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NATURE OF ACTIVITY AND SELECTIVITY OF CATALYSTS BASED ON DEALUMINIZED ZEOLITES. COMMUNICATION 2. ACTIVITY OF DEALUMINIZED Y ZEOLITES AND MORDENITE IN CRACKING STRAIGHT-CHAIN HYDROCARBONS

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Dealuminization of zeolites changes their catalytic properties very substantially. The character of these changes has been studied for many years, but thus far no satisfactory explanation has been obtained for the complex relationships that are observed [1-6]. In the work reported here, we have made an attempt to relate the changes in zeolite activity upon dealuminization to the changes in their acidity.

In order to determine what role in the changes of activity of dealuminized zeolites is played by chemical factors (changes in composition and acidity) and what role by diffusional factors, we investigated the activity of identical samples of dealuminized zeolites in the reaction of cracking various hydrocarbons differing in reactivity, but with approximately identical effective diameter of the molecule.

EXPERIMENTAL

We used the same samples of dealuminized zeolites as in [3, 7-9]: Y zeolite with SiO₂/ Al₂O₃ modulus M = 4.8, 5.6, 7.1, 10.0, and 22.8; and mordenite with M = 12.6, 17.8-20.0, 28.0, 47.2-50.0, and 118-125. The rates of cracking n-pentane, n-hexane, n-decane, and nhexadecane were compared with the previously measured rates of cracking l-hexene [7]. The measurements were performed in a pulse microreactor. The catalyst bed volume was 0.1-0.3 cm³, grain size 0.25-0.5 mm. The carrier gas (He) flow rate was 0.5-1.0 ml/sec. The volume of the injected dose was 1-5 µl. The products were analyzed chromatographically, the sorbent consisting of 15% squalane on Chromatone N-AW. In connection with the substantially different reactivities of the substrates that were selected and the different activities of the zeolites, the measurements of cracking activity were performed at different temperatures so that the total conversion would be no higher than 20% in any case. The cracking experiments were alternated with oxidative regeneration of the catalyst by air at 500°C until the activity had lined out (usually three cracking/regeneration cycles). As a characteristic of the activity we used the mean cracking rate on three or four different samples of each catalyst.

The heats of adsorption of n-butylamine and NH_3 on the test samples of dealuminized Y zeolite and mordenite at 30°C were measured in [8, 9]. In the present work, we obtained data on the heats of adsorption of NH_3 at 300°C on the H forms of these zeolites. With the aim of characterizing the change in diffusional permeability of the mordenite when it was dealuminized, we measured diffusion coefficients of 2,2,4-trimethylpentane. The measurements were made gravimetrically, taking kinetic curves for the sorption at 30°C.

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DISCUSSION OF RESULTS

The dependence of the activity of the faujasite samples on the Al/(Al + Si) ratio (α) is extremal (Fig. 1), the same as in the case of the dealuminized mordenites (Fig. 2). This same sort of variation of activity of dealuminized mordenite in cracking n-hexane was observed in [4, 5].

Among the faujasites, the highest activity in conversions of n-pentane and n-hexane was that of the sample with M = 5.6 (α = 0.26). In contrast, the activity of the dealuminized mordenites depends on the hydrocarbon chain length: For the n-pentane, the maximum activity is shown by the samples with M = 30-50, for the n-hexane with M = 28.8, for the n-decane with M = 20, and for the n-hexadecane with M = 12-18. Thus, the lower the molecular weight of the hydrocarbon, the greater is the degree of mordenite dealuminization required to achieve the maximum reaction rate.

Although the reactions were carried out at substantailly different temperatures, it was shown by special experiments on n-hexane and n-decane cracking in the temperature interval 300-500°C. that the maximum on the curve for the activity as a function of Al content in the zeolites is independent of the temperature.

Under the conditions of cracking, adsorption factors do not play any significant role, and in any case, they do not change substantially with changes in the length of the alkane chain [10]. Therefore, the observed relationship between the activity of the dealuminized mordenites and the number of carbon atoms in the molecule should apparently be attributed to a change in reactivity.

The data of Fig. 3 support the conclusion that changes in acidity must be responsible for the changes in cracking activity upon dealuminization. As can be seen from these data, in full agreement with the results reported in [4], the diffusional permeability of the mordenite increases steadily as Al atoms are removed from the lattice.

Upon dealuminization of the faujasite, the number of acidic centers decreases, but their strength remains unchanged [9]. The falling branch of the curves in Figs. 1 and 2 can be explained by a decrease in the number of acidic centers at high degrees of dealuminization. From this point of view, the rising branch of the curve does not find any satisfactory explanation.

Measurements of the heat of NH₃ adsorption on dealuminized mordenites [8] showed that when Al is removed from the zeolite, the total number of protonic centers decreases, but new high-strength centers are formed. In the examples of skeletal isomerization and double bond shift in 1-hexene, isomerization of o-xylene, and oligomerization of propylene, it was shown in [3] that the character of the changes in activity of dealuminized mordenite samples depends on the activation energy of the conversions that take place. For reactions with a high activation energy, the activity increases with increasing degree of dealuminization, in correspondence with the increase in the number of strong centers. In contrast, in reactions that do not require the participation of strong acidic centers, the activity of the mordenite decreases, since dealuminization reduces the total number of protonic centers; and for reactions taking place on moderate-strength centers, the dependence of the activity on the degree of dealuminization passes through a maximum.

The results shown in Fig. 2 are in good agreement with such an explanation of the changes in catalyst activity of mordenite upon dealuminization. With increasing length of the carbon chain, the alkane reactivity increases, and the cracking activation energy decreases [10]. The reaction proceeds on weaker centers, the maximum number of which is reached at a lower degree of dealuminization [3, 8]. The lower the reactivity of the hydrocarbon, the greater is the degree of dealuminization required to obtain the most effective mordenite catalyst. Upon dealuminization of faujasite, there is no change in the strength of the acidic centers [9]; and correspondingly, the optimal degree of dealuminization for the conversion of n-alkanes with different molecular weights likewise remains unchanged.

The data on the cracking of 1-bexene (Fig. 2) do not fit the general correlation between the hydrocarbon reactivity and the cracking activity of the dealuminized mordenites. The reactivity of alkenes is higher than that of alkanes; and for the 1-bexene, the maximum on the curve could be expected at a higher ratio A1/(A1 + Si). However, the cracking of the alkene takes place at a temperature 200-300°C lower than that of the alkane. Such a substantial difference in reactivity cannot be explained by adsorption or diffusional factors. The



Fig. 1. Activity of H faujasites in cracking hydrocarbons, as a function of degree of dealuminization: 1) n-pentane (500°C); 2) n-hexane (500°C); 3) 1-hexene (140°C), according to data of [7].

Fig. 2. Cracking activity of H mordenite as a function of degree of dealuminization: 1) n-pentane (500°C); 2) n-hexane (450°C); 3) n-decane (400°C); 4) n-hexadecane (350°C); 5) 1-hexene (250°C).

Catalyst		SiO2	H faujasites				H mordenites				
Al/(Al+Si) SiO2 : Al2O3		_	0,29 4,8	0,22 7,1	0,16 10,0	0,08 22,8	0,14 12,6	0,09 20,0	0,06 28,8	0,04 47,2	0,016 125
1-Hexene cracking	140° 250°	0,07	2,1	3,7	2,4	- 8	0,24		0,06	0,46	0,16
Hexane cracking	450°	-	1,8	4,5	s	12,4	1,4	3,6	s	ŝ	3,5

TABLE 1. Relative Yield of Propane in Cracking 1-Hexene on Zeolites with Different Degrees of Dealuminization, %

cracking of olefins apparently proceeds through a different mechanism, or with the participation of other active centers.

The substantially different mechanism of low-temperature cracking of olefins is also indicated by data on the relative yield of saturated products (Table 1). In [7], it was shown that dealuminized faujasites have high activities and dealuminized mordenites have low activities in the reaction of hydrogen redistribution in the cracking of 1-hexene at low temperatures. The paraffin/olefin ratio in the cracked products can be used as an approximate measure of the catalyst activity in the secondary reaction of hydrogen redistribution. This ratio is also considerably dependent on the degree of substrate conversion. However, as can



Fig. 3. Changes in diffusional permeability of H mordenite with respect to 2,2,4-trimethylpentane as the mordenite is dealuminized.

Fig. 4. Heat of ammonia adsorption at 300° C as a function of coverage on zeolites: 1) HM; 2) HY.

be seen from Table 1, the difference in the relative yield of propane, for example in the cracking of 1-hexene on the faujasite and mordenite samples, is so large that it cannot be explained by the difference in the degree of conversion, particularly since, as indicated above, the experimental conditions were selected so that the conversion would not be higher than 20%.

The data of Table 1 show that, for both types of zeolite, the behavior with respect to the hydrogen redistribution reaction changes when the temperature is raised. This change is particularly sharp for the dealuminized mordenites, which do not manifest any activity in the hydrogen redistribution reaction at 250° C and are not inferior to the dealuminized faujasites in this respect at 450° C. In a similar manner, with respect to activity in the primary reaction of fragmentation, the faujasites are far more active than the mordenites in the low-temperature region, such that the cracking of 1-hexene on the dealuminized mordenite had to be conducted at a temperature 100° higher than the cracking temperature on faujasite [7]. At the same time, as can be seen from Figs. 1 and 2, when the cracking is carried out in the high-temperature region, the activity of the dealuminized mordenite is an order of magnitude higher than that of the faujasite samples that were investigated.

It can be assumed that the low-temperature reactions have relatively low activation energies and thus require the participation of moderate-strength acidic centers in the catalytic act, the faujasite having considerably more of these centers than the mordenite [7-9]. The mechanism of the conversions that predominate in the high-temperature region is related primarily to the high-strength acidic centers, the presence of which is characteristic for mordenite [8].

Of particular interest from this point of view are the data on the heats of high-temperature adsorption of NH_3 on the faujasite and mordenite samples. The results shown in Fig. 4 confirm the substantial difference between the two types of zeolite in the presence of acidic centers of different strengths. On the Y zeolite, the ammonia is adsorbed with a heat of 95-110 kJ/mole, whereas the centers that are characteristic for the mordenite give heats of 170 and 143 kJ/mole. Upon dealuminization, the number of acidic centers is reduced, but the ratio between the heats of adsorption for the two types of zeolite remains the same.

Let us note also that the formation of completely saturated products has been observed in the cracking of hexane and hexene at low temperatures [11, 12]. According to [12], the absence of olefins in the cracked products is not a consequence of the occurrence of the homomolecular reaction of hydrogen redistribution, but rather is explained by an irreversible consumption of H atoms of the surface hydroxyl groups of the zeolites. However, the data of Table 1 do not support this view.

As already pointed out, according to the measurements of heats of adsorption of bases, the total number of acidic groups in the faujasite and mordenite decreases upon dealuminization. According to the stoichiometry, this should reduce the capability of the zeolites for forming saturated products in the cracking. However, it can be seen from Table 1 that the $C_{3}H_{8}/C_{3}H_{6}$ ratio in the products from n-hexane cracking on both types of zeolitic catalysts shows a sharp increase as the Al/(Al + Si) ratio is lowered; and the $C_{3}H_{8}/C_{3}H_{6}$ ratio begins to decrease only when almost all of the Al has been removed from the lattice.

On the other hand, on the samples of faujasite with a high degree of dealuminzation, as shown by data reported in [9], there are also silanol groups, the same as in silica gel. In this connection, we investigated the cracking of 1-hexene on a sample of Grade KSM silica gel under comparable conditions (Table 1). Even though the silica gel does have a certain activity in cracking reactions, this is nothing like the activity of thedealuminized faujasite, in which strong acidic centers are present, even though in small quantities.

These studies have shown that the complex character of the changes in zeolite activity in hydrocarbon cracking reactions are determined by the changes in the nature of acidity when they are dealuminized.

CONCLUSIONS

1. Cracking rates of the n-alkanes pentane, hexane, decane, and hexadecane on the H forms of dealuminized Y zeolite and mordenite have been measured, and also the heats of adsorption of ammonia and the diffusivity of 2,2,4-trimethylpentane.

2. As the degree of dealuminization is increased, the zeolite activity passes through a maximum. In the cracking of alkanes with different chain lengths on the faujasites, the optimal degree of dealuminization is the same for all of the alkanes. In the case of the mordenites, the lower the molecular weight of the alkane, the greater is the degree of dealuminization required to obtain an effective cracking catalyst.

3. Diffusional factors do not play a decisive role, and the activity of the zeolites, both in the primary fragmentation reaction and in the secondary hydrogen distribution reaction, is determined by the changes in their acidity upon dealuminization.

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