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Comparative study of IPTBE synthesis on HZSM-5 and ion-exchange resin catalysts

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Abstract

The title ether was synthesized using a batch reactor at 70–90°C and 1.6 MPa. The ion-exchange resins Amberlyst 15, Amberlyst 35 and Purolite CT275, and HZSM-5 zeolites with a SiO_2/Al_2O_3 ratio between 28 and 120 were used as catalysts. IPTBE synthesis rapidly reaches chemical equilibrium in the presence of resins with selectivities of 95–97%, diisobutene being the main byproduct. HZSM-5 zeolites are less active and selective than resin catalysts. Resins, especially Amberlyst 35, are suitable catalysts for obtaining IPTBE industrially.

Keywords: IPTBE; Isopropanol; Isobutene; Etherification; Amberlyst 15; Amberlyst 35; Purolite CT275; HZSM-5

1. Introduction

The US Clean Air Act Amendments of 1990 were designed to correct the changes in fuel composition associated with the lead phase-down, and drove the marketing of reformulated gasolines (RFG) everywhere. The objectives were to limit volatile organic compounds, NO_x, and toxic emissions. RFG composition requires oxygen, which is related directly to the control of CO emissions, and compliance with specifications on total aromatics, benzene and olefin content, and Reid vapor pressure (Rvp) [1]. Methyl *tert*-butyl ether (MTBE) is at present the main source for oxygen. It is a good substitute for aromatics because of its high octane number. In addition, its relatively low boiling temperature also improves the distillation characteristics and driveability performance of the fuel. MTBE has been in recent years under severe environmental pressure [2] and refiners have been examining alternative gasoline blending ethers including *tert*-amyl methyl ether (TAME), ethyl *tert*-butyl ether (ETBE), isopropyl *tert*-butyl ether (IPTBE), etc. [3]. These all have lower Rvp than MTBE, and they provide a good tool for refiners to reduce evaporative emissions. Besides, more volume of these ethers is needed to achieve a target oxygen content owing to their lower oxygen content. Therefore, they provide significant dilution of contaminants such as high boiling compounds.

Of the fuel ethers seriously being considered, IPTBE has the triple advantages of: (i) highest octane blending values, (ii) lowest oxygen content and (iii) low vapor pressure. It is to be noted that IPTBE is a completely refinery-based ether because the oxygen source is water, and its production is certainly interesting if it is combined with that of diisopropyl ether (DIPE) [4]. On the other hand, IPTBE has a lower volatility and water solubility than diethyl ether and DIPE, which accounts for its potential use as a solvent in the chemical and pharmaceutical industries. Still, to date interest towards it has been only academic. Only a few papers can be found in literature

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Nomenclature

a_j	activity of component j (dimensionless)
E	apparent activation energy (kJ mol^{-1})
ΔH^0	standard enthalpy of reaction (kJ mol^{-1})
k	apparent rate coefficient (mol (g h)$^{-1}$)
n_j	mole number of component j (mol)
r^0	reaction rate at $t = 0$ (mol (g h)$^{-1}$)
$R_{A/O}$	initial molar ratio of isopropanol-to-isobutene
S	selectivity
t	time (min)
T	temperature (°C)
W	dry mass of catalyst (g)
X	degree of conversion
Y	yield

Greek symbol

ν	stoichiometric coefficient

concerning the etherification of isobutene with 2-propanol in the liquid phase [5–8].

The acid-catalyzed etherification of isobutene with 2-propanol is the main route to IPTBE. The reaction takes place on ion-exchange resins at mild conditions: 40–80°C and a pressure of about 1.5 MPa:

$$(CH_3)_2CHOH + (CH_3)_2C{=}CH_2 \leftrightarrow (CH_3)_3COCH(CH_3)_2$$

The reaction is less favored than the related reactions of MTBE and ETBE syntheses. Because of the rather low isobutene equilibrium conversion, side reactions can easily take place reducing the selectivity to IPTBE. Main side reactions involved are [6]:

1. Isobutene dimerization:

   2-isobutene↔2,4,4-trimethyl-1-pentene (TMP-1),

   2-isobutene↔2,4,4-trimethyl-2-pentene (TMP-2)

2. Isobutene hydration:

   isobutene + water ↔ *tert*-butanol (TBA)

3. Isopropanol dehydration:

   2-isopropanol ↔ DIPE + water

4. Isopropanol dehydration:

   isopropanol ↔ propene + water

5. Decomposition of IPTBE:

   IPTBE ↔ TBA + propene

6. Etherification of 1-butene (only when a C_4 stream is used):

   1-butene + isopropanol ↔ IPTBE

The paper is devoted to study the IPTBE synthesis in liquid-phase on: (i) the conventional commercial Amberlyst 15 resin, (ii) the acidic poly-sulfonated resins Amberlyst 35, and Purolite CT275 and (iii) HZSM-5 zeolites. Compared to ion-exchange resins the zeolites are thermally stable, give no acid effluent when overheating, and are less sensitive to the alcohol/isobutene ratio. The HZSM-5 zeolites were selected since in the liquid-phase synthesis of MTBE [9,10] and ETBE [11] they gave higher selectivity than Amberlyst-15 in a wider range of methanol/isobutene ratios. The effect of the initial isopropanol-to-isobutene molar ratio ($R_{A/O}$) and temperature on isobutene conversion (X_{IB}), IPTBE yield ($Y_{IPTBE/IB}$) and IPTBE selectivity to byproducts was examined. Apparent activation energies were also determined.

2. Experimental

2.1. Materials

Isopropanol (>99.9%, water < 0.01%) was obtained from ROMIL Chemicals, and stored over 3 Å molecular sieves (Fluka). Isobutene (>99%) was supplied by SEO, and used without further purification. IPTBE (99.8% pure, GC) was prepared in our lab. TBA (>99%) supplied by Merck, and DIPE (>99%), TMP-1 and TMP-2 (>98%) obtained from Fluka, were used for analysis.

The catalysts used were the ion-exchange resins Amberlyst 15 (A15) and Amberlyst 35 (A35) from Rohm and Haas, and CT275 supplied by Purolite (P275), and HZSM-5 zeolites from Degussa (Z28, Z55, and Z120, respectively). Characteristics of these catalysts are given in Table 1.

2.2. Apparatus

The experiments were performed in a jacketed 250 mL capacity autoclave operating in batch mode.

Table 1
Characteristics of assayed catalysts

	A15	A35	P275	Z28	Z55	Z120
Surface area ($m^2\,g^{-1}$)	42	34	28	401	412	400
Capacity (eq. $H^+\,kg^{-1}$)	4.75	5.32	5.2	1.08	0.52	0.29
Average pore diameter (Å)	343	329	601			
Pore volume ($cm^3\,g^{-1}$)	0.36	0.28	0.42			
SiO_2/Al_2O_3				28	55	120
Pore size (Å)				5.3 × 5.6, 5.5 × 5.1	5.3 × 5.6, 5.5 × 5.1	5.3 × 5.6, 5.5 × 5.1

The reaction medium was agitated at 500 rpm by a magnetic drive turbine and mixing baffles on the reactor walls were used to improve the mixing.

2.3. Analysis

The composition of the reacting mixture was analyzed by injecting 0.2 μL of pressurized liquid using a split mode operation into a gas chromatograph (HP5890A) equipped with an FID detector. A 50 m × 0.2 mm × 0.5 μm methyl silicone capillary column was used to separate and determine 2-propanol, isobutene, IPTBE, TBA, DIPE, and isobutene dimers. The column was temperature programmed with a 7 min initial hold at 313 K followed by a 20 K min^{-1} ramp up to 433 K and held for 10 min. Helium was used as the carrier gas, at a flow rate of 30 mL min^{-1}.

2.4. Procedure

A calculated amount of 2-propanol and the dry catalyst were first charged into the reactor and, after looking for leaks, heated to the desired temperature. Then the corresponding amount of isobutene liquid was volumetrically measured at 0.8 MPa in a pressurized burette and charged into the reactor using nitrogen as a carrier. To maintain the reacting mixture in liquid phase over the whole temperature range, the pressure was set at 1.6 MPa. The time of introduction of the isobutene into the reactor was taken as the starting point of the reaction. The experiments were conducted at 70–90°C, and $R_{A/O}$ between 0.7 and 2 were used. To follow the concentration variation of chemicals with time liquid samples were periodically removed and analyzed.

Ion-exchange resins were ground, and the fraction with particle diameter between 0.08 and 0.1 mm was selected. Resin samples of 0.4–1 g (catalyst loading of ca. 1% of liquid mixture) were vacuum dried at 110°C for 3 h. The zeolites used were in the form of fine powders (crystal size of ca. 5 μm). Zeolite samples of 10–30 g (catalyst loading ranging from 5 to 15%) were activated at 400°C for 3 h.

3. Results and discussion

3.1. Ion-exchange resins

Experiments performed on resins were free of mass transfer effects since at 500 rpm external mass transfer do not influence the reaction rate of IPTBE synthesis on A35 [12], and etherification reactions are free of diffusion effects for particles smaller than 0.1 mm [13,14]. Fig. 1 shows a typical plot of the IPTBE and byproducts mole evolution in the presence of A35. IPTBE synthesis is fast and reaches chemical equilibrium at ca. 1.5 h. Byproducts appear as early as the reaction begins although their total amount is small at 3 h reaction time. Diisobutene, especially TMP-1, is the main byproduct. Olefin oligomers were not detected in the course of the experiments. TBA forms initially as a result of the presence of traces of water introduced in the system by the resin and the alcohol. Additional TBA forms all through the experiment because of water produced in isopropanol dehydration to DIPE. However, the extension of this reaction is very low.

As indicated in Table 2, it was observed that at a fixed temperature the isobutene equilibrium conversion increases as $R_{A/O}$ increases, since the initial amount of isobutene is smaller in the reacting mixture. On the other hand, X_{IB} at equilibrium decreases as temperature increases, as expected for an exothermic reaction ($\Delta H^0 = -22.9\,kJ\,mol^{-1}$ [5],

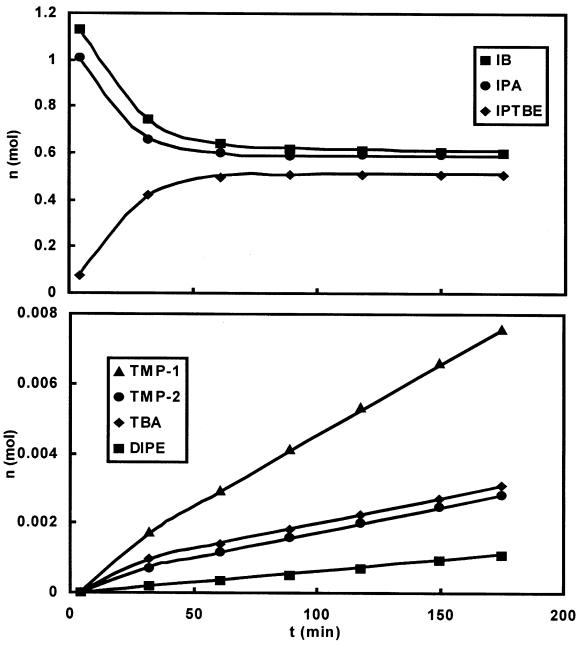

Fig. 1. IPTBE and byproducts formation on A35 at 79.4°C and $R_{A/O} = 1$. Catalyst weight 0.54 g (dry basis).

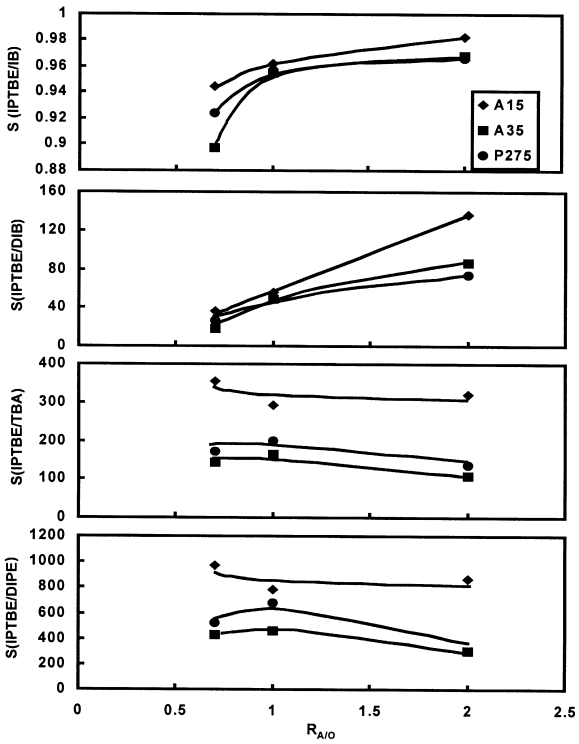

Fig. 2. Selectivity of IPTBE at chemical equilibrium with respect to isobutene, diisobutene, TBA, and DIPE at 79.4°C for A15, A35, and P275 resins.

$-25.5\,\mathrm{kJ\,mol^{-1}}$ [8]). Differences observed between the three resins were not significant, and can be explained because of the experimental error. Since X_{IB} at equilibrium is far lower than that of MTBE and ETBE syntheses, IPTBE is an ideal candidate to be produced industrially by catalytic distillation. The IPTBE formed would be removed from the reaction zone, thus suppressing the reverse reaction and allowing higher conversions into IPTBE.

Selectivity to IPTBE ($S_{IPTBE/IB}$) at equilibrium is also modified by $R_{A/O}$ and temperature. Fig. 2 shows that $S_{IPTBE/IB}$ is very high and increases as $R_{A/O}$ increases because the lower extent of main side reaction, i.e. olefin dimerization. With respect to temperature, as can be seen in Fig. 3, $S_{IPTBE/IB}$ on A35, and P275 decreases as temperature increases whereas it hardly varies on A15. This is because the larger extension of side reactions on the two poly-sulfonated resins.

Table 2
IPTBE conversion and yield at equilibrium on ion-exchange resins

		69.3°C (1)[a]	79.4°C (0.7)	79.4°C (1)	79.4°C (2)	89.5°C (1)
A35	X_{IB}	0.567	0.435	0.483	0.538	0.432
	$Y_{IPTBE/IB}$	0.552	0.396	0.449	0.475	0.406
P275	X_{IB}	0.556	0.484	0.497	0.510	0.385
	$Y_{IPTBE/IB}$	0.541	0.435	0.469	0.494	0.364
A15	X_{IB}	0.546	0.473	0.491	0.509	0.412
	$Y_{IPTBE/IB}$	0.531	0.458	0.481	0.502	0.400

[a] T°C ($R_{A/O}$).

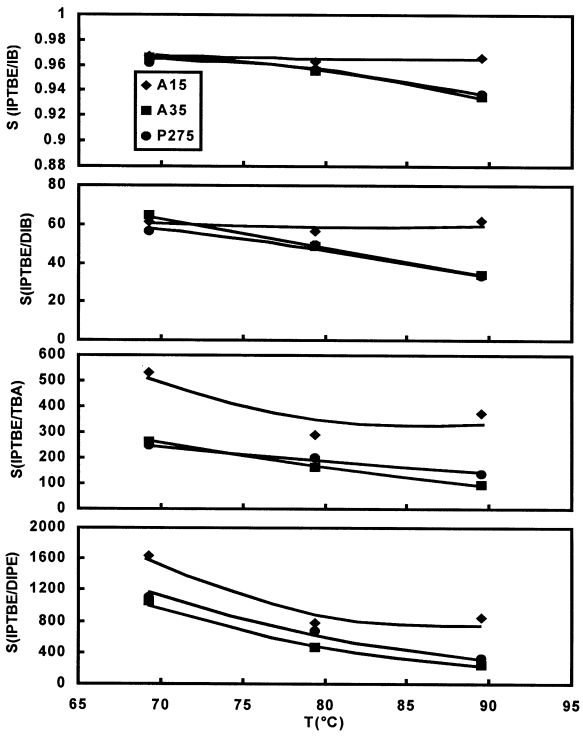

Fig. 3. Selectivity of IPTBE at chemical equilibrium with respect to isobutene, diisobutene, TBA, and DIPE at $R_{A/O} = 1$ for A15, A35, and P275 resins.

Finally, IPTBE yield at equilibrium is rather low and quite similar for the three resins (see Table 2).

In order to assess quantitatively the presence of each byproduct, it is worth to introduce the selectivity of IPTBE relative to byproducts. Thus, selectivity relative to dimers, $S_{IPTBE/DIB}$, is defined as moles of IPTBE produced per mole of dimers generated. As can be seen in Fig. 2, $S_{IPTBE/DIB}$ at equilibrium increases on increasing $R_{A/O}$ since the reaction rate of the isobutene dimerization decreases as the initial amount of the olefin decreases. Fig. 3 shows that $S_{IPTBE/DIB}$ decreases slightly as temperature increases. This fact is explained because the extent of IPTBE synthesis is limited by chemical equilibrium when temperature increases.

The amount of water in the reaction medium is very small since resins were dried at vacuum. Therefore the amounts of TBA formed are small and independent of the composition of reaction medium. $S_{IPTBE/TBA}$ at equilibrium decreases on increasing temperature (Fig. 3). Isobutene hydration is an exothermic reaction, and its equilibrium constants decrease on increasing temperature much more than those of IPTBE synthesis [5,15]. Thus, formation of TBA is more unfavorable thermodynamically than IPTBE synthesis.

Finally, $S_{IPTBE/DIPE}$ at equilibrium hardly varies with $R_{A/O}$, but decreases on increasing temperature. This is because the dehydration of isopropanol is more temperature sensitive than IPTBE synthesis.

Figs. 2 and 3 show that A15 is the most selective resin followed by P275, and A35. The resin with the highest number of active centers is thus the least selective. Selectivity values illustrate that on the three resins diisobutene is the main byproduct. In all the cases DIPE is formed in very small amounts.

Initial reaction rates were obtained from the slope of the curve of isobutene conversion vs. time at $t = 0$ according to the following expression:

$$r^0 = -\frac{n_{IB,0}}{W\nu_{IB}}\left(\frac{dX_{IB}}{dt}\right)_{t=0} \quad (1)$$

It has been observed that kinetic behavior of IPTBE synthesis is similar to that of MTBE [16,17], and ETBE [13] syntheses, and in line with previous IPTBE studies [8,18]. The initial reaction rate decreases as $R_{A/O}$ increases, i.e. when the alcohol concentration increases. Such behavior can be explained by a mechanism in which 2-propanol is hydrogen bonded in the three-dimensional network of $-SO_3H$ groups anchored on the resin, blocking partially the acidic active sites.

In the recent literature on addition reaction of alcohols to olefins catalyzed by ion-exchange resins, it is well accepted that these reacting systems behave non-ideally [8,13,17,19]. So, the kinetic analysis will be done using components activities instead of concentrations. The UNIFAC method was applied for the calculation of activity coefficients. In a previous work conducted on Bayer K2631 beads [18], initial reaction rates for IPTBE synthesis were found to fit well the following kinetic expression:

$$r^0 = k\frac{a_{IB}}{a_{IPA}^2} \quad (2)$$

obtained from a potential fit, and fully compatible with various kinetic mechanisms in which isobutene adsorption extent on the active centers

Table 3
Rate constants and apparent activation energies

	$k \times 10^3$ (mol (g min)$^{-1}$)			E (kJ mol^{-1})
	69.3°C	79.4°C	89.5°C	
A35	11.6	21.3±0.9	44	68±4
P275	8.3	20±1	33	70±9
A15	7.8	14±1	32	72±6
Z28	0.0120	0.0425±0.0008	0.101	109±10
Z55	0.0019	0.0046±0.0005	0.017	111±14

is negligible by comparing to isopropanol adsorption (Langmuir–Hinshelwood mechanism) or which isobutene does not adsorb (Eley–Rideal one). This kinetic view is compatible with a molecular mechanism wherein isobutene is protonated by a proton solvated by the isopropanol, followed by the interaction between the formed *tert*-butyl cation and isopropanol.

Fit of Eq. (2) to initial reaction rates yields the values for k listed in Table 3. These are thermodynamically consistent since they increase as temperature increases, and they indicate that the activity order of tested resins is A35, P275, and A15. If it is assumed that the kinetic constant follows an Arrhenius model, apparent activation energies (E) listed in Table 3 are obtained. As can be seen the lower E value corresponds to the most active resin, i.e. the resin A35 that contains the highest number of active centers. However, E values are the same for all resins within the limits of the experimental error. They are in good agreement with the value of 75.5 kJ mol^{-1} reported in a kinetic study on Bayer K2631 beads [18], and also with the range 70.3–78.4 kJ mol^{-1} determined in a calorimetric study [7].

3.2. HZSM-5 zeolites

Since zeolites were used as a powder, it is assumed that the experiments performed on HZSM-5 zeolites are free of external mass transfer effects. However, as IPTBE and byproducts molecules have roughly the same size as the zeolite pores we think that both main and side reactions are highly influenced by configurational diffusion. In this way, some diffusion retardation effect was observed for the less active zeolites especially in alcohol excess. Fig. 4 shows a typical plot of IPTBE and byproducts formation over an experiment

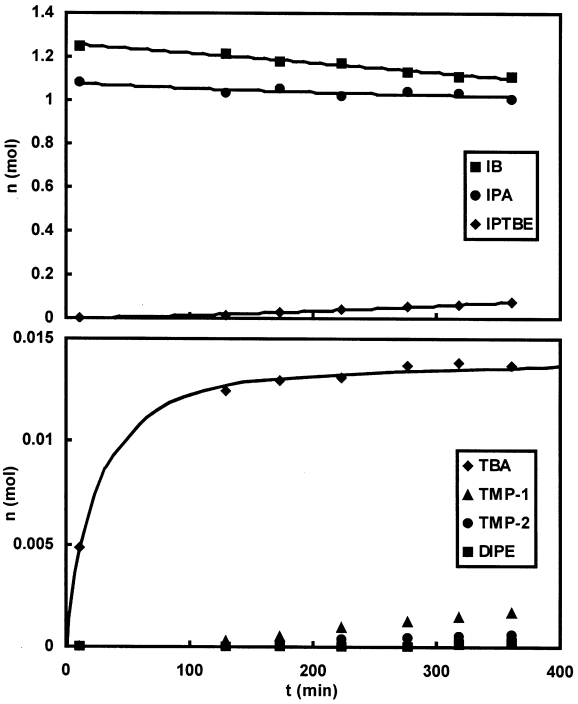

Fig. 4. IPTBE and byproducts formation on Z55 at 79.4°C and $R_{A/O} = 1$. Catalyst weight 17.2 g (dry basis).

on Z55. As can be seen, despite zeolite weight was 40 times higher than in the case of resins, IPTBE synthesis was still far from equilibrium at 6 h reaction time. Main byproduct is TBA. It forms fast at the start of experiment from traces of water in the reacting mixture. Then it increases slowly because the water released in the formation of DIPE. Diisobutene and DIPE also appear, but in smaller amounts than TBA.

To compare activity of catalysts properly it is important to examine experimental data at relatively short reaction times. As Table 4 shows, IPTBE synthesis

Table 4
Isobutene conversion, selectivity to IPTBE, and IPTBE yield at 1 h reaction time and 89.5°C ($R_{A/O} = 1$)

	X_{IB}	$S_{IPTBE/IB}$	$Y_{IPTBE/IB}$
A35	0.406	0.963	0.391
P275	0.395	0.973	0.384
A15	0.393	0.976	0.384
Z28	0.084	0.927	0.078
Z55	0.038	0.621	0.024

Table 5
Isobutene conversion, and IPTBE yield on HZSM-5 at 5 h reaction time

		69.4°C (1)[a]	79.5°C (0.7)	79.5°C (1)	79.5°C (2)	89.5°C (1)
Z28	X_{IB}	0.158	0.291	0.275	0.272	0.390
	$Y_{IPTBE/IB}$	0.139	0.271	0.255	0.250	0.354
Z55	X_{IB}	0.040	0.084	0.077	0.062	0.129
	$Y_{IPTBE/IB}$	0.027	0.073	0.062	0.049	0.109

[a] T°C ($R_{A/O}$).

on acidic resins is close to equilibrium at 1 h reaction time, but despite the higher catalyst mass used, for zeolites X_{IB} is very small. In the presence of Z28, $S_{IPTBE/IB}$ is a bit lower than on resins, but of the same order. The lower selectivity to IPTBE of Z28 and Z55 is mainly due to the fact that IPTBE synthesis is slower than on the assayed resins. On the other hand, activity of the HZSM-5 zeolites highly decreases as their aluminum content decreases. Under assayed conditions, Z120 was active only at 89.5°C, IPTBE being obtained in very small amounts, practically at the limits of chromatographic detection. Finally, by comparing with isobutene conversion on resins we can conclude that HZSM-5 zeolites are far less active than resins.

Initial reaction rates clearly indicated that Z28 is far more active than Z55. Similar to resins, initial reaction rates decrease as $R_{A/O}$ increases. HZSM-5 zeolites and resins adsorb large quantities of alcohol and isobutene [20]. Therefore reaction mechanisms on both catalysts are probably similar. Obtained rate constants from Eq. (2) are thermodynamically consistent (Table 3). Apparent activation energies for assayed zeolites are greater than for resins, showing a higher sensitivity of IPTBE synthesis to temperature.

Long reaction times are suitable to draw inferences of industrial interest, and to roughly compare with selectivity values obtained on resins at equilibrium. Table 5 shows X_{IB}, and $Y_{IPTBE/IB}$ on zeolites at 5 h reaction time. As can be seen, at $R_{A/O} = 1$ and 89.5°C X_{IB} is close to equilibrium only on Z28. Since the reaction is far from equilibrium, X_{IB} and $Y_{IPTBE/IB}$ increase with temperature, and decrease very slightly on increasing $R_{A/O}$. Therefore, IPTBE synthesis is more temperature sensitive than side reactions and accordingly selectivity to IPTBE increases with temperature. Fig. 5 shows that $S_{IPTBE/IB}$ decreases very slowly as $R_{A/O}$ increases, because of the lower extension of the dimerization of isobutene. It is to be noted that $S_{IPTBE/IB}$ is lower than in the presence of resins, and also less sensitive to composition of reaction medium.

As for side reactions, Figs. 5 and 6 show $S_{IPTBE/TBA}$, $S_{IPTBE/DIB}$ and $S_{IPTBE/DIPE}$ values at

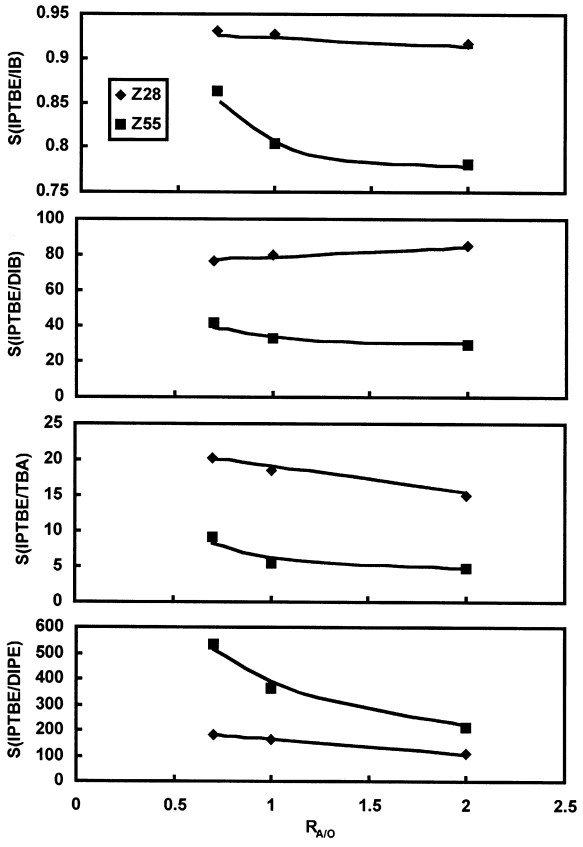

Fig. 5. Selectivity of IPTBE with respect to isobutene, diisobutene, TBA, and DIPE at 79.4°C for Z28 and Z55 at 5 h reaction time.

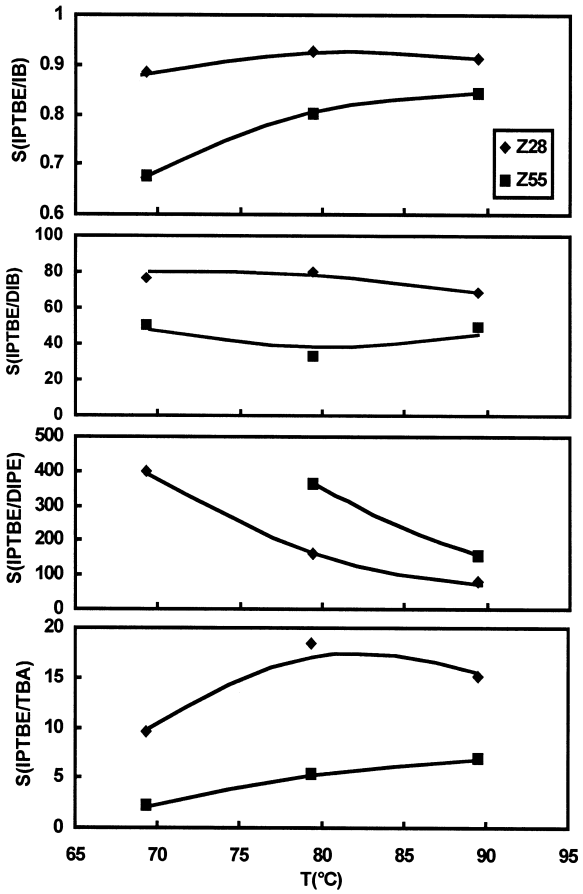

Fig. 6. Selectivity of IPTBE with respect to isobutene, diisobutene, TBA, and DIPE at $R_{A/O} = 1$ for Z28 and Z55 at 5 h reaction time.

5 h reaction time. As can be seen, TBA is the main byproduct whereas DIPE is the less important. Since TBA formation is also thermodynamically limited, $S_{IPTBE/TBA}$ increases as temperature increases, and decreases slightly as $R_{A/O}$ increases. $S_{ITBE/DIPE}$ hardly varies with $R_{A/O}$ and temperature showing that sensitivity to temperature of IPTBE synthesis and isobutene dimerization is similar. $S_{IPTBE/DIB}$ is little sensitive to composition of reaction medium probably because isobutene dimers and IPTBE can barely pass through the pores of zeolites. $S_{IPTBE/DIPE}$ decreases on increasing $R_{A/O}$ because the alcohol concentration increases, but it decreases as temperature increases since DIPE formation is more sensitive to temperature than IPTBE synthesis.

By comparing Figs. 2, 3, 5 and 6, we can see that $S_{IPTBE/DIB}$ on resins and zeolites are similar. However, $S_{IPTBE/TBA}$ is far less on zeolites which could explain that TBA amounts observed were higher than in the presence of resins. This could be explained because TBA have a less restricted motion than IPTBE in zeolite pores. Moreover, it is possible that some IPTBE decomposes into TBA and propene within pores of HZSM-5. "Finally, despite DIPE formation is very low on all the catalyst $S_{IPTBE/DIPE}$ is twice on resins, probably because configurational diffusion of DIPE is less hindered than that of IPTBE".

4. Conclusions

An ion-exchange resin, specifically Amberlyst 35, is suitable for obtaining IPTBE at working temperatures of industrial interest (ca. 60°C or even lower, in order to obtain isobutene equilibrium conversions as high as possible). Medium pore zeolites HZSM-5 are less active and selective than resins. Recently, it has been shown that H-beta zeolites are as efficient as Amberlyst 15 in the liquid phase synthesis of MTBE [21]. Therefore, it is likely that large pore zeolites, including faujasite or mordenite, would be more suitable than HZSM-5 for IPTBE synthesis. Anyway, much more work is needed to find the most suitable zeolite catalyst for this reaction.

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