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CATALYSIS

Isomerization of *n*-Butane on Dealuminated Mordenite Promoted with Zirconium Dioxide

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Abstract—Zirconiun dioxide promotes the catalytic activity of a dealuminated mordenite in *n*-butane isomerization. A method is suggested for preparing, without any solvents, a sulfated mordenite-zirconium catalyst active at relatively low temperatures.

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Isomerization of *n*-butane is one of the most important processes of petrochemical industry in production of alkylates and other valuable products [1, 2]. To perform this reaction, different heterogeneous catalysts have been suggested. Among them the chlorinated platinum-alumina catalysts, metallozeolites, and sulfated zirconium dioxide are of particular interest [1–8]. Each of these catalysts has advantages and disadvantages. For instance, chlorinated platinum-alumina catalyst require a thorough pretreatment of the raw material and are environmetally unfavorable. Isomerization with metallozeolites is performed at high temperatures; they are favorable in isomerization of C_5 and C_5–C_6 paraffins. Sulfated zirconium dioxide is active at relatively low temperatures. However, additional studies are required to improve the stability and reproducibility of its catalytic properties.

Due to cellular structure and possibility of purposeful modification of the physicochemical properties, zeolites are promising catalysts for *n*-butane isomerization. It was shown in [9, 10] that dealumination of H-mordenite enchances its isomerization activity. The activity of dealuminated H-mordenite can be further raised by choosing appropriate promoters [11, 12].

In this study, we examined the catalytic properties of binary mordenite-zirconium and ternary sulfated mordenite-zirconium catalysts to find the probable synergism of such systems and to develop on their base low-temperature catalysts of *n*-butane isomerization.

EXPERIMENTAL

The catalysts were prepared from dealuminated H-mordenite with the SiO_2/Al_2O_3 ratio of 17 (sample HM_{17}). To promote HM_{17} with zirconium dioxide, we used impregnation and mechanical mixing of the zeolite with $ZrO(NO_3)_2$ or $ZrO(OH)_2$, with subsequent decomposition of the mixture at 823–873 K [the samples were denoted as $a ZrO_2/HM_{17}$ (impregnation) and HM_{17}–$a ZrO_2$ (mixing), where a is the ZrO_2 content, wt %]. The samples obtained were sulfated by their treatment with 2 M solution of $(NH_4)_2SO_4$. Catalysts were molded with aluminum hydroxide as a binding agent, dried at 383–393 K, and calcined at 823–873 K.

The conversion of *n*-butane was studied in a flow-type apparatus at atmospheric pressure within the 433–523 K range. A 2 cm^3 portion of cylindrical catalyst granules 1–3 mm in size was charged into a quartz reactor and activated in an air flow at 773 K for 3 h. After the experiments, the catalyst was regenerated under the same conditions. After activation or regeneration, catalysts were cooled in an N_2 flow to the reaction temperature, and *n*-butane was started to be delivered at a flow rate of 300 ml h^{-1}. No carrier gas was used.

The induction period of the reaction was 20–30 min, depending on the experimental conditions. During this time, the isobutane yield reached the maximum and then decreased to a constant value. The data reported in this paper are related to 20th minute of the reaction run. The reaction products were monitored chromatographically, and catalysts, by powder X-ray diffraction (DRON-3M X-ray diffractometer) and thermal analysis (Q-1500D derivatograph).

Zirconium dioxide synthesized by decomposition of $ZrO(NO_3)_2 \cdot 2H_2O$ and calcination of $ZrO(OH)_2$ hydrogel precipitated with NH_4OH solution shows low activity in *n*-butane isomerization. Sulfation of ZrO_2 preliminarily calcined at 823–873 K does not raise the isobutane yield. The active catalyst is formed after treatment with an $(NH_4)_2SO_4$ solution of $ZrO(OH)_2$ dried at room temperature. In this case, the *n*-butane conversion is 22.0% at 493 K; the yield of isobutane reaches 16.9% (the residue consists of propane and *n*- and isopentanes).

Impregnation of dealuminated mordenite HM_{17} with $ZrO(NO_3)_2$ aqueous solution, with further calcinations at 823 K, substantially improves the catalyst activity, which appears in a rise in the isobutane and isopentane yield and in a decrease in the optimal temperature of the reaction. That is, ZrO_2 has a promoting effect on the activity of dealuminated mordenite.

It should be noted that, in contrast to HM_{17}, whose sulfation does not substantially affect its isomerization activity, $a ZrO_2/HM_{17}$ samples (a = 2.5–10.0 wt %) show after sulfation a higher activity in *n*-butane isomerization at relatively low temperatures. These data show that, in contrast to ZrO_2, which directly promotes HM_{17}, sulfate ions raise the activity of dealuminated mordenite only when the latter contains zirconium dioxide. The data obtained are listed in Table 1.

Depending on the ZrO_2 content in mordenite-zirconium and sulfated mordenite-zirconium catalysts, the *n*-butane conversion and the total yield of isoparaffins (isobutane and isopentane) pass through maxima. As can be seen from the figure, the maximal activity of the catalysts prepared by impregnation is observed for samples containing 5.0–7.5 wt % ZrO_2.

The same extremal dependences are observed for catalysts prepared more simply by mechanical mixing of HM_{17} and $ZrO(NO_3)_2 \cdot 2H_2O$ without any solvent, followed by molding with a binding agent, drying, and calcination. A comparison of samples containing from 5 to 20 wt % ZrO_2 showed that the HM_{17}–10 wt % ZrO_2 catalyst has the highest activity in *n*-butane isomerization. The corresponding data are listed in Table 2.

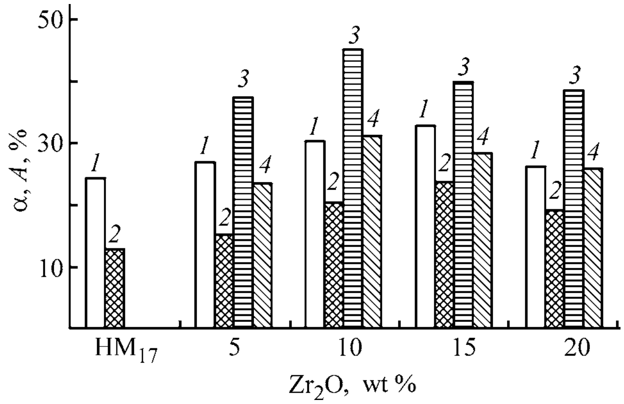
Table 1. Isomerization of *n*-butane on mordenite-containing catalysts prepared by impregnation

Catalyst	*T*, K	*n*-Butane conversion, %	Yield, wt %	
			isobutene	isopentane
HM_{17}	523	28.0	16.1	2.5
4% SO_4^{2-}/HM_{17}	523	28.2	15.4	3.7
27% SO_4^{2-}/ZrO_2	493	22.0	16.9	2.4
5% ZrO_2/HM_{17}	493	30.0	18.5	3.0
4% SO_4^{2-}/5% ZrO_2/HM_{17}	463	34.5	21.3	4.0

Table 2. Isomerization of *n*-butane on mordenite-zirconium catalysts prepared by mechanical mixing of HM_{17} and $ZrO(NO_3)_2 \cdot 2H_2O$

Sample no.	Catalyst	*T*, K	*n*-Butane conversion, %	Yield, wt %	
				isobutene	isopentane
1	HM_{17}	493	24.5	12.0	0.6
2	HM_{17}–5% ZrO_2	493	48.2	25.9	3.1
3	HM_{17}–10% ZrO_2	463	12.7	9.1	1.6
		493	54.5	28.5	5.3
4	HM_{17}–15% ZrO_2	463	3.0	2.6	–
		493	52.7	25.5	3.4
5	HM_{17}–20% ZrO_2	493	33.5	19.9	4.6
6	HM_{17}–$ZrO(OH)_2$ (as calculated for 10% ZrO_2)	463	5.8	4.5	0.6
		493	31.8	20.2	2.9
7	ZrO_2	493	0.9	0.5	–

It should be noted that such an extremal dependence of the activity on the ZrO_2 content is observed for the catalysts prepared by mechanical mixing of HM_{17} with a $ZrO(OH)_2$ hydrogel synthesized by precipitation from $ZrOCl_2 \cdot 8H_2O$ solution with aqueous NH_4OH. However, at the same ZrO_2 content, the activity of catalysts prepared using a zirconium salt (Table 2, sample 3) is higher than the activity of



(*1*, *3*) conversion α of *n*-butane and (*2*, *4*) total yield of isoparaffins *A* vs. the ZrO_2 content in (*1*, *2*) $a ZrO_2/HM_{17}$ and (*3*, *4*) 4% $SO_4^{2-}/a ZrO_2/HM_{17}$ catalysts.

Table 3. *n*-Butane conversion in an apparatus with two series-connected reactors (catalyst HM_{17}–10% ZrO_2–4% SO_4^{2-})

Temperature, K		*n*-Butane conversion, %	Yiels, %	
reactor 1	reactor 2		isobutene	isopentane
448	–	8.9	7.4	0.2
463	–	36.3	19.2	2.3
493	–	51.6	26.0	4.9
448	463	37.2	25.3	3.4
463	463	43.9	28.9	4.1

the sample prepared from ZrO(OH) hydrogel (Table 2, sample 6).

The difference in the properties of mordenite-zirconium catalysts prepared by impregnation or mechanical mixing is also manifested in that sulfation of impregnated catalysts $a$$ZrO_2$/$HM_{17}$ calcined at 823 K raised their activity, while sulfation of the HM_{17}–$a$$ZrO_2$ (mixed catalysts) samples calcined at the same temperature does not substantially affect the activity.

The three-component catalyst HM_{17}–10% ZrO_2–4% SO_4^{2-} prepared by simultaneous mixing of HM_{17}, $ZrO(NO_3)_2 \cdot 2H_2O$, and $(NH_4)_2SO_4$ followed by thermal treatment under the above standard conditions has a higher isomerization activity. At 463–493 K, the yield of isobutane and isopentane on this catalyst was 19.2–26.0 and 2.3–4.9%, respectively, at an *n*-butane conversion of 36.3–51.6%. The yield of the main by-product of the reaction, propane, decreases substantially faster as compared to the isobutane yield, and the selectivity of the reaction correspondingly increases.

Taking into account the data obtained, we studied the conversion of *n*-butane on a catalytic apparatus with two series-connected reactors. In this case, a higher yield of isoparaffins and selectivity can be reached at lower temperatures. The data on *n*-butane conversion and the yield of isoparaffins after the first and second reactors at various temperatures are listed in Table 3. As seen, the yield of isobutane in the two-reactor system at 448–463 K increases to 25.3–28.9% at a small decrease in the isopentane yield. The reaction selectivity with respect to isoparaffins increases to 75% due to a substantial decrease in the propane yield. These results are of certain interest because the catalyst used contained no precious metals (Pt, Pd) and was prepared by a simple and convenient method at atmospheric pressure and without any carrier gas. Such catalysts can be used as a basis for preparation of more active catalysts for isomerization of *n*-paraffins.

The high catalytic activity of sulfated ZrO_2 promoted with various metals (Mn, Fe, Ga, Pt, etc.) was discussed in a number papers [6–8, 13–17]. In this study, we showed that zirconium compounds promote the activity of dealuminated mordenite, whereas sulfation does not affect isomerization activity of mordenite itself, but substantially improves that of the mordenite-zirconium catalysts. This fact suggests that the promoting effect of sulfate ions is caused by the presence of ZrO_2 in the catalysts. At the same time, it should be noted that dealuminated mordenite is not only a support for ZrO_2 and SO_4^{2-}, but is the dominating component of the mordenite-zirconium catalysts, as indicated by the attainment of the maximal catalytic activity at small concentrations of ZrO_2 and SO_4^{2-} and by the preservation of the same features of the reaction before and after promotion of HM_{17}. The parallel variation of the yields of propane, isobutane, and isopentane with time can be caused by the bimolecular mechanism of the reaction. However, this matter requires a further study.

The thermal analysis of the systems HM_{17}, 5% ZrO_2/HM_{17} and 4% SO_4^{2-}/5% ZrO_2/HM_{17} and of samples prepared by mechanical mixing (HM_{17}–10% ZrO_2 and HM_{17}–10% ZrO_2–6% SO_4^{2-}) does not show any substantial difference in their thermal behavior. Only one endothermic peak at 388 K, caused by elimination of adsorbed water, exists in the DTA curve of HM_{17}. After impregnation of HM_{17} with $ZrO(NO_3)_2$, this peak shifts to 398 K and a weak endothermic peak appears at 628 K.

These facts are probably caused by dehydration and decomposition of the zirconium salts. The high-temperature peaks of sulfate decomposition were not found, probably, because of the small amounts of sulfate groups in the samples examined.

The X-ray diffraction patterns show that the crystal structure of H-mordenite is preserved after dealumination and promotion with zirconium dioxide. In the diffraction patterns of a powder with the composition 7.5% ZrO_2/HM_{17} and ZrO_2, prepared by decomposition of $ZrO(NO_3)_2 \cdot 2H_2O$ at 873 K, reflections characteristic of tetragonal ZrO_2 at $2\theta = 30^\circ$ were observed [18]. Based on the data obtained, we can suggest that impregnation of HM_{17} with a $ZrO(NO_3)_2$ aqueous solution, followed by thermal treatment at 823–873 K, yields a mixed mordenite-zirconium system with a higher isomerization activity at relatively low temperatures because of the interaction between the decomposing zirconium salt and HM_{17}. This process affects the specific texture and acid–base properties of the catalytic mixture.

CONCLUSIONS

(1) The promoting effect of ZrO_2 on the catalytic activity of dealuminated mordenite in isomerization of *n*-butane was found.

(2) It was shown that the sulfated mordenite-zirconium catalyst prepared by a simple and convenient method shows high activity in *n*-butane isomerization at atmospheric pressure and relatively low temperatures.

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