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Optimization of SiO_2/Al_2O_3 Mole Ratio of Mordenite for *n*-Pentane Isomerization

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Partially dealuminated H-mordenite, with a Group VIII metal, has been employed as a catalyst in the isomerization of *n*-pentane. As dealumination proceeds the catalytic activity goes through a maximum at a SiO_2/Al_2O_3 mole ratio of 17/1 which appears to coincide with the maximum in the total number of Bronsted acid sites. The dependence of isomerization activity on the nature, quantity, and state of reduction of the supported metal has also been investigated.

INTRODUCTION

Catalytic isomerization of low-molecular weight normal paraffins is well known and of significant importance in the petroleum refining industry. The use of zeolite catalysts, specifically mordenite, in the past several years, as the acidic component in dual function hydroisomerization catalysts had made the light paraffin hydroisomerization process even more appealing (*1–3*).

While providing all the advantages of the conventional (amorphous support) dual function catalysts, the zeolite-based catalysts eliminate some undesirable side effects, such as corrosion, and operate at considerably lower temperatures. With mordenite, acceptable light paraffin isomerization reaction rates and good selectivities have been reported by various workers (*4, 5*).

In their study of *n*-pentane isomerization, Voorhies and Bryant (*6*) have concluded that a range of 10/1 to 50/1 for the SiO_2/Al_2O_3 mole ratio of mordenite is required for maximum activity. In the present investigation, we report studies conducted on modified mordenites wherein the SiO_2/Al_2O_3 mole ratios are of intermediate value.

This paper also discusses studies on the dependence of *n*-pentane isomerization activity on the nature and content of the supported metal.

Our previous results (*7*) on several mordenite samples showed that partial dealumination results in a substantial increase in the quantity of very strong sites.[2] Since isomerization is known to proceed through a carbonium ion mechanism, we then undertook the present investigation to establish if there existed any correlation between maximum acidity and optimum *n*-pentane isomerization activity of Pd-H-mordenite.

EXPERIMENTAL

The mordenite samples employed in this study were prepared according to the procedure reported in an earlier publication (*7*). Before catalytic testing, the samples were metal exchanged and washed. They were then pilled with a binder and calcined at 550°C in dry air.

The metal exchanged, pilled, and calcined catalysts were tested for *n*-pentane isomerization. These measurements were made using a fixed bed continuous flow

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[2] As dealumination proceeds, the total acid site concentration increases, however, the concentration of Bronsted sites ($\geq 48\%$ H_2SO_4 or $pk_a > -3.0$ or ir absorption at 1435 cm^{-1} after NH_3 absorption at 150°C) goes through a maximum. The concentration of *strong* Bronsted sites (ir absorption at 1435 cm^{-1} after NH_3 absorption at 300°C) increases.

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TABLE 1

Catalyst Activity for Pd Loaded H-M

Catalyst[a]	SiO_2/Al_2O_3 mole ratio	Isomer ratio[b] i-$C_5/\Sigma C_5$	Selectivity to i-C_5 (%)
1	10.8	0.185	95.0
2	11.8	0.306	95.4
3	12.5	0.315	95.7
4	14.6	0.450	97.9
5	15.6	0.570	97.2
6	16.9	0.564	99.1
7	17.3	0.550	98.9
7a	17.3	0.680	98.2
8	17.9	0.591	97.6
9	21.7	0.510	97.3
10	28.7	0.191	95.6

[a] Catalysts were ion exchanged with palladium to ~0.5 wt% and mixed with a bonding agent prior to activity test.

[b] Catalyst isomerization activity was determined using the following process variables: temperature = 260°C; pressure = 31.67 kg/cm^2; H_2/C_5 = 1.81; n-C_5 room temperature feed rate = 20 cm^3/hr; LHSV = 1.00 cm^3/cm^3 hr; catalyst volume = 20 cm^3.

[c] Equilibrium isomer ratio, i-$C_5/\Sigma C_5$ = 0.745 at 260°C.

reactor. The feedstock in every case was Fisher certified n-pentane. A Hewlett-Packard Model 5830A gas chromatograph was used to analyze the product gases.

RESULTS AND DISCUSSION

The n-pentane isomerization activity of 10 Pd-exchanged H-M samples is shown in Table 1. The acidity measurements for some of these samples are reported elsewhere (*7*). The catalyst activity is expressed as the ratio of i-C_5 to total C_5's in the reactor product. The SiO_2/Al_2O_3 mole ratio shown is that determined for the catalyst after treatment to enhance its surface acidity. It is important to emphasize that some structural alumina is removed by these treatments since the SiO_2/Al_2O_3 mole ratio in synthetic mordenite is close to 10/1. The partial dealumination of mordenite effected its n-pentane isomerization activity. Of course, the most interesting feature is the maximum in activity with increasing SiO_2/Al_2O_3 mole ratios. This is apparent in both the isomer ratio (i-$C_5/\Sigma C_5$) and i-C_5 selectivity of the product (Table 1). Figure 1 clearly demonstrates that at an SiO_2/Al_2O_3 mole ratio of 17/1 the isomerization activity of the dealuminated Pd-H-mordenite reaches a maximum. In addition, it can be stated that selectivity is also correlated to activity (the highest activity is accompanied by the highest selectivity).

Using the free energy data (*8*), the equilibrium isomer ratio was calculated to be 0.745 at 260°C. Apparently, in the present studies the equilibrium value of i-$C_5/\Sigma C_5$ was not reached. When sample 7 was subjected to further modifications the resulting sample 7a, with the optimum SiO_2/Al_2O_3, showed an increase in the isomer ratio from 0.55 to 0.68.

As was mentioned earlier, Voorhies and Bryant (*6*) have reported a range of 10/1 to 50/1 for the SiO_2/Al_2O_3 mole ratio required for maximum n-pentane isomerization activity of mordenite. More careful control of the SiO_2/Al_2O_3 mole ratio is what enabled us to determine the optimum value of 17/1.

The best confirmatory evidence that has been published is provided by Bremer *et al.* (*9*) whereby nickel-exchanged mordenite was employed in the hydrocracking of n- and iso-octane. These workers reported that maximum hydrocracking activity was obtained at a SiO_2/Al_2O_3 mole ratio of about 23/1. Selectivity was also found to be

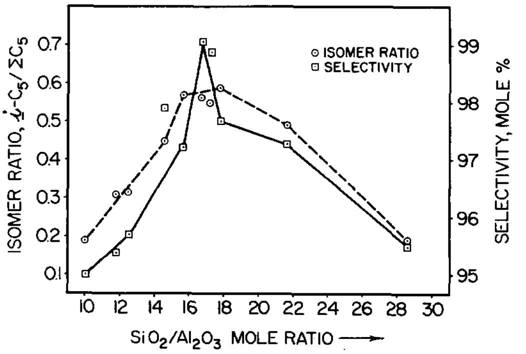

FIG. 1. Isomer ratio and selectivity versus SiO_2/Al_2O_3 mole ratio of modified H-M in the isomerization of n-pentane.

directly correlated to the activity, i.e., catalysts possessing the highest activity exhibited the highest selectivity. The plot of cracking activity (k_n) and selectivity versus SiO_2/Al_2O_3 mole ratio, reported by these researchers, has been reproduced in Fig. 2.

The use of a zeolite for isomerization, but in the absence of metal hydrogenation component, leads to the accumulation of carbonaceous deposits which rapidly deactivate the catalyst. The incorporation of a noble metal onto a hydrogen mordenite not only prevents catalyst deactivation, but also increases the selectivity (*5*).

The dependence of isomerization activity on the nature and content of the supported metal has therefore been investigated. The isomerization results for catalysts containing various amounts of ion-exchanged metal are presented in Table 2. A comparison of catalysts eleven, thirteen, and sixteen reveals that the isomerization activity is highly dependent upon the nature of the metal. The relative activities decline in the order Ni > Pd ≫ Rh.

The results from Table 2 also indicate that the isomerization activity is dependent upon the metal loading. A similar dependence of isomerization activity on metal loading has been reported elsewhere (*10*).

Minachev and co-workers have investigated the activity of several zeolite-supported metals in the hydrogenation of benzene (*11–13*). The most active was a rhodium catalyst; next were iridium, platinum, and palladium catalysts, and finally nickel and rhenium. It is apparent that the isomerization activity and hydrogenation activity of these metals are related. More specifically, the present results and those of Minachev indicate that an inverse relationship exists, i.e., less active hydrogenation metals are more active in the isomerization reaction. At least, this is true for *n*-pentane isomerization. In addition to providing hydrodehydrogenation sites, one cannot eliminate the possibility that the supported metal also influences the acid sites. Indeed, an interaction between the supported metal and the acid site has recently been reported (*14*). Further studies of this possible interaction are required.

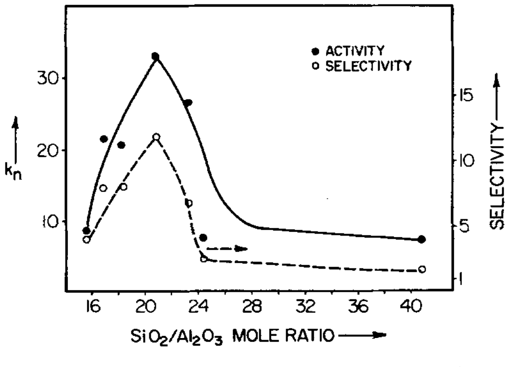

FIG. 2. Activity and selectivity versus SiO_2/Al_2O_3 mole ratio of modified H-M in the cracking of *n*- and iso-octane (*8*).

TABLE 2

Influence of the Supported Metal

Catalyst	Metal	Weight percent	Isomer ratio[a] i-$C_5/\Sigma C_5$	Selectivity to i-C_5 (%)
11	Pd	0.080	0.492	97.1
12	Pd	0.600	0.526	96.7
13	Ni	0.082	0.567	93.8
14	Ni	0.043	0.613	92.7
15	Ni	0.021	0.623	94.2
16	Rh	0.050	0.165	10.6

[a] Catalyst isomerization activities were determined using the following process variables: temperature = 249°C; pressure = 31.67 kg/cm^2; H_2/C_5 = 1.81; LHSV = 1.00 cm^3/cm^3 hr; catalyst volume = 20.0 cm^3.

Table 3 shows the importance of prereduction of supported metal prior to catalytic reaction. If the reduction temperatures are not very high the redox equilibrium in the system M^{2+}–zeolite + H_2 → M^0 + $2H^+$–zeolite will be reversible. The present results suggest that at prereduction temperatures below 354°C, the palladium ions are not sufficiently reduced by hydrogen. Under severe reduction conditions, M^0 atoms migrate to the external surface of zeolite crystals to form aggregates (*15*). The 354°C prereduction tem-

TABLE 3

Effect of Metal Reduction Temperature on Catalyst Activity

Reduction temperature[a] (°C)	Isomer ratio[b] $i\text{-}C_5/\Sigma C_5$	Selectivity to $i\text{-}C_5$ (%)
227	0.524	97.7
308	0.640	97.8
354	0.656	97.9

[a] Catalyst contained 0.60 wt% Pd and was reduced in a flowing hydrogen atmosphere.

[b] Process variables: temperature = 260°C; pressure = 31.67 kg/cm^2; H_2/C_5 = 1.81; LHSV = 1.00 cm^3/cm^3 hr; catalyst volume = 20.0 cm^3.

perature does not appear to be severe enough to cause metal migration since no decrease in activity was observed up to this temperature.

Studies of *n*-pentane isomerization over Pt and Pd zeolites of the faujasite and mordenite types provided evidence that this reaction proceeds according to a dual function mechanism (*16*). The currently accepted mechanism for the hydroisomerization of a normal paraffin is a three-step process, with a dehydrogenation reaction occurring on a metal site and a subsequent structural rearrangement of the normal olefin on an acidic site. The resulting iso-olefin is thought to be hydrogenated to an iso-paraffin at another metal site.

CONCLUSION

In the isomerization of *n*-pentane, partially dealuminated H-mordenite with a Group VIII metal has been employed as a catalyst. As dealumination proceeds, the catalytic activity goes through a maximum which is observed at a SiO_2/Al_2O_3 mole ratio of 17/1. The present investigation further reinforces the existing literature reports that an increase in the number of strong Bronsted acid sites increases the isomerization catalytic activity. It is interesting that the optimum SiO_2/Al_2O_3 mole ratio for the isomerization of *n*-pentane is very close to that reported by Bremer *et al.* (*8*) for the hydrocracking of *n*- and iso-octane. The current results also show the influence of isomerization activity of the nature, quantity, and state of reduction of the supported metal. The relative activities are found to decline in the order $\text{Ni} > \text{Pd} \gg \text{Rh}$. The optimum prereduction temperature of the supported metal prior to catalytic reaction is established at 354°C.

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