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The Effect of Exchange Cations on Acidity, Activity, and Selectivity of Faujasite Cracking Catalysts

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Several studies have shown that the removal of exchanged sodium increases activity for paraffin cracking as would be expected of a solid Brønsted acid. However, it has also been observed that at low unit cell sizes the presence of low levels of sodium affects selectivity but not activity for gas oil cracking. This paper describes how cation exchange affects the distribution of acid sites in dealuminated faujasite over a range of unit cell sizes and how this in turn affects the activity and selectivity of USY at a unit cell size of ~2.440 nm for gas oil and heptane cracking. The acidic properties were determined by NH_3/TPD measurements, by pyridine adsorption followed by IR measurements, and by isopropylamine TPD experiments. Activities and selectivities were measured by gas chromatographic analysis of the products of heptane and gas oil cracking. The results show that alkali exchange of dealuminated faujasite has little or no effect on activities for gas oil cracking, but a very strong effect on activity for heptane cracking. While the results show that exchange by alkali cations reduces the number of cracking sites, the major effect is to reduce the intrinsic activity per site by an order of magnitude or more. The deactivating effect of individual cations is a strong function of size. The activity follows the order $H^+ \sim Mg^{2+} \sim Li^+ > Na^+ > K^+$.

INTRODUCTION

Catalysts containing dealuminated faujasite are widely used in the petroleum refining industry (*1*). The selectivity and activity of these catalysts for gas oil cracking is controlled by the number of aluminum acid sites per unit cell of the faujasite as measured by the unit cell size after deactivation in the regenerator. Typically unit cell sizes of 2.426–2.430 nm are achieved. At this unit cell size there are about seven aluminum atoms per unit cell or about one per super cage. It is believed that the number of sites relates to the strength of the site, isolated sites being stronger, and to the hydrogen transfer activity. It has also been proposed that nonframework alumina plays a role in determining the strength and activity of the site.

The relationship between the activity and the sodium level of zeolites is not entirely clear. Studies have shown that cracking activity is proportional to the degree of removal of cations such as sodium from either Y (*2, 3*) or dealuminated Y (*4, 5*) as would be expected of a solid Brønsted acid. Sodium exchange of greater than 30% of the active sites in a sample of hydrogen Y entirely deactivated the sample for paraffin cracking (*3*). In the case of dealuminated Y samples, sodium poisoning reduces cracking activity much more dramatically than would be expected simply on the basis of the numbers of sites poisoned compared to the number of sites remaining. While sodium is a very strong poison, potassium was shown to be an even stronger poison (*5*). Other studies based primarily on results obtained with pyridine poisoned catalysts have distinguished between strong acidity required for alkane cracking and a weaker acidity required for the cracking of olefins and for

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other acid catalyzed reactions (*6*). Experimental poisoning experiments with ammonium showed an unexpectedly sharp drop to zero activity for alkane cracking after only about 10% of the sites were poisoned (*7*). These experiments suggest that a small number of easily poisoned strong sites are responsible for alkane cracking. Sodium exchange may be less effective in controlling the numbers of weaker sites. In an important study of the effect of unit cell size on selectivity, the degree of sodium exchange was observed to have little effect on activity for gas oil cracking. In this study, high levels of sodium had a major effect on octane (olefin) selectivity (*8*). It has also been proposed that both activity and selectivity in certain reactions may be related to the local electrostatic potential gradient resulting from differently charged atoms present within the small zeolite cages (*9*). This work also showed that sodium exchange had a very strong effect on *n*-decane cracking activity.

In this paper, the intention is to discover how cation exchange affects the strength and distribution of the acid site in dealuminated faujasite and how this in turn affects the intrinsic catalyst activity and selectivity for gas oil cracking. The acidic properties of a variety of zeolites were determined by ammonia TPD, isopropylamine TPD, and by pyridine/DRIFTS measurements. The activity and selectivity were measured by gas chromatographic analysis of the products of gas oil cracking as well as heptane cracking. Faujasites were prepared and tested for this study at unit cell sizes of 2.460 nm and ~2.440 nm.

METHODS

Samples of dealuminated Y (DEALY) were prepared with <1% Na_2O by steam dealumination at different severity levels to give DEALY with a 2.439-nm unit cell size. After the steam dealumination the USY samples were slurried at 80°C in a solution containing an amount of ammonium sulfate equal in weight to the zeolite and adjusted to pH 2.9 with sulfuric acid. This procedure prepares the zeolite in the ammonium form and removes sodium as well as nonframework alumina. A wash at a lower pH with 0.1 *M* HCl can dealuminate the framework and also lacks the buffering capacity to dissolve the nonframework alumina in the pH region required for alumina solubility. Alumina is soluble below pH ~3.5. Nonframework aluminum removal was nearly complete as measured by a comparison (Table 1) of the aluminum content measured chemically and by reference to the relationship between unit cell size and framework aluminum content (*10*). After washing there was a slight increase in the unit cell size from 2.439 to 2.441 nm as a result of cation removal. After calcination at 500°C, the temperature of reaction, a small amount of octahedral nonframework alumina is observed by ^{27}Al MASNMR, either as a result of dealumination during the calcination or as a result of nonframework alumina remaining after the washing procedure. The unit cell size is not observed to change after the 500°C calcination.

TABLE 1

Zeolite Properties

Unit cell (nm)	2.457	2.441
#Al/uc	36	19
% Crystallinity	95	116
Surface area (m^3/g)	790	878
Si/Al (Chem anal.)	—	8.61
#Al/uc	—	20

Catalysts containing 35% USY at ~2.440 nm unit cell size were prepared by grinding and sieving a dried slurry of exchanged zeolite and Ludox AS40, 0.08% Na_2O, 0.16% ammonia, and 40% silica sol obtained from E.I. Du Pont. Spray dried catalysts containing 35% DEALY with a unit cell size of 2.458 nm were prepared by spray drying a slurry of zeolite, clay and 20% silica binder followed by exchange. The cation exchange was carried out with approximately neutral chloride salts of rare earth (pH ~5), magnesium, sodium, potassum, lithium, or ammonium followed by extensive hot (80°C) water washing. The clay contains about 0.1% sodium and does not retain significant amounts of cation after water washing. The unit cell of the zeolites changed slightly with exchange, decreasing by 0.002 nm or less. Prior to use all catalyst samples were calcined for 2 h at 538°C. Properties of the zeolites used to prepare the calcined catalysts are summarized in Table 1.

Chemical analyses were done by ICP. Activity for gas oil cracking was measured using standard MAT conditions as given by ASTM test 3907. The reactor temperature was 527°C. Coke and hydrogen were determined using a LECO instrument and by a GOW MAC thermal conductivity detector connected to a 13 × molecular sieve packed column. Heptane cracking experiments were done at 502°C. The heptane was picked up in a 100 cm^3/min nitrogen flow through a bubbler at 22°C. The heptane flow was measured at 1.19 g/h over 0.2 grams of a catalyst containing 35% zeolite. The catalyst was mixed in the reactor with about 16 g of alundum. Alundum was also used for the preheater section. Hydrogen was measured with a thermal conductivity detector. Reproducibility of the cracking runs was within 10% at 20% conversion.

Pyridine DRIFTS spectra were obtained using Nicolet 60 SX-FTIR. Prior to obtaining the spectra, the samples were evacuated for 1 h to 0.5 Torr at 550°C, exposed to pyridine for 1 h at 150°C at atmospheric pressure, evacuated again for 2 h to 0.5 Torr at 150°C, and transferred to the spectrometer under helium pressure. Samples were prepared for ammonia TPD measurements by heating to 550°C in flowing helium for 2 h, exposed to ammonia at 110°C for 2 h, and flushed with helium. The desorption was carried out from 110 to 550°C at 20°C/min. A thermal conductivity detector was used to monitor the desorbed ammonia.

Isopropylamine TPD experiments were carried out as follows: 20 mg of sample was outgassed in helium or one hour at 550°C and cooled to 100°C. The sample was treated with a total of 5 ml of 2-propylamine at 100°C picked up in a stream of flowing helium passing over the isopropylamine. The total amount of amine picked up by the sample at this point is not measured. The sample was flushed for four hours with helium to remove excess amine (zero base line for m/e of 44 at the detector) and temperature programmed at 10°C/min to 550°C. The calibrated mass spectrometer detector monitored m/e of 44 (2-propylamine), 41 (propylene), and 17 (ammonia). The amount of isopropylamine desorbed as cracked product (propylene) was measured and is reported in Table 5. The amount of desorbed isopropylamine was not measured.

TABLE 2

Relative Activities for Gas Oil Cracking of Catalysts Containing MgDEALY, RENaDEALY, and NaHDEALY Prepared from NaHY Sieve Dealuminated to 2.458 nm Unit Cell (Cat/Oil 2.0, 526°C, 32 WHSV)

	Exchange cation			
	Re^{3+}	Mg^{2+}	Na^{+}	H^{+}
Composition (wt%)				
Na_2O	0.31	0.26	2.54	0.34
RE_2O_3	3.08	0.0	0.0	0.0
MgO	0.0	1.14	0.0	0.0
Unit cell (nm)	2.458	2.459	2.459	2.453
% Exchange	50	45	68	—
Pyridine adsorption (DRIFTS)				
1543 cm^{-1} (Brønsted)	2.6	2.1	1.7	2.5
1445 cm^{-1} (Lewis)	1.8	2.7	2.7	2.2
Ammonia TPD				
μmol/g ammonia	1090	940	800	790
Activity and selectivity (wt%)				
Conversion	73.4	72.7	74.3	70.9
Hydrogen	0.17	0.17	0.12	0.18
C1 + C2	3.63	3.73	3.53	3.83
C3	8.8	9.1	7.8	9.8
C4	24.2	24.3	21.8	25.4
C5 + gasoline	36.2	36.1	40.0	32.3
Coke	12.8	12.2	12.3	13.1

RESULTS

Gas Oil Cracking

Activities and selectivities of RE^{3+}-, Mg^{2+}-, and Na^+-exchanged catalysts containing 35% of dealuminated Y zeolite with a unit cell size of 2.458 nm, and H^+-exchanged catalysts containing the same

TABLE 3

Relative Activities for Gas Oil Cracking of Catalysts Containing 35% of Alkalai-Exchanged Dealuminated Y (2.440 nm unit cell) (Cat/Oil 4.0, 526°C, 32WHSV)

	Exchange cation				
	Li$^+$	Na$^+$	K$^+$	H$^+$	Mg^{2+}
NB# 16156-35-	2	4	3	—	1
Zeolite composition (wt%)					
Li_2O	1.26	0.0	0.0	0.0	0.0
Na_2O	0.06	3.23	0.04	0.05	0.07
K_2O	0.0	0.0	4.87	0.0	0.0
MgO	0.01	0.01	0.01	0.01	1.77
% Exchange	48	59	57	—	51
Gas oil cracking, activity and selectivity (wt%)					
Conversion	85.6	86.9	85.3	86.7	83.9
Hydrogen	0.21	0.22	0.19	0.22	0.20
C1 + C2	5.0	5.15	4.1	5.1	4.7
C3=	3.0	3.4	3.8	3.0	3.1
C3	8.0	6.6	4.5	9.8	8.1
Total C3	11.0	10.0	8.3	12.8	11.2
NC4	3.9	3.5	2.9	4.4	3.7
IC4	8.6	9.4	8.9	9.8	7.9
Total C4	14.5	15.1	14.1	16.1	13.9
C5 + gasoline	36.9	38.6	42.4	37.4	37.8
Coke	17.7	17.6	16.0	14.5	15.9
Steamed 4 h at 815°C, 100% steam					
Activity and selectivity (wt%)					
Conversion	48.5	49.3	54.8	38.1	52.3
Hydrogen	0.08	0.07	0.07	.10	0.08
C1 + C2	1.27	1.34	1.47	1.47	1.73
C3=	2.9	2.9	3.3	2.3	3.1
C3	0.5	0.5	0.5	0.6	0.9
Total C3	3.4	3.4	3.8	2.8	3.9
NC4	0.4	0.3	0.4	.4	0.7
IC4	1.7	1.6	1.9	1.2	2.5
Total C4	5.7	6.0	6.8	4.4	6.5
C5 + gasoline	35.7	36.5	40.1	27.2	37.0
Coke	2.2	1.9	2.4	2.0	2.8
Unit cell (nm)	2.425	2.424	2.424	2.426	2.427

TABLE 4

Relative Activities of Catalysts Containing NaY, RENAY, and NAHY for Gas Oil Cracking (526°C, 32WHSV)

	Cat/oil ratio		
	0.7	1.0	1.37
NaY	18.2	23.4	22.9
RENaY	52.1	55.0	78.8
NaHY	35.2	45.5	78.8

amount of dealuminated Y at a unit cell size of 2.453 nm are summarized in Table 2. The results show that the activity for gas oil cracking is nearly independent of the cation. Activities of Li$^+$-, Na$^+$-, K$^+$-, or H$^+$-exchanged catalysts at ~2.440-nm unit cell size were also found to be independent of the identity of the exchanged cation; see Table 3. For comparison, the gas oil cracking activities of variously exchanged HY based catalysts were also measured; see Table 4. The results showed the normal behavior. The sodium exchange decreased activity.

At both unit cell sizes selectivities appear to be somewhat affected by alkali exchange. The Na$^+$-exchanged catalyst makes less H_2, a less olefinic gasoline, and more gasoline compared to RE^{3+}-, Mg^{2+}-, or H$^+$-exchanged catalysts. The ability of Na$^+$ to neutralize Brønsted acid sites appears to affect selectivity more strongly than the activity of the catalyst.

Acidity Measurements

1. Pyridine DRIFTS. The effects of cation exchange are observable by conventional methods of acidity measurement. Alkali exchange should reduce the number of protonic acid sites. This effect is observed by pyridine DRIFTS experiments; see Fig. 1. The Na$^+$-exchanged 2.458-nm unit cell size catalyst has the least intensity associated

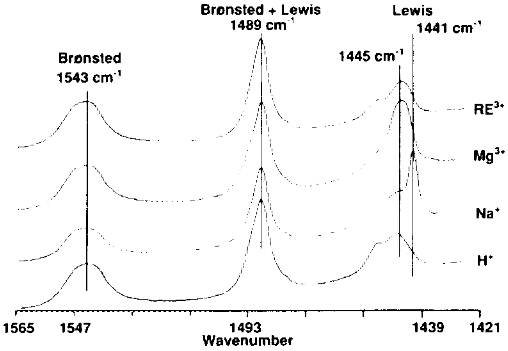

FIG. 1. Pyridine adsorption/DRIFTS spectra of catalysts containing 35% of a mildly dealuminated and exchanged Y prepared at a unit cell of 2.458 nm (RE^{3+}, Mg^{2+}, Na$^+$) and 2.453 nm (H$^+$).

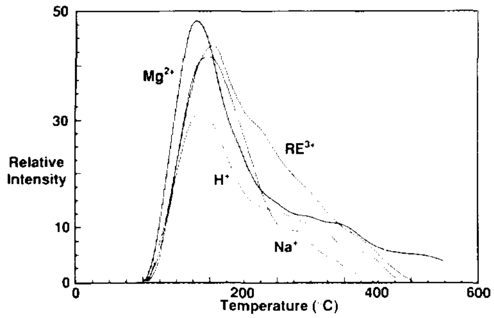

FIG. 2. Ammonia TPD of catalysts containing 35% of a mildly dealuminated and exchanged Y prepared at a unit cell of 2.458 nm (RE^{2+} Mg^{2+}, Na^+) and 2.453 nm (H^+).

with protonic acid sites and the RE^{3+}-exchanged catalyst has the greatest intensity. In terms of efficiency for neutralizing Brønsted sites, the cations rank in the order $Na^+ > Mg^{2+} > RE^{3+}$. The multivalent cations can hydrolyze and are not expected to neutralize Brønsted acid sites as effectively as the monovalent cation (*11*). In the case of Lewis sites the Mg^{2+}- and the Na^+-exchanged catalysts have the greatest intensity and the RE^{3+}-exchanged catalyst has the least intensity. Relative intensities are listed in Table 2.

2. Ammonia TPD. Two peaks commonly appear in the ammonia TPD spectrum of zeolites. The lower temperature peak is identified with weaker acidity and the higher temperature peak with higher acidity. Although the weaker acidity is sometimes further identified with Lewis sites and the stronger acidity with protonic sites, in many cases the source of the acidity cannot be demonstrated. NH_3 TPD profiles of the RE^{3+}-, Mg^{2+}-, and H^+-exchanged catalyst at 2.458 nm are shown in Fig. 2. Amounts of desorbed ammonia are given in Table 2.

The hydrogen and rare earth forms produced a distribution characterized by a sharp first peak conventionally interpreted as weak acidity and a second broad region corresponding to stronger acidity. In the case of the Mg^{2+} exchanged material, the intensity of the weak acidity peak increased with respect to the strong acidity region compared to the spectrum of the hydrogen and rare earth forms. Sodium exchange produced a sharp profile in the weak acidity region and much less strong acidity indicating that the stronger, possibly protonic, sites were neutralized by the sodium. The hydrogen form prepared from the ammonium form had a lower unit cell than the cation exchanged sieves and desorbed less total ammonia consistent with a slightly lower unit cell, a result of dealumination occurring during the thermal decomposition of the ammonium Y.

Excluding the hydrogen exchanged form, the ammonium TPD results show that the total number of acid sites counted is $RE^{3+} > Mg^{2+} > Na^+$. The sodium form desorbs less ammonium than the magnesium or rare earth forms implying the conventional interpretation, that sodium neutralizes protonic sites, while neutralization with rare earth and magnesium is incomplete.

3. Isopropyl amine TPD. Isopropyl amine TPD is a recently developed method of counting active acid sites capable of catalyzing cracking reactions. Since the desorbed species is propene and ammonia, products of cracking of the isopropyl amine, the sites counted by this method are those involved in the cracking reaction. The method has the advantage of measuring the number of sites independently of the zeolite type and the strength of the sites (*12*). Isopropylamine TPD profiles for the samples of catalysts prepared from the variously exchanged ~2.440-nm DEALY were obtained and the quantitative results are given in Table 5. These results agree with the ammonia TPD results in that the alkali exchange reduces the number of acid sites by about half, while exchange with a divalent cation such as magnesium does not.

4. Heptane cracking. Activity for heptane cracking is a measure of both the number of sites as well as the intrinsic activity of the available sites. Activities and selectivities for heptane cracking by the catalysts described in Table 3 are given in Table 5. Ex-

TABLE 5

Relative Activities of Alkali Exchanged Dealuminated Y (2.440 nm unit cell) for Heptane Cracking (502°C, 0.2 g Catalyst, 35% zeolite, 47 μmol Heptane/s-g Zeolite)

	Exchange cation				
	Li^+	Na^+	K^+	H^+	Mg^{2+}
Zeolite composition (wt%)					
Li_2O	1.26	0.0	0.0	0.0	0.0
Na_2O	0.06	3.23	0.04	0.05	0.07
K_2O	0.0	0.0	4.87	0.0	0.0
MgO	0.01	0.01	0.01	0.01	1.77
% Exchange	48	59	57	—	51
# sites/unit cell	9.9	7.8	8.2	19	9.8
Isopropylamine TPD					
#sites/uc	5.9	4.1	4.5	7.0	7.2
		Heptane cracking			
% *n*C7 Converted	22.3	2.4	0.9	37.3	25.9
Rate μmol $g^{-1} s^{-1}$	10.6	1.16	0.42	17.8	12.3
Site time yield × 10^2	2.1	0.3	0.1	2.9	2.0
Selectivities (gc-FID)					
H2	0.0106	0.0186	—	0.0154	0.0078
C1	0.13	0.045	0.028	0.19	0.12
C2	0.40	0.13	0.06	0.59	0.36
C2=	0.47	0.13	0.11	0.85	0.52
C3	3.81	0.21	0.03	7.06	4.70
C3=	6.12	0.62	0.20	9.94	6.98
IC4	3.01	0.09	0	5.63	3.86
NC4	2.42	0.19	0.03	4.06	2.80
C4=	4.44	0.60	0.21	6.21	4.67
*n*C7	77.72	97.56	99.11	62.7	74.1

change with alkali cations modified the acidity of these dealuminated Y catalysts without affecting the activity for gas oil cracking. However, there are dramatic differences in the activity for heptane cracking. In Table 5 the rate is given as μmol of heptane cracked per s per g of zeolite. Since the number of cracking sites per unit cell for these catalysts is available from the isopropylamine TPD experiments, the heptane cracking experiments provide estimates of the yield per site per s associated with the available sites also calculated in Table 5. The results show that although alkali exchange does not reduce the number of active sites, the major effect is a dramatic reduction in the activity of the sites. Larger cations are much more effective in reducing activity, while the smallest cation, Li^+, does not significantly affect the activity. The same is true of the divalent magnesium cation. Magnesium exchange does not reduce either the number or the activity of the active sites.

DISCUSSION

The cracking of paraffins by strongly acidic catalysts is proposed to occur by direct protonation to form a pentacoordinated carbonium ion (*13*). This organic cation decomposes by releasing hydrogen, methane, and possibility ethane and other saturated hydrocarbons. The remaining carbenium reacts by chain propagation or by chain termination involving hydrogen transfer. The results obtained here demonstrate the operation of at least two different sets of cracking sites, one involving the cracking of gas oil and one the cracking of heptane.

Heptane Cracking

The sites involved in heptane cracking are strongly influenced by cation exchange. Although exchange by alkali cations does reduce the numbers of available acid sites, the major effect is on the yield per site per s a measure of the average intrinsic activity of the sites. The exchange either eliminates or reduces the activity of the most active sites.

Selectivities for hydrogen, methane and ethane appear to change depending on the catalyst as well as the conversion level. The zeolite in the protonic form makes relatively more hydrogen, methane, and ethane than the cation-exchanged forms, suggesting a greater degree of initiation by a carbonium ion mechanism and a shorter chain length. The less active Na^+ and K^+ exchanged catalysts also produced more methane, ethane, and hydrogen relative to the total conversion, implying a shorter chain length. However, in these cases differing conversion levels weaken the conclusion. The results suggest that the mechanism as well as the type of sites involved in cracking may vary with the changes in activity induced by cation exchange.

Gas Oil Cracking

In the case of gas oil cracking, ion exchange of dealuminated Y has little effect on activity and a small effect on selectivity. Since the activity of unsteamed HY for gas oil cracking is strongly influenced by cation exchange, the implication is that the dealumination process introduces new sites that are active for gas oil cracking and that these sites do not deactivate by alkali cation exchange. They may be more weakly acidic sites favoring chain propagation rather than chain initiation or termination steps. The observation that the same treatment, cation exchange, influences selectivity for gas oil cracking and strongly influences activity for alkane cracking suggests that the kinds of strongly acidic sites active for alkane cracking may be associated with deleterious selectivities in gas oil cracking. This is not unreasonable. Alkanes typically used in cracking experiments occur in the gasoline range. Excessive activity for the cracking of molecules in this carbon number range would be expected to reduce gasoline yield.

CONCLUSIONS

Since cation exchange of dealuminated Y catalysts affects gas oil cracking and heptane cracking in very different ways, the cracking of gas oil and of small alkanes such as heptane does not appear to occur by the same mechanism or on the same sites. Consequently the cracking of heptane or other small alkanes may not be a good model for gas oil cracking. In the case of alkane cracking, while exchange by alkali cations reduces the number of cracking sites, the major effect is to reduce the intrinsic activity per site by an order of magnitude or more. The deactivating effect of individual cations is a strong function of size in the order $K^+ > Na^+ > Li^+ \sim Mg^{2+}$.

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