for the formation of DIPE. The rate-determining step is protonation of propylene. Hydration of propylene takes place in the temperature range of 303 K - 353 K and the etherification (bimolecular dehydration) to DIPE takes place in the temperature range of 393 K - 453 K. Catalytic production of DIPE was carried out either by single step integrated process or by a two step process (hydration and etherification separately). Amberlyst resin was demonstrated as catalyst for the production of DIPE from propylene feedstock with both single step integrated process and two step processes. In the two step process, two zone reactor was employed in which the reactors can be operated either under the same conditions or at different conditions. In the first zone, propylene was converted to IPA and thus formed IPA was further converted to DIPE in the second zone.

Integrated process was developed for the production of DIPE from propane feedstock by dehydrogenation followed by etherification. The catalysts employed are Pt for dehydrogenation and A-36 for etherification (Marker *et al.*, 1998). In this process, propane is allowed through the dehydrogenation zone where propylene is formed which is further transformed to IPA and DIPE. The product formed from the first zone is allowed to go through the etherification zone where water is passed simultaneously which converts propylene to isopropanol. In the same zone, DIPE is formed either by bimolecular dehydration of IPA or etherification of IPA with propylene. The reactors have been designed in such a way that unreacted propylene and IPA can be recycled to enhance the yield economically. Processes have also been developed to increase the lifetime of ion exchange resin by simultaneous removal of SO_3H before recycling step. Child *et al*, (1990) also developed a two-stage process for the production of DIPE from propylene over catalysts namely MCM-22 (hydration) and A-15 (etherification). The formed ether was allowed to recycle to the hydration zone, which suppresses the temperature of the reaction there by reducing the oligomerisation. It was found that the reaction temperature was reduced to 283 K as a result of recycling the product (Child *et al.*, 1990).

Hydration and etherification process for the production of DIPE was developed over MCM-36 mesoporous materials. MCM-36 affords high selectivity towards IPA (88 %), compared to DIPE (11%) for the feedstock containing only propylene and water. However, the selectivity of DIPE (87 %) was higher when the feed contains additional IPA along with mixture of propylene and water. The conversion and selectivity of DIPE was found to increase with increase in reaction time (Le and Yokomizo, 1993). Heses *et al*, (1999) have developed a process for the production of DIPE in a single step employing A-15 resin as catalysts. The advantage of this process is that both hydration and etherification occurs in a single step. They have studied the influence of feed ratio of reactant, contact time and pressure on the catalytic activity in detail. The selectivity of the catalysts was found to be higher for IPA compared to DIPE without byproduct formation (Heses *et al.*, 1999).

DIPE is widely prepared from IPA by bimolecular condensation of isopropanol; alternately DIPE can also be prepared from the mixture of IPA and propylene. In this route protonated propylene reacts with IPA to give DIPE over acidic catalysts. Nippon Oil Company in 1980 developed a process for the production of DIPE from propylene and isopropanol over the A-15 in the temperature range of 373 K - 403 K. In this process in order to produce high purity DIPE, product stream was allowed to pass through the acid neutralizing zone, which contains hydrotalcite ($6MgO.Al_2O_3CO_2.12\ H_2O$). The purpose for employing neutralizing zone is to remove acidic materials present in the product, which is eluted from the resin catalyst. The effluent from the neutralizing zone was subjected to distillation and solvent extraction in order to get pure DIPE (Imaizumi *et al.*, 1980). DIPE production from isopropanol and propylene with montmorillonite (K-10) clay as catalyst was studied in liquid phase (Woods *et al.*, 1977). They have studied the influence of temperature, reactant ratio and pressure on the formation of DIPE. The conversion of reactants such as IPA and propylene was found to be 48.2 % and 7.6 %, respectively with the reaction yield of 28.2 %. It has also been observed that stoichiometric amount of reactants favor the formation of DIPE. Sulfuric acid treated clays are promising catalysts for the production of DIPE from IPA and propylene. The same authors have studied the influence of the temperature on bimolecular dehydration over clay and observed that conversion increases while selectivity decreases with temperature. The decrease in selectivity attributed to formation of propylene.

Zeolites were exploited extensively compared to any other solid acid catalysts due to their uniform pore size, high thermal stability and desired product selectivity. Among the available zeolites, appropriate zeolite was selected on the basis of constrained index and acidity function. H-ZSM-5, H-ZSM-12, H-ZSM-35, H-zeolite-ß, H-zeolite-Y, REY and H-mordenite (Harandi *et al.,* 1992; Bell *et al.*, 1996; Harandi *et al.,* 1993) are examples of zeolites utilized for the production of DIPE. Zeolite catalysed synthesis of DIPE was demonstrated for both two-step process (hydration and etherification separately) and single step process (hydration and etherification are combined together). Etherification of IPA to DIPE was carried out as separate process over acidic catalyst in order to understand the reaction mechanism thoroughly. Bimolecular condensation of isopropanol results in the formation of DIPE in presence of acidic sites. Harandi *et al,* (1993) have studied the influence of water present in the feed of IPA for the production of DIPE over H-zeolite-β as catalyst at a temperature of 433 K and a pressure of 1000 PSI. The results showed that feed containing 15 % water decreased the activity significantly compared to pure IPA feed. Pure IPA gave rise to and yield close to equilibrium value at a space velocity of less than 5, whereas IPA containing 15 wt % water reduced the activity by 4 fold in the case of self bound H-zeolite-β. The authors also compared the activity of H-zeolite-β with H-ZSM-5, H-zeolite-Y, REY and A-36 catalysts (Harandi *et al* ., 1993).

Sorensen *et al,* (1989) have developed a two-step process by employing a multi-bed propylene conversion unit. The unit consists of two reaction zones namely, zone A (hydration zone) and zone B (etherification zone), featuring multiple points of olefin introduction. H-ZSM-35 and H-zeolite-ß were employed as catalysts for hydration and etherification, respectively. In hydration zone optimum conditions were maintained to get maximum conversion of propylene to IPA with little co-production of DIPE. Etherification zone was operated under different conditions, which maximize the conversion of IPA formed in zone A. This process gave rise to only 1 wt % or less of oligomer (Sorensen *et al.*, 1989).

Beech *et al,* (1992) have studied the production of DIPE in three zone adiabatic reactor over alumina and silica bound H-zeolite-β catalysts. The adiabatic three zone reactor has been interconnected to each other. The reaction was carried out at 438 K and a pressure of 100 bar using fixed bed reactor. The authors studied the influence of recycling the product mixture (IPA + DIPE) on yield of DIPE. Zeolites are susceptible to the deactivation by coke formation and hydrothermal attack of excess water, the process of recycling product or residual reactant is one of the methods to suppress the coke formation and maintaining single phase of reactant. It was observed that recycling of product mixture results in high conversion of propylene, higher yield of IPA and DIPE (conversion = 36.7 %, IPA = 14.1 % and DIPE 38.6) compared to reaction without recycling (conversion = 32.7, IPA =14.1 and DIPE = 32.6). Recycling the product stream being able to dissolve the coke and maintain a homogeneous phase for the reaction which results in the higher activity and sustained stability of catalyst (Beech et *al.*, 1992).

Deactivation of zeolites due to coke formation can be prevented by recycling the product or reactant. Apart from recycling, the deactivated zeolite can be regenerated by conventional method by calcining under air atmosphere at high temperatures. The problem associated with the calcination in air is that the steam formed during the process can destroy the active sites of the catalyst. The alternate process developed for regeneration is to use non-oxidizing gas under milder conditions. Hydrogen activation has been found to be a promising method for regeneration of spent catalyst, which restores the activity of the catalyst. The method employed for regeneration is as follows: initially nitrogen gas was purged through the catalyst bed at 600 psig for 24 h. The nitrogen gas was then discontinued and hydrogen was passed at pressure of 600psig at 644 K and the temperature was raised to 727 K and maintained for 72 h. The temperature was subsequently reduced to 338 K and after 16 h, hydrogen was discontinued again and nitrogen gas was allowed to pass through the catalyst. Since the activation involves the nitrogen purging, these authors have also compared the catalysts regenerated by the above method and spent catalyst purged with only nitrogen. The results showed that activity of the spent catalyst could not be restored only by nitrogen activation. Hydrogen activation effectively removes the coke formed during the reaction and the activity of the catalyst restored after hydrogen activation for DIPE production without destroying the structure of the catalyst (Beech *et al.*, 1995).

The influence of inert solvent on the production of DIPE from propylene in integrated process has been studied in detail in the presence of zeolite catalyst. The primary role of solvent in these reactions is to increase the solubility of propylene (non polar gas) in water (polar). The other advantage of using a solvent is that it dissolves the coke formed during reaction and prevents the dealumination of zeolites. The characteristics of the solvent are that it should be miscible with water and hydrocarbon, stable to acid, reactant and product upto 477 K and the boiling point should be below 373 K at 1 atm. The possible candidates satisfying these characteristics are 1, 4-dioxane, DME, THF 1, 3- dioxane, alkyl ether and ethylene glycol. Dioxane was found to increase the yield of IPA (28.5 %) and DIPE (28.0 %) compared to the process without solvent (IPA = 15.0 % and DIPE = 20.6%) (Brown *et al*., 1998).

DIPE and IPA formation from propylene and water by direct hydration involves the formation of carbon-oxygen bond which tends to decrease the stability of the catalyst by coke formation and hydrothermal attack of zeolites. Moreover the reaction medium is not homogeneous during the reaction in case of direct hydration. These problems can be overcome by avoiding direct hydration and employing indirect hydration route from the mixture of DIPE and water. In this route, reaction of DIPE and water leads to the formation of IPA and IPA was further converted to DIPE either by bimolecular dehydration or by reacting with propylene. Beech and coworkers (1996) have developed a process for the production of DIPE and IPA from propylene by indirect hydration route over H-zeolite-ß catalyst. The reaction was carried out using serially connected, multistage fixed bed reactor which promotes the indirect hydration of propylene with inter-stage injection of water and other reactants. According to the requirement of desired product, one can designe the process to get either DIPE or IPA. Bell *et al,* (1996) have developed a process for the production of IPA and DIPE. In this process, a single phase was maintained throughout the reaction and the reactor was designed in such a way that one reactor gave DIPE in large amount and the other yielded IPA. The catalytic activity of H-zeolite-ß, A-15 and H-ZSM-5 is evaluated for the production of DIPE and compared with direct hydration of propylene. It was observed that indirect route gave rise to 43 wt % of DIPE which is closer to equilibrium value of 49 wt %, whereas direct pathway gave 12 wt % of DIPE (Bell *et al.*, 1996).

1.12.2. Diisopropyl ether production from acetone feed stock

Texaco chemical Company has developed an alternate route to produce DIPE based on crude acetone as feedstock. The advantage of this process is that the acetone feedstock is available from propylene oxide industry as by-product. Acetone is converted to DIPE in a two step process involving hydrogenation to IPA, followed by etherification of IPA to DIPE which is extensively studied using bifunctional catalysts in vapor phase under high pressure condition (Taylor *et al.*, 1996; Knifton an Dai, 1995). 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 (1999) have developed a process for the production of DIPE from acetone by employing three different acidic catalysts namely Ni-Cu/H-zeolite-ß, Fe-Cr-Mn/H-zeolite-ß and dealuminated H-zeolite- Y. The influence of different types of reactors and temperature on the production of DIPE has been investigated in detail. Apart from two-step process, an integrated single step process (hydrogenation an etherification together) is also employed for the production of DIPE (Knifton and Dai, 1999)

Shell chemical company has developed and demonstrated a process for selective conversion of crude acetone stream to DIPE in a two-step process (Knifton and Dai, 1999). In this process Ni-Cu/H-zeolite-ß, Pd/H-zeolite-ß, Fe-Cr-Mn/H-zeolite-ß, and dealuminated H-zeolite-Y were employed as etherification catalysts and Ni-2175 was employed as hydrogenation catalyst for the production of DIPE. In the first step acetone which contains significant amount of methanol and TBA was converted to IPA at 433 K and 50 bar which results in a product composition of 48.3 % IPA, 15.8 % MeOH and 30.8 % of TBA. The product of first step was converted to DIPE in the temperature range 393 K - 453 K and a pressure of 50 bar. Investigations 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. The influence of temperature on DIPE formation and IPA conversion was investigated over Ni-Cu/H-zeolite-ß, Fe-Cr-Mn/H-zeolite-ß and dealuminated zeolite-Y. It was observed that the Ni-Cu/H-zeolite-ß system showed more etherification sites as compared to other catalyst systems investigated. Pt/50 % H-zeolite-ß/Al_2O_3 and Linday type zeolite-Y (LZY) were also employed as catalyst for the DIPE formation from IPA in the temperature range of 393-453 K. Maximum yield of 12.3 % DIPE was obtained in the case of Pt/H-zeolite- ß where as 3.8 % was obtained for LZY at 453 K (Knifton and Dai, 1999)

Single step integrated process for the generation of DIPE along with MTBE and IPTBE was developed by Texaco chemical company by employing bifunctional catalysts. The microreactor used possesses two reactors in series separated by quench zone. The top reactor was loaded with 4 ml catalyst and the bottom reactor contains two catalyst beds separated by inert material. On the whole, 12 ml of catalyst has been loaded on this type of reactor. Bifunctional catalyst employed for this process consists of hydrogenation active part like Ni-Cu and etherification active part like H-zeolite -ß. Catalytic activity of 32% Ni-Cu/10 wt % H-zeolite- β/Al_2O_3, 32wt % Ni-Cu/50 wt % H-zeolite-β/Al_2O_3, 32 wt % Ni-Cu/60 wt % H-zeolite-β/Al_2O_3 and Ni-Cu-Cr/HZM-5 for the production DIPE and IPA was evaluated. The influence of temperature on DIPE and IPA production over 32 wt % Ni-Cu /50 wt % H–zeolite-β/Al_2O_3 and 32% Ni-Cu/10 wt % H-zeolite-β/Al_2O_3 has been investigated. Their results showed that there is an increase in the ether yield with increase in temperature, whereas IPA yield decreases in the temperature range 372 K - 435 K. The decrease in the yield of IPA is attributed to the DIPE formed at the expense of bimolecular dehydration of IPA. Among the bifunctional catalysts, 32 % Ni-Cu/60 % H-zeolite-ß/Al_2O_3 is more active than other catalysts affording 25 % DIPE. The influence of temperature on DIPE formation has also been studied by employing Pt/50 wt% H-zeolite-ß/Al_2O_3 and LZY in the temperature range of 393 K - 453 K. The study has shown that increase in temperature results in increase in the DIPE yield with decreasing yield of IPA, which is consumed for the formation of DIPE (Knifton and Dai, 1999).

Texaco chemical Company (Taylor *et al.,* 1996) developed a process in which three types of integrated reactors such as two zone reactors with options for interstage separation, integrated process without interstage separation and integrated process with catalytic distillation for etherification portion were employed for the production of DIPE. In two zone reactors, 32%Ni-Cu/Al_2O_3 was loaded on top reactor and 32%Ni-Cu/80 H-zeolite-ß/Al_2O_3 was loaded in bottom reactor. The temperature was varied to investigate the effect of temperature. The yield of DIPE increases with increase in temperature on DIPE formation with complete conversion of acetone. In another type of reactor without changing the top zone catalyst, the bottom zone catalyst was varied with different zeolite loading on alumina to evaluate the acidity of zeolite on catalytic activity. The maximum yield of 36 % of DIPE was obtained with 60/40 H-zeolite-ß/Al_2O_3 at etherification temperature of 416 K. These results demonstrated that a high yield of IPA and DIPE can be obtained from an integrated process where acetone is hydrogenated over a alumina supported Ni-Cu catalyst and the resulting IPA is converted to DIPE over an acidic alumina supported H-zeolite-ß with or without additional hydrogenation function (Taylor *et al.*, 1996).

Taylor *et al*, (1996) developed process by employing two zone reactors with two different catalysts for the synthesis of DIPE from acetone feedstock. Acetone was passed through first zone where hydrogenation active catalyst was loaded which hydrogenates acetone to IPA. The formed IPA was then passed through the second zone where etherification catalyst namely Ni-Cu/zeolite has been loaded. In this zone, unconverted acetone was converted to IPA and IPA was further converted to DIPE. 36 % of DIPE was obtained using Ni-Cu/Al_2O_3 as catalyst in the first zone at 392 K and 32%Ni-Cu/60 % H-zeolite-ß/ Al_2O_3 in second zone at 419 K. The combination of Ni-Cu/Al_2O_3 and Ni-Cu/80 % H-zeolite-ß/Al_2O_3 produced 30 % of DIPE at reactor temperatures of 388 K and 410 K respectively. Under similar conditions; Ni-Cu/Al_2O_3 and Ni-Cu/30 % H-zeolite-ß/Al_2O_3 produced 25 % of DIPE at 388 K and 408 K respectively (Taylor *et al.*, 1996).

Gradient reactors, which consist of three-catalyst zone, have been employed for the efficient production of DIPE from acetone. The first zone was loaded with 4 cc of hydrogenation catalyst, second zone loaded with the catalyst which is having medium hydrogenation and etherification activity. The bottom of catalyst zone was loaded with active etherification catalyst. The combination of Ni-Cu/Al_2O_3, Ni-Cu/50% H-zeolite-ß/Al_2O_3 and 80 % H-zeolite-ß/Al_2O_3 with the temperature sequence of 377 K – 432 K -419 K gave 38 % DIPE and 98 % yield of IPA + DIPE and is more active than other temperature sequences and other combination of catalyst. The temperature sequence of 378 K – 415 K - 409 K with combination Ni-Cu/Al_2O_3, Ni-Cu/50 % H-zeolite-ß/Al_2O_3 and Ni-Cu/ 80 % H-zeolite-ß/Al_2O_3 give rise to 26 % DIPE (Taylor *et al.,* 1996).

Single step synthesis of DIPE by employing gradient reactor with multi-catalyst bed has been described by Taylor *et al,* (2000). The catalyst employed for these reactions are bifunctional catalysts such as Ni-Cu/ H-zeolite-ß with varying percentage of zeolite, Ni-Cu-Cr/H-ZSM-5 and PW/SiO_2-Al_2O_3. Three types of reactors were employed for this purpose namely two bed reactor with single catalyst for both beds, two zone reactor with two different catalysts and a gradient reactor using three types of catalysts. In this study, DIPE is also produced using two-zone reactor with single catalyst for both the zones. The temperature of the reaction was varied from 373 K - 433 K. Ni-Cu/10 % H-zeolite-ß/ Al_2O_3, Ni-Cu/50 % H-zeolite-ß/Al_2O_3, Ni-Cu/60 % H-zeolite-ß/Al_2O_3, Ni-Cu-Cr/H-ZSM-5 and PW/SiO_2-Al_2O_3 were employed as catalysts for this reaction. Among these catalysts Ni-Cu/60%H-zeolite-ß/Al_2O_3 gave higher yield of DIPE (24.8% at 397 K) compared to other catalysts. The Ni-Cu/10% H- zeolite-ß/Al_2O_3 is more selective to IPA at lower temperature. At high temperature, IPA is converted to DIPE. The same trend is also followed for Ni-Cu/50%H-zeolite-ß/Al_2O_3 (Taylor *et al.*, 2000).

H-zeolite-ß appears to be more active for etherification of IPA to DIPE. High activity was attributed to appropriate pore size and medium acidity of H-zeolite-ß based on constraint index (pore size) and alpha value (which is a measure of acidity) for the etherification of IPA to DIPE. H-zeolite-ß is active for etherification without any unimolecular dehydration in the desired temperature window (393 K - 453 K). In the case of hydrogenation active part of the bifunctional catalyst (mostly Ni-Cu), 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 favors 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 that inhibits the hydrogenating activity.

1.13 OBJECTIVE AND SCOPE OF THE PRESENT STUDY

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, complete miscibility with gasoline and low water solubility. These characteristics make it as an attractive alternate as oxygenate. DIPE can be prepared from acetone and propylene, which are by-products in propylene oxide industry and available in refineries (in fluid catalytic cracking unit) respectively. This has motivated to prepare DIPE from propylene, isopropanol and acetone using different zeolites, heteropolyacids and ion exchange resins based solid on 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, is a 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-ß supported trimetallic catalyst has been identified to show maximum activity and selectivity for MIBK production.

Similarly, new energy sources with cleaner technology like Direct Methanol Fuel Cell (DMFC) have also to be evaluated to meet the future demand for energy. Development of anode electro-catalyst with maximum utilization of Pt on different type of carbon support for methanol oxidation is another area of research interest in this study.

The main objectives of this thesis include

1. Catalytic production of isopropyl alcohol (IPA) and DIPE by employing solid acids such as heteropolyacids, ion exchange resins and zeolites.

2. Preparation and catalytic studies on H-zeolite supported Ni, Ni-Cu and Ni-Cu-Cr metallic particles for DIPE production from acetone.

3. Evaluation of the effect of reaction parameters such as metal loading, temperature and pressure for optimum DIPE production using the supported metallic catalysts.

4. Production of MIBK from acetone using Ni-Cu-Mg/H-zeolite and Ni-Cu-Cr/H-zeolite-β catalysts and

5. Preparation of Pt/CDX-975 supported catalysts with varying metal loading for application as anode electro-catalyst for methanol oxidation in DMFC application.