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The Promotional Effect of Hydrogen on the Catalytic Properties of Rare-Earth Zeolites

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Under high hydrogen pressure, zeolites X and Y exchanged with Ce, La, or mixed rare-earth ions showed sustained catalytic activity in cracking *n*-hexadecane. The carbon number distribution of the cracked product agrees well with that obtained with hydrocracking catalysts containing a weak hydrogenation function, such as sulfided nickel or tungsten. The promotional effect of molecular hydrogen was further confirmed by comparable runs made with helium and nitrogen. In either case, the conversion was lower and the activity declines with time-on-stream. Reversing the gas from helium or nitrogen to hydrogen was found to reversibly restore the catalyst to its steady-state activity in hydrogen. Using cyclohexene as a diagnostic tool, rare-earth-exchanged zeolite X was shown to possess only cracking, hydrogen transfer, and isomerization activities which are characteristics of an acid catalyst. No hydrogenation activity was observed. It is reasoned that rare-earth cations in zeolites behave similarly to supported sulfided nickel or tungsten as a weak hydrogenation function. They cannot hydrogenate olefinic hydrocarbons but can hydrogenate diolefin intermediates formed in the hydrogen transfer process and thus prevent catalyst fouling.

INTRODUCTION

Minachev and his co-workers (*1*) reported in 1968 the hydrogenation of butylene on CaY and NaY without adding any known hydrogenating agent. Their subsequent studies on the hydrogenation of benzene and other aromatics over various alkali and alkaline earth metal cation forms of mordenite (*2–5*) suggested the participation of such cations associated with mordenite in the hydrogenation/dehydrogenation reactions. Although aromatic hydrogenation reactions have not been reported on other zeolites, the dehydrogenation of cyclohexane over NaY (*6*) and the hydrogenation of olefins (*7–10*) and oxygenates (*11–13*) over a number of zeolites including the small-pore NaA have been reported by a number of investigators. The hydrogenation of 2-methyl-2-butene (*8*) and furan (*12*) over NaA is particularly intriguing, since neither molecule can be sorbed by the zeolite.

The promotional effect of hydrogen was also reported by Beaumont and Barthomeuf (*14*) in the cracking of isooctane over NaHX and NaHY. They found a sharp rise in cracking activity with 1 atm of hydrogen when 35 to 45% of the Na^+ in NaY is replaced by H^+. Such a sharp rise in activity was not observed with helium. They postulated that strong acid sites are liberated in the presence of hydrogen. These sites also possess hydrogenation activity which kept the active sites from rapid fouling.

In this paper we present the results of a study on the promoting effect of hydrogen under hydrocracking conditions at 2000 psig of total pressure. Catalysts studied

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included rare-earth-exchanged X and hydrogen Y. Experiments were conducted both in hydrogen and nitrogen or helium with *n*-hexadecane or cyclohexene as the feed.

EXPERIMENTAL

A. Materials

Rare-earth-exchanged X was prepared by treating NaX with a 0.5 *M* mixed rare-earth chloride solution at 180°F. The exchanged product was filtered, washed, dried and calcined, and then reexchanged with the rare-earth chloride solution.

CeX and LaX were prepared in the same manner except $Ce(NO_3)_3$ and $La(NO_3)_3$ solutions were used.

HY was prepared from NH_4Y by deep-bed calcination (*15*). A significant contraction of unit cell dimension from 24.72 (NH_4Y) to 24.35 Å was noted after calcination. This indicates that the HY sample was a stabilized Y.

The compositions of the catalysts are shown in Table 1. Trace metal analysis showed that all catalysts contained 100–1000 ppm of Fe and less than 100 ppm of Cu. The catalysts were pretreated at atmospheric pressure in the reactor for 2 hr at 900°F with hydrogen before use. The reactants were reagent grade *n*-hexadecane and cyclohexene.

TABLE 1

Catalyst Compositions

Component	Composition (wt%)			
	REX catalyst	CeX catalyst	LaX catalyst	HY catalyst
SiO_2	44.4	39.9	40.3	73.8
Al_2O_3	30.6	28.1	27.2	24.9
RE_2O_3	25.2	29.8	29.6	—
Na_2O	0.3	0.6	0.3	0.4
CaO	<0.01	<0.01	<0.01	<0.01
MgO	0.01–0.1	0.01–0.1	0.01–0.1	0.01–0.1
Fe	0.01–0.1	0.01–0.1	0.01–0.1	0.01–0.1
Cu	<0.01	<0.01	<0.01	<0.01

TABLE 2

n-Hexadecane Conversion at 2000 psig, 750°F[a]

Conversion in the presence of	Conversion (wt%)			
	REX catalyst	CeX catalyst	LaX catalyst	HY catalyst
H_2	61	92[a]	51	52
N_2	23	15	13[b]	32
H_2	48	46	77[b]	29
He	7	—	—	—
H_2	47	—	—	—

[a] Initial activity, 2 hr on-stream; 2-hr prerun in other series.

[b] 0.3 LHSV.

B. Apparatus

Details of the micropressure reactor have been described elsewhere (*16*). The unit was operated at 2000 psig of total pressure with a mole ratio of hydrogen to hydrocarbon of 30–40 to 1. The hydrocarbons were fed to 0.6 LHSV, unless otherwise noted. When the gas was switched from hydrogen to helium or vice versa, at least 4 hr were allowed to elapse before a material balance was taken.

Mass spectrometry analyses were used to analyze the gaseous reactor effluents, and gas chromatography (silicone gum rubber column) was used for the liquid products.

RESULTS

A. Conversion of n-Hexadecane in the Presence of Hydrogen or Inert Gases (Nitrogen or Helium)

The effect of each gas on the activity of four catalysts (REX, CeX, LaX, and HY) was investigated by starting the run in hydrogen and switching to a different gas each day. As shown by the data in Table 2, the nature of the gas has a pronounced influence on the conversion of hexadecane. In hydrogen, all four catalysts exhibited an initial high activity which rapidly declined to a steady-state activity of about 50 to 60% conversion. In nitrogen or helium, however, all the catalysts continued to lose activity. With rare-earth-exchanged

TABLE 3

Normalized Carbon Number Distribution Data for REX and HY

Carbon number	Carbon number distribution (wt%)			
	REX catalyst			HY catalyst
	H_2 atmosphere		N_2 atmosphere	H_2 atmosphere
	61%[a]	48%[a]	23%[a]	52%[a]
C_1	0.1	0.4	0.2	0.6
C_2	1.5	2.1	5.7	0.8
C_3	14.1	16.9	23.5	10.2
C_4	21.0	26.0	29.2	17.4
C_5	17.4	13.4	8.3	17.2
C_6	11.9	12.5	6.5	14.3
C_7	8.8	10.4	6.1	9.6
C_8	7.7	6.9	5.2	6.8
C_9	6.2	5.4	5.7	5.1
C_{10}	4.8	3.3	4.8	4.9
C_{11}	4.8	1.9	2.6	5.7
C_{12}	1.8	0.8	2.2	2.5
$C_{13} + C_{14}$	—	—	—	5.1

[a] Conversion, weight percent.

zeolites, switching back to hydrogen reversibly restored the catalyst activity to its steady-state activity in hydrogen. The ability of rare-earth-exchanged zeolites to sustain the conversion of hexadecane in hydrogen without an added hydrogenating agent has thus been demonstrated. In the case of HY, a change to hydrogen did not recover the catalyst activity. However, the lower activity level was sustained in hydrogen without further deactivation.

B. Comparison of Products Obtained in Hydrogen and in Nitrogen

TABLE 4

Olefins in C_5^- Products

	REX catalyst			HY catalyst
	H_2 atmosphere		N_2 atmosphere	H_2 atmosphere
	61%[a]	48%[a]	23%[a]	52%[a]
$C_3^=$'s in C_3's	1.2	3.5	3.0	4.6
$C_4^=$'s in C_4's	0.2	1.1	0.3	3.0
$C_5^=$'s in C_5's	0	0.7	0	0.3

[a] Conversion, weight percent.

TABLE 5

Reactions of Cyclohexene over REX at 2000 psig

Product	Product (wt%)		
	650°F 10%[a]	750°F 65%[a]	800°F 74%[a]
Cyclohexane	30	—	—
Methylcyclopentane	5	15	24
Benzene	50	63	57
Cracked products	15	22	19

[a] Conversion, weight percent.

Although hydrogen has varying degrees of promotional effect on different catalysts, analyses of the reactor effluent showed that the composition of the cracked products was substantially the same for all four catalysts and, furthermore, it was not affected by the choice of the gas used. Shown in Table 3 are the normalized carbon number distribution data for REX and HY. Data in Table 4 shows that the olefin concentrations in the C_5^- products were quite low, indicating extensive hydrogenation or hydrogen transfer reactions. In view of the fact that the choice of nitrogen or hydrogen made little difference, we conclude that these saturated hydrocarbon products are largely the result of hydrogen transfer reactions.

The lack of hydrogenation activity was also demonstrated by the reaction of cyclohexene over REX in hydrogen at 2000 psig and 650 to 800°F. These condi-

TABLE 6

Reactions of Cyclohexene at Atmospheric Pressure

Product	Product (wt%)		
	REX at 550°F		NiREX at 93°F[a]
	H_2 atmosphere 94%[b]	He atmosphere 93%[b]	H_2 atmosphere 100%[b]
Cyclohexane	<1	<1	97
Methylcyclopentane	78	86	3
Benzene	21	14	0
Cracked product	<1	<1	<1

[a] Impregnated with 4% Ni.
[b] Conversion, weight percent.

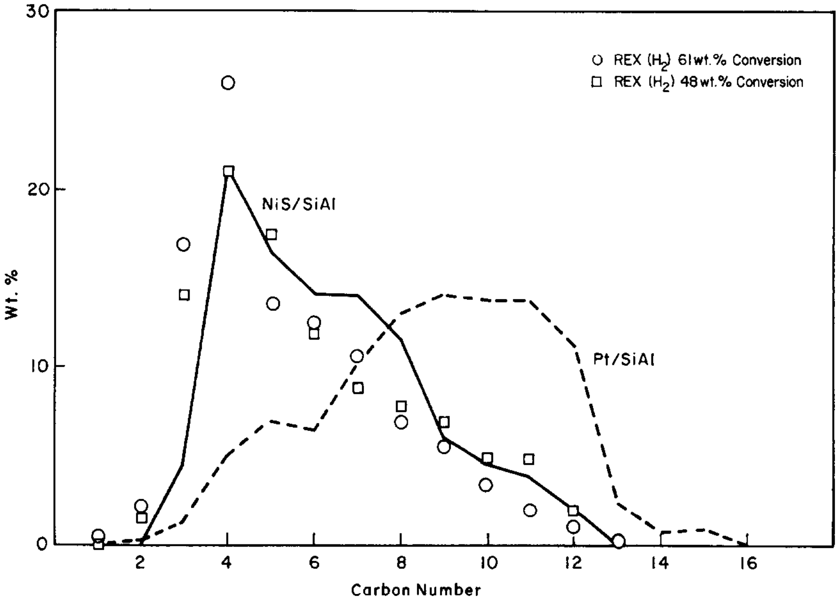

FIG. 1. Product distribution from *n*-hexadecane.

tions are highly favorable for the complete hydrogenation of cyclohexene. Instead, the data as shown in Table 5 indicate that the predominant reactions found are hydrogen transfer, cracking, and isomerization reactions typical of those expected from an acid catalyst.

A separate set of experiments was made with cyclohexene at atmospheric pressure to compare REX in hydrogen and helium and the effect of added nickel to the REX catalyst. The runs were made with 0.5-cm^3 catalyst in a 7-mm-i.d. flow reactor. The catalysts were calcined in flowing air at 1000°F for 1 hr, cooled to 900°F in helium, reduced in hydrogen at 900°F for 1 hr, then cooled to the reaction temperature in hydrogen or helium. The reaction was carried out at 0.6 LHSV, 4.4/1 mole ratio of hydrogen (or helium) to cyclohexene. The data are summarized in Table 6.

The result on NiREX presents a sharp contrast to that of REX alone. Again, with REX, the choice of gas used made little difference on the product distribution. In either case, the yield of methylcyclopentane was higher than expected from the reaction stoichiometry:

$$3C_6H_{10} \rightarrow C_6H_6 + 2C_6H_{12}.$$

Instead of attributing the excess yield of methylcyclopentane to the hydrogenation activity, it is more likely that the extra hydrogen came from hydrogen transfer and condensation reactions which yielded unsaturates of higher molecular weights that remained on the catalysts, since continuous catalyst aging was observed at 1 atm.

C. Comparison of Products with Those from Conventional Hydrocracking

Marked differences in the hydrocracked product distribution have been observed depending on the strength of the hydrogenation function (*17*). Shown in Fig. 1 is a comparison of the results of the present study with those of hydrocracking *n*-hexadecane over a Pt/SiAl catalyst and a NiS/SiAl catalyst. The similarity between the product distribution of REX andNiS/SiAl suggests that the rare-earth ions also serve as a weak hydrogenation function like NiS.

DISCUSSION

The major observations of the present study may be summarized as follows.

1. The catalytic activity of rare-earth zeolite X and HY for the conversion of hexadecane can be sustained under a high partial pressure of hydrogen but not in inert gases.
2. The predominant reaction products are independent of the diluent gases used and can be attributed to cracking, hydrogen transfer, and isomerization reactions typical of an acid catalyst.
3. The product distribution is similar to that obtained from hydrocracking over a nickel sulfide on silica alumina catalyst.
4. The catalysts (REX, HY) do not hydrogenate olefins.

These results are consistent with the proposed hydrocracking mechanisms. There are two distinct classes of hydrocracking catalysts: One contains a strong hydrogenation function, such as Pt or Pd, the other contains a weak hydrogenation function such as sulfided nickel or tungsten.

Hydrocracking of *n*-hexadecane in the presence of a strong hydrogenation component follows the classical dual functional mechanism (*18*): The *n*-hexadecane molecule is dehydrogenated to *n*-hexadecene on the metal site, followed by cleavage split to two olefins on the acid site, and then is rehydrogenated on the metal site to form paraffinic products. There is very little secondary splitting of the products except at high conversion. The carbon number distribution of the hydrocracked products is similar to that of the acid cracking of an olefin (*19*). A typical product distribution from the hydrocracking reaction of *n*-hexadecane over Pt/SiAl, taken from Ref. (*19*), is shown in Fig. 1. However, hydrocracking in the presence of a weak hydrogenation component follows the typical carbonium ion mechanism as in acid cracking. The products from hydrocracking *n*-hexadecane (*17*) over NiS/SiAl are strikingly similar to those of catalytic cracking (*20*). Extensive secondary C–C bond scission takes place. The products are characterized by high isobutane yield due to the isomerization of the carbonium ion intermediate followed by β-scission and hydrogen transfer reactions. The hydrogenation component in this case does not play a dual functional role but serves primarily to prevent catalyst fouling. Initiation of the C–C bond scission reaction is the same as in catalytic cracking, except that the reaction can proceed at a lower temperature because the catalytic sites are kept clean by the weak hydrogenation function. The effect of catalyst fouling on the observable rate of cracking of *n*-paraffins was vividly demonstrated by Nace in his study of the instantaneous rate measurement for hexadecane cracking (*21*).

Our data suggest that the rare-earth cations, and to some extent the cations in the stabilized HY, serve the same antifouling function as the sulfided nickel or tungsten component of hydrocracking catalysts. Although they do not have sufficient activity for olefin hydrogenation, they can hydrogenate polyunsaturated coke precursors produced via acid-catalyzed hydrogen transfer reactions. Thus, catalyst deactivation is lessened. The difference between rare-earth zeolite X and HY appears to be in the strength of this hydrogenation function. REX, having a stronger hydrogenation function, can recover its activity in hydrogen after a deliberate deactivation.

The participation of molecular hydrogen in the conversion of hexadecane over REX and HY has been clearly demonstrated, but we cannot definitely rule out the possible activity of trace metals. All the catalysts in this study contained 100 to 1000 ppm of iron, as were the catalysts used by Minachev *et al.* (*3*). These workers concluded that iron was not involved in the catalytic process because large variations in catalyst activity depended upon the type of cations in the zeolite rather than the iron concentration. However, more recent studies indicated that the oxidation state of a reducible metal ion in a zeolite depends on the acidity of the zeolite (*22*). For example, nickel ion in a Na zeolite is easily reducible, while nickel ion in a hydrogen zeolite is not easily reduced. Similarly, the state of trace iron and its hydrogenation activity may also depend on the cationic form of the zeolite. Thus, the role of iron, though it may be minor, cannot be definitively ruled out without further experimentation.

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