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Isomerization of isobutyraldehyde to methyl ethyl ketone on zeolite catalysts

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The isomerization of isobutyraldehyde (IBH) was studied over aluminium-free ZSM-5 zeolite catalysts with different boron content in the framework. The selectivity to methyl ethyl ketone (MEK) is high, ca. 83 wt%. With the increase of boron content, the conversion of IBH increased but the selectivity to MEK decreased. The effects of Na content, cation-exchange, 500°C-steam treatment and temperature on catalyst activity were investigated. It was observed that cation-exchange resulted in the decrease of conversion of IBH and increase of selectivity to MEK, but 500°C-steam treatment resulted in the decrease of selectivity to MEK.

Keywords: isomerization; isobutyraldehyde; methyl ethyl ketone (butanone); BZSM-5 zeolite

1. Introduction

Isobutyraldehyde (IBH), which is produced in considerable quantity as a by-product in the oxonation reaction of propylene, has a very low commercial value and, therefore, attracts considerable interest in its economic upgrading. Among the reactions considered, isomerization is one of the most promising from an economic standpoint, since the isomeric ketone, methyl ethyl ketone (MEK), is a very desirable solvent.

Thermodynamically, the isomerization of IBH to MEK is possible [1]. This reaction is acid catalyzed. Traditionally, the reaction was investigated using alumina, silica and alumina–silica as catalysts [2–4]. The disadvantages of such catalysts are the very low selectivity to MEK and rapid deactivity. In order to obtain better results, water co-feed is indispensable. This, however, increases the difficulty in separation.

ZSM-5 zeolite catalysts for the isomerization have been reported [5], but the

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selectivity to MEK is also low due to their strong acidity. Recently, BZSM-5 showed high activity as a catalyst in the isomerization of IBH to MEK [6]. But there is only scant information on the isomerization over BZSM-5 zeolite catalysts. In the present work, in order to obtain more information, the effects of boron content, cation-exchange, steam-treatment and temperature on the isomerization were studied.

2. Experimental

The BZSM-5 type zeolites with different boron content were hydrothermally synthesized from the system $Na_2O{\cdot}SiO_2{\cdot}B_2O_3{\cdot}H_2O{\cdot}TPABr$ by varying the boron contents (samples B_1Z, N-2, N-4, B_2Z, of which the Si/B molar ratios in the starting gels are 70/16, 70/8, 70/2, 70/1, respectively). The products were filtered, washed and dried in an oven at 383 K for 12 h, then calcined at 823 K in air for 12 h. It has been demonstrated from XRD, unit cell volume and IR spectroscopy that boron incorporated into the ZSM-5 framework [7].

The proton form of BZSM-5 zeolite was prepared treating the above NaBZSM-5 sample with a 0.5–1.0 M aqueous solution of NH_4NO_3, using a solid-to-liquid weight ratio of 1/20 at 353–373 K for 1 h, under stirring, followed by drying at 383 K and ulterior calcination at 773 K in air for 3 h (samples HB_1Z, HN-2, NH-4, HB_2Z).

Metal ion-exchanged BZSM-5 zeolite was obtained by conventional exchange of NH_4BZSM-5 zeolite with a 0.1 M aqueous solution of $Cu(NO_3)_2$, $Mg(NO_3)_2$ or $CuCl_2$ in the above weight ratio and subsequently washed, dried and calcined at 573 K for 1 h, 773 K for 3 h (samples MHB_nZ).

A schematic drawing of the apparatus is shown in fig. 1. The carrier gas

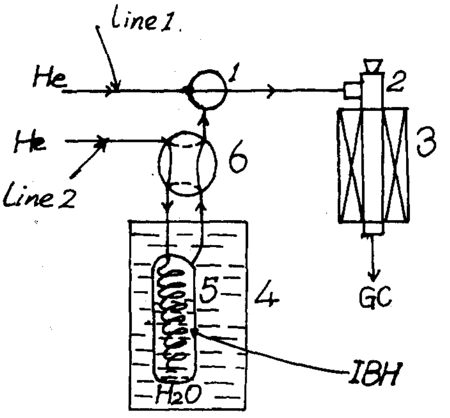

Fig. 1. Scheme of the apparatus: (1) three-way joint, (2) reactor (i.d. 5 mm), (3) heater, (4) thermostat, (5) saturator, (6) four-way valve (GC) gas chromatograph, (line 1) as dilute gas, (line 2) as carrier gas. All feed lines were heated sufficiently.

(helium) was passed through the saturator with IBH at a definite temperature, chosen so as to ensure a suitable IBH WHSV and contact time.

Catalytic runs were carried out at atmospheric pressure in a continuous downflow mode with a fixed bed stainless steel reactor. The catalyst charge was 0.1 g. The product analysis was done on stream in a 103 type GC (manufactured by Shanghai Anal. Instruments factory) equipped with TCD and He as carrier gas.

Materials: $Cu(NO_3)_2$, $Mg(NO_3)_2$, $ZnCl_2$, NH_4NO_3 and IBH, etc. are all of analytical purity.

The contact time is defined as follows:

$$\text{contact time (s)} = \frac{\text{volume of catalyst (ml)}}{\text{total flow of gases (ml/s)}}.$$

3. Results and discussion

3.1. THE INFLUENCE OF BORON CONTENT ON THE ISOMERIZATION

The three samples HN-2, HN-4 and HB_2Z – with contents of framework boron decreasing in this same sequence – were compared in the IBH isomerization reaction (fig. 2). It was obvious that the activities of the catalysts were very high. The conversion of IBH increased with increasing boron content while the selectivity to MEK decreased. The isomerization reactivity of samples obtained by different times of ion-exchange with an aqueous solution of NH_4NO_3 is shown in table 1.

From table 1 we can obtain the following facts:

(1) On Na-type BZSM-5 catalyst, on which no Brønsted acid sites are present, both the conversion of IBH and selectivity to MEK are very low, i.e. the Na-type BZSM-5 displays negligible activity below 500°C.

(2) Times of cation-exchange, i.e. Brønsted acid density or Na content have an obvious influence on the reactivity, the difference between one time and double times of cation-exchange is especially obvious. With the increase of the times of cation-exchange, the conversion of IBH increased, but the selectivity to MEK decreased. Meanwhile, big molecular by-products (aromatics, etc.) owing to polymerization were produced. From the above, we assume that the Brønsted acid in the catalysts surface is indispensable for effectively converting IBH to MEK, but the presence of excess Brønsted acid is more favorable for the cracking reaction of IBH, producing gas components.

3.2. THE EFFECT OF TEMPERATURE ON THE ISOMERIZATION OF IBH

The reaction data were taken using Mg^{2+} exchanged HBZSM-5 zeolites. Fig. 3 shows the reaction temperature dependence of the reaction of IBH over $MgHB_2Z$. The conversion of IBH increased monotonously with increasing temperature and

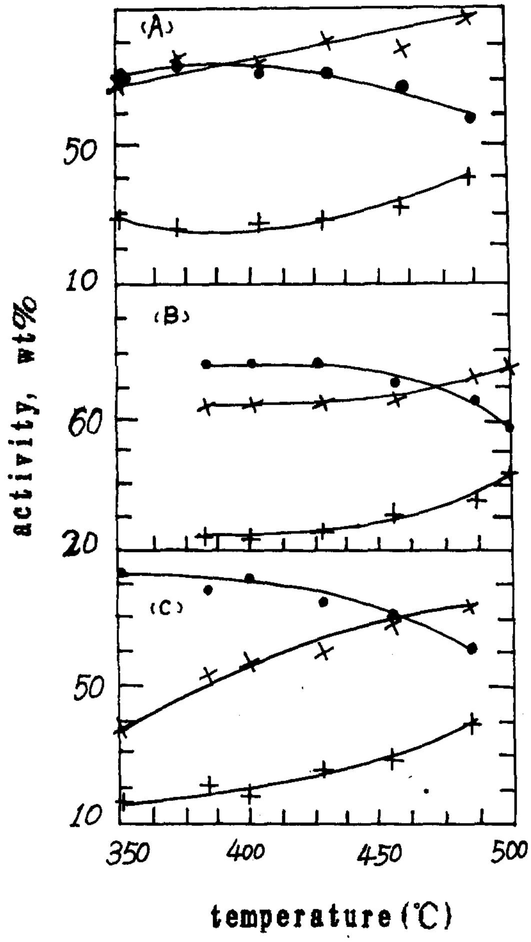

Fig. 2. Effect of boron content on catalyst activity. WHSV = 3.4 h^{-1}, contact time = 0.3 s. (A) HN-2, (B) HN-4, (C) HB_2Z. (×) Conversion of IBH, (+) selectivity to gases, (●) selectivity to MEK.

Table 1
Reaction results for IBH over varying times of NH_4^+-exchanged BZSM-5 zeolite catalysts. (WHSV= 3.4 h^{-1}, contact time 1.1 s)

Sample	Reaction temperature (°C)	Conversion (wt%)	Selectivity (wt%)	
			MEK	gases
B_2Z[a]	500	5.1	44.5	55.5
HB_2Z-1[b]	385	51.1	80.5	19.5
HB_2Z-2[b]	385	88.4	77.7	16.4
HB_2Z[b]	385	91.4	73.8	19.8

[a] WHSV = 4.5 h^{-1}, contact time = 1.7 s.

[b] HB_2Z-1, HB_2Z-2, HB_2Z denote one, double and five times NH_4^+-exchanged B_2Z catalyst, respectively.

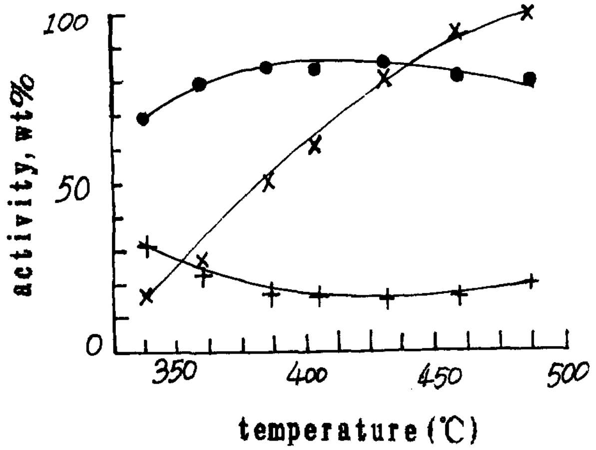

Fig. 3. Effect of reaction temperature on the isomerization over $MgHB_2Z$ catalyst. WHSV $= 3.4\ h^{-1}$, contact time = 1.1 s. Symbols as in fig. 2.

reached ca. 80% at 430°C. The selectivity to MEK increased with a rise in reaction temperature and had a maximum of ca. 84 wt% in the range 380–430°C. MEK and products of cracking of IBH were mainly produced below 480°C. Not more than 1 wt% of other by-products, such as *n*-butyraldehyde, were obtained above 480°C. Thereafter, the isomerization of IBH to *n*-butyraldehyde, which is expected to occur over the acidic catalyst, is negligible.

Fig. 4 shows the effect of the preheating temperature on the isomerization of IBH over $CuHB_1Z$. The treatment to catalysts was performed in situ in the reactor in the presence of helium. The conversion of IBH and selectivity to MEK decreased slowly with increasing temperature and were minimum at 540°C. Then, they increased above 540°C.

3.3.THE EFFECTS OF CATIONS AND STEAM-TREATMENT ON THE ISOMERIZATION OF IBH

Two samples of different boron content, HB_1Z and HB_2Z, of which the Brønsted acid density on HB_1Z is higher than on HB_2Z from IR measurement and, correspondingly, the ion-exchange capacity for HB_1Z is greater, were cation-exchanged. A few selected runs are listed in table 2. The selectivity to MEK is very high over HB_2Z based catalysts, although the reactions were performed at relatively low temperature, and no large molecular compounds were observed as by-products. It is also evident that the modification by cation-exchange resulted in the increase of the selectivity to MEK. But the most striking results are the dropping of conversion of IBH on modified HB_1Z and $CuHB_2Z$ catalysts. The conversion is inversely correlative to rq (radius multiplied by electric charge) of the cation; i.e. $(rq)_{Zn^{2+}} > (rq)_{Cu^{2+}}$ and $(rq)_{Cu^{2+}} > (rq)_{Mg^{2+}}$, but the conversion is: $ZnHB_1Z < CuHB_1Z$ and $CuHB_2Z < MgHB_2Z$.

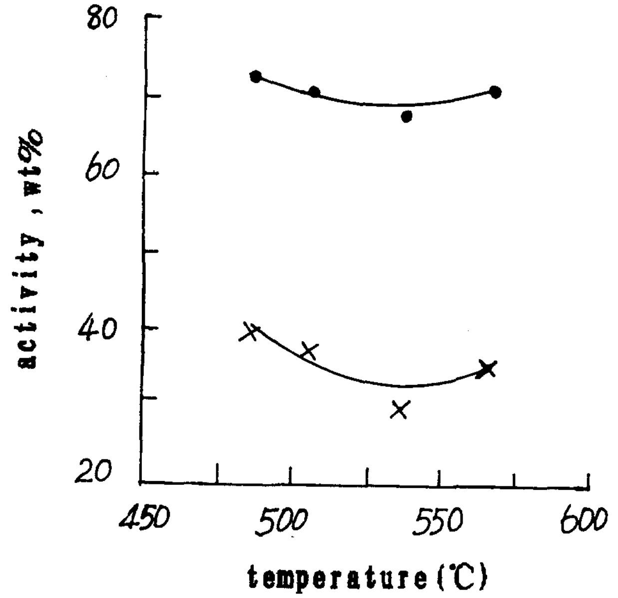

Fig. 4. Effect of preheating temperature on the isomerization over $CuHB_1Z$ catalyst. WHSV = 4.5 h^{-1}, contact time = 1.7 s, reaction temperature = 385°C, treatment time = 0.5 h. Symbols as in fig. 2.

The catalytic activities of 500°C-steam treated $MgHB_2Z$ and $CuHB_2Z$ (abbreviated as $MgHB_2Z$-500 and $CuHB_2Z$-500, respectively) are also listed in table 2. Compared with the results obtained for $MgHB_2Z$ and $CuHB_2Z$, 500°C-steam treatment resulted in a decrease of selectivity to MEK, but an increase of conversion of IBH over the $MgHB_2Z$ based catalyst and no obvious change in conversion over the $CuHB_2Z$ based catalyst.

Table 2
Reaction results for IBH over various cation-exchanged HBZSM-5 zeolite catalysts [a]

Sample	Reaction temperature (°C)	Conversion (wt%)	Selectivity (wt%)		rq of M^{n+}
			MEK	gases	
HB_1Z	385	97	50		
$ZnHB_1Z$	385	22.4	60.9		1.66
$CuHB_1Z$	385	39.8	72.7		1.60
HB_2Z	358	40.5	73.1	26.9	
$CuHB_2Z$	356	11.6	76.9	23.1	1.60
$CuHB_2Z$-500	355	11.6	70	30	
$MgHB_2Z$	358	26.9	78.3	21.7	1.30
$MgHB_2Z$-500	358	34.4	71.5	28.5	

[a] WHSV= 4.5 h^{-1}, contact time = 1.7 s for HB_1Z based catalysts; WHSV = 3.4 h^{-1}, contact time = 1.1 s for HB_2Z based catalysts.

4. Conclusion

The presence of Brønsted acid sites on the zeolite surface appears to be very important for IBH isomerization to MEK. A relatively low weak Brønsted acid density is suitable for IBH isomerization to MEK in high selectivity. A better result was obtained over HB_2Z catalyst.

Cation-exchange resulted in the increase of the selectivity to MEK and the decrease of conversion of IBH. The conversion is inversely correlative to *rq* of the cation. The high selectivity to MEK and conversion of IBH were obtained over $MgHB_2Z$ catalyst. 500°C-steam treatment resulted in a decrease of selectivity to MEK, but an increase of conversion of IBH over $MgHB_2Z$ based catalyst and no obvious change in conversion over $CuHB_2Z$ based catalyst. The preheating temperature of the catalysts also influenced the catalyst activity.

References

[1] V.V. Alexandrov, V.A. Smirnov and S.I. Kryukov, Neftekhimiya 25 (1985) 645.
[2] W.H. Ploder, J. Catal. 23 (1971) 358.
[3] V.M. Zubkov, Zh. Prikl. Khim. (Leningrad) 64 (1991) 448.
[4] B.P. 1,049,990 (1966).
[5] US 4,537,995 (1985).
[6] US 4,694,107 (1987).
[7] J. Wang, Masters thesis, Dalian Institute of Chem. Phys., CAS (1993).