M_xO_y/SO_4^{2-}/Dealuminated Zeolite β (M=Ti, Fe) as Novel Catalysts for Alkylation of Isobutane with 1-Butene

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A new kind of M_xO_y/SO_4^{2-}/H-form dealuminated β (DHβ) catalysts prepared here were applied to alkylation of isobutane with 1-butene. The group of M_xO_y/SO_4^{2-}/DHβ (M = Ti, Fe) catalysts has a lower rate of deactivation and higher selectivity of this alkylation than other group of Hβ and DHβ. It is proposed that the strong acid sites corresponding to the active sites for this alkylation can be formed by the interaction among DHβ, M_xO_y, and SO_4^{2-}.

Alkylation of isobutane with butenes is an important route to obtain high octane number gasoline. Many investigators have searched for effective solid acid catalysts[1-3] instead of hazardous sulfuric and hydrofluoric acids. Recently, zeolite beta (β), a high-silica and large pore three dimensions zeolite, has been shown to have higher activity and selectivity than other zeolites for alkylation[4-5] of isobutane with butenes. In present work, a new type of solid acid catalysts, TiO_2/SO_4^{2-}/DHβ (Ti-SDHβ) and Fe_2O_3/SO_4^{2-}/DHβ (Fe-SDHβ), which only contain small amounts of TiO_2 or Fe_2O_3 and SO_4^{2-}, have been found to have high activity and selectivity for trimethylpentane (TMP) in the alkylation of isobutane with 1-butene.

Hβ was synthesized according to Ref.6. DHβ was prepared by treating Hβ with 0.1 M oxlaic acid (solid: acid =1:10 in weight) for 2 h × 3 times at 80 °C. The Ti-SDHβ was prepared from DHβ, which was firstly passed through $TiCl_4$ vapor at 350 °C under N_2 flow of 30 ml/min for 2-3 h, washed till free Cl^-, then promoted with SO_4^{2-} (1% $(NH_4)_2SO_4$), dried at 105 °C for 24 h, and finally calcined at 540 °C for 3 h. The Fe-SDHβ was obtained by impregnation of DHβ with Fe^{3+} (2% $NH_4Fe(SO_4)_2$) under pH = 2-3, then following treated with the same procedures as that of Ti-SDHβ described above. The content of TiO_2 (or Fe_2O_3) and SO_4^{2-} in catalysts was 2% and 1.5%, respectively. Those catalysts were characterized by X-ray powder diffraction (XRD), temperature-programmed desorption of NH_3 (NH_3-TPD), temperature-programmed desorption of pyridine measured by IR (Py-IR-TPD) and BET method for surface area. Liquid phase alkylation of isobutane with 1-butene was performed in a continuous fixed-bed reactor at reaction temperature of 353 K, total pressure of 2.2 MPa, the isobutane/1-butene molar ratio of 14, and the weight space velocity (WHSV) of 1-butene for 1.5 h^{-1}. The catalysts were pelletized to particle size of 40-60 mesh without binder. The reaction products were vaporized on line to enter GC for analysis with a 50m capillary column (fused silica, OV-101) and a flame ion detector (FID). The C_5-C_8 hydrocarbons were identified by GC-MS and available reference standards.

The acid amount, BET surface area and crystallinity of samples are shown in Table 1. The crystallinities calculated from patterns of XRD of different catalysts are almost at the same level except for Zr/Sβ (mechanically mixed sample contained superacid ZrO_2/SO_4^{2-} of 25% and Hβ of 75%) and DHβ. The BET surface area of M_xO_y/SO_4^{2-}/DHβ is low compared with Hβ or DHβ. This means that the M_xO_y and SO_4^{2-} enter the channels or cages of zeolite but don't destroy β structure. The bulk Si/Al ratios of Hβ, DHβ, Ti-SDHβ, and Fe-SDHβ were 14.1, 20.9, 21.5, and 20.5, respectively. The profiles of NH_3-TPD on different catalysts show that the M_xO_y/SO_4^{2-}/DHβ (M = Ti, Fe) samples have three desorption peaks (Table1). The peak at ca. 495 K is corresponding to weak acid sites and the two peaks at high temperatures are associated to medium-strong and strong acid sites, respectively. Zr/Sβ and DHβ don't have the highest third peak corresponding to the strong acid sites. These results suggest that the strong acid sites of M_xO_y/SO_4^{2-}/DHβ (M = Fe, Ti) catalysts might arise from the interaction between the DHβ and small amounts of M_xO_y and SO_4^{2-} in the zeolite. The strong acid numbers in these samples are in order as: Ti-SDHβ ≅ Fe-SDHβ > Hβ > Zr/Sβ > DHβ, but the total acid amounts decrease as follows: Fe-SDHβ > Ti-SDHβ > Hβ > Zr/Sβ > DHβ.

Table 1. Characterization results on different catalysts

Catalysts	Crystallinity(%)	SA[a] (m/g)	Temp.Peak(K)[b]			Acid numbers[c] (10^{20}/g-cat.)	
			T_1	T_2	T_3	N_1	N_{2+3}
Ti-SDHβ	91	412	491	680	873	1.95	1.97
Fe-SDHβ	99	480	495	678	863	2.43	1.94
Zr/Sβ	72	378	493	665		1.68	1.12
Hβ	100	497	490	667		1.70	1.25
DHβ	79	465	494	670		1.63	0.93

Catalysts	Py-IR acid sites numbers(10^{19}/g-cat.)[d] Bronsted			Lewis		
	120[e]	320[e]	$(S/W)_B$[f]	120[e]	320[e]	$(S/W)_L$[f]
Ti-SDHβ	2.01	0.44	0.22	4.56	0.98	0.22
Fe-SDHβ	2.96	0.76	0.26	4.96	1.56.	0.32
Hβ	2.61	0.34	0.13	3.46	0.38	0.11
DHβ	2.15	0.24	0.11	1.96	0.15	0.08

[a]BET surface area (m^2/g); [b]The peak temperatures of NH_3-TPD profile; [c]The acid sites numbers were calculated from the amount of desorbed ammonia; [d]The extinction coefficients from Ref. 7; [e]Desorption temperatues (°C); [f]The ratio of strong acid sites to weak ones measured by Py-IR at desorption temperature of 120°C and 320°C, respectively.

1-Butene conversions on different catalysts are presented in Figure 1. It can be clearly seen that all catalysts decay with increase of time on stream (TOS). At the early reaction stage (TOS ≤ 90 min), the M_xO_y/SO_4^{2-}/DHβ largely surpasses the Hβ, DHβ and Zr/Sβ in activity. This is in accordance to the order of the strong acid numbers measured by NH_3-TPD and Py-IR-TPD. The Hβ, DHβ and Zr/Sβ under this reaction condition have a low activity because of their less strong acid amounts

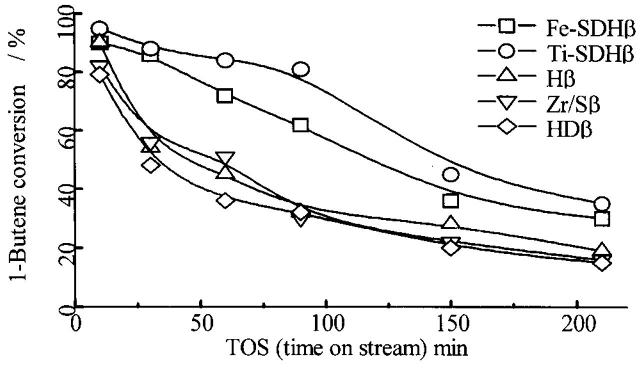

Figure 1. 1-Butene conversions on different catalysts with TOS.

Table 2. Products distribution on different catalysts at TOS=30 min

Catalysts	Ti-SDHβ	Fe-SDHβ	Zr/Sβ	DHβ	Hβ
nC_4^0(%)	2.0	1.8	0.8	0.6	0.5
in C_{5+}(%) wt.					
C_{5-7}	5.9	4.0	5.5	5.4	7.8
C_8	85.3	90.7	74.5	79.0	81.0
C_{9+}	8.8	5.3	20.0	15.5	12.2
in C_8 (%)					
TMP(total)	68.3	70.8	51.9	58.5	59.3
2,2,4-TMP	21.4	20.9	23.5	31.7	30.1
2,2,3-TMP[a]	4.5	3.5	10.4	12.6	13.1
2,3,4-TMP	10.9	9.7	11.0	7.8	9.0
2,3,3-TMP	31.5	36.7	7.1	5.4	7.0
DMH(total)	13.6	12.2	23.3	21.4	19.1
$C_8^=$ olefins	18.1	17.0	24.8	20.6	21.6

[a] The result includes 2,4-DMH.

(see Table 1). The rate of deactivation on the group of Ti-SDHβ and Fe-SDHβ catalysts is clearly slower than that on other group of ones (Hβ, DHβ).

Table 2 shows the products distribution of alkylates produced on the different catalysts at TOS = 30 min. The selectivity of C_8 on Ti-SDHβ and Fe-SDHβ catalysts is higher than that on Hβ, DHβ and Zr/Sβ. The amounts of trimethylpentanes (TMP), the most desired products, on different catalysts are in the following order: Fe-SDHβ > Ti-SDHβ > Hβ, Zr/Sβ and DHβ. Within total TMPs, the 2,3,3-TMP is preferably formed on Fe-SDHβ and Ti-SDHβ, but 2,2,4-TMP is predominant on other ones (Hβ, Zr/Sβ and DHβ). The Py-IR-TPD results tell us that Ti-SDHβ and Fe-SDHβ have high ratios of strong/weak acid sites for both Bronsted and Lewis acid sites (Table 1), which are in favour of the formation of TMP. In addition, the dimethylhexanes (DMH) and C_8 olefins formed on Ti-SDHβ and Fe-SDHβ are always less than that on Hβ, DHβ and Zr/Sβ (Table 2).

We have found butane formed during initial alkylation time. According to Corma et al,[8] the hydrogen transfer activity of catalysts may be expressed by the content of butane. Table 2 also lists the content of butane at TOS = 30 min. The more amounts of butane formed in alkylation processes may suggest that the more alkylates are produced.

A promising solid acid catalysts, Ti-SDHβ and Fe-SDHβ which only contain small amounts of TiO_2 or Fe_2O_3 and SO_4^{2-} are found to have more stable activity and higher selectivity of TMPs than Hβ and DHβ zeolites for alkylation of isobutane with 1-butene. The good catalytic performance of M_xO_y/SO_4^{2-} /DHβ may be closely related to the strong acid sites, which could be produced by the interaction among M_xO_y, SO_4^{2-} and DHβ zeolites.

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References

1 F. W. Kirsch, J. D. Potts, and D. S. Barmby, *J. Catal.*, **27**, 142 (1972).
2 J. Weitkamp, *Proc. 5th Int. Zeolite Conf.*, **5**, 858 (1980).
3 A. Corma, A. Martinez, and C. Martinez, *J. Catal.*, **149**, 52 (1994).
4 S. Univerricht, S. Ernst, and J. Weitkamp, *Stud. Surf. Sci. Catal.*, **84**, 1693 (1994).
5 K. P. de. Jong, C. M. A. Maesters, P. T. M. Van Bugge, and C. de Groot, *Chem. Eng. Sci.*, **51**, 2053 (1996).
6 M. A. Camblor, and J. P. Pariente, *Zeolites*, **11**, 202 (1991).
7 I. Kiricsi, C. Felego, G. Pazzuconi, and G. Bellussi, *J. Phys. Chem.*, **98**, 4627 (1994).
8 A. Corma, A. Martinez, and C. Martinez, *J. Catal.*, **146**, 185 (1994).