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Active Sites in Zeolites

III. Selective Poisoning of Bronsted Sites on Synthetic Y Zeolites

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2,6-Dimethylpyridine and pyridine adsorption on CaY, HY and NaY zeolites is followed by quantitative infrared spectroscopy. 2,6-Dimethylpyridine reacts selectively with the hydroxyl groups. After adsorption of the base at temperatures from 25 up to 400°C the OH groups are titrated first and only thereafter the Lewis sites interact with the base. The selectivity of pyridine towards Brønsted and Lewis sites is much less pronounced. Infrared identification of the ion or of the Lewis bound base was made through the frequency shift of the ν_{8a} and ν_{8b} vibrations.

Poisoning with 2,6-dimethylpyridine of the cumene cracking activity of the HY samples amounts to an upper limit of active sites of 1.8×10^{20} per gram. This number is much lower than the amount titrated with pyridine.

INTRODUCTION

Poisoning experiments with basic molecules as pyridine, quinoline, ammonia and aliphatic amines have been widely used to determine the number of sites responsible for the carboniogenic activity on cracking catalysts.

The requirements of a good poison for acid-catalyzed reactions are that the basic molecules neutralize the seat of catalytic activity under reaction conditions in a quantitative and selective way.

On zeolites, Turkevich and Ono (*1*) have pointed out that for the cumene dealkylation reaction, the amount of quinoline needed to poison the activity agreed well with the number of hydroxyl groups. The same authors claim that at 325°C quinoline does not react with Lewis sites but only with Brønsted sites. Boreskova, Topchieva and Piguzova (*2*) described similar poisoning experiments and have found that the amount of quinoline exceeds several times the number of Al atoms and therefore the hydroxyl group concentration. On the other hand, Goldstein and Morgan (*3*) reported that quinoline does indeed poison the activity of molecular sieves Y for the acid-catalyzed cracking of cumene. However, the concentration of quinoline required to poison the activity of the zeolite is equal to the density of supercages. A single molecule of quinoline per supercage is able to block cumene from the active sites, whatever their concentration may be.

Pyridine adsorption at 150°C followed by infrared spectroscopy is generally used as a quantitative measurement of both the Lewis and Brønsted site concentration (*4, 5*). Jacobs, Leeman and Uytterhoeven (*6*) using pyridine as a poison for the cumene cracking activity on zeolites, found that the amount of poison agrees with the hydroxyl group concentration if no Lewis sites are present. If both types of sites are present simultaneously, pyridine does not titrate them in a selective way. Although on hydrogen Y zeolites the agreement between the amount of poison and hydroxyl groups was good, data from other techniques indicated that possibly only a small fraction of the hydroxyl groups act as active centers and pyridine does not react as a selective poison.

Recently Benesi (*7*) showed that chemisorption measurements of sterically hindered amines have potential utility as an index of catalytic activity on acidic solids. On alumina, the amount of chemisorbed pyridine exceeds that of 2,6-dimethylpyridine, while the opposite is true for silica–alumina. 2,6-Dimethylpyridine appears to show reasonable degree of specificity for proton acidity at 400°C. Knözinger and Stolz (*8*) on alumina showed by infrared spectroscopy that the surface bond to Lewis acid sites of 4-methylpyridine is stronger than that of pyridine because of its higher basicity. 2,4,6-Trimethylpyridine despite its higher basicity is more weakly bound than pyridine due to steric hindrance between reagent and adsorbent. In view of these results, the sterically hindered pyridines seem to react more specifically with protons, compared to the commonly used poisons.

In this work, the specificity of 2,6-dimethylpyridine for protons in the presence of Lewis sites and its possible use as a selective poison for acid-catalyzed reactions is investigated.

EXPERIMENTAL METHODS

Materials

Linde NaY zeolite was exchanged with 0.1 *N* NH_4Cl or $CaCl_2$ solutions. After the necessary washings the samples were dried at ambient temperature. The NH_4Y and CaY samples were exchanged to 70 and 90%, respectively.

Pyridine (Py) and 2,6-dimethylpyridine (2,6-DMPy) from Fluka were Uvasol grade. They were degassed under vacuum by the pump–freeze–thaw technique before being passed over a drying train of activated molecular sieve 4A. Cumene was from Fluka and was distilled under vacuum before use and stored over molecular sieve 4A.

Equipment

A pulse microcatalytic reactor equipped with catharometer detection was used (*6*). Chemisorption measurements were carried out by injection of 0.1 μl pulses of the base into the carrier gas stream until the peak area of the reactant desorbing from the catalyst remained constant.

Poisoning experiments were carried out by alternating 5 μl pulses of poison with 50 μl pulses of cumene.

The infrared spectra were scanned on a Beckman IR12 spectrometer in conditions suitable for quantitative measurements (*9*). Apparent integrated absorption intensities for several bands of the adsorbed species were calculated from the integrated form of Beer's law as described elsewhere (*10*). The method used for the separation of overlapping bands was similar to the one described by Hughes and White (*12*).

Procedure

In the pulse microreactor 300 mg of catalyst was used with particle size between 30 and 60 mesh. The samples were activated under a flow of dry helium, the sample temperature being raised very slowly (*6*).

Infrared platelets were degassed under vacuum and heated slowly to the temperature of the final activation. The sample temperature is known accurately by means of a thermocouple in close contact with the platelets. Room temperature refers to 25°C.

The samples derived from NH_4Y are denoted by HY followed by the temperature of activation. NaY and CaY samples are denoted in the same way.

RESULTS AND DISCUSSION

Assignment of Bands in the 2000–1200 cm^{-1} Region

Since pyridine (Py) and 2,6-dimethylpyridine (2,6-DMPy) belong to the same symmetry point group C_{2v}, the same normal vibrations may be expected to appear in the adsorbed state. In Fig. 1, Py and 2,6-DMPy are adsorbed on a NaY-400 sample. In Fig. 2, increasing amounts of 2,6-DMPy are adsorbed on zeolite HY-400 (spectrum a, b, c). Comparable amounts of pyridine are adsorbed on the same sample (spectrum d). The adsorbed species on NaY-400 are denoted as Lewis bound (Py:L or 2,6-DMPy:L). The adsorbate interacts only with the residual Na^+ ions, since the samples are far from saturation. On sample HY-400

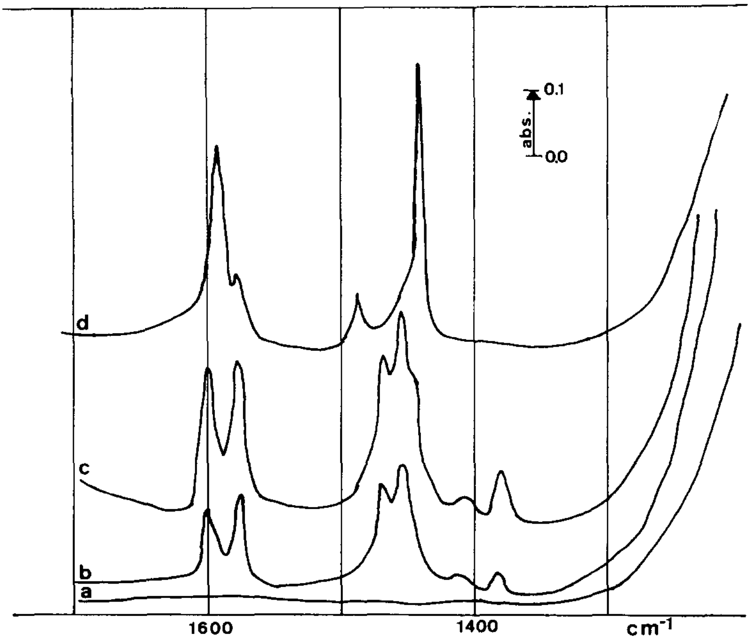

FIG. 1. Infrared spectra of 2,6-DMPy and Py adsorbed at room temperature on NaY-400 (film thickness, 3.5 mg cm^{-2}). Background (a); addition of 0.2 (b) and 0.5 μmole 2,6-DMPy (c); addition of 0.5 μmole Py (d).

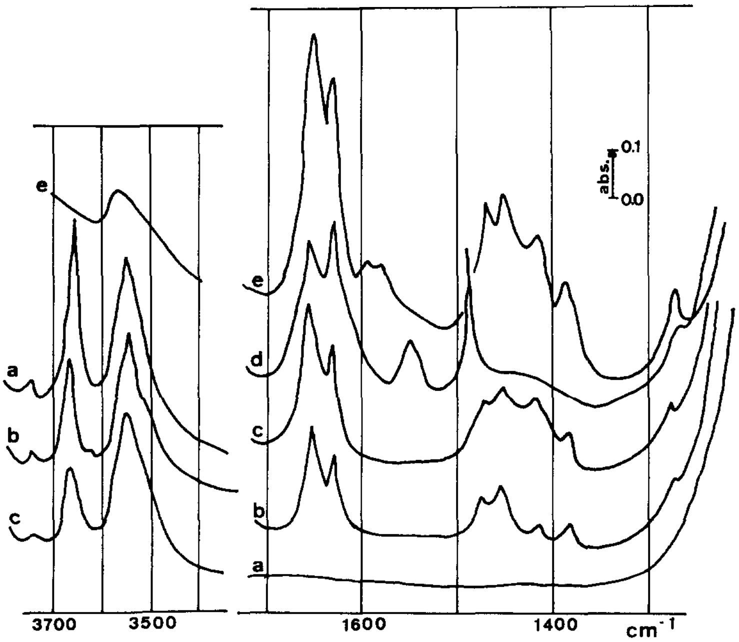

FIG. 2. Infrared spectra of 2,6-DMPy and Py adsorbed on HY-400 (film thickness, 3.5 mg cm^{-2}). Background (a); adsorption of 0.2 (b) and 0.5 μmole 2,6-DMPy (c) at room temperature; adsorption of 0.5 μmole Py(d) at room temperature; adsorption of 50 μmole 2,6-DMPy (e) at 400°C, followed by outgassing at 400°C.

TABLE 1

ASSIGNMENT OF VIBRATIONAL MODES OF 2,6-DMPy AND Py ADSORBED ON ZEOLITES[a]

Vibrational modes	Liquid 2,6-DMPy	2,4,6-TMPy on alumina [from Ref. (*8*)]	2,6-DMPyH$^+$	2,6-DMPy: L	Py liquid	PyH$^+$	Py:L
8*a*; $\nu_{cc(N)}$ (A_1)	1605 m	1634	1650 s	1603 s	1579 s	1655 s	1595 vs
8*b*; $\nu_{cc(N)}$ (B_1)	1580 s	1566	1630 s	1580 s	1572 m	1627 s	1575 m
19*a*; $\nu_{cc(N)}$ (A_1)	1480 s	1500	1473 s	1477 s	1478 s	1490 vs	1490 s
$\delta_{as}CH_3$	1455 m	1455	1452 s	1455 s	—	—	—
19*b*; $\nu_{cc(N)}$ (B_1)	1410 w	1415	1415 w	1410 w	1439 vs	1550 m	(1455–1442) vs
δ_sCH_3	1375 w	1383	1385 m	1380 m	—	—	—
9*b* (B_1) $\delta(CNH^+)$			1277 m			1275 w	
9*a* (A_1)	1230 w	1237	1235 w	1235 w		1235 vw	1227 w

[a] w = weak; m = medium; s = strong; vs = very strong.

only PyH$^+$ and 2,6-DMPyH$^+$ ions are formed through interaction with hydroxyl groups. In Table 1, the frequencies of the ring vibrations (ν_{8a}, ν_{8b}, ν_{19a}, ν_{19b}, ν_{9a}, ν_{9b}) are compared for Py and 2,6-DMPy in the liquid phase and adsorbed on Lewis and Brønsted sites of zeolite Y. Differences in frequencies and band intensities in the spectrum of Py and 2,6-DMPy in the liquid phase are due to charge disturbances in the six-ring by the electron donating effect of the substituents (*11*).

Compared to the frequencies in the liquid phase, 2,6-DMPy:L shows no frequency shift. This is not true for Py:L. The higher frequencies of Py:L compared to Py in the liquid phase indicate charge disturbance in the ring and therefore a stronger interaction with the Lewis sites. The vibration 8*a*, 8*b*, 9*a*, and 9*b* for PyH$^+$ and 2,6-DMPyH$^+$ are around the same frequencies (Table 1). The marked difference in the spectral behavior for both ions is in the frequency of ν_{19b}. In Py, this vibration is very sensitive towards coordination (1550 cm^{-1} in PyH$^+$ and 1455 in Py:L), while in 2,6-DMPy it is frequency invariant (1410–1415 cm^{-1}).

The spectra of Figs. 1 and 2 and the data of Table 1, show that Lewis bound 2,6-DMPy can be distinguished spectroscopically from 2,6-DMPyH$^+$ as is the case for Py:L and PyH$^+$. Bands characteristic for 2,6-DMPy:L are at 1603 and 1580 cm^{-1}. Bands at 1650, 1630 and 1275 cm^{-1} are characteristic for 2,6-DMPyH$^+$ and PyH$^+$.

Intensities of the Vibrational Modes

The apparent integrated intensities of ν_{8a} and ν_{8b} of adsorbed Py and 2,6-DMPy are shown in Table 2. Both bands can be used as quantitative indices of Lewis or Brønsted bound adsorbate. Both vibrational modes show always a higher intensity for adsorbed Py than for adsorbed 2,6-DMPy. For the calculation of the apparent integrated intensities, it was checked that the amount of adsorbate used was adsorbed without building up any residual pressure. From these data we calculated the minimal amount of 2,6-DMPy needed to obtain a spectrum

TABLE 2

APPARENT INTEGRATED INTENSITIES OF INFRARED BANDS OF ADSORBED 2,6-DMPy AND Py

Adsorbate	Wavenumber (cm^{-1})	Assignment	Adsorbent	Apparent integrated intensity (cm μmole^{-1}) ($\pm$0.2)
2,6-DMPy	1603	8a	NaY-400	3.0
Py	1595	8a	NaY-400	4.6
2,6-DMPy	1650	8a	HY-400	7.8
Py	1655	8a	HY-400	12.0
Py[a]	1620	8b	HY-300	12.9
2,6-DMPy	1627	8b	HY-400	10.0
2,6-DMPy	3640	ν_{OH}	HY-400	5.18
NH$_3$[b]	3640	ν_{OH}	HY-400	5.30

[a] From Ref. (*12*).

[b] From Ref. (*10*).

that can be used for quantitative interpretation. For 2,6-DMPy:L and 2,6-DMPyH$^+$ these amounts are, respectively, 3×10^{18} and 1×10^{18} molecules g^{-1} and correspond to the sensitivity of titration method.

As shown in Fig. 2, a, b, c, upon room temperature adsorption of 2,6-DMPy on HY-400, the 3640 cm^{-1} hydroxyl band disappears in a selective way. Only after adsorption at high temperatures (400°C) has the hydroxyl band at 3550 cm^{-1} decreased in intensity, probably due to migration of protons out of the sodalite cages and capture by the absorbate molecules. The integrated absorption intensity of the 3640 cm^{-1} band after room temperature adsorption of 2,6-DMPy is also given in Table 2 and compared with its capability for ammonium ion formation at room temperature. In previous work *(10)* it was concluded that NH_3 molecules react quantitatively with the 3640 cm^{-1} hydroxyls. Since the values of the apparent integrated intensities of the 3640 cm^{-1} band for both adsorbates are close together, the conclusion seems straightforward, at least under the experimental conditions used, that also in the case of 2,6-DMPy the 3640 cm^{-1} hydroxyls form 2,6-DMPyH$^+$ ions in a stoichiometric way.

Selective Adsorption of 2,6-DMPy

In Fig. 3, increasing amounts of 2,6-DMPy are adsorbed at room temperature on HY-600. Pretreatment of the original NH_4Y sample *in vacuo* at 600°C causes considerable dehydroxylation of the sample *(6)* with the formation of trigonal coordi-

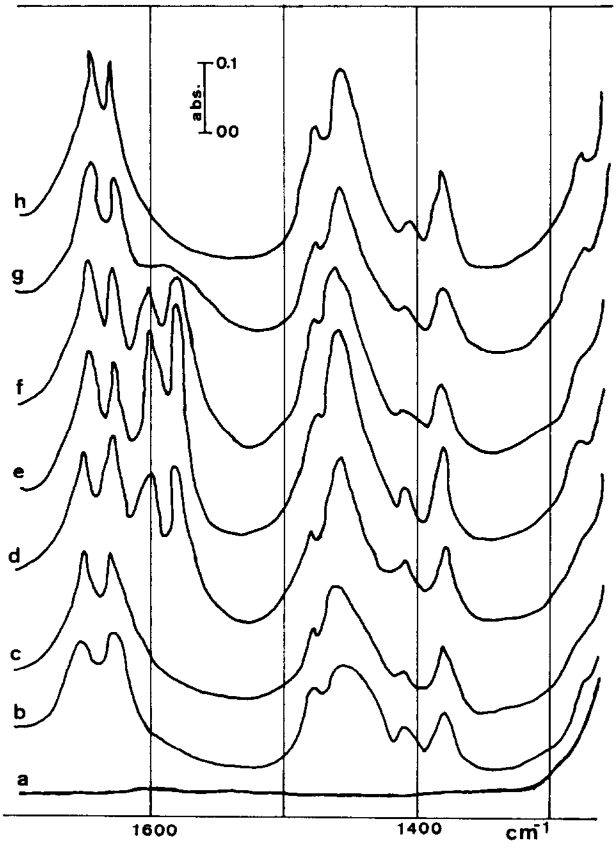

FIG. 3. Infrared spectra of 2,6-DMPy adsorbed on HY-600 (film thickness, 5 mg cm^{-2}). Background (a); room temperature adsorption of 0.18 (b); 0.28 (c), 0.50 (d), 0.98 (e) μmole 2,6-DMPy, followed by outgassing at 200 (f) and 400°C (g); adsorption of 50 μmole 2,6-DMPy at 400°C followed by outgassing at 400°C (h).

nated Al atoms acting as Lewis sites. In spectrum b and c, the bands at 1650, 1630 and 1277 cm^{-1} indicate increasing amounts of 2,6-DMPyH$^+$ formed. Only after the third introduction (d) do bands specific for 2,6-DMPy:L appear at 1603 and 1580 cm^{-1}. Further introduction of base (spectrum e) results only in the increase of the amount of Lewis bound 2,6-DMPy. The amount of ion formed after the second introduction (c) does not change significantly upon further addition of adsorbate. It seems that at room temperature, sufficiently small amounts of 2,6-DMPy neutralize first the hydroxyl groups and then start to neutralize the Lewis sites formed by dehydroxylation. The thermal stability of the two adsorbed species is illustrated in spectra f, g, h. After outgassing at 200°C, part of the 2,6-DMPy:L species have disappeared (f). At 400°C no residual Lewis bound base remains on the zeolite surface (g). The intensity of the bands attributable to 2,6-DMPyH$^+$ does not change even after outgassing at 400°C. Adding an excess of base at 400°C (h), followed by outgassing at the same temperature, results in the forma- of more ions. This can be explained by the migration of residual protons contained in the 3550 cm^{-1} band towards the supercages. These results clearly show that from room temperature up to 400°C 2,6-DMPy can be used to poison the hydroxyl groups selectively in the presence of Lewis sites.

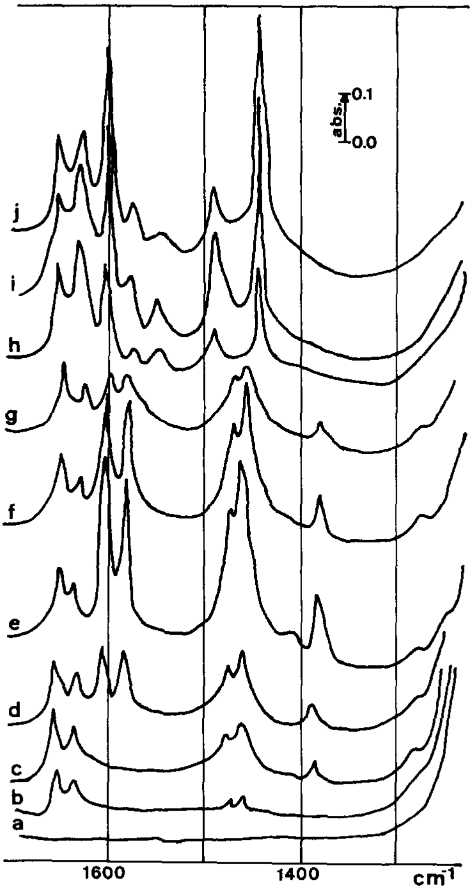

FIG. 4. Infrared spectra of 2,6-DMPy and Py adsorbed on CaY-400 (film thickness, 3.5 mg cm^{-2}). Background (a), adsorption at room temperature of 0.13 (b), 0.20 (c), 0.33 (d), 50 (e), μmole 2,6-DMPy followed by outgassing at 200 (f), and 400°C (g). Adsorption of 0.2 (h), and 50 (i), μmole Py at room temperature followed by outgassing at 400°C (j).

In Fig. 4 the selectivity of adsorption of 2,6-DMPy and Py on CaY-400 is illustrated. The Ca^{2+} ions exposed to the supercages and the 3640 cm^{-1} OH groups formed by dissociation of cation hydration water (*13–15*) possibly interact with adsorbed base. Increasing amounts of 2,6-DMPy in doses of about 8 × 10^{18} molecules g^{-1} added to CaY-400 at room temperature show that the hydroxyl groups are titrated in a selective way (spectra a, b, c) as shown by the appearance of bands at 1650 and 1630 cm^{-1}. Only upon further addition of base, increasing amounts of 2,6-DMPy:L are formed (d, e). Desorption at 200 and 400°C (f, g) shows that the species held by Lewis sites (Ca^{2+} ions) are thermally more stable compared to the sample HY-600. Spectrum h shows adsorbed Py on the same sample. The amount of base added corresponds to spectrum c. Assignment of the different peaks shows the presence of both PyH$^+$ and Py:L. After addition of more pyridine the amount of PyH$^+$ and Py:L increases (i). After desorption at 400°C (j) the amount of PyH$^+$ has decreased, and the amount of Py:L adsorbed remains unaltered. This is in contrast to the behavior after adsorption of 2,6-DMPy.

The data of Fig. 4 show that 2,6-DMPy reacts in a selective way with the hydroxyl groups. Only after neutralization of these

TABLE 3

CHEMISORPTION CAPACITY AT 400°C FOR 2,6-DIMETHYLPYRIDINE (2,6-DMPy) AND PYRIDINE (Py) (molecules $g^{-1} \times 10^{-20}$)

Sample	2,6-DMPy	Py[a]	Sum (2,6-DMPy) + 2(Py)
HY-400	6.5	1.8	10.1
HY-600	1.9	3.1	8.1
CaY-400	4.4		

[a] The amount of Py chemisorbed afterwards, when the sample would no longer chemisorb 2,6-DMPy.

groups is a coordinative bond with the Ca^{2+} ions formed. Pyridine molecules adsorbed in the same conditions do not react in the same way. The Lewis held Py molecules are thermally more stable than the pyridinium ions.

In Table 3, 2,6-DMPy and Py were adsorbed at 400°C under reaction conditions on the zeolite samples indicated. In the pulse microcatalytic reactor, the amount of base chemisorbed is measured. The data are shown in Table 3 (column 2). At the moment that 2,6-DMPy molecules remain no longer chemisorbed on the zeolites, further addition of Py shows that a considerable amount of this species remains on the zeolite (Table 3, column 3). Infrared measurements on the same samples show that the first base is adsorbed as 2,6-$DMPyH^+$. After successive adsorption of Py only Py:L species are formed. This is further proved by the fact that the amount of 2,6-$DMPyH^+$ plus twice the amount of Py:L reaches a constant value (Table 3, column 4) on samples HY-400 and HY-600. Indeed, each Lewis site formed results from the condensation of two hydroxyl groups (*13*).

Active Sites for Cumene Cracking

The high selectivity of 2,6-DMPy for Brønsted sites has been demonstrated satisfactorily in previous sections. The action of such a poison on a Brønsted site catalyzed reaction, such as the cumene dealkylation, should enable us to evaluate an upper limit for the number of active sites. In the conditions (*6*) used for the chemisorption measurements cumene and poison molecules are injected alternatively. The amount of base used to reduce the cumene dealkylation activity to zero is given in Table 4 for the poisons 2,6-DMPy and Py. The amount of 2,6-DMPy used is equal for samples HY-400 and HY-600 and two orders of magnitude lower than the number of Al atoms in the zeolite structure. The amount of Py used is lower on HY-600 and considerably higher than the amount of 2,6-DMPy used.

TABLE 4

ACTIVE SITES FOR CUMENE CRACKING AS TITRATED WITH Py AND 2,6-DMPy (sites $g^{-1} \times 10^{-20}$)

Sample	2,6-DMPy	Py
HY-400	1.86	10.0
HY-600	1.80	6.3

CONCLUSION

The higher basicity of 2,6-dimethylpyridine compared to pyridine results in the formation of stronger ions on the zeolite surface. Due to the steric effects of the CH_3 groups in positions 2 and 6, weaker bonds are formed with the Lewis sites in the zeolite. Typical Lewis sites investigated are trigonal coordinated Al atoms, and compensating cations as Na^+ and Ca^{2+}, embedded partially in the zeolite six and four-rings. The 2,6-DMPy molecules show a high selectivity towards Brønsted sites in the presence of Lewis sites. The position and intensity of the vibrations ν_{8a} and ν_{8b} in the case of Brønsted or Lewis bound molecules can be used to follow quantitatively the nature of the acid sites. The sensitivity of the method is better than 3×10^{18} molecules g^{-1}.

The number of active sites in the cumene dealkylation reaction measured with Py is much higher than with 2,6-DMPy. On HY samples the number of active sites titrated with 2,6-DMPy is about 1.8×10^{20} molecules g^{-1} and does not depend on the pretreatment temperature of the sample.

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