Influence of polar components in the dimerization of isobutene

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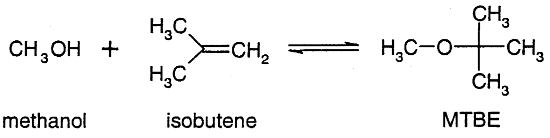
Isooctane is seen as a potential replacement for methyl *tert*-butyl ether (MTBE) in gasoline. Isooctane can be produced via the indirect alkylation route in two steps. Isobutene is first dimerized to isooctenes, which are then further hydrogenated to isooctane. In the dimerization a polar component is used to enhance the selectivity for diisobutenes. In this study the effects of *tert*-butyl alcohol (TBA), methanol and MTBE in the dimerization reaction were compared on the basis of experimental results. All the oxygenates studied induced similar effects: higher selectivity for diisobutenes and lower isobutene conversion as the oxygenate content increased and temperature decreased. The different polarity of the components causes the need for more methanol or MTBE than TBA to get the same conversion and selectivity.

KEY WORDS: isobutene dimerization; isooctene; isooctane; ion exchange resins as catalysts.

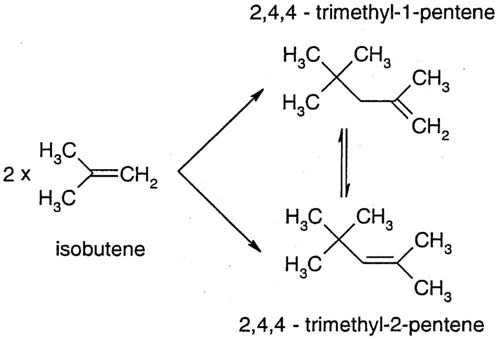
1. Introduction

In recent years there has been growing interest in components in gasoline that can replace methyl *tert*-butyl ether (MTBE, 2-methoxy-2-methyl propane). MTBE has a very high octane number and as an oxygen-containing compound it assists in clean burning of fuels. However, MTBE is soluble in water and can enter ground water from leaking storage tanks. California has banned the use of MTBE in gasoline with effect from the end of 2003 [1,2].

MTBE could be replaced by, for example, the product of isobutene (IB, 2-methyl propene) dimerization, *i.e.* a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene. Isobutene dimerization uses the same isobutene feedstock as MTBE synthesis (schemes 1 and 2). The diisobutenes (isooctene, DIB) have high octane numbers (RON/MON = 100/89) [3] and are not as soluble in water as MTBE. Diisobutenes can also be used as a feedstock to produce other high-octane components like isooctane (2,2,4-trimethyl pentane) or ethers like 2-methoxy-2,4,4-trimethyl pentane and 2-ethoxy-2,4,4-trimethyl pentane [4,5]. One advantage of the dimerization process is that existing MTBE plants can be converted to produce isooctane [6], even though the changes needed are sometimes underestimated.



Scheme 1. Formation of MTBE.



Scheme 2. Dimerization of isobutene.

The dimerization of isobutene has been widely studied as a side reaction of MTBE synthesis [7–9]. When dimerization is conducted without etherification using an ion exchange resin catalyst, as well as diisobutenes, significant amounts of various triisobutenes and also some tetraisobutenes are produced [10]. These higher oligomers are not useful components in gasoline because of their high molecular weight and low volatility [8]. The selectivity for diisobutenes can, however, be increased by feeding methanol together with isobutene (methanol/isobutene = 0.2–0.6 mol/mol) into the reactor [3]. The use of other polar components such as ethanol and isopropanol has also been reported [11].

The drawback of feeding methanol together with isobutene is the formation of MTBE. Its separation from the product is fairly difficult and therefore it would be an advantage to use an additive that does not form an ether with isobutene. *Tert*-butyl alcohol (TBA, 2-methyl-2-propanol) is an example of such a polar component [12]. The only significant side reaction here is the dehydration of TBA which produces water and isobutene, as shown in scheme 3. This is why water can also be used to enhance the selectivity.

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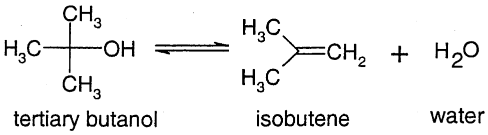

Scheme 3. Dehydration of TBA.

Several technologies are available for commercialization. Snamprogetti has developed Isoether processes to produce isooctane [13–15] and together with Catalytic Distillation Technologies (CDTECH) they also offer combined CD*Isoether* technology [16]. In these technologies isobutene can be dimerized to diisobutenes or partially dimerized and partially etherified. Depending on the case, TBA or methanol or both can be used to enhance the selectivity.

UOP's InAlk process uses solid phosphoric acid or sulfonic acid ion exchange resin catalysts in the dimerization [17]. Water is added in both cases to control the activity and selectivity of the operation. The NExOCTANE^{TM} process developed by Fortum Oy and Kellogg Brown & Root also uses water (TBA) as an additive [6,18]. As a result, diisobutenes are produced free of MTBE and with a high diisobutene yield.

Even though several commercial processes exist, the scientific understanding of the reaction is still limited. In this article we confirm the importance of the polar component in the dimerization of isobutene on an ion exchange resin catalyst. The results from experiments with two different alcohols, methanol and TBA, are compared. To study the difference in the effects of methanol and MTBE, experiments with MTBE in the feed were also performed. From the results the conversion of isobutene and selectivity for diisobutenes were determined. Their dependence on the temperature and additive content was established, allowing some speculation on the effect of the polar component. Furthermore, the deactivation level of the used catalyst was determined by measuring the hydrocarbon content of the catalyst by ^{13}C NMR.

2. Experimental

2.1. Reactor system

The reactor used in the dimerization experiments was a continuous stirred tank reactor (CSTR) that operated in the liquid phase. The volume of the reactor was 50 cm^3 and it was stirred with a six-blade mechanical stirrer. The reactor included a mixing baffle and a metal gauze basket in which the catalyst (1 g) was placed.

Two feeding tanks (2 dm^3) were used in the reactor system. One tank contained isobutene as a liquid, and the other contained a mixture of the polar component and the solvent. The feeding tanks were pressurized with nitrogen to 1.8 MPa. The flow through the reactor was achieved with a pressure difference, as the pressure in the reactor was kept at 1.5 MPa. The tubes in which TBA flowed were heated to 33–35 °C due to its high melting point (23–25 °C). The reactor was heated with hot oil flowing through a jacket.

An automation system using Wonderware Factory-Suite 2000 software gathered measurements on-line. This also made the control of the temperature in the reactor possible according to a predetermined plan.

2.2. Analytical methods

The flows to and from the reactor were analyzed with an on-line Hewlett-Packard 5890 Series II gas chromatograph (GC). The GC was equipped with a capillary column, HP-1, the length of which was 60 m, film thickness 1.00 μm and diameter 0.25 mm. A flame ionization detector was used in the GC.

In order to obtain quantitative results from the analysis, response factors were determined for the different compounds. For di- and triisobutenes these were obtained from mixtures of these compounds. Tetraisobutenes were assumed to have the same response factor as triisobutenes.

2.3. Catalyst

A commercial ion exchange resin was used as a catalyst. This resin consisted of a styrene–divinylbenzene-based support in which sulfonic acid groups had been added as active sites. The concentration of the active sites on the catalyst was 5 eq/kg, the surface area 45 m^2/g and the average particle size 0.8 mm.

2.4. Reactants and solvents

The reactants used included isobutene (Aga, 99%), methanol (Riedel-de Haën, >99.8%) and TBA (MERCK-Schuchardt, >99%). MTBE was supplied by Fortum Oil and Gas Oy (>95%). Isopentane (Fluka Chemika AG, ≥99%) was used as a solvent.

2.5. Procedure

Before use the catalyst was dried in an oven at about 100 °C overnight. Dried catalyst (about 1 g) was packed into the catalyst basket and placed into the reactor. The mixing was fixed at 900 rpm. The feeding tanks were filled and pressurized. The flow of isobutene was set at 11.4 g/h and the flow of isopentane and additive mixture at 24.3 g/h, resulting in an isobutene to isopentane and additive molar feed ratio of about 0.6. The additive content in the feed was varied between 0 and 19.0 mol% in the experiments.

At the beginning of the experiment the mixed isobutene, isopentane and additive flow was analyzed using the gas chromatograph. When the flow had stabilized and the feed had been analyzed accurately, the flow was fed into the reactor. The reaction at one temperature was continued until the change in the concentrations was smaller than ±1 mol%. This was considered a steady state. After it was reached the temperature could be changed. Experiments were carried out at temperatures of 60, 80 and 100 °C.

2.6. Calculation

During the experiments the contents of the flows to and from the reactor could be analyzed. With these data the conversion of isobutene to oligomers X, the selectivity for diisobutenes S and the diisobutene yield Y could be calculated. When MTBE formation was taken into account in the calculations the following equations were used:

$$X = \frac{2\dot{n}_{\mathrm{DIB}} + 3\dot{n}_{\mathrm{TRIB}} + 4\dot{n}_{\mathrm{TETRAB}} + \dot{n}_{\mathrm{MTBE}}}{\dot{n}_{\mathrm{IB,in}}} \times 100\%, \tag{1}$$

$$S = \frac{2\dot{n}_{\mathrm{DIB}}}{2\dot{n}_{\mathrm{DIB}} + 3\dot{n}_{\mathrm{TRIB}} + 4\dot{n}_{\mathrm{TETRAB}} + \dot{n}_{\mathrm{MTBE}}} \times 100\%, \tag{2}$$

$$Y = \frac{XS}{100\%}. \tag{3}$$

2.7. Measuring the hydrocarbon content of the catalysts used

The hydrocarbon content of some of the catalysts after the dimerization experiments was calculated from ^{13}C CPMAS NMR spectra. Before the measurements the samples were heated in a vacuum at 110 °C for 3 h to remove volatile compounds and water. A Chemagnetics Infinity spectrometer at 270 MHz was used for the measurements, and the peak areas in the aliphatic region of the fresh and used catalysts were compared. The method was based on the studies of Law *et al.* [19,20].

3. Results

3.1. Conversion and selectivity

Experiments were initially carried out without polar components. In figure 1 the result of the experiment at 80 °C is presented as molar fractions of products as a function of time. A stationary state was reached after about 14 h. It is clearly seen that at first diisobutenes are the main products (66 mol%). In the stationary state though, the amount of triisobutenes is already 71 mol% of the product. The tetraisobutene content is still fairly low: only 5 mol%.

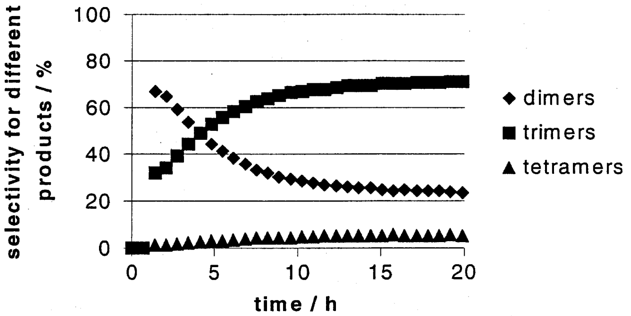

Figure 1. Molar fractions of formed oligomers as a function of time in an experiment without polar components at 80 °C.

One experiment with methanol as an additive and one with TBA were carried out. The results are presented in figures 2 and 3, showing the molar fractions of products as a function of time. The experiments were carried out at 80 °C and there was 2.0 mol% methanol (figure 2) and 0.9 mol% TBA (figure 3) in the feed. These two experiments were chosen because in these the diisobutene yield was almost the same (43% and 46%).

In figures 2 and 3 the remarkable effect of the polar component can be seen. With methanol the stationary state is reached in about 12 h under the conditions used. Methanol reacts almost completely to MTBE and there are about 45 mol% triisobutenes and 2 mol% tetraisobutenes in the product. With TBA the stationary state is achieved in about 7 h and the molar fraction of oligomers is even smaller: 14 mol% triisobutenes and 0.4 mol% tetraisobutenes. Clearly, with TBA better selectivity for diisobutenes is achieved.

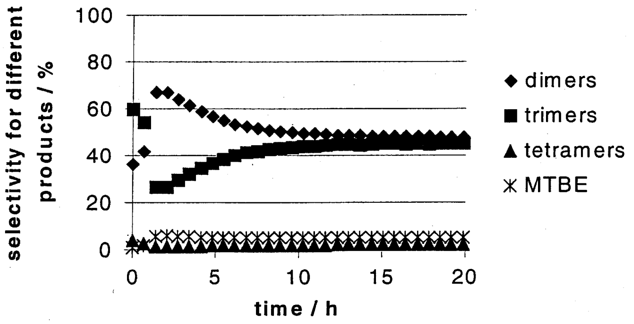

Figure 2. Molar fractions of formed oligomers as a function of time in an experiment with 2.0 mol% methanol at 80 °C.

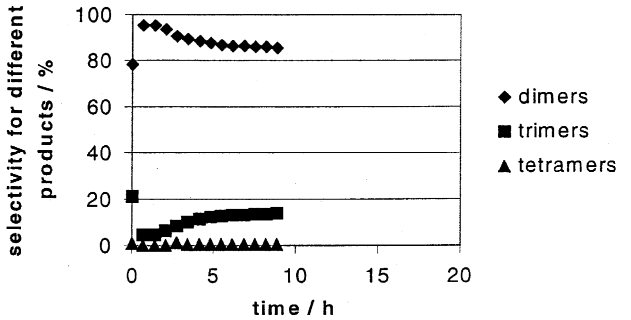

Figure 3. Molar fractions of formed oligomers as a function of time in an experiment with 0.9 mol% TBA at 80 °C.

Table 1
Conversion of isobutene, selectivity for diisobutenes and diisobutene yield for experiments at 80 °C

	Conversion	Selectivity	Yield
Without alcohol	97	24	23
With 2.0 mol% MeOH	89	48	43
With 0.9 mol% TBA	53	86	46

The conversions, selectivities and yields of the two experiments are compared with the results of the experiment with no polar component in table 1. It can be seen that although the best selectivity for diisobutenes is achieved with TBA, the conversion is then very low compared to the other experiments. However, the improved selectivity increases the diisobutene yield considerably.

Experiments were also carried out with MTBE in the feed. In these experiments, hardly any methanol was produced. The results of the experiments with all three additives and different additive content are presented in figures 4 and 5. It can be seen that there is a dramatic increase in the diisobutene selectivity in the experiments as the TBA content increases. The effect is not as clear with methanol. In experiments with MTBE the conversion is lower and selectivity higher than in experiments with methanol.

In experiments with high methanol content, the formation of MTBE clearly affects both the conversion of isobutene and the selectivity for diisobutenes. Figures 6 and 7 also give the conversions and selectivities as a function of additive content, but the formation of MTBE is not taken into account in the calculations. Now the dimerization reaction without etherification can be studied. The difference between the methanol and MTBE experiments seen in figures 4 and 5 is not seen in figures 6 and 7.

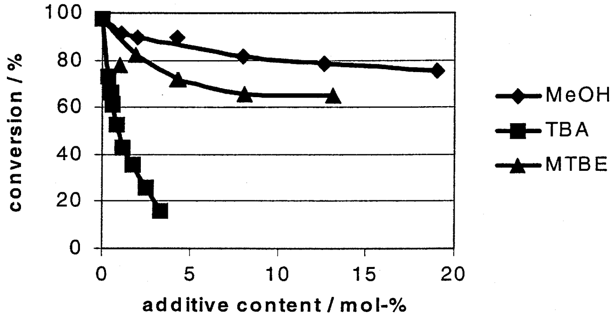

Figure 4. Total conversion of isobutene as a function of additive content in the feed at 80 °C.

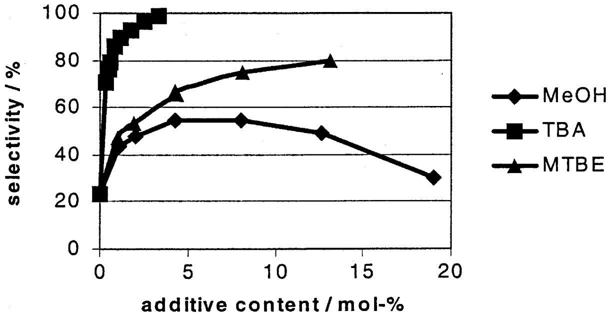

Figure 5. Selectivity for diisobutenes as a function of additive content in the feed at 80 °C.

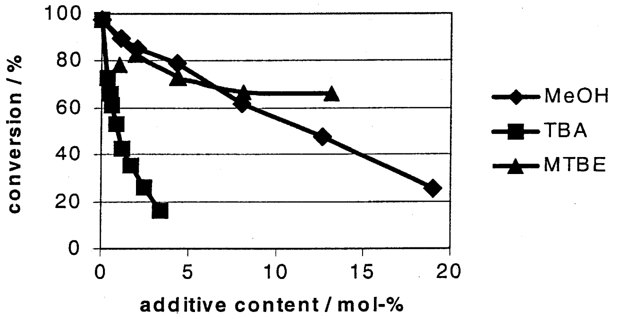

Figure 6. Conversion of isobutene to oligomers as a function of additive content in the feed at 80 °C.

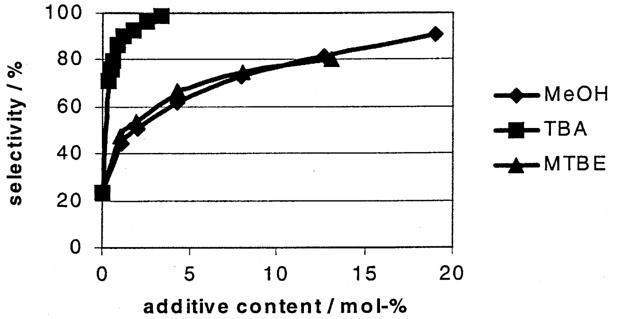

Figure 7. Selectivity for diisobutenes as a function of additive content in the feed at 80 °C when MTBE formation is not taken into account in the calculations.

The conversion and selectivity as a function of methanol or TBA content in the feed at different temperatures is presented in figures 8 and 9. It is seen that as the alcohol content is increased, selectivity increases. The temperature has only a small effect on selectivity in all experiments. With low alcohol content though, as the temperature increases, the selectivity decreases. The conversion of isobutene shows the

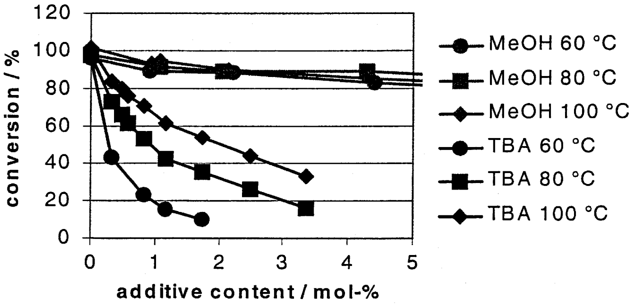

Figure 8. Total conversion of isobutene as a function of additive content in the feed at different temperatures.

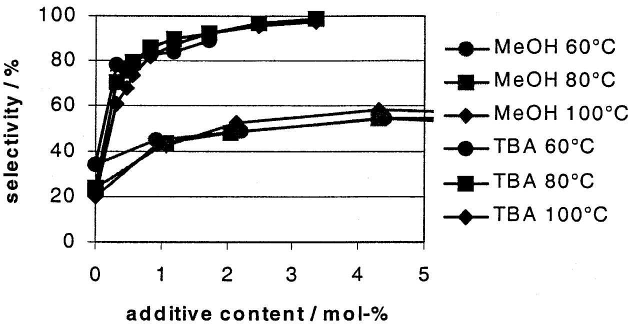

Figure 9. Selectivity for diisobutenes as a function of additive content in the feed at different temperatures.

opposite behavior: it decreases as the alcohol content increases and the temperature decreases. With methanol the temperature has hardly any effect on the conversion of isobutene. All these effects are summarized in table 2.

The yields of the experiments at 80 °C are presented in figure 10. The diisobutene yield has a maximum, 50%, at about 0.5 mol% of TBA. With methanol the best yield is 48% with an alcohol content of about 4.3 mol%.

3.2. *Hydrocarbon formation on the catalyst in the experiments with alcohols*

In the hydrocarbon (HC) content measurements all remaining HC after drying is assumed to be trapped in the pores, *i.e.* the HC content shows the potential deactivation level of the catalyst even though no deactivation was observed in these short experiments. The relative hydrocarbon content of some of the catalysts used in the dimerization experiments is presented in figure 11. It can be seen that, with alcohols present in the dimerization, the hydrocarbon content of the catalyst decreases. With TBA there is a low hydrocarbon content, *i.e.* negligible deactivation already with low TBA content. With methanol, however, the decrease is not as fast.

Table 2
The effect of alcohol content and temperature on the conversion of isobutene and the selectivity for diisobutenes

	TBA		MeOH	
	Conversion	Selectivity	Conversion	Selectivity
Increasing alcohol content	↓	↑	↘	↗
Increasing temperature	↗	↔	↔	↔

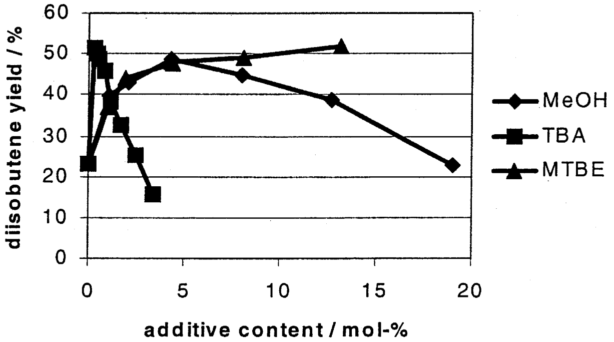

Figure 10. Diisobutene yield as a function of additive content in the feed at 80 °C.

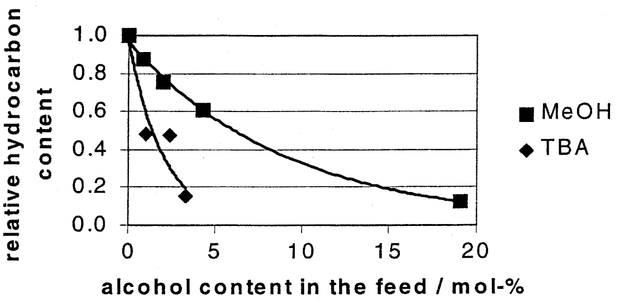

Figure 11. Relative hydrocarbon content of the catalysts used in the dimerization experiments with different amounts of methanol and TBA.

4. Discussion

4.1. *Dimerization without polar components*

From the experiments without polar components it can be seen that diisobutenes are the main products at the beginning. After a while their content decreases as the amount of triisobutenes increases. This suggests that triisobutenes are formed in a consecutive reaction via diisobutenes. In the experiments without polar components triisobutenes are the main products in the stationary state. Furthermore, the isobutene conversion is high, indicating a very active state of the catalyst.

4.2. *Methanol versus MTBE experiments*

Figures 6 and 7 show the conversion of isobutene and the diisobutene selectivity when the formation of MTBE is not taken into account in the calculations. These figures show that there is about the same selectivity and conversion in both the methanol and the MTBE experiments. This suggests that there is about the same amount of MTBE and methanol on the catalyst in experiments with both additives. As there is hardly any methanol produced in the MTBE experiments, it can be concluded that almost all methanol reacts to MTBE. The differences in figures 4 and 5 between the methanol and MTBE experiments are thus explained by MTBE formation when methanol is fed into the reactor.

Based on the previous observations, it seems that MTBE, not methanol, affects the selectivity in both the methanol and the MTBE experiments. This means that we have to consider the properties of MTBE and not methanol when we want to study the differences between the effects of the polar components.

4.3. *Effect of polar component on conversion and selectivity*

Increasing the amount of polar component results in a decrease in conversion. Similar effects of polar components on ion exchange resins have been reported in the literature. Thornton and Gates [21], for example, studied different structures of the acid sites of ion exchange resins in the presence of polar components with infrared spectroscopy and the catalytic activities of these resins in the dehydration of alcohols. They concluded that the active sites of the ion exchange resin are hydrogen-bonded sulfonic acid sites. The catalytic activity of these sites is a consequence of their strong proton-donating tendencies. As polar components come into contact with the resin, they place themselves between hydrogen bonds and in this way dissociate the protons of the acid groups. The resulting structure has a smaller proton donor strength than the original one and in this way is also less catalytically active.

Di Girolamo *et al.* [3,22], on the other hand, studied the effect of methanol on the dimerization reaction using ion exchange resins as catalysts. They reasoned that methanol adsorbs on the active sites considerably because of its high polarity. They also thought, like Thornton and Gates [21], that the species formed (MeOH_2^+) are not as acidic as the original sulfonic acid site. This results in a decrease in the rate of oligomerization reactions.

More polar components usually adsorb on the active sites more strongly than less polar components [23]. This was confirmed by Karinen *et al.* [5], who studied the etherification and isomerization of alkenes and found that both rates increased with decreasing polarity of the alcohol, among other features. These studies suggest that we can compare different additives in the dimerization by their polarities. As an alcohol TBA is more polar than MTBE (dielectric constant for TBA at 30 °C = 10.9 [24] and for MTBE = 2.6 [25]). The effect of TBA on oligomerization rates is thus strong already with low content. With MTBE the effect is considerably weaker. The high polarity of methanol (dielectric constant at 25 °C = 32.6 [24]) cannot be utilized because of the immediate conversion of methanol to MTBE, as noted earlier.

The reduced reaction rates in the presence of polar components result in increased selectivity. There are fewer isobutenes and oligomers adsorbed on neighboring active sites, which prevents the formation of higher oligomers. In addition, as conversion decreases there is less starting material for the formation of triisobutenes.

It would be interesting to know whether there are any differences in the intrinsic behavior of the polar components and whether we can get higher conversion and higher selectivity with one polar component than with the other. The selectivity for diisobutenes as a function of conversion at 80 °C is plotted in figure 12 (MTBE formation was not taken into account in the calculations). The figure shows that the relationships are very similar with different additives. This suggests that both MTBE and TBA affect the catalyst in the same way: as polar components they solvate the protons of the acid sites of the catalyst and thus reduce the reaction rates, which increases selectivity for diisobutenes. The only difference is their different polarity. A smaller amount of the compound with higher polarity is needed to get high selectivity than of the compound with lower polarity.

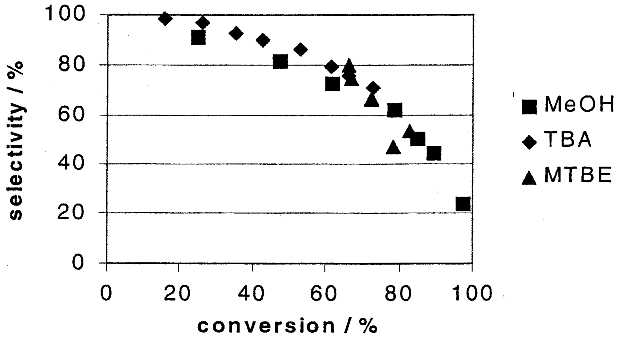

Figure 12. Selectivity for diisobutenes as a function of isobutene conversion at 80 °C.

The discovery that the correlation between selectivity and conversion is the same for all the additives explains many of the experimental results. For example, the time needed to reach the stationary state was 14 h without polar components, 12 h with methanol and 7 h with TBA. With higher triisobutene content it takes longer to reach a stationary state than with lower content. The yields in the alcohol experiments were almost the same but the conversions and selectivities were very different. In the methanol experiments it took longer to reach a stationary state but the conversion was higher and selectivity lower than with the experiment with TBA. This means that because MTBE was less polar, its effect was not as strong as with TBA and the results in the MTBE experiments more closely resemble those without polar components. The hydrocarbon contents of the used catalysts can be explained similarly.

4.4. *Effect of temperature on conversion and selectivity*

Figure 8 shows that as the temperature increases, the conversion increases. Both dimerization and oligomerization rates increase, which results in a decrease in the diisobutene selectivity. This is seen with low additive content. With higher content the selectivity is already so high that the differences are not seen.

The effect of temperature was not as clear in the experiments with methanol as with TBA. This could be because conversion is already so high that it cannot be increased by increasing the temperature. As the conversion remains unchanged, selectivity also does not change.

5. Conclusions

The effects of polar components on the dimerization of isobutene using ion exchange resin catalysts were studied. It was confirmed that in this reaction polar components improve the selectivity for diisobutenes, which are the desired products. Without them the diisobutenes react further to triisobutenes in significant amounts.

The effects of methanol and TBA in the dimerization reaction were compared. In the experiments almost all the methanol reacted with isobutene to produce MTBE. This is why MTBE was concluded to be the selectivity-controlling component rather than methanol. High diisobutene yields were achieved, but the MTBE content in the product was also considerable.

Unlike methanol, TBA does not form an ether with isobutene and only water is formed in a side reaction. The experiments showed that high selectivity was achieved already with low TBA content. The higher selectivity in the TBA experiments than in the MTBE (methanol) experiments was concluded to be due to TBA's higher polarity. However, all the polar components gave the same correlation between isobutene conversion and diisobutene selectivity: as conversion increases, selectivity decreases. This similarity indicates that a polar component in the dimerization decreases the activity of the catalyst. The selectivity improvement is caused by this reduced catalytic activity.

Low TBA content is needed for an MTBE-free diisobutene product. Based on the results, TBA will be used as an additive in further studies which will include the modeling of reaction kinetics.

6. Notation

DIB = diisobutenes, dimers (2,4,4-trimethyl pentenes)
IB = isobutene (2-methyl propene)
MeOH = methanol
MTBE = methyl *tert*-butyl ether (2-methoxy-2-methyl propane)
$\dot{n}$ = molar flow in a stationary state
TBA = *tert*-butyl alcohol (2-methyl-2-propanol)
TETRAB = tetraisobutenes, tetramers
TRIB = triisobutenes, trimers

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