Simultaneous dehydrogenation and isomerization of n-butane to isobutene over ZSM-22 and zinc-modified ZSM-5 zeolites

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Direct formation of isobutene from n-butane was investigated over a zinc-impregnated potassium-ion-exchanged ZSM-5 dehydrogenation catalyst and an acidic shape-selective ZSM-22 skeletal isomerization catalyst. The experiments were performed in a fixed-bed microreactor system operating at near-atmospheric pressure. High selectivity to n-butene was obtained over the zinc-impregnated potassium-ion-exchanged ZSM-5 dehydrogenation catalysts. The yield of isobutene increased after adding the acidic ZSM-22 skeletal isomerization catalyst, although the selectivity to butene isomers slightly decreased because the skeletal isomerization of n-butene was competing with other acid-catalyzed reactions such as cracking and aromatization.

Keywords: dehydrogenation, skeletal isomerization, n-butane, isobutene

1. Introduction

Different processes for isobutene production, especially skeletal isomerization of 1-butene [1–3], have received a lot of attention during recent years since isobutene is used in reaction with methanol to produce MTBE (methyl *tert*-butyl ether). The production of MTBE is at present limited by the supply of isobutene. Since large amounts of butane are readily available from refinery processes, the future demand for isobutene is likely to be satisfied by dehydrogenation [4]. Direct conversion of n-butane to isobutene is an interesting alternative to the currently practiced twin reactor system where an isomerization step is followed by a dehydrogenation step or vice versa.

Dehydrogenation of alkanes to alkenes can be performed under oxidative or non-oxidative conditions. The main advantage with oxidative dehydrogenation is to remove the thermodynamic limitations that make the non-oxidative route less attractive [5,6]. On the other hand, the non-oxidative route used in the experiments presented in this paper can be more selective to alkenes since there is no additional combustion of hydrocarbons to carbon dioxide or partial oxidation to aldehydes or acids.

Bifunctional zinc-modified ZSM-5 zeolites can be used in aromatization of n-butane [7,8], where the metals provide the dehydrogenation activity while Brønsted acid sites are active in dimerization and cyclodimerization reactions. It is of interest to note that zinc-impregnated ZSM-5 is a selective dehydrogenation catalyst for transforming n-butane to n-butene provided Brønsted acid sites are removed by potassium ion exchange before the zinc impregnation. On the other hand, Brønsted acidity is needed in order to obtain isobutene from n-butane. Relatively high selectivity to isobutene can be obtained directly from n-butane if the Brønsted acidity is provided by a shape-selective skeletal isomerization catalyst such as ZSM-22.

2. Experimental

The skeletal isomerization catalyst used in the experiments was as-synthesized ZSM-22 (Si/Al ratio 53) obtained directly after calcination without further modifications. The ZSM-22 catalyst was synthesized as described in [3]. The ZSM-5 (Si/Al ratio 40) zeolite was synthesized as described in [9] with some modification. The phase purity and structure of the synthesized zeolites were determined by X-ray powder diffraction (XRD). After calcination in nitrogen for 7 h at 550 °C followed by an additional 8 h in air, the ZSM-5 dehydrogenation catalyst was ion-exchanged for 24 h in a 1 M KNO_3 solution at room temperature, impregnated with $Zn(NO_3)_2{\cdot}6H_2O$ (10 wt% zinc) or ion-exchanged in a 1 M $Zn(NO_3)_2{\cdot}6H_2O$ solution for 48 h. The zinc-modified zeolites were finally calcined in air for 4 h at 500 °C.

The catalytic activity of the synthesized zeolites in dehydrogenation and dehydroisomerization of n-butane was investigated in a fixed-bed microreactor system at near-atmospheric total pressure. Dehydroisomerization was performed using a mixed bed of Zn/K-ZSM-5 and H-ZSM-22 as well as two consecutive beds of the two catalysts. n-butane (99.9% purity, AGA) was diluted with nitrogen (99.999% purity, AGA) and the molar ratio between n-butane and nitrogen was $1:1$. The temperature used in all the experiments presented in this paper was 500 °C. Products from the reactor were analyzed by a gas chromatograph (Varian 3700) equipped with a FID detector. A capillary column (50 m × 0.32 mm i.d. fused-silica PLOT Al_2O_3–KCl) was used for product separation.

Table 1
Activity of as-synthesized, potassium-ion-exchanged, potassium- and zinc-ion-exchanged, and potassium-ion-exchanged and zinc-impregnated ZSM-5 zeolites.

	As-synth. ZSM-5	K-ZSM-5	Zn(ion)/K-ZSM-5	Zn(imp)/K-ZSM-5
Yield (mass%)				
Cracking prod. (C_1–C_3)	9.8	0.7	29.9	1.4
Isobutane	0.4	0.0	2.8	0.0
Dehydrogenation prod. (butenes)	1.6	0.1	2.4	15.3
Aromatics	0.2	0.0	33.8	0.3
Conversion (mass%)	12.2	0.8	69.1	17.1

3. Results and discussion

Potassium ion exchange followed by zinc ion exchange was not sufficient to give low Brønsted acidity, although the catalytic activity of potassium-ion-exchanged ZSM-5 catalyst was very low as can be seen from the results presented in table 1. The potassium- and zinc-ion-exchanged ZSM-5 zeolite still demonstrated high activity in aromatization reactions. The weight hourly space velocity (WHSV) of n-butane and time on stream (TOS) used in the experiments presented in table 1 were 2 h^{-1} and 10 min. High selectivity to butene isomers (86 mass%) was only obtained when the incipient wetness impregnation method was used in order to introduce zinc to the potassium-ion-exchanged ZSM-5 zeolite. The dehydrogenation activity of Zn(imp)/K-ZSM-5 as a function of time on stream (TOS) is presented in figure 1.

The dehydrogenation activity of Zn(imp)/K-γ-Al_2O_3, Zn(imp)/K-ZSM-22 and Zn(imp)/K-ZSM-5 are compared in figure 2. The main advantage of using zeolites as support for zinc was observed in the stability as a function of TOS. Coke deactivation of Zn(imp)/K-γ-Al_2O_3 was much more rapid compared to Zn(imp)/K-ZSM-5, when both the catalysts were prepared in the same way. The dehydrogenation activity of Zn(imp)/K-ZSM-5 was higher compared to Zn(imp)/K-ZSM-22.

The skeletal isomerization activity of the Zn(imp)/K-ZSM-5 catalyst was low, as can be seen from the results presented in figure 1. In order to improve the skeletal isomerization activity, Zn(imp)/K-ZSM-5 was mixed with H-ZSM-22. Results over Zn(imp)/K-ZSM-5 mixed with H-ZSM-22 in the ratio 2 : 1 are presented in figure 3. Considering the activity of Zn(imp)/K-ZSM-5 in dehydrogenation and H-ZSM-22 in skeletal isomerization, excess amount of H-ZSM-22 was used in the beginning of the experiment in order to compensate for the rapid initial coke deactivation of H-ZSM-22. Low selectivity to isobutene and other dehydrogenation products was obtained in the beginning of TOS as a result of the excess amount of H-ZSM-22, because the acidic skeletal isomerization catalyst was active in cracking and aromatization of n-butane. The main reason for the exceptionally rapid deactivation of H-ZSM-22 in dehydroisomerization of n-butane was 1,3-butadiene produced over the dehydrogenation catalyst. Regeneration of deactivated catalysts was possible in air at 550 °C.

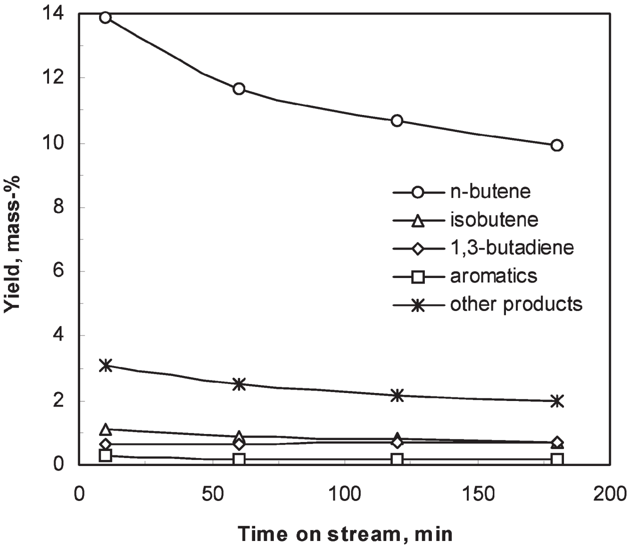

Figure 1. Dehydrogenation activity of Zn(imp)/K-ZSM-5 as a function of TOS. The WHSV of n-butane in the experiment was 2 h^{-1}.

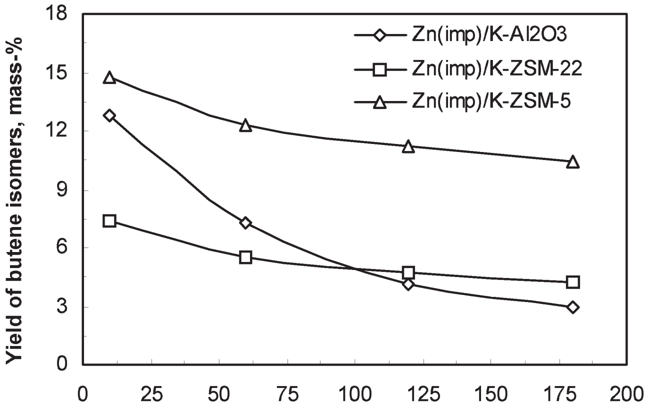

Figure 2. Dehydrogenation activity of Zn(imp)/K-γ-Al_2O_3, Zn(imp)/K-ZSM-22 and Zn(imp)/K-ZSM-5 as a function of TOS. The WHSV in the experiment was 2 h^{-1}.

Yields of different products obtained over Zn(imp)/K-ZSM-5 and the mixture of Zn(imp)/K-ZSM-5 and H-ZSM-22 are compared in figure 4 at 14.5 mass% conversion of n-butane. The yield of isobutene increased after mixing the Zn(imp)/K-ZSM-5 dehydrogenation catalyst with the acidic H-ZSM-22 skeletal isomerization catalyst, but the selectivity to butene isomers decreased because other acid-

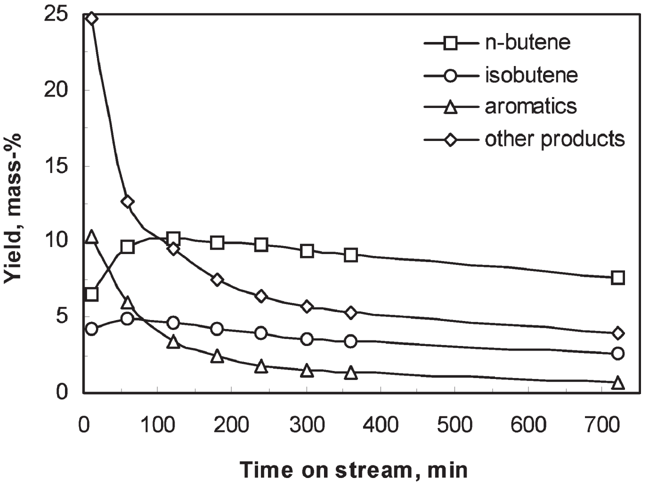

Figure 3. Yield of different products over Zn(imp)/K-ZSM-5 mixed with H-ZSM-22 in the ratio 2 : 1. The WHSV of n-butane in the experiment was 0.7 h^{-1}.

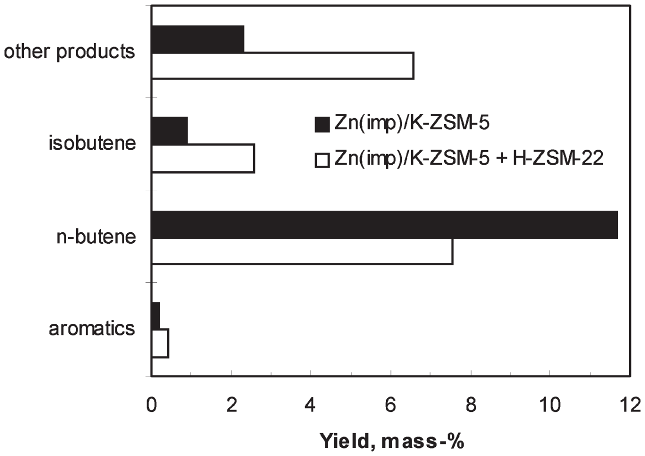

Figure 4. Yield of different products at 14.5 mass% conversion of n-butane over Zn(imp)/K-ZSM-5 and Zn(imp)/K-ZSM-5 mixed with H-ZSM-22 in the ratio 2 : 1. The results were obtained after 720 min TOS.

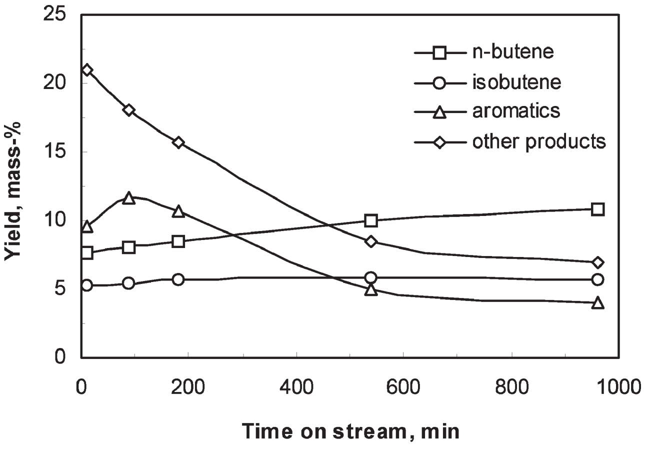

Figure 5. Yield of different products over consecutive beds of Zn(imp)/K-ZSM-5 and H-ZSM-22 in the ratio 5 : 1. The WHSV of n-butane in the experiment was 0.8 h^{-1}.

catalyzed reactions such as cracking (formation of methane, ethane, ethene, propane and propene) and aromatization (formation of benzene, toluene and xylenes) were competing with skeletal isomerization.

Results over Zn(imp)/K-ZSM-5 followed by H-ZSM-22 (separate beds) as a function of TOS are presented in figure 5. The main difference between using mixed beds or two consecutive beds was observed in the deactivation of the H-ZSM-22 catalysts. The rate of deactivation was much higher when the dehydrogenation and isomerization catalysts were mixed together. Since the deactivation of H-ZSM-22 was lower when two consecutive beds were used, less amount of the H-ZSM-22 was used in the experiments presented in figure 5 compared to the mixed-bed experiment presented in figure 3. The reaction conditions used in the TOS experiments presented in figures 3 and 5 are not optimal since according to additional experiments higher selectivity to isobutene can be obtained using lower partial pressure of n-butane, and higher WHSV of n-butane should be used in the beginning of the experiments in order to reduce the formation of by-products. The dehydrogenation activity of Zn(imp)/K-ZSM-5 can also be increased by increasing the temperature.

4. Conclusion

It is well known that zinc-modified ZSM-5 zeolites can be used in aromatization of light alkanes [7,8]. On the other hand, the results presented in this paper indicate that zinc-impregnated ZSM-5 is also a selective dehydrogenation catalyst provided Brønsted acidity is reduced by potassium ion exchange before zinc impregnation. Furthermore, if Brønsted acidity is provided by a shape-selective isomerization catalyst such as ZSM-22, relatively high selectivity to isobutene can be obtained directly from n-butane (figure 6).

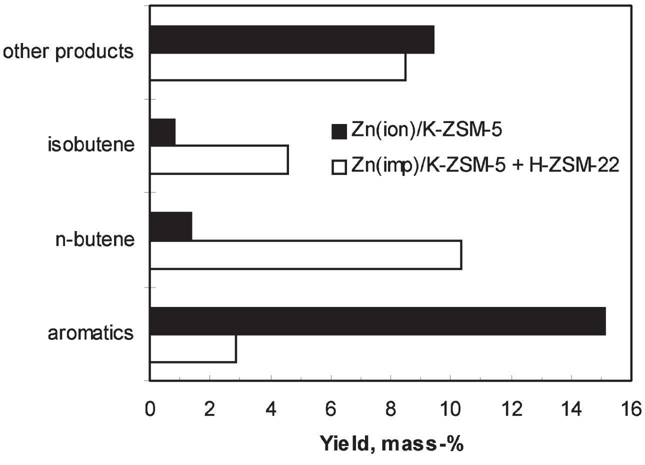

Figure 6. Yield of different products at 27 mass% of n-butane conversion over Zn(ion)/K-ZSM-5 (aromatization) and Zn(imp)/K-ZSM-5 mixed with H-ZSM-22 (dehydroisomerization) after 10 min TOS.

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