Comparison of the catalytic properties of Al-ZSM-22 and Fe-ZSM-22 in the skeletal isomerization of 1-butene

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The catalytic activities of Al-ZSM-22 (Al in the framework) and Fe-ZSM-22 (Fe in the framework) were compared in the skeletal isomerization of 1-butene to isobutene. The catalysts synthesized in the laboratory were characterized by means of XRD, FTIR spectroscopy, SEM and surface area measurements. The activity of the zeolites was investigated using a fixed-bed microreactor system. Al-ZSM-22 demonstrated higher activity in 1-butene transformation compared to Fe-ZSM-22, while the selectivity to isobutene, on the other hand, was higher over Fe-ZSM-22. Coke formation was monitored using a microbalance and the results showed that the weight gain of Fe-ZSM-22 was slightly higher compared to Al-ZSM-22.

Keywords: ZSM-22, skeletal isomerization, isobutene production, acid strength

1. Introduction

There is an increasing interest in the skeletal isomerization of n-butene to isobutene over zeolites as isobutene can be used in the reaction with methanol to produce MTBE (methyl *tert*-butyl ether). Branched ethers like MTBE have become an important and highly demanded part of reformulated gasoline since they enhance the octane number. As the current supply of isobutene from catalytic cracking is insufficient to meet the increasing demand for MTBE, considerable interest has been devoted to producing isobutene from n-butene.

Several papers have demonstrated the importance of shape selectivity in order to obtain high selectivity to isobutene from 1-butene [1,2]. The most promising 1-butene skeletal isomerization catalysts such as ZSM-22 [3,4], ZSM-23 [5], ZSM-35 [6–8] and SAPO-11 [9,10] all have 10-membered-ring pore systems. Another important parameter, which needs to be taken into consideration when developing a selective skeletal isomerization catalyst, is acid strength. It is known that the acid strength required for acid catalyzed conversion of hydrocarbons can be ranked as cracking $\approx$ oligomerization $>$ skeletal isomerization $\gg$ double-bond isomerization [11]. Since isobutene is most likely produced through a monomolecular reaction mechanism [8,10], the ideal skeletal isomerization catalyst should have acidity, which is strong enough for skeletal isomerization, but weak enough to avoid oligomerization and cracking in order to reduce the formation of by-products such as octenes, propene and pentenes.

Brønsted acid sites in zeolites are associated with framework trivalent atoms. The acid strength depends on the nature of the framework trivalent atoms. The acid strength of zeolites decreases in the sequence: Al $>$ Ga $>$ Fe $\gg$ B [12]. ZSM-5 with framework Al, Ga, Fe and B has previously been investigated in the skeletal isomerization of 1-butene [13]. The conclusion was that Fe-ZSM-5 was more selective to isobutene compared to both Al-ZSM-5 and Ga-ZSM-5 because of its lower acid strength. B-ZSM-5 was not sufficiently acidic to catalyze skeletal isomerization of 1-butene.

To the best of our knowledge, there has been no publication where ZSM-22 with Fe in the framework has been investigated in the skeletal isomerization of 1-butene. Because of its one-dimensional channel system of 10-membered-rings with channel diameters of 4.5×5.5 Å and no cavities [14], ZSM-22 is a much more shape-selective catalyst than ZSM-5. The latter has a three-dimensional channel system and the large cavities formed in the intersections of the 10-membered ring channels cannot prevent dimerization of butene, and therefore production of by-products is higher over ZSM-5 than ZSM-22.

2. Experimental

2.1. Synthesis of the zeolites

The synthesis method used in the preparation of Al-ZSM-22 has previously been described in [4]. Fe-ZSM-22 was synthesized using the method described in [15] with some modifications. The main modification was in the choice of reagents for the synthesis. The reagents used in the synthesis of Fe-ZSM-22 were: sodium silicate solution (Merck), $Fe(NO_3) \cdot 9H_2O$ (Fluka), 1-ethylpyridinium bromide (TCI), sulfuric acid (Merck) and distilled water.

The obtained zeolites were washed thoroughly with distilled water and dried at 100 °C for 12 h. The as-synthesized form of the zeolites was obtained after the organic template was removed in a calcination step at 550 °C in a flow of nitrogen for 6 h, followed by air for an additional 10 h. Before calcination the zeolite powder was pressed, crushed and finally sieved to 0.125–0.250 mm particle size. The proton form of the zeolites was obtained after ion exchanging the as-synthesized zeolites for 24 h in a 1 M NH_4Cl solution, followed by washing, drying and, finally, calcination using the same procedure as in the removal of the organic template. The difference in activity of the as-synthesized and proton form of the zeolites was determined in 1-butene transformation. The activities of the as-synthesized and the proton form of Al-ZSM-22 were similar [4,8]. On the other hand, the conversion over Fe-ZSM-22 increased substantially after the ion exchange. The as-synthesized form of Al-ZSM-22 (Si/Al = 53) and the proton form of Fe-ZSM-22 (Si/Fe = 56) were used in all the following experiments.

2.2. Characterization of the zeolites

The structure and phase purity of the synthesized zeolites were determined by X-ray powder diffraction (XRD) using Cu Kα radiation (Philips pw 1830). Except for one additional peak in the Fe-ZSM-22 diffraction pattern at $2\theta = 22°$, the XRD patterns of Al- and Fe-ZSM-22 were identical and similar to those previously reported in the literature [3].

The acidities of the zeolites were characterized using FTIR analysis of adsorbed pyridine (ATI Mattson infinity spectrometer). The method used for pyridine adsorption has previously been described in [8]. The FTIR spectra for Al- and Fe-ZSM-22 are compared in figure 1. The band at 1548 cm^{-1} which is characteristic for pyridine adsorbed on Brønsted acid sites, and the band at 1453 cm^{-1} associated with pyridine adsorbed on Lewis acid sites, were present in both the zeolites. The band at 1491 cm^{-1} is usually associated with pyridine adsorbed on both Lewis and Brønsted acid sites. The number of Brønsted acid sites was lower in Fe-ZSM-22 compared to Al-ZSM-22, as can be seen by comparing peak areas at 1548 cm^{-1}.

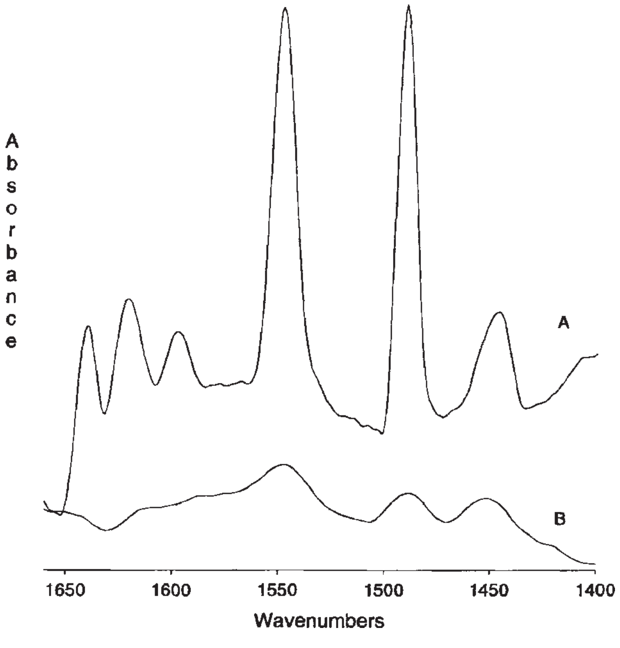

Figure 1. The FTIR spectra for Al-ZSM-22 (A) and Fe-ZSM-22 (B) after adsorption of pyridine.

The shape and size of the crystals were determined from scanning electron microscopy (SEM) pictures (Leica Cambridge Stereoscan 360). The average width of the needle shaped Al-ZSM-22 crystals was found to be 0.4 μm and the length was 2.9 μm. The corresponding sizes of the needle shaped Fe-ZSM-22 crystals were 0.4 and 4.0 μm.

The surface areas of the zeolites were determined by nitrogen adsorption (Carlo Erba Instruments) and the Dubinin method was used in the calculations. The surface area of the Fe-ZSM-22 zeolite was 271 m^2/g, which was less than the 330 m^2/g surface area of Al-ZSM-22.

2.3. Catalyst testing

The catalytic activity of the synthesized zeolites in the skeletal isomerization of 1-butene (99.0% purity, AGA) to isobutene was investigated using a fixed-bed microreactor system operating at near atmospheric pressure. The reactant was diluted with nitrogen (99.999% purity, AGA) to reduce the partial pressure of 1-butene. The products from the reactor were analyzed using a gas chromatograph (Varian 3700) equipped with a flame-ionization detector (FID). A capillary column (50 m × 0.32 mm i.d. fused-silica PLOT Al_2O_3-KCL) was used for product separation. The formation of coke deposits from 1-butene was measured using a microbalance (Cahn D 200).

3. Results and discussion

The product distribution obtained over Al- and Fe-ZSM-22 at a similar level of conversion is presented in table 1. The selectivity to isobutene was higher over Fe-ZSM-22 compared to Al-ZSM-22, mainly because of lower selectiv-

Table 1

Product selectivity in skeletal isomerization of 1-butene over Al- and Fe-ZSM-22. Temperature, partial pressure of 1-butene and TOS in the experiments were 400 °C, 0.6 atm and 10 min.

	Al-ZSM-22	Fe-ZSM-22
WHSV (h^{-1})	300	25
Selectivity (mol%)		
Ethene	0.0	0.3
Propane	0.1	0.1
Propene	9.1	5.2
Isobutane	0.3	0.4
n-butane	2.4	1.7
Isobutene	76.9	84.7
Pentenes	6.2	3.6
Hexenes	0.6	0.1
Heptenes	0.5	0.0
Octenes	3.5	3.6
Yield of isobutene (mol%)	22.9	26.3
Conversion (mol%)	29.8	31.7

ity to propene and pentenes. The results in table 1 indicate that isobutene is produced in monomolecular reactions and propene and pentenes are produced through dimerization of butene isomers followed by cracking (bimolecular reactions). Since the acid strength of Fe-ZSM-22 is weaker than that of Al-ZSM-22 [16], the Fe-ZSM-22 catalyst is not able to catalyze dimerization to the same extent as Al-ZSM-22. As mentioned earlier, dimerization reactions require higher acid strength than skeletal isomerization. On the other hand, Al-ZSM-22 was more active compared to Fe-ZSM-22 since similar conversion was obtained using considerably higher WHSV of 1-butene. The higher activity of Al-ZSM-22 could be a consequence of the higher number of acid sites in Al-ZSM-22 compared to Fe-ZSM-22 (figure 1).

Conversion, yield of isobutene and selectivity to isobutene as a function of time on stream (TOS) over Al- and Fe-ZSM-22 are presented in figures 2 and 3, respectively. The decrease in activity over Fe-ZSM-22 as a function of TOS was higher compared to Al-ZSM-22. After 14 h TOS it was found that the conversion over Fe-ZSM-22 had decreased to 5.7% and the surface area of the deactivated catalyst had decreased to 28 m^2/g. The surface area of Al-ZSM-22 after 20 h TOS was 92 m^2/g [8]. The weight gain because of coke deposits as a function of TOS for both the catalysts is presented in figure 4. The weight gain was at a higher level over Fe-ZSM-22 compared to Al-ZSM-22. There are several possible explanations for the more rapid deactivation of Fe-ZSM-22 compared to Al-ZSM-22. Acid strength, particle size or defects in the crystalline structure could all influence the rate of coke formation. For both the catalysts the rate of coke formation was high during the first few minutes, as non-selective acid sites probably situated on the external surface of zeolite crystals became deactivated. It was possible to regenerate the deactivated catalysts in air at 550 °C since the deactivation was due to coke formation.

The selectivity to isobutene also depends on the temperature, partial pressure and WHSV of 1-butene. The selectivity to isobutene increased with increasing temperature (figure 5), decreasing partial pressure of 1-butene (figure 6)

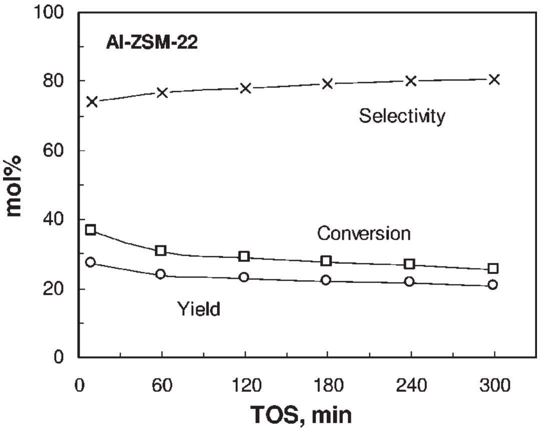

Figure 2. Conversion of n-butene, yield of isobutene and selectivity to isobutene as a function of TOS over Al-ZSM-22. Temperature, WHSV of 1-butene and partial pressure of 1-butene in the experiment were 400 °C, 200 h^{-1} and 0.6 atm, respectively.

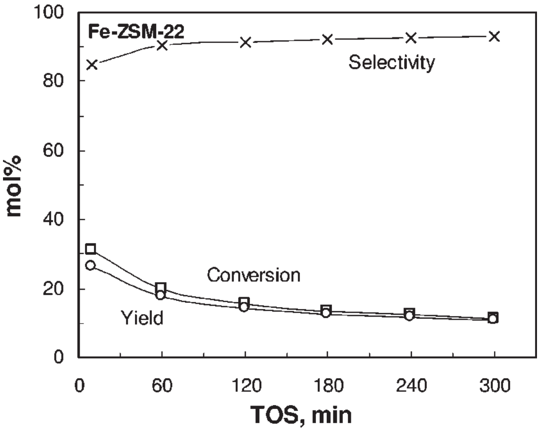

Figure 3. Conversion of n-butene, yield of isobutene and selectivity to isobutene as a function of TOS over Fe-ZSM-22. Temperature, WHSV of 1-butene and partial pressure of 1-butene in the experiment were 400 °C, 25 h^{-1} and 0.6 atm, respectively.

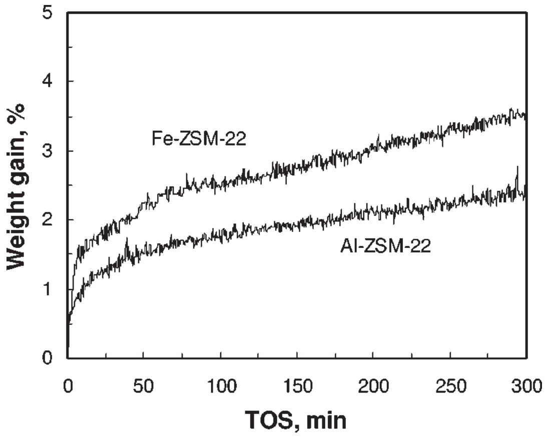

Figure 4. Weight gain over Al- and Fe-ZSM-22 as a function of TOS. Temperature, WHSV of 1-butene and partial pressure of 1-butene in the experiment were 400 °C, 150 h^{-1} and 0.5 atm, respectively.

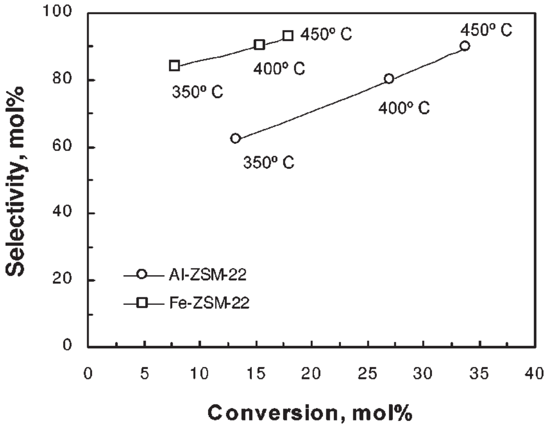

Figure 5. Effect of temperature on conversion of n-butene and selectivity to isobutene. The WHSV of 1-butene in the experiments over deactivated (TOS > 300 min) Al- and Fe-ZSM-22 were 200 and 10 h^{-1}, respectively. The partial pressure of 1-butene in the experiments was 0.6 atm.

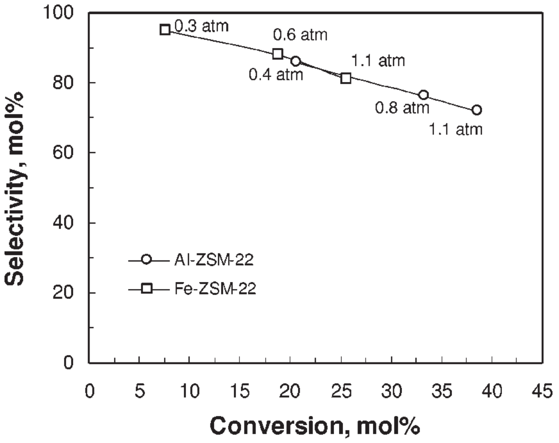

Figure 6. Effect of partial pressure on conversion of n-butene and selectivity to isobutene. The WHSV of 1-butene in the experiments over deactivated (TOS $>$ 300 min) Al- and Fe-ZSM-22 were 200 and 10 h^{-1}, respectively. The temperature in the experiments was 400 °C.

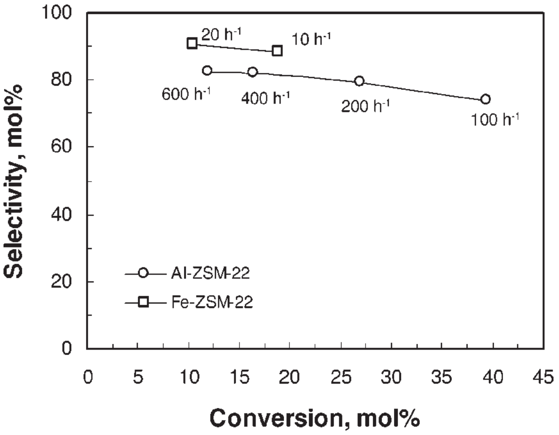

Figure 7. Effect of WHSV on conversion of n-butene and selectivity to isobutene. The temperature and partial pressure of 1-butene in the experiments over deactivated (TOS $>$ 300 min) Al- and Fe-ZSM-22 were 400 °C and 0.6 atm.

and increasing WHSV (figure 7) over both the catalysts. The higher selectivity to isobutene at high temperature and low partial pressure of 1-butene indicate that isobutene is produced in monomolecular reactions and by-products in bimolecular reactions. Bimolecular reactions (dimerization of butene isomers) are more favorable at low temperature and at high partial pressure of 1-butene. The selectivity to isobutene increased with increasing WHSV of 1-butene because of decreasing yield of isobutene. Isobutene is more reactive in dimerization reactions than n-butene.

4. Conclusions

The results obtained in this work revealed that Fe-ZSM-22 was active in skeletal isomerization of 1-butene to isobutene, which indicates the presence of Fe in the zeolite framework. The FTIR spectra of adsorbed pyridine demonstrated that Brønsted acid sites were present in both the zeolites, although the number of acid sites was lower in Fe-ZSM-22 compared to Al-ZSM-22. This is in agreement with the results from 1-butene transformation since Al-ZSM-22 was more active compared to Fe-ZSM-22. However, probably because of its lower acid strength, the selectivity to isobutene was higher over Fe-ZSM-22 compared to Al-ZSM-22, when the catalysts were compared at similar conversions.

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