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Active Sites in Zeolites

I. Cumene Cracking Activity of NH_4Y Zeolites After Different Reactor Pretreatments

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The dealkylation of cumene was investigated in a pulse microreactor. The catalysts were zeolites Y in the hydrogen form and partially hydrolyzed HY pretreated at temperatures between 500° and 800°C. The hydroxyl content of the samples was derived from infrared spectra taken from samples pretreated in identical conditions. Brønsted and Lewis sites were determined by adsorption of ammonia and pyridine, and poisoning experiments with pyridine were also carried out.

A good correlation was found between the number of hydroxyls and the amount of pyridine needed for complete poisoning. Nevertheless, the initial activity after different pretreatments decreased much more slowly than the concentration of acidic hydroxyls. It was concluded that only a fraction of the hydroxyls are involved in the reaction.

The activity varied with the pulse number. This was ascribed to the formation of a polymer by the propylene formed in the reaction. This polymer is catalytically active per se. On the HY samples the presence of the polymer resulted in a decrease of the initial activity. On the hydrolyzed sample the polymeric species had a favorable effect on the catalytic activity.

INTRODUCTION

One of the standard tests for the characterization of cracking catalysts is the dealkylation reaction of cumene. Previous papers concerning this reaction on zeolites have recently been reviewed (*1*, *2*). The reaction is of the Friedel-Crafts type and is generally rationalized in terms of proton attack at an aromatic carbon atom with displacement of the sidechain as a carbonium ion (*3*) and was investigated several times on deammoniated X and Y zeolites (*4*-*9*). Turkevich *et al.* (*4*, *5*) found that the amount of base needed for a complete poisoning of the dealkylation activity corresponded to the number of hydroxyl groups. On the other hand, Boreskova *et al.* (*8*) found that for a complete poisoning an amount of quinoline was needed which was several times higher than the hydroxyl group concentration. Ward (*7*) reported that the hydroxyl groups are involved in the cumene cracking. At 250°C only the hydroxyl groups of the infrared band at 3640 cm^{-1} were involved. The 3550 cm^{-1} hydroxyls were only affected at reaction temperatures higher than 365°C. The changes in the hydroxyl group concentration could also be attributed to the formation of surface species (*7*).

For several cracking reactions over NH_4Y catalysts, the catalytic activity decreases with increasing pretreatment temperatures, while the Lewis acid concentration increases (*9*-*12*). This suggests that the Lewis site is not the primary active site. However, the maximum cracking activity of NH_4Y does not occur at the maximum

Brønsted acidity but after some dehydroxylation has occurred (*11, 12*). It is therefore possible that only a fraction of the acid groups is important (*10*) or that the acid strength of the hydroxyls is influenced by neighboring dehydroxylated sites (*13*).

For the investigation of possible relationships between catalytic activity of NH_4Y zeolites and surface acidity, several points should be taken into account. The relation between catalytic activity and surface acidity requires the combination of reactor data and the results of chemical or physicochemical methods (*10–13*). It is known that NH_4Y samples are very sensitive to hydrolyzing effects during the pretreatment, and that the geometry of the zeolite bed during calcination significantly affects the nature of the final product (*14*). Moreover, this treatment enhances considerably the concentration and the nature of the hydroxyls (*15–17*). In order to establish valuable correlations, it is necessary that the samples used in the different techniques are completely identical. This was not always ensured in earlier work.

Aging of the catalyst results in a change in nature or number of catalytic sites, or in the accessibility of sites for the reactant molecules (*18*). Therefore, it is necessary to define catalytic activity in terms of initial and steady state activity, in order to make the comparison with the active sites on a clean surface meaningful.

In this work, the influence of different pretreatments including hydrolyzing effects on the initial and constant conversion of cumene were investigated at different temperatures.

EXPERIMENTAL

Materials

The NaY zeolite obtained from Linde had the unit cell composition $Na_{55}(AlO_2)_{55}(SiO_2)_{137}$. Impurity cations were removed after repeated exchanges with 0.1 *N* NaCl solution. By ion exchange with a 0.1 *N* NH_4Cl solution followed by the necessary washings a sample was obtained with the composition $Na_{16.5}(NH_4)_{38.5}(AlO_2)_{55}(SiO_2)_{137}$. Compressed platelets as used for infrared experiments (*15*) were cracked and passed through a laboratory sieve. The 30–60 mesh fraction was retained for catalytic and for adsorption experiments. The samples were stored under a 70% relative humidity atmosphere and had a moisture content of 29.5% by weight. The NH_4–Na–Y sample was deammoniated in the reactor at temperatures between 400° and 800°C.

Hydrogen Y(HY) or dehydroxylated HY samples were prepared under a flow (120 ml min^{-1}) of dry helium gas in a quartz tube reactor. The samples were first heated by raising the temperature to 120°C over a period of 2 hr, and held at 120°C for another 2-hr period. The temperature was then raised slowly, at a rate of 1°C min^{-1}. to 400°C and held there for 2 hr. Subsequently, the temperature was raised at the same rate to different temperatures between 500° and 800°C. The notation HY600 indicates that the outgassing procedure was as described, the final evacuation being at 600°C.

Hydrolyzed samples (HYh) were obtained by plunging the reactor containing the NH_4–Na–Y sample under an atmosphere of helium into an oven preheated between 500° and 800°C. After 3 hr, the volatile products were evacuated under a flow of He, and after two more hours, the samples were cooled to reaction temperature.

Pyridine, cumene, benzene, and toluene of "Uvasol" quality were from Fluka. Cumene and pyridine were distilled in vacuo before use. Ammonia gas from J. T. Baker (99.5% purity) was dried before use.

Methods

The catalytic activity was studied in a pulse microreactor. The apparatus consisted of an injection system in series with a reactor, a product trap, an analytical column, and a Gow-Mac catharometer. Each element could be bypassed. The reactor was a U-shaped quartz tube which could be maintained at constant temperature within 1°C. The flow rate was 120 cc min^{-1}. The analytical column consisted of a 6 m ¼ inch Inox tube packed with 10% Apiezon L and

10% Bentone on Chromosorb W and was maintained at 150°C. The size of the zeolite sample was 0.100 gm, packed between quartz wool plugs.

Pulses of 15 μl cumene were injected into the system by a microsyringe. The products were collected in the product trap. When the reaction was over, the products were flash-evaporated using a hot oven and analyzed. Successive pulses were injected until constant conversion was reached. The reaction temperature varied between 200° and 400°C.

Retention volumes were determined in the 200°–300°C temperature region. In order to determine the net retention volume a small amount of dry air was added to the 5 μl pulse of the hydrocarbons. The corrected specific retention volume V_R (ml gm^{-1}) was calculated by means of the equation:

$$V_R = (t - t_o)\frac{T}{298}\cdot\frac{3}{2}\cdot\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}\cdot\frac{F}{W}.$$

t and t_o are the retention times of the hydrocarbon and the inert gases, respectively; T is the column temperature (°K), P_i and P_o are the reactor inlet and outlet pressure, respectively; F is the carrier gas flow rate and W the weight of the packed zeolite. It is found that V_R is independent of the partial pressure of the adsorbate and the particle size of the zeolite. This enables us to calculate the initial heat of adsorption from a plot of log V_R/RT against $1/T$ (*19*).

Poisoning experiments with pyridine were carried out, so as to reduce the initial activity to zero. Adsorption of N_2 was carried out in a conventional system with a McLeod gauge for measuring low pressures. The system was connected to the reactor. The amount of extractable aluminum was determined by extraction with NaOH following the method of Kerr (*14*). Infrared films were made from reactor pretreated samples. To avoid readsorption of water during the time needed for the preparation of a film and the transport of the film to the infrared cell, carbon dioxide at atmospheric pressure was adsorbed on the pretreated sample. Examination in the spectrometer showed that no water was readsorbed. The preparation of films and the spectroscopic conditions used for quantitative work have been described in detail elsewhere (*15*). Gas phase spectra were excluded by the use of a reference cell of identical path length.

The Brønsted acid concentration was estimated (±4%) from the δNH_4^+ vibration at 1430 cm^{-1} after room temperature adsorption of NH_3 followed by degassing at ambient temperature. Pyridine was adsorbed at 150°C followed by evacuation at the same temperature. The Lewis acid site concentration was determined from the intensity of the 1450 cm^{-1} band of adsorbed pyridine molecules. The integrated absorption coefficient of the bands was determined from comparison of the infrared spectra with adsorption experiments in a Mettler thermobalance.

RESULTS

Physicochemical Properties of the Samples

The samples HY and HYh pretreated between 400° and 750°C show good X-ray crystallinity. The sorption capacity for N_2 (Table 1) shows that no pronounced deterioration of the porosity occurred. For the HYh samples, the amount of aluminum extractable with NaOH increases with the pretreatment temperature (Table 1). From the HY samples no aluminum could be extracted.

The retention volume of benzene at 300°C is shown in Fig. 1. For the HY samples, V_R increases when dehydroxylated sites develop. The adsorptive properties show a

TABLE 1

N_2-SORPTION CAPACITY (ml gm^{-1}) AT −196°C AND $P/P_0 = 0.2$

Sample	Pretreatment temperature (°C)		
	500	600	700
HY	243	230	225
HYh	225	215	200
	% extractable Al		
HYh	10	38	45

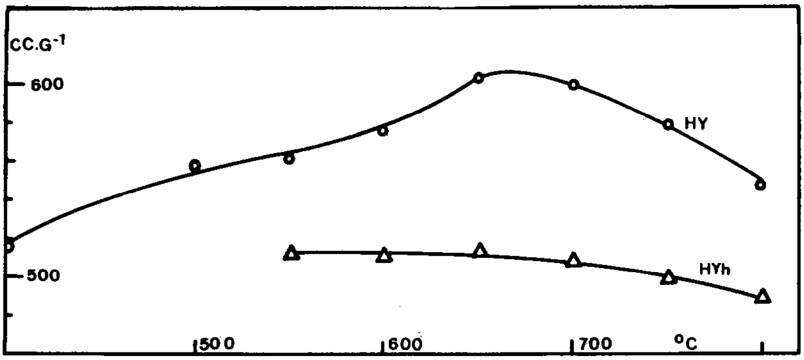


FIG. 1. Retention volume of benzene on the samples as a function of pretreatment temperature.

maximum for pretreatment between 650° and 750°C. The HYh samples show a gradual decrease in retention volume. The retention volumes for toluene are higher but show identical changes with the pretreatment procedure. The initial heat of adsorption, measured between 300° and 400°C, for benzene and toluene is shown in Fig. 2. For HY samples, the heat of adsorption increases with the pretreatment temperature. For HYh samples, there is a slight increase, followed by a gradual decrease after pretreatment temperatures higher than 500°C.

In Fig. 3, the concentration of Brønsted and Lewis acids is shown for the HY samples after pretreatment at different temperatures. Above 500°C, the number of Brønsted sites (curve a) decreases gradually and the number of Lewis sites simultaneously increases (curve b). The decrease of Brønsted acidity is about twice the increase of the Lewis acidity. The sum of both kinds of site at each temperature is shown

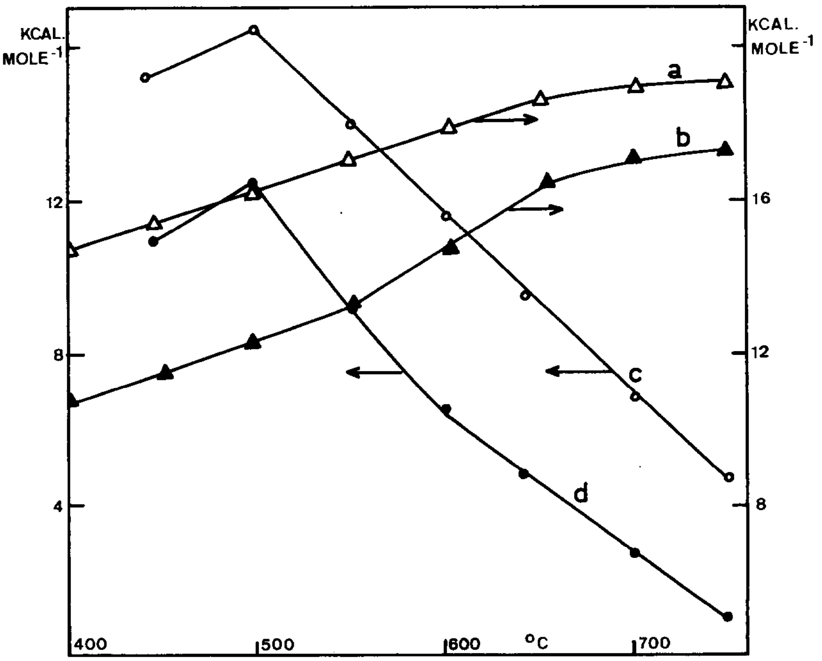


FIG. 2. Initial heat of adsorption on the samples in the range from 300° to 400°C. a, toluene on HY; b, benzene on HY; c, toluene on HYh; d, benzene on HYh.

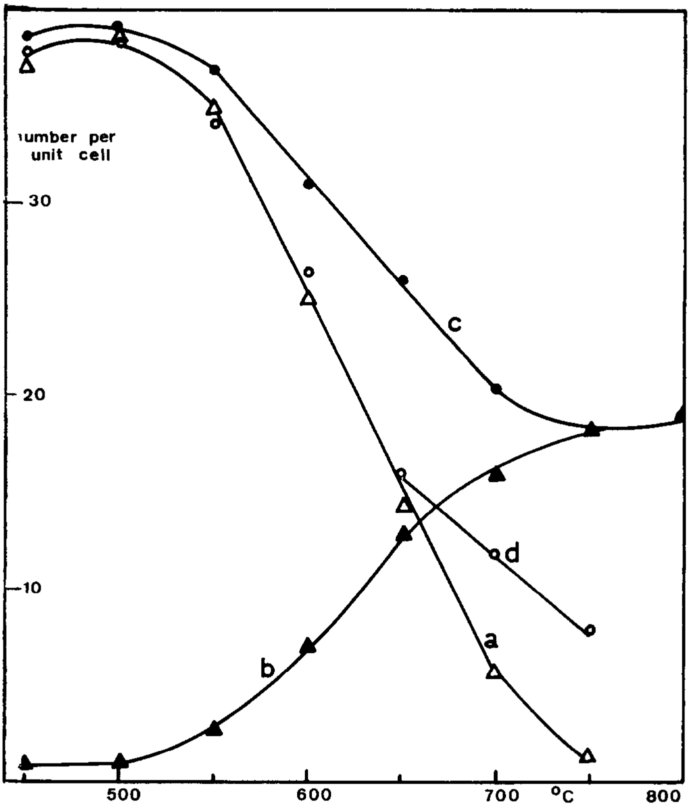


FIG. 3. Change in the amount of Brønsted sites (a), Lewis sites (b), sum of Lewis and Brønsted sites (c), and the amount of pyridine molecules (d) needed to reduce the initial activity to zero on HY samples at different pretreatment temperatures.

on curve c. In Fig. 4, the same data are shown for the HYh samples. For these samples the Brønsted and Lewis site concentration decreases gradually at higher outgassing temperatures, which is in contrast with the behavior of the HY samples.

Catalytic Tests

The main products of the dealkylation of cumene on the catalysts investigated were benzene and propylene. The mass balance of the products showed a deficiency in propylene. Since the measurements of the retention volumes showed that the adsorption of benzene was reversible, the conversion data are calculated from the concentration of benzene in the products. Depending on the pretreatment of the catalyst, the activity increases or decreases with the pulse number. After five pulses of cumene a constant conversion was obtained. It was checked that the activity remained constant up to pulse number 30. The initial and constant conversion mentioned in the text were those determined after the first and the fifth pulse, respectively.

The catalytic activity at 250°C is shown in Fig. 5 for the HY and HYh samples. For the HY samples, the initial activity decreased with the pretreatment temperature (curve a), while the constant conversion (curve b) increased and showed a shallow maximum for pretreatments between 600° and 700°C. Below 700°C the catalysts are less active compared to their initial activity. Above 700°C, the irreversible adsorption of propylene molecules has a favorable effect on the catalytic activity. For the HYh samples, the initial activity (curve c) decreases slowly at higher outgassing temperatures and is lower than for the HY samples, except for outgassing above 700°C. The con-

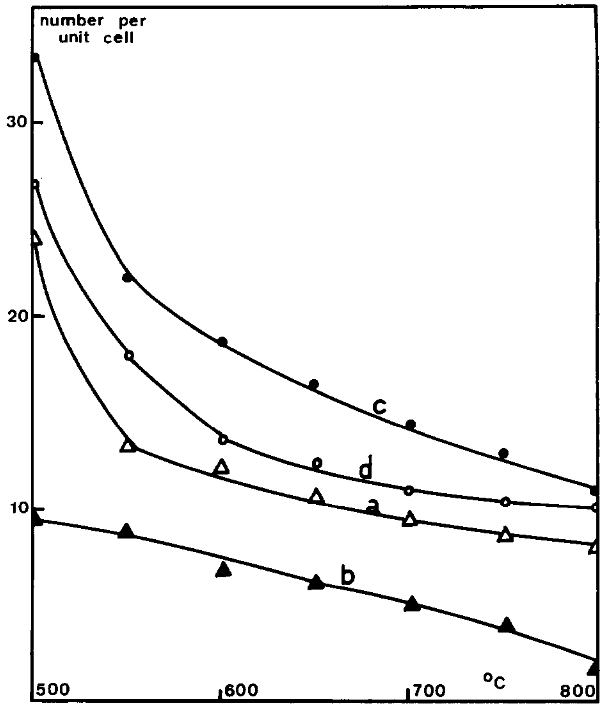


FIG. 4. Same notation as for Fig. 3, but for HYh samples.

stant activity (curve d) shows also a shallow maximum and is higher than the initial activity on the same samples.

The amount of pyridine needed to reduce the initial activity to zero at 400°C is given in Fig. 3 (d) for the HY samples. After outgassing below 650°C, the amount of pyridine used agrees with the number of

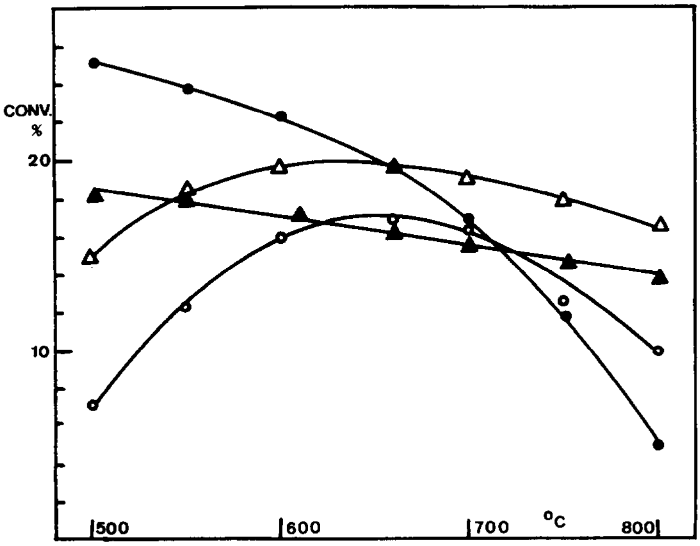


FIG. 5. Initial and constant activity for cumene dealkylation of the samples at 250°C. a, initial and b constant activity of HY. c, initial and d, constant activity of HYh.

TABLE 2
INITIAL ACTIVITY PER ACTIVE SITE
(% CONVERSION PER OH GROUP)

Pretreatment temperature	HY[a]		HYh[a]	
	(a)	(b)	(a)	(b)
500	0.65	0.66	0.67	0.75
550	0.71	0.68	0.98	1.45
600	0.85	0.88	1.21	1.63
700	1.42	2.80	1.44	1.75
750	1.50		1.45	1.74

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

Brønsted sites. Above 650°C, the amount of poison used is higher than the Brønsted site concentration. For the HYh samples, the corresponding data are shown in Fig. 4 (d). The amount of pyridine, at each temperature, is slightly higher than the number of Brønsted sites. In a separate experiment, the samples HY600 and HYh600 were poisoned with 1.5 10^{19} molecules of NH_3 gm^{-1} at 500°C. The initial activity decreased by as much as 50%.

The initial activity per active site for the different catalysts is shown in Table 2. The number of active sites used is determined by pyridine poisoning at 400°C (a) or by ammonia titration at room temperature (b). The specific activity increases at higher pretreatment temperatures. This is less pronounced for the HYh samples pretreated between 550° and 750°C.

Residue Formation

The amount of residue formed on the different catalysts at constant conversion is given in Table 3. The values obtained from the deficiency of propylene in the products agree with the data obtained by combustion of the residue. For the HY samples, the amount increases at higher pretreatment temperatures. The amount of residue on the HYh samples is much less dependent on the outgassing temperature and is of the same order of magnitude as on HY600.

In Fig. 6, infrared spectra of cumene adsorbed on HY400 are shown. After physisorption of 10 torr of cumene at room temperature, the 3650 cm^{-1} hydroxyl band disappeared, while a new broad band appeared around 3385 cm^{-1} (spectrum b). This is consistent with the formation of a hydrogen bond between the supercage hydroxyls and cumene. Specific bands for the benzene ring are at 1603 and 1495 cm^{-1} (*21*). The isopropyl group shows characteristic bands at 1386 and 1367 cm^{-1}, due to δCH_3 symmetrical (*22*). After adsorption and subsequent desorption of cumene at 300°C (spectrum c) a residual chemisorbed species is left on the catalyst. The benzene bands (1603 and 1495 cm^{-1}) have disappeared. A new band appeared at 1585 cm^{-1}. Besides the ν_{CH_3} asymmetric (2970 cm^{-1}), a new band of equal intensity appeared at 2920 cm^{-1} in the region of ν_{CH_2} asymmetric (*23*). Readsorption of cumene at room temperature on the sample of spectrum c, showed that the sorption capacity for cumene decreased (compare spectra b and d). For comparison, spectrum e shows the HY400 sample taken from the reactor at 300°C after constant conversion was reached. The spectrum is similar to curve c: a band is present around 1585 cm^{-1} while a new band is observed at 1547 cm^{-1}.

Figure 7 shows the effect of propylene adsorbed on HY400. After room temperature adsorption, the 3650 cm^{-1} band disappeared and a broad band is found at 3230 cm^{-1} (spectrum a, b). This indicates that propylene molecules form a stronger hydrogen bond with the 3650 cm^{-1} hydroxyl groups, compared to cumene. Assignment of the important modes is in agreement with other work (*24*). After 2 hr at room temperature (spectrum c), the intensity of the $\nu_{C=C}$ vibration (1635 cm^{-1}) decreases, while the δCH_3 and δCH_2 (around 1460 cm^{-1}) modes increase in intensity. This spectral behavior is consistent with the formation of hexane (*24*). After adsorption of propylene at 10 torr and 300°C for 30 min (spectrum d) the $\nu_{C=C}$ vibration is absent, while bands are observed at 1585 and 1540 cm^{-1}. Spectrum d is identical to spectrum c in Fig. 6. After adsorption of propylene for 1 hr (spectrum e) bands are present at 1573 and 1355 cm^{-1}. The 2940 cm^{-1} band (ν_{CH_2} asymmetric) has the same

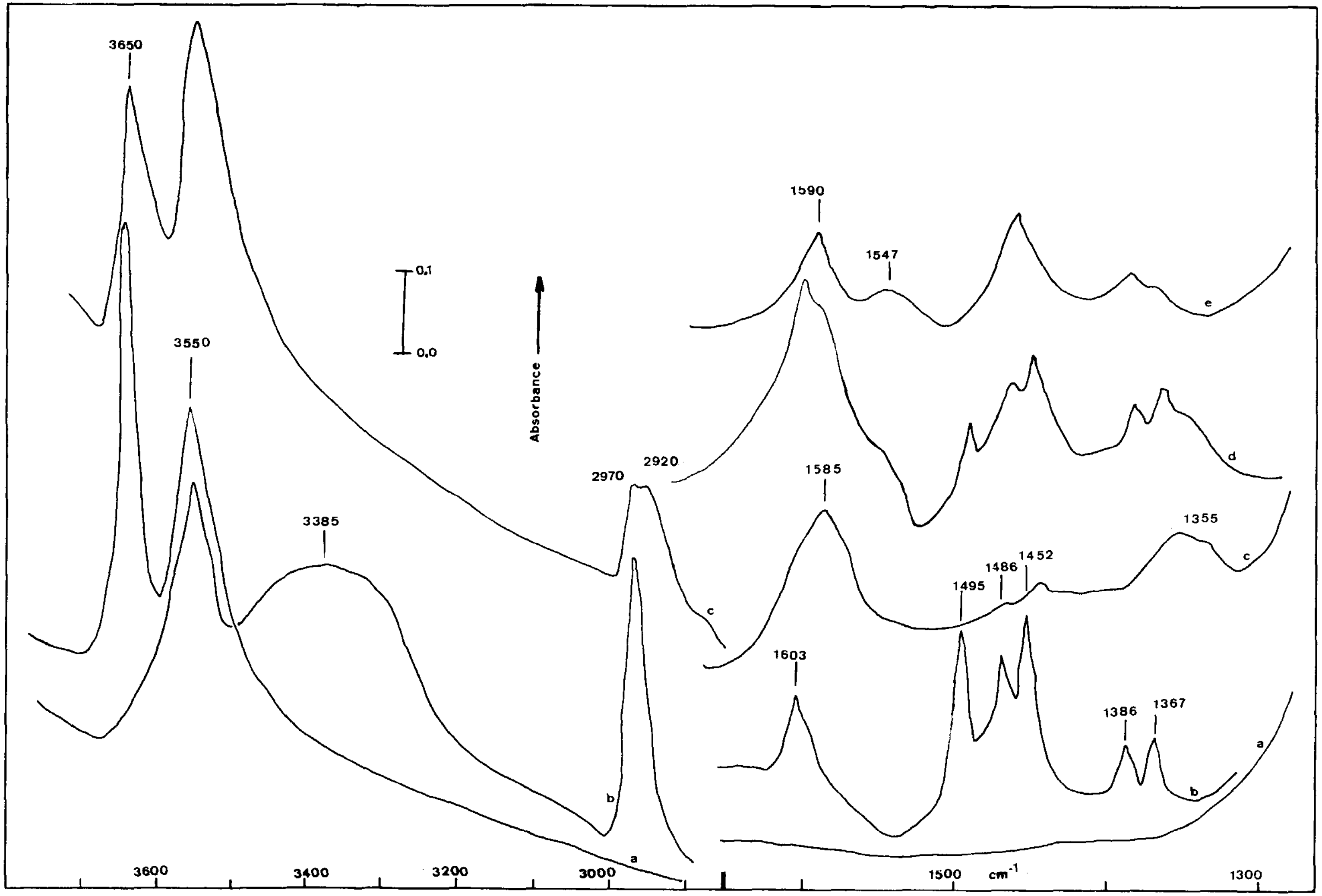


FIG. 6. Room temperature infrared spectra of cumene on HY400. a, background spectrum of HY400; b, adsorption of cumene at 10 torr and 11°C; c, adsorption of cumene at 10 torr and 300°C for 1 hr, followed by evacuation at 300°C for 2 hr; d, readsorption of cumene on c at 10 torr and room temperature; e, spectrum of the HY400 catalyst, after constant conversion was reached at 300°C.

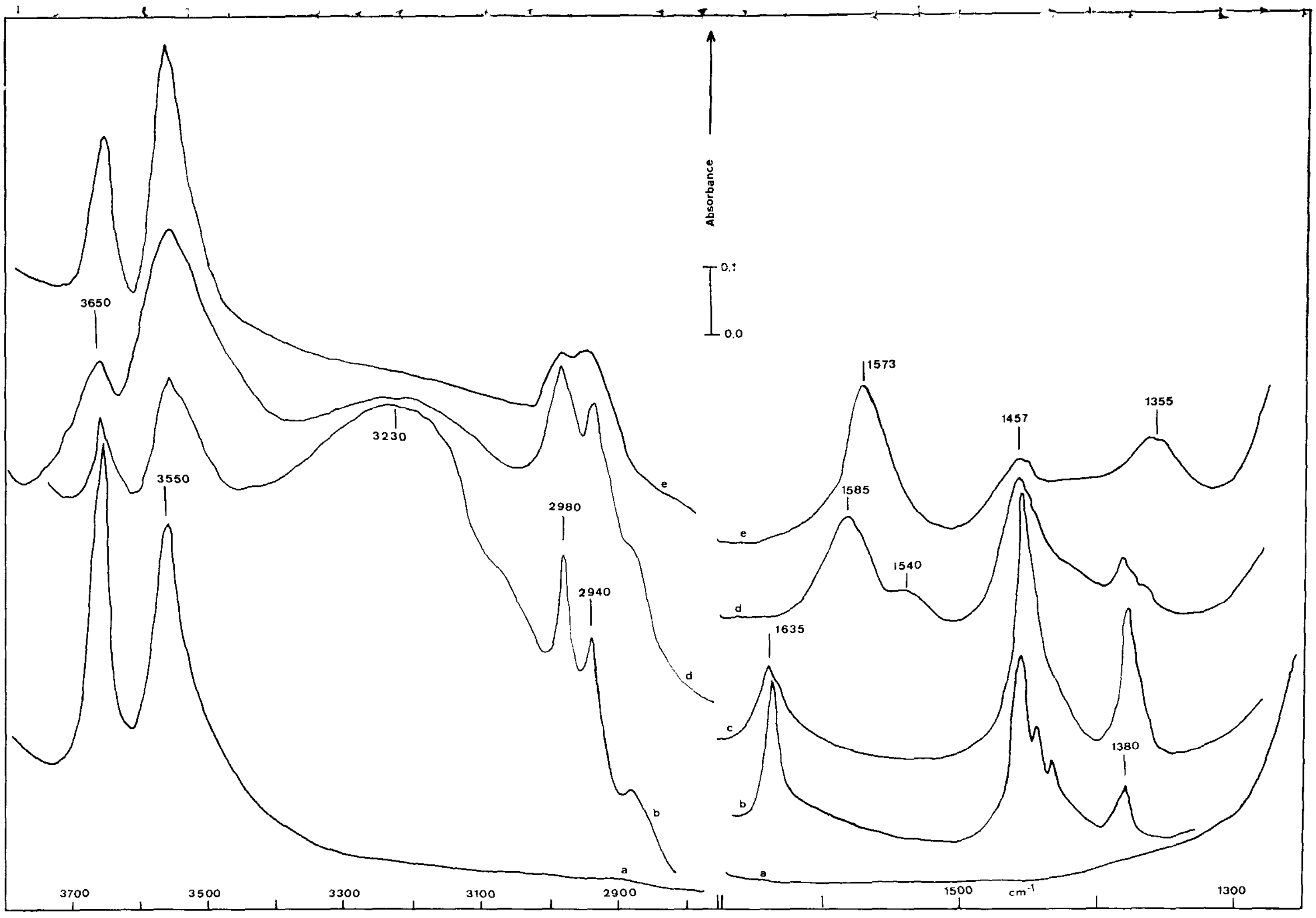


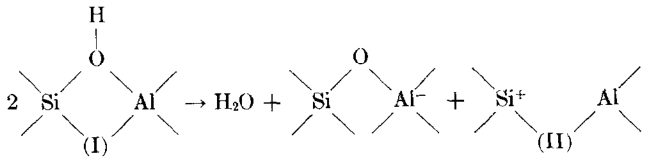
Fig. 7. Room temperature infrared spectra of propylene on HY400. a, background spectrum of HY400; b, room temperature adsorption of propyleneat 10 torr after admission of the gas; c, as b, but after 1 hr; d, adsorption of propylene at 10 torr and 300°C for 30 min followed by evacuation at 300° C; e, as d, but with the contact time of 1 hr.

intensity as the 2980 cm^{-1} band (ν_{CH_3} asymmetric). The latter spectrum is similar to spectrum c of Fig. 6. After adsorption of cumene or propylene at 300°C on HY or HYh pretreated at higher temperatures, comparable spectral changes are observed.

DISCUSSION

Nature of the Solids

The infrared results show that the HY samples contain Brønsted (I) and Lewis (II) sites. Their concentration at different temperatures fits quantitatively the scheme for dehydroxylation proposed by Uytterhoeven *et al.* (*25*).



The hydroxyl groups titrated with ammonia correspond to the OH groups involved in both the 3650 and 3550 cm^{-1} bands. In the temperature range for cumene cracking, the protons are mobile and jump from one lattice oxygen to another (*26*). The acidity of the protons is therefore determined by their jump frequency and as a consequence by the lifetime of a proton on a surface site (*27*). In view of this, it is difficult to compare the catalytic activity with the hydroxyl concentration in the supercages (3650 cm^{-1}) as titrated with pyridine at 150°C, since an increasing fraction of hydrogen atoms which are not directly accessible for the gas phase may become trapped in the supercages by adsorption of the reactant.

The adsorptive properties of HY samples for benzene in the temperature range of interest increase with the pretreatment temperature. The initial heat of adsorption of benzene and toluene shows the same behavior. This seems to indicate that the Lewis sites are stronger adsorption sites than the hydroxyl groups and the residual Na$^+$ ions, in agreement with the work of Matsumoto *et al.* (*19*).

In the HYh samples, the amount of extractable Al increases at higher pretreatment temperatures. At the same time, the Brønsted and Lewis site concentration decreases. This is in contrast to the HY samples, but is consistent with the observations on ultrastable faujasites (*28*). The contact of water at higher temperatures causes hydrolysis and extraction of lattice aluminium which appears at cationic positions. At the same time, higher outgassing temperatures produce a structural rearrangement of the faujasite. This was viewed as a recrystallization process involving silica migration from regions with structural breakdown into the vacancies created by dealumination (*17*, *28*, *29*). The decrease in sorption properties at higher temperatures indicates that the stronger adsorption sites (Lewis sites) are not formed in the HYh samples, and certainly not following the stoichiometry observed for the samples HY. However, both the presence of residual OH groups and Lewis sites at higher temperatures prove that the process of silica transport and recrystallization does not occur in our pretreatment conditions to the same extent as in the preparation of real ultrastable samples.

Active Sites for the Initial Activity

For HY samples, the initial activity for cumene dealkylation and the total hydroxyl concentration show the same overall changes with the pretreatment temperature. Identical changes of the cracking activity with the calcination temperature were reported earlier for conversion of the first pulses of cumene on the same samples (*9*). Also, Ward (*10*) reported a correlation between hydroxyl concentration and cumene cracking activity on HY zeolites. However, the Brønsted sites and the sum of Brønsted and

Lewis sites (Fig. 3a,c) at different temperatures change in the same way. The nature of the active sites can not therefore be established only on the basis of a similar behavior of catalytic activity and OH concentration. The amount of pyridine used to poison the initial activity at 400°C corresponds to the total number of acidic hydroxyl groups. Turkevich *et al.* (*4, 5*) reported similar results for quinoline poisoning. Therefore, a straightforward conclusion is that the Lewis sites are not the primary active sites and that the variation of the catalytic activity agrees rather well with the variation of the acidic hydroxyls.

For the HYh samples, the initial cumene conversion and the number of acidic OH groups decreases nearly linearly with the outgassing temperature. The amount of pyridine used as a poison agrees fairly well with the number of acidic hydroxyls. Therefore, the conclusion for the HY samples, namely that the acidic OH groups are the primary active sites and even that the acidic protons not available for direct interaction are potentially active sites, seems also to hold for the HYh samples. The fact that the enhanced thermal stability of the HYh samples (*14–16*) and of the lattice hydroxyls (*15*) is accompanied by a less pronounced decline in catalytic activity especially at higher temperatures, supports this hypothesis.

Pyridine molecules, however, do not react selectively with Brønsted sites at 400°C in the presence of dehydroxylated spots in the structure. Indeed, there are indications (*30*) that at 400°C pyridine molecules prefer Lewis sites. Therefore this amount should only be considered as a measure of the upper limit of active sites, although there is a rather good agreement between the number of acidic protons and the amount of poison used. On the one hand, since the interaction between strong bases and hydroxyl groups at 400°C is thermodynamically favored, pyridine molecules may react with OH groups without displaying any selectivity (*1*). On the other hand, pore mouth blocking may occur. In this way more than one proton per pyridine molecule may be shielded from interaction with the reactant. In view of these considerations, our poisoning results can also be explained if one assumes that pyridine molecules titrate both the Lewis and Brønsted sites, while only a fraction of the hydroxyls are active in the cumene cracking reaction. This applies to both series of samples.

This interpretation is strengthened by the information of Fig. 8. The initial activity and acidic proton concentration are compared in relative units. For the HY and HYh samples, the OH concentration decreases much faster than the initial catalytic activity. This can only be explained if a small fraction of the hydroxyl groups play an active role in the dealkylation reaction. The considerable activity of the HY750 sample, which shows practically no hydroxyl groups in the infrared spectrum, is also in favor of the hypothesis that only a low number of OH groups are operative. This interpretation also agrees with the ammonia poisoning experiment. Indeed, 1.9×10^{19} NH_3 molecules per gram (0.6% of the lattice aluminium) have a drastic effect on the catalytic activity. This is also consistent with the observations of Hildebrandt and Skala (*34*), who found that a HY500 sample retained 4.2×10^{19} molecules of ammonia per gram, which is comparable to our poisoning data on the HY550 sample. These residual NH_4^+ ions liberate "ultra-active" hydroxyl groups after outgassing at 550°C. This implies that the active OH groups on the different HY and HYh samples are heterogeneous in nature at different pretreatment temperatures, which is indeed reflected in the values of the initial activity per active site. These values increase at higher pretreatment temperatures, but the changes are less pronounced for the HYh samples. Also the concentration of Lewis sites does not change in the same way on the two series of samples. Therefore the hypothesis of Lunsford (*13*) can be invoked to explain the changes of the activity per active site. Lunsford assumed an inductive effect of the dehydroxylated sites on the hydroxyl groups through the zeolite lattice resulting in the formation of stronger acids.

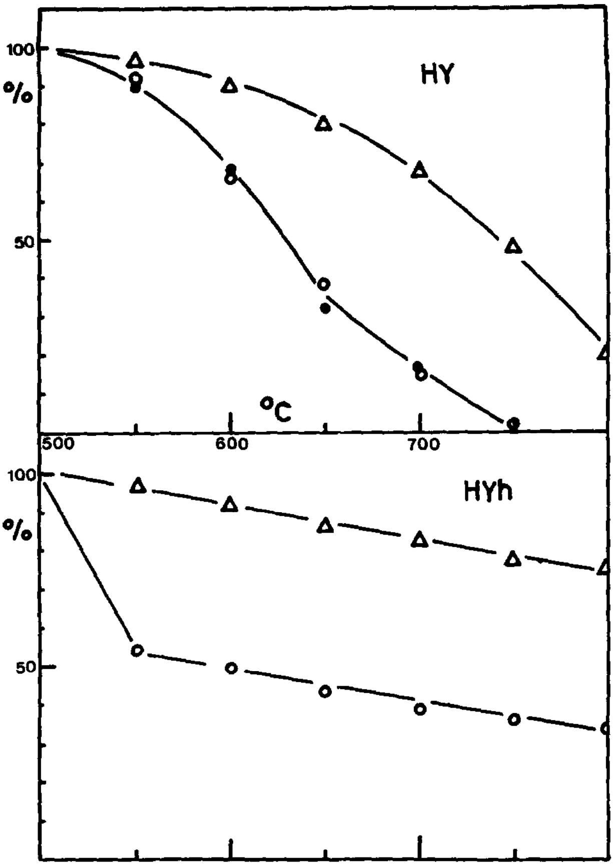


FIG. 8. Relation between the initial cumene conversion (△), acidic hydroxyls as titrated with NH_3 (○), and the hydroxyls of the 3650 cm^{-1} band (●).

Constant Activity and Active Sites

In HY samples, the formation of residue results in a decrease of the initial activity. The difference between initial and constant activity decreases after pretreatment at higher temperatures. After outgassing above 650°C the initial activity is lower than the constant activity. In the HYh samples, a favorable effect of the residue on the constant activity is observed even after outgassing at 550°C. It seems that on samples with a high initial activity and hydroxyl concentration the initial catalyst activity is poisoned. On samples with a high initial Lewis acid concentration and/or relatively low OH concentration residue formation increases the initial activity.

On silica–alumina, several authors (*34–37*) have shown evidence for the formation of a polymeric complex on a Lewis site. The residue is formed during the first minutes of the reaction and the catalytic activity of the solid decreases. On the HY samples our observations are similar. Ward (*7*) showed that after several hours on-stream, the OH groups disappear practically completely. Therefore it might be possible that at the steady conversion in a continuous flow reactor, these polymeric species are the catalytically active sites. However, since at constant conversion in our pulse reactor only part of the hydroxyls are consumed, both the polymeric species and some hydroxyl groups can act as active sites, at least for the HYh samples and the HY samples pretreated above 650°C. For the alkylation reaction of benzene, Venuto *et al.* (*31*, *32*) found that steady conversion is obtained after a rapid increase in activity followed by a slow ageing of the catalyst.

TABLE 3
Residue on the Samples as Propylene Molecules per Gram of Catalyst

Sample	Propylene/gm × 10^{-20}	
	From mass balance	From combustion to CO_2
HY400	4.5	3.2
HY600	8.0	7.5
HYh550	6.9	5.9
HYh650	7.3	7.0

The different behavior of our HY and HYh samples may therefore simply be due to a different activity–time curve for the two series of catalysts.

The infrared data can give more information on the nature of the polymeric complex. The presence of two bands at 1585 and 1540 cm^{-1} are indicative of a diene type structure (*22*). After longer contact times, these bands disappear and a new band at 1573 cm^{-1} appears, characteristic for the carbon skeleton vibration of an aromatic ring structure (*22*, *38*). At the same time the two bands around 1350 cm^{-1} indicative for isopropylic groups remain on the samples. The appearance of ν_{CH_2} at 2920 cm^{-1} is indicative for the polymerization process. These spectral changes suggest an acid catalyzed polymerization of propylene to an aliphatic polymer of low molecular weight. This can be transformed by intermolecular hydrogen-transfer, dehydrogenation, and skeletal isomerization reactions to a highly branched diene type polymer after rather short contact times. Thereafter, cyclization and cracking reactions can build up hydrogen-deficient aromatics. Venuto *et al.* (*32*) came to the same conclusion for alkylation reactions with low molecular weight olefins on faujasite catalysts. For alkylation temperatures below 120°C liquid aliphatic polymer remained on the catalyst. Above 180°C, exclusively aromatic polymers were retained. Similar hydrogen-transfer reactions were reported for the polymerization of propylene over silica–alumina (*39*).

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