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Structure and Catalytic Properties of Thermally and Hydrothermally Treated Zeolites

Acid Strength Distribution of REX and REY

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Acidity distributions of REX and REY zeolites have been determined after pretreatment under various conditions. These acidities are correlated with the catalytic performance of the zeolites in gas oil cracking. It was found that hydrothermal treatment of the zeolites leads to a decreased number of strong acid sites, while the number of sites with intermediate and weak acid strength remain unchanged.

The disappearance of the strong acid sites results in an increased cracking selectivity, especially for the REY type zeolites. This study shows that the selectivity in catalytic cracking for gasoline, gas and coke production is very much dependent on the total number of acid sites as also on the acidity distribution in the catalyst.

INTRODUCTION

Rare earth exchanged X and Y type zeolites are commonly used as sieve components in molecular sieve cracking catalysts. They have a higher activity and better selectivity than amorphous silica–alumina catalysts. To obtain this selectivity, a hydrothermal treatment is essential [Eastwood, Plank and Weisz (*1*)].

The present paper deals with changes of the acidity distribution as introduced by steaming, and correlations between acidity distribution and activity/selectivity for gas oil cracking.

EXPERIMENTAL METHODS

Materials

NaX and NaY zeolites, obtained from Union Carbide Corp. Linde Division, were purified from free sodium silicate by repeated washing with demineralized water. The molar ratios of the zeolites were:

NaX: $Na_2O/Al_2O_3/SiO_2 = 1.00/1.00/2.51$;

NaY: $Na_2O/Al_2O_3/SiO_2 = 0.98/1.00/5.03$.

The rare earth Y zeolites were obtained by repeated exchange of NaY with $RECl_3$ solutions at pH 5.5, with intermediate drying at 120°C. The distribution of rare earths in the $RECl_3$ solution used was approximately: 50% CeO_2, 29% La_2O_3, 15% Nd_2O_3, 4% Pr_6O_{11} and 2% other rare earth oxides.

The X zeolite was exchanged with $RECl_3$, calcined 1 hr at 600°C, followed by another exchange with $RECl_3$. The composition of the rare earth exchanged zeolites was:

REX: $Na_2O/RE_2O_3/Al_2O_3/SiO_2 = 0.01/0.34/1.00/2.60$;

REY: $Na_2O/RE_2O_3/Al_2O_3/SiO_2 = 0.027/0.32/1.00/5.03$.

Thermal treatment was carried out by placing the zeolite in a muffle furnace, heating to the desired temperature in about 0.5 hr and maintaining this temperature during the calcination period.

TABLE 1
Properties of Mid Continent Gasoil Feedstock

Specific gravity (60°F)	0.866 g/cc
API gravity	31.9
Boiling range	272–405°C

Hydrothermal treatment was carried out by heating the zeolite to the desired temperature, followed by subjecting the zeolite to steam with a pressure of 1 atm during 17 hr.

Acidity Measurements.

The zeolite acidity has been determined according to the Benesi method (*2*, *3*) which is based on the successive neutralization of acid sites with *n*-butylamine in nonaqueous suspension. The acid strength of the strongest sites not yet neutralized, is measured with adsorbed indicators. Hirschler (*4*) pointed out that difficulties may arise with Hammett (H_0) indicators if the color change is due to the Lewis acid sites. Therefore we also used three H_r indicators. In our experiments there is a good correspondence between the points determined with H_0 and H_r indicators as shown in the figures.

Cracking Activity and Selectivity

The catalytic properties have been determined by cracking of Mid Continent Gasoil. The properties of this feed are summarized in Table 1. Two test methods were applied, the microactivity test (MAT) (*5*) and the cyclic fixed bed test (*6*). The principal properties of these tests are given in Table 2, indicating that the main difference between the tests is a difference in the process time. The cyclic fixed bed test is a very sensitive method for determining the product selectivity. The selectivity of the zeolite action has been compared with that of a standard amorphous silica–alumina catalyst, containing 13% Al_2O_3, and is expressed in terms of factors for produced gasoline, gas and coke, e.g.:

TABLE 2
Test Methods

	Cyclic fixed bed	Microactivity
WHSV ($g_{oil}hr^{-1}g_{cat}^{-1}$)	2.0	4.0
Process time (min)	10[a]	2.5
Catalyst (g)	15 10 wt % zeolite in SiO_2	6 10 wt % zeolite in SiO_2
Temp (°C)	500	484

[a] The products were collected during the period $t = 3$ till $t = 13$.

gasoline factor

$$= \frac{\text{gasoline produced by the sample}}{\text{gasoline produced by the standard}} \quad \text{at equal conversion.}$$

The samples for these cracking tests were prepared by diluting zeolite with inert silica (10 wt % zeolite and 90 wt % silica).

Results and Discussion

Acidity Distributions

The acidity distributions of a number of calcined and steam-treated zeolites are shown in Figs. 1 and 2. Following the assumptions of Hirschler and Schneider (7) we consider only the acidity stronger than $H_0 = +3.3$ as relevant for the catalytic activity. Sites with an acidity $H_0 < -8.2$ are called strong acid sites, with $-8.2 < H_0 < -3.0$ intermediate acid sites and with $-3.0 < H_0 < +3.3$ weak acid sites.

Comparison of the calcined and steamed REY zeolites shows that steam-activation results in a pronounced decrease of the number of strong acid sites, while the distributions of the intermediate and weak acid sites show a small change only. This can be deduced from the nearly parallel shape of the curves. REX zeolites show the same acidity behavior. X zeolites are less stable than Y zeolites, therefore lower steam temperatures have been used.

Otouma, Yoshima and Ukihashi (*8*) have investigated the acidity distributions of some calcined zeolites. They reported higher total acidities than in the present study. The differences may perhaps be ascribed to the vacuum calcination that

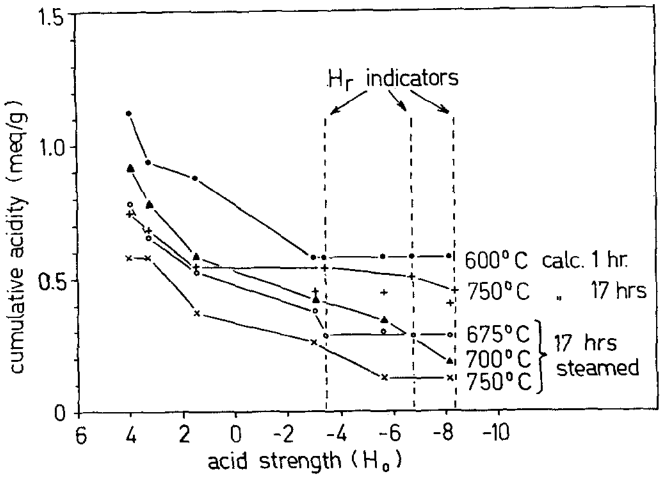

FIG. 1. Acidity distributions of REY zeolites.

Otouma, Yoshima and Ukihashi applied as zeolite pretreatment.

The presence of an appreciable amount of sites with intermediate and weak acid strength for zeolites compared to amorphous aluminosilicates agrees with the work of Otouma, Yoshima and Ukihasi.

Catalytic Performance

The cracking of model compounds is often used as a measure for the activity of catalysts. Cracking of hexane (*9*, *10*) and cumene (*11*, *12*) are well-known examples. The question of selectivity cannot play an important role in such model reactions. Cumene splits into benzene and propene; hexane is cracked only once and saturation of the formed propene by hydrogen transfer is the only important secondary reaction. Relations between the number of acid sites and the activity for these types of model reaction have been investigated intensively. It is generally found that catalysts with the highest number of acid sites are the most active ones (*9*, *11*).

The prime interest in gas oil cracking is often the production of as much gasoline as possible while cracking into gas and coke are unwanted reactions. Coke formation also decreases the activity of the catalyst by blocking the active sites. The

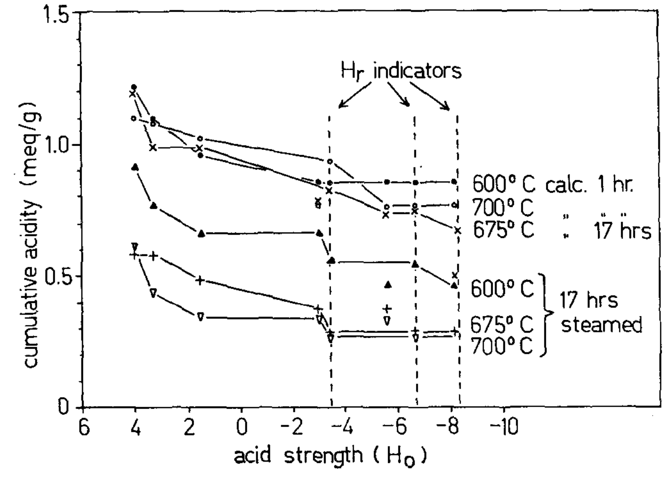

FIG. 2. Acidity distributions of REX zeolites.

TABLE 3
MAT RESULTS FOR REY AND REX ZEOLITES

	REY					REX		
	Calcined		Steamed		NaOH added calcined	Calcined		Steamed
	1 hr 600°C	17 hr 750°C	17 hr 675°C	17 hr 750°C	1 hr 600°C	17 hr 675°C	1 hr 700°C	17 hr 675°C
WHSV	3.94	4.35	3.92	3.71	3.82	3.99	3.79	3.98
Conversion	88.0	86.5	88.9	87.85	88.8	89.7	85.4	78.5
H_2 wt %	0.14	0.09	0.07	0.06	0.11	0.09	0.11	0.10
C_1	1.16	0.98	0.83	0.74	0.96	1.08	0.91	0.99
C_2	2.39	2.02	1.76	1.63	2.18	2.12	1.89	1.74
C_3	8.11	4.23	3.69	3.34	5.03	4.47	4.14	2.37
$C_3^=$	2.53	3.56	3.69	3.62	3.56	3.59	3.46	3.91
iC_4	13.77	11.15	10.33	9.31	11.81	11.25	10.74	7.63
nC_4	5.03	3.12	3.13	2.95	4.05	3.33	3.28	1.94
$C_4^=$	1.68	2.25	2.32	2.52	2.18	2.40	2.47	3.26
C_5^+	46.87	54.94	58.50	59.35	54.14	54.22	51.44	52.11
Cycle oil	11.94	13.53	11.09	12.15	11.15	10.24	14.59	21.49
Coke	6.39	4.14	4.59	4.33	4.83	7.21	6.97	4.46

TABLE 4
CYCLIC FIXED BED TEST RESULTS FOR REX AND REY ZEOLITES

Pretreatment	Time (hr)	Temp (°C)	Conversion (wt %)	C_5^+ (wt %)	Selectivity factors		
					C_4^-	C_5^+	Coke
REY zeolites							
Calcination	1	600	64.4	37.3	0.78	1.09	1.16
	72	600	67.9	43.1	0.67	1.22	0.87
	17	750	70.6	47.7	0.62	1.33	0.53
Steaming	17	600	69.3	43.7	0.67	1.23	0.80
	17	650	70.5	46.1	0.62	1.29	0.77
	17	675	70.5	46.6	0.61	1.30	0.74
	17	700	74.4	49.5	0.58	1.36	0.61
	17	750	73.2	50.8	0.56	1.40	0.46
	17	775	70.8	47.3	0.64	1.32	0.50
	17	800	54.5	35.8	0.81	1.16	0.61
REY + 1% Na_2O calcination	1	600	66.3	43.1	0.71	1.19	0.93
REX zeolites							
Calcination	1	600	57.6	36.6	0.72	1.14	1.21
	1	700	59.6	38.6	0.72	1.18	0.92
	17	675	61.7	39.0	0.71	1.17	1.07
Steaming	17	600	63.2	37.7	0.80	1.11	0.95
	17	675	65.5	42.1	0.70	1.22	0.79
	17	700	64.5	42.9	0.68	1.25	0.66

influence of the changed acidity by steaming on the activity and selectivity for gas oil cracking has been investigated here.

The results of the microactivity test for REX and REY zeolites are shown in Table 3. All these tests have been performed under the same conditions. The product distribution is expressed as weight percentages of the feed.

On steaming the REY zeolites, no big differences are found in conversion, although the steamed catalysts have lost an appreciable part of the original number of acid sites. The selectivity changes on steaming have also been determined with the cyclic fixed bed test. The conversion and gasoline yield in weight percentages, together with the selectivity factors are summarized in Table 4. It was found that increased steam temperatures give increased amounts of gasoline. The structural collapse of the zeolites determines the upper limit for the activation temperature. A plot of the relative crystallinity versus steam temperature is given in Fig. 3 and illustrates that around 775°C structural collapse takes place for the REY zeolites. This is reflected in a loss of activity and a changed selectivity.

A gradual loss in crystallinity is observed for the REX zeolites on steaming (Fig. 3). This explains the decrease in activity of the REX zeolites observed with the MAT test (Table 3). An improvement of the selectivity is also found for the REX zeolites; especially a lower coke make is noticed. In Fig. 4, the gasoline and coke factors of REY zeolites, determined with the cyclic test, are given as a function of the number of strong acid sites. These data indicate that the decrease of the number of strong acid sites on steaming results in an increased gasoline yield and decreased coke and gas make. That this change in acid strength is a very important factor determining the activity/selectivity for gas oil cracking can be shown by partly neutralizing the acid sites of a REY zeolite. The acidity distribution of a RENaY zeolite containing 1 wt % Na_2O shows a decreased number of strong acid sites, resulting also in an increase in selectivity (Table 3).

Comparison of the activities and selectivities of REX and REY zeolites shows that after thermal activation these zeolites have comparable activities and selectivities. The REY zeolites show an improved selectivity on steaming, which is also found to a lesser degree for the REX zeolites.

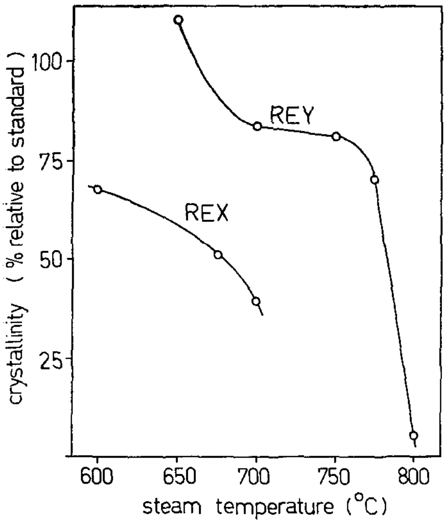

FIG. 3. Effect of steam temperature on crystallinity of REX and REY zeolites.

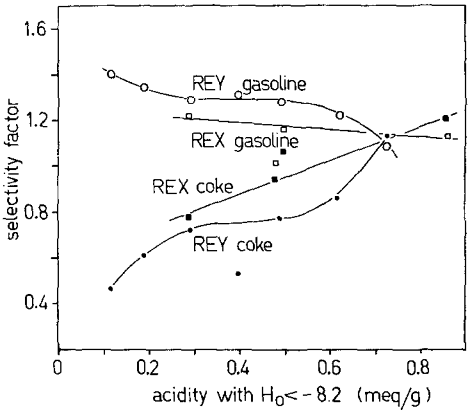

FIG. 4. Effect of zeolite acidity on cracking selectivity factors.

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