Active Sites in Zeolites

II. Cumene Cracking and Toluene Disproportionation Activity of Stabilized Faujasite Structures

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The concentration of acidic hydroxyl groups, sorptive properties, and catalytic activity for cumene cracking and toluene disproportionation were compared for different stabilized catalysts, viz., "deep-bed" "ultrastable," and aluminum-deficient Y zeolites. It was concluded that only a fraction of the acidic hydroxyls could be catalytically active. The toluene disproportionation reaction requires hydroxyl groups with higher acidity. Several structural properties have a favorable effect on the nature of the active sites for both reactions.
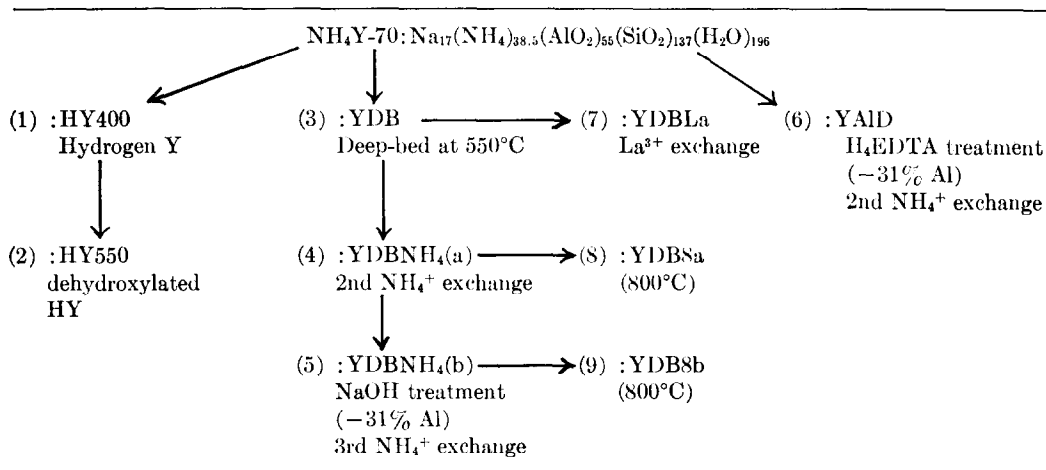
INTRODUCTION

Stabilized faujasites derived from NH₄Y zeolites have raised considerable interest due to their chemical and thermal stability. Samples of improved stability can be prepared after several severe calcination steps around 800°C and are known as ultrastable zeolites (1–4). The geometry of the bed or the hydrolyzing conditions during a milder calcination around 550°C result in the formation of the so-called "deep-bed" products (5–9). Samples with increased stability can also be prepared by extraction of lattice aluminum by chemical reagents (9–13).

Several techniques, such as sorption measurements (1, 6), infrared spectroscopy of the hydroxyl (3, 4, 6–8, 14) and skeletal region (3, 10), ESR spectroscopy (9), and X-ray diffraction (2), help to define more or less precisely the changes of the framework and surface during the stabilization process. Partially hydrolyzed samples of the deep-bed type show a deficiency of O_1 oxygen atoms, a considerable amount of extra-lattice aluminum, and a character-

istic OH spectrum (2, 5–8). Ultrastable zeolites are characterized by a low hydroxyl concentration but also by a low concentration of Lewis sites. This seems to be due to structural rearrangements involving silica migration into vacancies created by the dealumination process (1–4). Aluminum-deficient catalysts prepared by extraction with organic acids (10–13) show a hydroxyl spectrum very similar to the deep-bed samples. The concentration of Lewis sites is also lower than in the original samples.

The catalytic activity of such stabilized structures has rarely been reported (1). Only the isooctane (12, 13) and cumene (15) cracking activity of samples dealuminated by chemical agents has been investigated systematically.

In this work, the activity for cumene cracking and toluene disproportionation of several stabilized structures is reported. The catalytic activities are related to certain physicochemical properties, so that comparison with samples described in the literature is possible.

TABLE 1

Sample Treatment

NH_4Y-70: $Na_{17}(NH_4)_{38.5}(AlO_2)_{55}(SiO_2)_{137}(H_2O)_{196}$

(1) :HY400
Hydrogen Y

(3) :YDB $\longrightarrow$ (7) :YDBLa
Deep-bed at 550°C La^{3+} exchange

(6) :YAlD
H_4EDTA treatment
$(-31\% Al)$
2nd NH_4^+ exchange

(2) :HY550
dehydroxylated
HY

(4) :YDBNH$_4$(a) $\longrightarrow$ (8) :YDBSa
2nd NH_4^+ exchange   (800°C)

(5) :YDBNH$_4$(b) $\longrightarrow$ (9) :YDB8b
NaOH treatment   (800°C)
$(-31\% Al)$
3rd NH_4^+ exchange

EXPERIMENTAL

Materials

A Linde NaY zeolite was exchanged with 0.1 N NH_4Cl and a sample with the following unit cell composition was obtained:

$$Na_{16}(NH_4)_{38.5}(AlO_2)_{55}(SiO_2)_{137}(H_2O)_{196}.$$
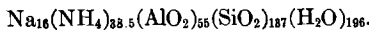
The procedure is described in Part I of this work (*16*). This sample was treated in several ways, as summarized in Table 1. The samples HY400 and HY550 were prepared in the reactor using the same conditions as in Part 1 (*16*).

About 40 gm of the sample NH_4Y-70 contained in a covered crucible were introduced into a muffle furnace preheated at 550°C and left there for 4 hr. The dimensions of the calcination bed were 1.5 cm diameter × 7 cm bed height. Part of the product obtained (YDB) was exchanged with 0.1 N NH_4Cl solution. The residual Na^+ in YDB could be exchanged completely for NH_4^+. The sample YDBNH$_4$-(a) was obtained in this way. Part of the YDBNH$_4$(a) sample was treated with 0.1 N NaOH at 70°C using the method of Kerr (*17*) and the Na^+ ions exchanged again for NH_4^+ to give the sample YDBNH$_4^+$(b). During the NaOH treatment 31% of the lattice aluminum could

be extracted. The residual ions of the YDB sample were also exchanged for La^{3+} with a 0.1 N $La(NO_3)_3$ solution (YDBLa). The samples YDBNH$_4$(a) and YDBNH$_4$(b), with 30% by weight of hydration water, were introduced into the furnace at 800°C and left there for 8 hr. The calcination bed had a diameter of 1 cm and a height of 3 cm. The calcination was carried out in a covered crucible. The products obtained are denoted as YDB8a and YDB8b, respectively. The NH_4Y-70 sample was also treated with a sufficient amount of a 0.05 N solution of H_4EDTA to extract 31% of the lattice aluminum. The residual Na^+ ions were then exchanged with a 0.1 N NH_4Cl solution (YAlD). Before being used in any experiment, the samples were heated in the reactor at 400°C in the same conditions as the sample HY400.

For comparison, an LaY sample with 70% Na exchanged for La and a MgY sample with 72% Na exchanged for Mg were prepared by ion exchange with a 0.1 N $La(NO_3)_3$ and a 0.1 N $MgCl_2$ solution, respectively. The samples were dehydrated slowly at 400°C in the reactor in the same conditions as the HY400 sample. The reactor containing the hydrated samples LaY (28% of H_2O) and MgY (30% of water) in a helium atmosphere was also plunged at 550°C into the reactor oven and left there for 2 hr, and then outgassed at 550°C

TABLE 2

PHYSICOCHEMICAL PROPERTIES OF THE SAMPLES

Sample	Catalyst number	Lattice parameter $(a_o \pm 0.003 \text{ Å})$	Water (25°C) (weight%) $(P/P_o = 0.5)$	Benzene (25°C) (cc g^{-1}) $(P/P_o = 0.2)$	N$_2$ (cc g^{-1}) (−196°C) $P/P_o = 0.2$
HY400	1	24.601	32.5	70.5	245
HY550	2		31.9		232
YDB	3	24.550	26.9	58.4	220
YDBNH₄(a)	4	24.500	26.5		210
DB^b			27.9		
YDBNH₄(b)	5	24.480	26.3		216
DB^a		24.31–24.41			
YAlD	6	24.520			215
YDBLa	7	24.550	25.0		211
YDB8a	8	24.402	22.34	50.5	190
YDB8b	9	24.401	22.00	51.1	186
Ultrastable^c		24.45		51.7	184
MgY	10	24.680	31.00	74.3	250
MgDB	11	24.600	27.90	69.3	
LaY	12				255
LaDB	13				225

^{a} Ref. (5).

^{b} Ref. (6).

^{c} Ref. (1).

for 2 hr. The new materials are denoted as LaDB and MgDB, respectively.

Methods

The pulse microcatalytic reactor was described in Part 1 (16). The sorption measurements of water, benzene, and nitrogen were carried out in the dosing system attached to the reactor and equipped with a McLeod gauge. The measurements of the retention volume and heat of adsorption of benzene between 300° and 400°C and the conditions used in the infrared spectroscopic measurements were described in detail in Part 1 (16). The results of the pyridine poisoning experiments refer to the number of pyridine molecules needed to reduce the initial activity to zero.

The initial and constant conversion of cumene is taken after the first and fifth pulse as specified in Part 1 (16). The activity for the toluene disproportionation was calculated from the conversion of toluene. The major products of the reaction were benzene and a mixture of the xylenes. The same equipment was used as for the

cracking of cumene. Constant conversion was reached usually after the seventh pulse.

RESULTS AND DISCUSSION

Physicochemical Properties of the Samples

A synoptic list of the samples is given in Table 2, in which the catalysts are numbered. In order to allow comparison with other stabilized samples described in the literature, some physicochemical properties are also given in Table 2. The deep-bed calcined and ultrastable samples have a smaller lattice parameter and a lower sorption capacity than the hydrogen Y sample (HY400). The YDB (No. 3) sample has about the same sorption capacity as the deep-bed samples examined by Kerr (5) and Ward (6). The YDB8a (No. 8) sample has the same overall physicochemical properties as the ultrastable sample prepared by McDaniel and Maher (1). Although the parent sample used in our work was only exchanged for 70%, while in other work (5, 6) it was exchanged for about 90%, the overall physicochemical

properties of the deep-bed products showed no pronounced differences.

The infrared spectra of the hydroxyl region for these samples have been analyzed in detail and published elsewhere (8). In Fig. 1 is given the number of acidic protons titrated with pyridine (a) and ammonia (b) contained by the different catalysts. The OH groups titrated with pyridine at 150°C are acidic (3650 cm^{-1}) and the major part is located in the supercages (18). The OH groups titrated with ammonia include the acidic groups in the supercage and sodalite cages (bands at 3650 and 3550 cm^{-1}) (18). The dehydroxylation of these two OH groups is more pronounced for a thermal treatment in hydrolyzing conditions (catalyst No. 3) than for a treatment in vacuo (catalyst No. 2). The residual Na$^+$ ions present in the YDB (No. 3) sample are exchangeable by NH$_4^+$ ions. After decomposition, these NH$_4^+$ ions give protons that are attached preferentially to the lattice oxygens of the sodalite cages (No. 4). This is in agreement with the data of Ward and Hansford (19), who showed that decomposition of the last NH$_4^+$ ions exchanged in the Y samples give

protons that contribute preferentially to the 3550 cm^{-1} OH band (18, 20). Extraction of the extralattice aluminum formed during the deep-bed treatment has no influence on the number of acidic OH groups (No. 5). When the same amount of lattice aluminum is extracted with an organic acid (No. 6), only the supercage hydroxyls show a slightly lower concentration. The way the lattice aluminum is removed has therefore no influence on the protonic acidity (Nos. 5, 6). Exchange of the residual Na$^+$ for La^{3+} in the YDB sample does not form new OH groups (No. 7). The OH concentration of the samples treated at 800°C is reduced to $\frac{1}{5}$ of the hydroxyls of the HY sample, whether the extralattice aluminum is still in cationic positions (No. 8) or not (No. 9). The acidic OH concentration of the samples LaY (No. 12) and MgY (No. 10) is also lower after deep-
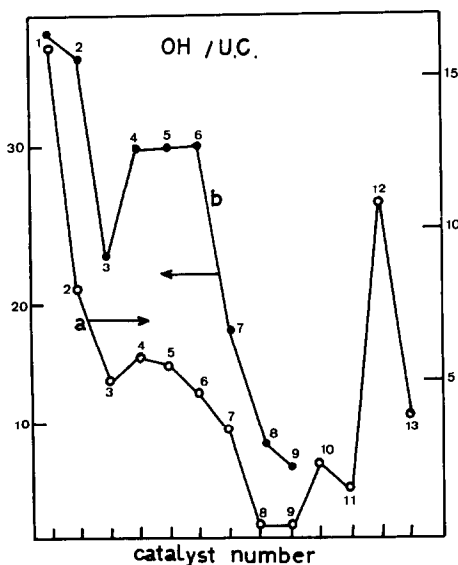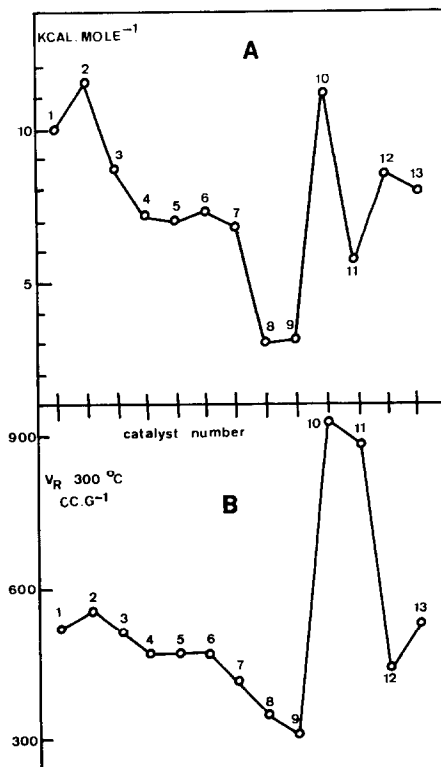

FIG. 1. Hydroxyl concentration per unit cell of the different catalysts. Curve a: hydroxyl groups titrated with pyridine (150°C). Curve b: hydroxyl groups titrated with ammonia (25°C).

FIG. 2. Initial heat of adsorption of benzene (300°–400°C) on the catalysts (part A) and retention volume (V_R) of benzene on the different catalysts (part B).

bed calcination (Nos. 11, 13). All the samples contain OH bands around 3700 and 3600 cm⁻¹ (8). These hydroxyl groups are not reactive toward bases in the conditions used here and are therefore not included in the concentrations reported in Fig. 1. Indeed, on the samples YDB (No. 3) and YDBNH$_4$ (Nos. 4, 5) only about 50% of the area under the OH absorption curve disappears when NH$_3$ is adsorbed.

The retention volume and heat of adsorption of benzene on the different samples is shown in Fig. 2. It was reported previously (16) that Lewis sites are the strongest adsorption sites for benzene molecules. This is indeed reflected in Fig. 2 for samples 1, 2, and 3. The effect of the hydroxyls on the sorption of benzene can be seen by comparing the change in sorption properties for the samples No. 4 to No. 9. These properties change in a way closely related to the acidic supercage OH groups (Fig. 1a), and to the total OH concentration titrated with NH$_3$ (Fig. 1b). This can only be explained if under the conditions of adsorption, an increasing part of the acidic hydroxyls located on O_2, O_3, or O_4 (20) are mobile and become accessible in the supercages, depending on the pressure of the reactant. Proof for the mobility of protons in zeolites has already been given (23). Cant and Hall (21) mentioned the proton mobility after adsorption of propylene on HY. The rather high values of V_R on MgY (No. 10) and MgDB (No. 11) can be explained by the presence of polyvalent cations in the supercages. The YDBLa (No. 7) sample fits into the series of deep-bed samples, indicating that no La^{3+} ions are in the supercages but the heat of adsorption is higher for the samples LaY (No. 12) and LaDB (No. 13) which can be due to the presence La^{3+} ions in the supercage.

Cumene Cracking Activity of the Samples

The initial and constant activity for the dealkylation of cumene are shown in Figs. 3A and 3C. Since the catalysts show pronounced differences in cracking activity, the cumene conversion at 250°C (Fig. 3A)

and the temperature for 50% dealkylation (Fig. 3C) are used to characterize the catalytic activity.

The difference in initial activity for samples No. 1 to 3 is explained in Part 1. The presence of a minor amount of NH$_4$$^+$ ions and a possible inductive effect exerted by the Lewis sites are invoked. The samples YDBNH$_4$(a) (No. 4), YDBNH$_4$(b) (No. 5), and YAlD (No. 6) show a higher activity than the YDB and even the HY sample. They have a very low Na$^+$ content. The hydroxyls derived from the NH$_4$$^+$ ions introduced during the extra exchange step confer on the sample a higher catalytic activity, although they appear in the infrared spectra at 3550 cm⁻¹ which indicates that they are located at less accessible sites. Samples YDBNH$_4$(b) (No. 5) and YAlD (No. 6) have the same catalytic activity. They also have the same chemical composition and the same hydroxyl population and sorptive capacity, although they were prepared in a different way. Sample YDBNH$_4$(a) (No. 4) contains 31% of extralattice aluminum at cationic positions, while the samples YDBNH$_4$(b) (No. 5) and YAlD (No. 6) do not. The former of these samples has higher activity and also higher stability of the lattice and of the lattice hydroxyls. This is possibly due to a stabilizing effect of polynuclear cations of the Al-O-Al type in the cubo-octahedra (8).

From CO$_2$ adsorption experiments (26) we were able to conclude that the samples LaY and LaDB contained some La^{3+} ions in the large cavities, while in the sample YDBLa all the La^{3+} ions were located on sites inaccessible from the large cavity. Nevertheless, the introduction of the La ions in sample YDB (No. 3) resulted in an increase of the catalytic activity. However, when the catalytic results of sample YDBLa (No. 7) are compared to those of sample LaY (No. 12) and LaDB (No. 13), we must conclude that the presence of La^{3+} ions in the supercage has still a more pronounced effect on the catalytic activity. This can be explained by assuming an inductive effect of the La^{3+} ions on the OH groups, in the same way as proposed for
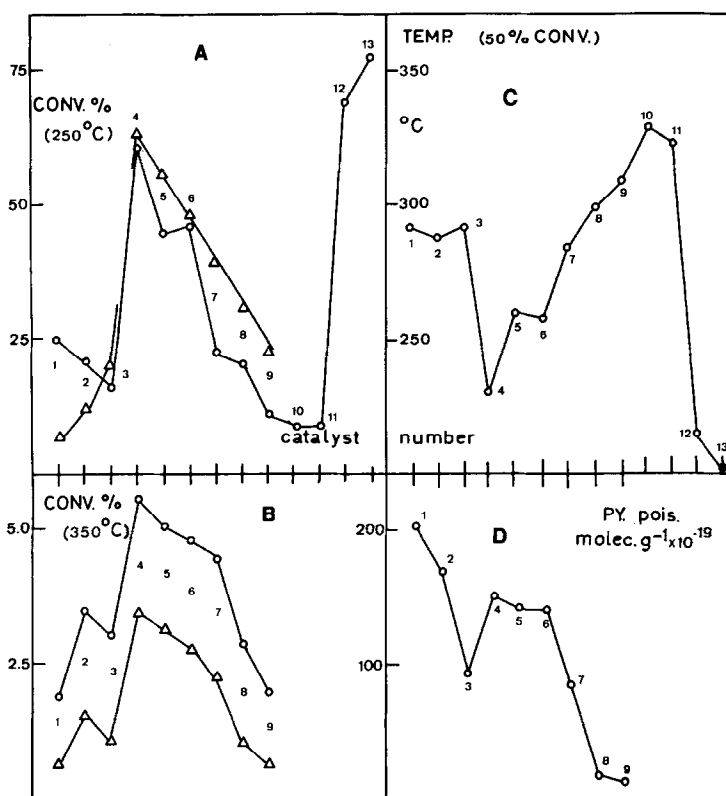
FIG. 3. Catalytic activity of the different catalysts. Part A: percentage of cumene dealkylation at 250°C. Part B: percentage of toluene disproportionation at 350°C. (○): initial activity. (△): steady state activity. Part C: temperature (°C) for 50% conversion of cumene (initial values) on the catalysts. Part D: number of pyridine molecules used to reduce the initial activity for cumene dealkylation to zero.

the action of the Lewis sites in dehydroxylated samples (16, 22). Furthermore the La^{3+} ions in YDBLa did not generate hydroxyls by dissociation of water like those in LaY samples (18).

The ultrastable samples (Nos. 8 and 9) have a relatively low cracking activity. Comparing the activity before (No. 8) and after (No. 9) extraction of aluminum, we conclude that the extralattice aluminum has a favorable effect on the cracking activity as stated already for the samples No. 4 and No. 5.

Pyridine poisoning (Fig. 3D) was carried out as described in Part I (16). Unambiguous conclusions cannot be drawn. For the samples No. 4 to No. 9 the number of pyridine molecules needed to suppress completely the cracking activity correlated very well with the total amount of acidic

hydroxyls. For samples No. 1–3 it correlated with the sum of Lewis sites and Brønsted sites. In the conditions used the pyridine titrates both the Lewis and the Brønsted sites, and therefore the figures obtained in the poisoning experiments must be considered only as an upper limit. The heats of adsorption of benzene on the samples Nos. 3–7 show only minor differences. In those samples the concentration of the Lewis sites is practically identical but the samples have considerable differences in cracking activities. That this difference is not reflected in the adsorption properties for benzene can only be understood by assuming that the amount of superactive hydroxyls is so small that they have no influence on the overall heat of adsorption.

The constant activity for the samples

No. 3 to No. 9 is higher than the initial activity. During the cracking of the first pulses propylene molecules polymerize on the catalyst, and a branched polyene type structure is formed. More details on this are given in Part 1 (16).

Toluene Disproportionation

The activity for disproportionation of toluene was maximum on H-zeolites after deammoniation at 600°C (24). This maximum activity was obtained after heating beyond the temperature at which ammonia evolution was last observed. Moreover, the hydrogen-free form was inactive. Therefore, the Brønsted acids were considered as the seat of activity (24). The disproportionation activity of our samples decreases rapidly with time. If initial and constant activity are compared (Fig. 3B), the relative changes from sample to sample remain unaltered. Compared to the cumene cracking activity, the activity sequence is not the same when the different samples are compared in the same order. This indicates that the same hydroxyls are not active for the two cracking reactions.

The enhanced activity of sample HY550 (No. 2) compared to sample HY400 (No. 1) is consistent with the removal of the last ammonia molecules and the liberation of protons that form ultra-active Brønsted sites. This indicates that in the toluene disproportionation reaction, hydroxyls of higher acidity are involved compared to cumene cracking activity. This is also substantiated by the fact that in the same conditions cumene is degraded to a much higher extent than toluene.

The difference in activity between YDB (No. 3) and HY550 (No. 2) can be due to the difference in concentration of active hydroxyls, but more probably to the difference in Lewis acid concentration on both samples (16). Again, an inductive effect exerted by the Lewis on the Brønsted sites can be invoked to explain the difference (22). For the other samples there are no pronounced differences between the samples in the relative activity changes for the two cracking reactions.

Nature of the Active Sites

The combination of the cracking data with the physicochemical properties shows that only a fraction of the surface hydroxyls can play an active part in the cracking reactions. The two reactions seem to require hydroxyl groups with different strength. On the samples pretreated above 550°C no new OH groups are generated since no residual NH_4^+ ions were left. If no other factors had an influence on the nature of the active groups, the initial activity per hydroxyl group would remain constant for the samples Nos. 2 to 9. Table 3 shows these data for the cumene cracking reaction. Since the values change from one sample to another, supplementary factors are involved which change the strength of the active OH groups. These are the concentration of Lewis sites (samples 2, 3) and the concentration of residual Na^+ ions (samples 3, 4). Turkevich et al. (24) also found in Na–H–Y zeolites that the activity per site increased with the number of sites and thus with the degree of ion exchange. Other factors that can change the nature of the active hydroxyl groups are the presence of extralattice aluminum (samples 4, 5 and 8, 9, respectively), and the extent of dealumination (samples 4, 8 and 5, 9, respectively). Topchieva et al. (15) reported

TABLE 3

INITIAL ACTIVITY FOR CUMENE CRACKING PER HYDROXYL GROUP[a]

Catalyst number	(a)[b]	(b)[b]
1	0.41	0.40
2	0.80	0.71
3	0.91	1.15
4	2.25	2.07
5	1.75	1.50
6	1.91	1.63
7	1.75	1.44
8	5.45	3.34
9	3.64	2.00
12	2.80	2.80

[a] % conversion per hydroxyl group.

[b] (a) OH concentration determined by NH_3 titration at room temperature and (b) by pyridine poisoning at 400°C.

that the cracking activity for cumene increased with increasing Si/Al ratio. Only when more than 35% of the lattice aluminum was extracted did the activity start to decrease. For the iso-octane cracking activity, Barthomeuf and Beaumont (12) reported a decrease around the same degree of dealumination. Also the presence of La^{3+} ions in the small cages (sample 7), must have an increasing effect on the acidity of the hydroxyls as explained earlier. This effect seems to be much more pronounced when La^{3+} ions are present in the supercages (sample 12).

CONCLUSIONS

The results of Part 1 and Part 2 allow us to draw some generalized conclusions.

1. It is highly probable that in cracking reactions initially only a fraction of the hydroxyls act as active sites. The disproportionation of toluene seems to require protons of higher acidity compared to the cracking of cumene.

2. Since in the temperature range required for cracking the protons show a considerable mobility, it is not possible to correlate the cracking activity with definite hydroxyl groups as observed in the infrared spectrum.

3. Our results show that several structural changes can have a drastic influence on the cracking activity.

ACKNOWLEDGMENTS

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