JOURNAL OF CATALYSIS **179,** 451–458 (1998)
ARTICLE NO. CA982233

2,6-Di-Tert-Butyl-Pyridine as a Probe Molecule to Measure External Acidity of Zeolites

A. Corma,*,[1] V. Fornés,* L. Forni,† F. Márquez,* J. Martínez-Triguero,* and D. Moscotti†

**Instituto de Tecnología Química, UPV-CSIC, Universidad Politécnica de Valencia, Avenida de los Naranjos s/n, 46022 Valencia, Spain;*
†Universitá di Milano, Dipartimento Di Chimica Fisica Ed Elettrochimica, Via Golgi 19, 20133 Milan, Italy

Received February 24, 1998; revised May 19, 1998; accepted July 15, 1998

The use of a large probe molecule like di-tert-butyl-pyridine (DTBPy) is showed to be adequate to characterize the acid sites located at the external surface of zeolites. Infrared spectroscopy, has been revealed as a good technique to monitor the adsorption of the base by following the N-H$^+$ stretching band at 3370 cm^{-1} of the protonated amine. In this way, zeolites with 10 and 12 member ring (MR) pores with uni-, bi-, and tridirectional system of channels have been studied. On some samples, the relative amount of external acid sites has been changed by modifying the crystal size or by selective Al leaching of the surface. The external surface acidity measured by this technique correlates well with the cracking activity for large reactant molecules that cannot penetrate inside the pores of the zeolites. © 1998 Academic Press

INTRODUCTION

It can be safely said that acid catalysis involves both the largest amount of catalysts used and the largest number of catalytic process (1). Among those catalysts zeolites have shown a great utility not only from the activity point of view but also for their selectivity associated to the shape and size of the pores. Thus, it is not surprising that great attention has been paid recently to enhance the shape selectivity of zeolites by passivating their external surface (2–4) and, as a consequence, much efforts have been devoted to find out a probe molecule that is able to measure the external surface sites which are the accessible ones when working with cumbersome molecules such as those typical of vacuum gasoil. Indeed, the shape selectivity of zeolitic catalysts is determined by the size of their pores and by the relative population of active sites on the external and internal surface. Some methods have been developed for characterizing the acid sites present at the external surface (5–11), but up to now no definitive results have been reached.

Adsorption and desorption of bases monitored by IR spectroscopy is a method widely used to characterize both total acidity and acid strength distribution on solid acid catalysts. Pyridine is largely employed as probe for large- and medium-pore zeolites since it can easily penetrate through the 10- and 12-membered ring (MR) channels of the zeolites and so interact with acid sites in channels and cavities.

It has been reported (12) that, whenever possible, the reactant itself should be used as a probe molecule. However, to obtain some general and standard results, it is advisable to select some molecules possessing peculiar characteristics for use in standard measurements. Among the general criteria for selecting probes for acid sites characterization by IR spectroscopy the following are the most important: (i) the probe should have dominating basic and rather weak acidic properties, so to interact primarily by its base function, with acid function hardly interacting with the solid; (ii) the IR spectrum of the adsorbed probe should allow to distinguish between sorption on Brønsted (B) and Lewis (L) acid sites through significant differences in the position of the IR adsorption bands; (iii) the probe should allow distinguishing between sites of the same type but of different strengths; (iv) the hardness of the probe molecule should be similar to that of reactants to characterize reliably the acid–base properties with respect to a particular reactant; (v) the size of the probe molecule should be comparable with that of the reactant, in order to determine the concentration of "useful" acid sites participating in a particular reaction (accessibility).

In a recent work (6) 2,6-di-tert-butyl-pyridine (DTBPy) has been employed for characterizing external B acid sites of a ZSM5 zeolite by means of thermogravimetric measurements. Previously, only a few references could be found on the use of DTBPy as a probe for acidity measurement. All of them refer to porous systems such as alumina (13–15), fluorinated alumina (16), or boron phosphate (17) and they report on the study of B acid sites without interference to L sites. On this basis DTBPy has been selected to measure Brønsted acid sites (6) and also to poison the external acid sites of ZSM catalysts (17,18). There exists some controversy (11,14) on the assignation of the infrared bands of

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[1] To whom correspondence should be addressed. E-mail: acorma@itq.upv.es.

0021-9517/98 $25.00

DTBPy in the range of 1700–1300 cm^{-1} to Brønsted, Lewis, or both types of acid centers. To elude the discussion in the present work we have selected the stretching band of the protonated amine group ($\equiv$N-H^+, at ca 3370 cm^{-1}), which is unequivocally related to the Brønsted acid groups. After a systematic study of the adsorption of DTBPy on a large number of zeolites with different pore sizes and topologies, we conclude that such a band is much more reliable than the previously selected ones and that DTBPy is a suitable probe for characterizing selectively the B acid sites present on the external surface of 10-MR and of mono-directional 12-MR zeolitic acid catalysts.

EXPERIMENTAL

Material

2,6 di-tert-buthyl-pyridine was of 97 wt% purity and used without further purification. Pyridine was of spectrophotometric grade (99+ wt%), with a water content lower than 0.05%. The reactants, 1,3,5-triisopropylbenzene (TIPB) and *n*-decane (*n*D) were 97 and 99 wt% pure, respectively. All such chemicals were used as purchased from Aldrich.

Apparatus and Procedure for Collecting IR Spectra

The IR spectra were collected at room temperature using a BIO-RAD FTS-40 FT-IR spectrometer, fully controlled through a VECTRA HP 486/25 VL PC, by means of the WIN-IR-BIORAD software.

The samples were finely ground in an agate mortar and than pressed in ca 10 mg/cm^2 self-supporting wafers in the absence of any binder. Before IR analysis all samples were heated at 673 K and high vacuum (10^{-2} Pa) overnight. After cooling to room temperature the reference spectrum of the so-activated sample was collected with 4 cm^{-1} resolution. Some preliminary experiments suggested the following proper operating conditions: adsorption of DTBPy by equilibrating the catalyst wafer with the probe vapor pressure for 12 min at 423 K, followed by 1 h degassing at the same temperature and by collection of the spectrum at room temperature, while Py was adsorbed by equilibrating the sample for 1 min with a 6×10^2 Pa vapor pressure of the probe at room temperature. The desorption procedure for the pyridine probe was monitored stepwise by evacuating the sample for 1 h at 523, 623, and 673 K and cooling down to room temperature after each step to record the spectrum.

Apparatus and Procedure for Collecting XPS Spectra

XPS measurements were carried out with a VG-Escalab-210 spectrometer, by using the Mg Kα (1253.6 eV) radiation of a twin anode in the constant analyzer energy mode, with a pass energy of 50 eV and X-ray power of 200 W. The chamber pressure was maintained at 5×10^{-10} mbar. Depth profiling experiments were carried out in a pretreatment chamber and the sputter erosion was performed using an Ar^+ ion beam of 4 keV primary energy at an angle of incidence of 45°. Calibration with at Ta_2O_5 standard gave a sputtering rate of ca 35 Å min^{-1} for this source.

TABLE 1

Standard Acid Catalysts

Sample	Structural type	Si/Al
Mordenite	MOR	10
Beta	BEA	12.5
Y	FAU	2.5
ZSM5	MFI	25
ZSM11	MEL	34
M50	MWW	50
SSZ24	AFI	50
SSZ26	CON	20

Standard Catalysts

The standard catalysts chosen for this work are listed in Table 1. All of them are of well-known porous structure and include 10-MR systems, such as ZSM5 and ZSM11; mono-directional 12-MR systems, such as mordenites and SSZ-24; bi-directional systems, with 10 × 12-MR structure, such as MCM-22; tri-directional systems with 10 × 12-MR structure (SSZ-26) and 12-MR channels, such as BETA and Y-zeolites. Parallel measurements were carried out over such catalysts, by adsorbing DTBPy and Py.

Catalysts with Different Concentration of External Acid Sites

A first series of two sets of catalysts with mordenite structure and with modulated concentration of external acid sites were prepared, starting from the previously mentioned (Table 1) commercial zeolite (CBV20A, ammonium-exchanged form Si/Al = 10, Na_2O = 0.2 wt% and SA = 550 m^2/g, purchased from P.Q. Zeolites B.V.). The sets differed in the concentration of external acid sites and were prepared by dealuminating with HCl the external layers of the parent zeolite. Since dealumination begins preferentially at the external surface and gradually proceeds toward the inner part of the crystals, this technique permits the modulation of the surface dealumination degree by simply modifying the operating conditions such as temperature, acid concentration, and time of treatment. Sample M1 was prepared by treating 15 g of the parent zeolite with 1000 cm^3 of 0.1 *M* HCl at a temperature of 353 K filtered and washed. Samples **M2** and **M3** were prepared by adding 15 g of the parent mordenite to 150 cm^3 of 1 *M* HCl. The slurry was stirred for 30 min and 3 h, respectively, at the same temperature, and then filtered and washed. To avoid precipitation of the extracted aluminum, washing was

TABLE 2

Physico-Chemical Characteristics of Dealuminated Mordenites

Catalyst	SiO_2(wt%)	Al_2O_3(wt%)	Na_2O(wt%)	Crystallinity %	Al/Al + Si(bulk)	Al/Al + Si(XPS)
M0	94.46	5.34	0.20	100	0.110	0.080
M1	95.52	4.46	0.03	95	0.099	0.070
M2	95.98	3.99	0.03	95	0.089	0.050
M3	96.44	3.53	0.03	89	0.079	0.045

carried out with several batches of HCl, 0.01 *M*, up to a total amount of 1000 cm^3, followed by about 2000 cm^3 of water, up to the disappearance of Cl^- ions in the washing solution. The solids were then dried overnight at 60°C. X-ray diffraction patterns of the original **M0** (CBV 20A) and of dealuminated mordenites clearly showed that all of the dealuminated samples maintained a good degree of crystallinity. The relevant characteristics of these catalysts are collected in Table 2.

A second series of catalysts, with ZSM5 structure and similar Si/Al ratio, but with different crystal size, have been obtained following four different preparations. The gel composition for **Z53** (1 μm) was the following: $Si/Al = 20$, $TPA^+/Si = 0.023$, $M_2O/Si = 45$, $OH^-/Si = 0.2$, $Na^+/Si = 0.25$, being the source of: SiO_2, Aerosil 200 (Degussa); Al; sodium aluminate (Carlo Erba, 56% Al_2O_3, 37% Na_2O); OH^-, NaOH (Probus); TPA^+, tetrapropyl ammonium bromide (Aldrich). The sample was crystallized at 423K for 21 h. For preparing **Z51** (0.1 μm), the synthesis gel composition was $Si/Al = 20$, $TPA+/Si = 0.02$, $H_2O/Si = 45$, $OH-/Si = 0.15$, $Na+/Si = 0.27$, $SO_4^{2-}/Si = 0.058$ being the reactants, the same as above. The crystallization temperature and time were 423 K and 20 h, respectively. The synthesis gel for preparing sample **Z52** (0.25μm) had the following synthesis composition: $Si/Al = 20$, $TPA^+/Si = 0.03$, $H_2O/Si = 45$, $OH/Si = 0.1$, $Na/Si = 0.16$. The starting materials were the same as above, except for Si that LUDOX was 40% in H_2O stabilized with ammonium. The same conditions as above were used for crystallization. Finally, sample **Z50** (0.04 μm) was prepared with a gel composition containing a $Si/Al = 20$, $TPA/Si = 0$, $H_2O/Si = 24$, $OH^-/Si = 0.2$, $Na/Si = 0.26$ being the starting materials and the crystallization conditions the same as for sample **Z52**.

The general synthesis procedure included the homogenization of the synthesis gel for 30 min, and the crystallization in a 500 ml autoclave (Autoclave Engineers) under agitation at 380 rpm. After the required time, the autoclave was cooled down and the solid was filtrated and washed with distilled water until the pH of the washing waters was lower than 9. The crystallinity of the samples was high (100%), except for the sample prepared in the absence of TPA^+ that was 85%.

Before used for reaction, the zeolites were calcined at 773 K, followed by exchange with a NH_4Cl solution (2 *M*, liquid/solid = 10 wt/wt). The exchange-calcination process was repeated two times. The crystallinity of the final samples was in all cases higher than 80%.

Catalytic Tests

Catalytic runs were carried out on dealuminated mordenites (Table 2) and ZSM-5 samples of different crystal sizes. Catalytic activity was studied in a fully computer-controlled microactivity test unit (MAT) (19) arranged for carrying out several reaction-regeneration cycles, following different scheduled procedures. A Pyrex tubular downstream reactor, loaded with 0.2 g of 0.60–0.80 mm catalyst particles, was used. The reactor dead volume preceding the catalyst bed was filled with quartz wool to favor complete vaporization of the liquid reactant. The reactant was injected by means of a syringe pump for 60 s at atmospheric pressure and time factor $\tau = W/F = 0.1$ to 0.3 min, W being the catalyst weight (g) and F (g/min) the feeding rate. Reaction temperature was 480°C. At the end of the injection time the products were stripped out of the reactor by a nitrogen flow. Liquid products were condensed in cooled sample holders, while gases were stored over water column. Catalyst activation and regeneration after each experiment were carried out *in situ*. Activation was performed at reaction temperature while regeneration was done at 520°C for 3.5 h by feeding 80 cm^3/min of air. Gases stored during reaction and nitrogen stripping were analyzed by a HP 5890 gas chromatograph, equipped with two capillary columns connected in series with two detectors (TCD and FID). The first column, a molecular sieve 15-m long × 0.53-mm ID, separated hydrogen, nitrogen, and methane, while the second column, alumina, 50-m long, separated hydrocarbons (C_2 to C_6). Liquid products were analyzed by a Varian 3400 gas chromatograph, equipped with FID and a SUPELCO PETROCOL DH 100 column, 100-m long × 0.25-mm ID. CO_2 produced during regeneration was monitored by an IR spectrometer, while water was absorbed on anhydrous $CaSO_4$.

RESULTS AND DISCUSSION

FT-IR Studies

Preliminary qualitative experiments, in which DTBPy was adsorbed on a sample of mordenite (CBV20A), showed

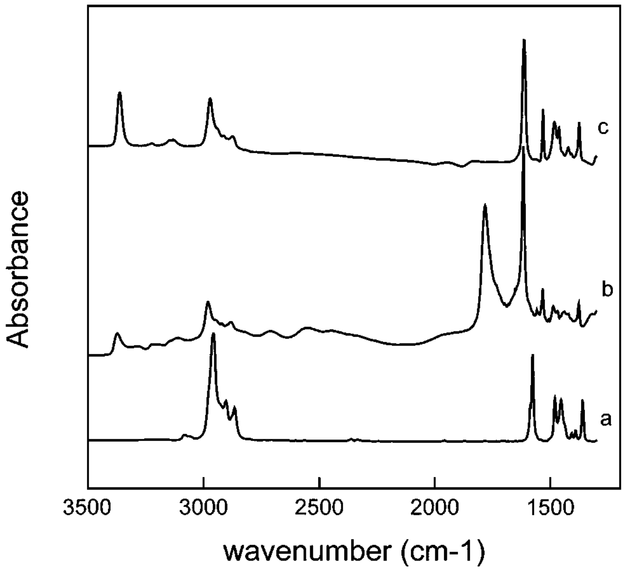

FIG. 1. IR spectra of: (a) pure DTBPy; (b) DTBPyH$^+$; (c) DTBPy, adsorbed on mordenite.

a number of bands in various regions of the IR spectrum (Fig. 1c). In order to evidence the most suitable bands for monitoring DTBPy adsorption on acid sites, the spectrum was compared with those of pure DTBPy and DTBPyH$^+$ (trifluoroacetic acid adduct) (Figs. 1a and b). These data point clearly to the bands at 3370, 1616, and 1530 cm^{-1} as characteristic signals of the DTBPyH$^+$ ion. Hence they can, in principle, be used to monitor B acid sites.

According to previous works (4) the bands at 1616 and 1530 cm^{-1} were assigned to the ring signals of the protonated probe. As for the band at 3370 cm^{-1}, by reacting DTBPy with trifluoroacetic acid (Fig. 1b), we observed that the -CH$_3$ stretching and symmetric deformation vibrations are displaced by about 20 cm^{-1} towards higher wavenumbers with respect to the pure base (Fig. 1a). Furthermore, the spectrum of DTBPy adsorbed on solid acid catalysts, such as mordenite (Fig. 1c), shows practically the same bands of the DTBPyH$^+$ ion in the 1700–1300 cm^{-1} region, besides the stretching band at 3370 cm^{-1}. In addition, the C-H stretching region presents the same characteristics and the shift to higher wavenumber is still present. Such a behavior confirms that the -CH$_3$ groups can interact with acid sites as reported by Knözinger *et al.* (15) and Miyata and Moffat (17). To conclude, these results let us to attribute the 3370 cm^{-1} band to the $\equiv$N-H$^+$ stretching of protonated DTBPy. Moreover, our data of adsorption experiments on the various standard catalysts point to such a band as the most adequate for characterizing B sites on solid acids. Indeed, this signal presents an acceptable intensity with all of the systems tested, while the two other typical bands (1616 and 1530 cm^{-1}) are not suitable, the first one being too much intense on the samples possessing a large amount of easily accessible Brønsted sites (BETA and Y zeolites) and the second being too weak for the samples with hardly accessible acid sites (ZSM5 and MCM-22).

When contacting DTBPy with 10-MR systems, such as ZSM5 or ZSM11, a very small amount of probe is adsorbed, accompanied by a correspondingly very small decrease of the signal of the acidic OH, while when adsorbing Py the complete disappearance of the latter band is observed. This clearly indicates that DTBPy cannot penetrate into the pore network of these catalysts. Thus we can reasonably admit that the adsorbed DTBPy interacts only with the acid sites situated on the external surface of the crystals. This behavior, i.e. the inability for DTBPy to enter the pores of 10-MR zeolites, has been confirmed by us also through calculations carried out by means of the BIOSYM molecular dynamic simulation program.

Mordenite and SSZ-24 zeolites possess a mono-directional 12-MR pore system. When adsorbing DTBPy on them, the small decrease in the intensity of the acidic OH band at about 3610 cm^{-1} shows that only a partial interaction of the probe with acid sites occurs, thus indicating that only the B sites closer to the mouth of the pore, besides the properly called external sites, interact with DTBPy (Fig. 2). Furthermore, when simulating the penetration of DTBPy

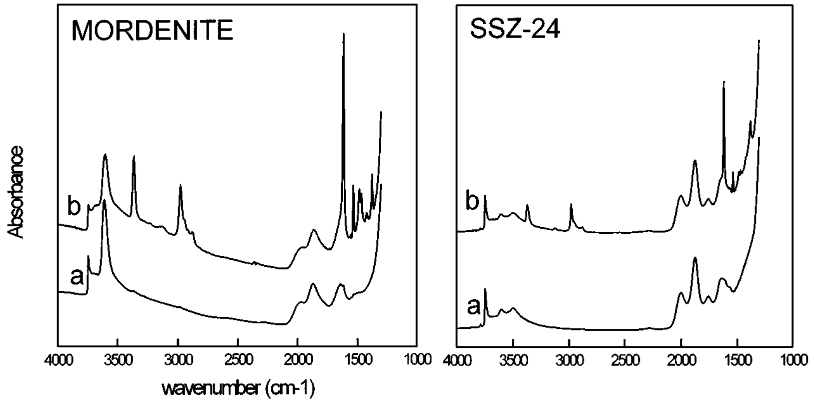

FIG. 2. IR spectra in the 4000–1300 cm^{-1} range, before (a) and after (b) adsorption of DTBPy on unidirectional 12MR zeolites, Mordenite, and SSZ-24.

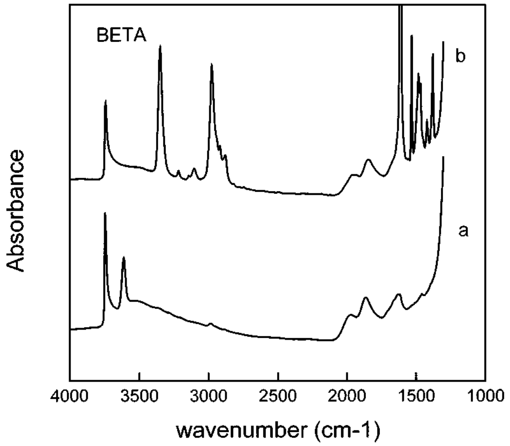

FIG. 3. IR spectra (a) before and (b) after adsorption of DTBPy on beta zeolite.

into mordenite channels by the BIOSYM program, strong Van der Waals interactions between the molecule and the lattice are observed.

In the case of tri-directional 12-MR systems, such as BETA zeolite, an easy penetration of DTBPy into their pore network and a complete disappearance of the OH acidic band at 3610 cm^{-1} was observed (Fig. 3). On the other hand for Y zeolites, as confirmed also with the docking simulation, only a limited number of DTBPy molecules can be fitted into the supercage, due to steric hindrance, and consequently, only a fraction of the B acid sites can interact with the probe.

In the case of zeolites possessing a 10 × 12-MR channel system, it has been observed that in SSZ-26 the two types of acidic hydroxyls are partially accessible. This may indicate that DTBPy reaches the sites, not only in the 12-MR, but also in the 10-MR pores, probably through their connections with the 12-MR. However, the limited accessibility of the probe indicates a behavior very similar to that of the unidirectional 12-MR-structured zeolites.

Finally, with MCM-22 possessing a structure of 10- and 12-MR pores, but with access to the 12-MR cavities only through the 10-MR pores (20), the DTBPy cannot enter in either of the two pore systems and the behavior is similar to that of ZSM5.

Scale of External Brønsted Acidity

In order to obtain a relative scale of external acidity, our experimental data have been elaborated as follows. Beta zeolite shows a complete accessibility to both Py and DTBPy, the adsorption of any of the two neutralizes all of their OH acidic groups, and the characteristic band at 3610 cm^{-1} disappears. Considering that the interaction B : DTBPy is 1 : 1, this means that the number of adsorbed probe molecules upon B acid sites is the same for the two probes.

This amount corresponds to the total amount of DTBPy adsorbed on B sites of the catalyst, since the experimental calculation has been carried out on the band at 3370 cm^{-1}, corresponding to the $\equiv$N-H^{+} stretching. Assuming that the number of adsorbed DTBPy molecules corresponds to that of Py (for BETA zeolite), the area of the 3370 cm^{-1} band, divided by the number of adsorbed μmol of DTBPy, yields the "μmol area" corresponding to the adsorbed probe. Then, from the area of the band of the Py spectrum at 1545 cm^{-1} the total amount of B acid sites of each catalyst is calculated, and multiplying this value by the "μmol area" of DTBPy, we can obtain the "theoretical" area of DTBPy by assuming that all the acid sites are accessible to the probe. Finally, dividing the measured area of the 3370 cm^{-1} band by the theoretical area of DTBPy, the fraction of the acid sites interacting with the probe is obtained. The above could be summarized in the following two equations:

$$S_{\text{DTBpy}}\,(\text{theoretical}) = \frac{\text{A Spy (zeolite problem)} \times S_{\text{DTBpy}}\,(\text{Beta})}{\text{A Spy (beta)}} \qquad [1]$$

$$\text{Fraction of acid sites interacting with DTBpy} = \frac{S_{\text{DTBpy}}\,(\text{zeolite problem})}{S_{\text{DTBpy}}\,(\text{theoretical})}, \qquad [2]$$

where A is the integrated molar extinction coefficient (IMEC) corrected by the weight of the sample irradiated by the beam. Notice from Eq. [1] that the corrected IMEC parameters are canceled out and, therefore, it is not necessary to know the particular values for obtaining the fraction of the acid sites interacting with the probe.

The results obtained for the different standard acid catalysts are shown in Table 3, giving an idea of the degree of penetration of the probe into the solid, thus indicating if the observed amount of adsorbed DTBP corresponds only to the external surface or to a major portion of the overall B acid sites.

This procedure presents, however, two main drawbacks when extended to zeolites which are too different in

TABLE 3

Accessibility of Protonic Acid Sites of Different Standard Zeolites

Samples	Si/Al	exp. DTBPy	Theor. DTBPy	Percentage interaction
Mordenite	10.0	7.3	20.3	36
Beta	12.5	22.0	22.0	100
Y	2.5	23.5	41.3	57
ZSM5	25.0	0.6	17.4	3
ZSM11	34.0	0.9	2.0	43
M50	50.0	0.7	10.2	6
SSZ24	50.0	1.5	4.8	30
SSZ26	20.0	4.5	13.8	33

topology. First, when the sample is not completely accessible to Py, as for mordenite, the result overestimates the interaction of DTBPy with the solid, since the calculated total amount of B acid sites is lower than the real one. Second, the catalysts presenting low interaction with DTBPy (e.g., ZSM5) show a very small band area. In this case the results are deeply affected by the inaccuracy in the determination of the areas, making the comparison among different catalysts difficult. The comparison is, in consequence, only semiquantitative and remains meaningful only for samples with similar pore structures.

Nevertheless, the results of Table 3 show that there are three types of zeolites with respect to the accessibility of acid sites of DTBPy:

a. Total accessibility to DTBPy. Such is the case of beta and Y zeolites with Si/Al ratios >10 and possessing a tridirectional 12MR pore system. In this case external and internal surfaces are accessible to the probe molecule. However, the case of the Y zeolite needs further discussion and this will be done below.

b. Partial accessibility (30–40%) as in the case of unidirectional 12-MR pore system zeolites like Mordenite and SSZ24. The tri-directional 12/10-MR zeolites, like SSZ26, are included, and the accessible surface corresponds to the external plus the mouths of the pores and defects.

c. Nonaccessible zeolites (<5%) which DTBPy adsorption corresponds exclusively to external surfaces. The ZSM5 and MCM22 samples are examples of this behavior.

Finally, the ZSM11 sample behaves as a 12-MR unidirectional zeolite while possessing a tridirectional 10-MR pore system. However, it must be take into account that this sample has a very small crystal size (<100 nm) and the proportion of external surface is strongly increased. In fact, this result is similar to that of **Z51** (ZSM5 < 100 nm) which is 44.5%.

Y zeolite must be considered separately, since the observed low interaction is related, not only to the inaccessibility of some sites located at the hexagonal prism and sodalite unit, but also to the inability of the probe molecule to neutralize all of the sites potentially accessible due to the size of the DTBPy which limits the number of molecules that can be fitted in the supercavities.

In the case of ZSM-5, when decreasing the crystal size of the sample while keeping constant the bulk Si/Al content, the ratio between the accessible acid sites located at the external surface and those that are inaccessible in the channels should increase. Then one should expect that the amount of DTBPy adsorbed on Brønsted acid sites will increase accordingly. Indeed, in Fig. 4, we can see that a good correlation between the external surface area of the zeolite and the amount of DTBPy adsorbed is obtained.

In the case of mordenite, the framework Si/Al ratio of the external surface was changed by acid treatment, and the external Si/Al composition was obtained from the XPS (Table 2). In Fig. 5 we are plotting the Si/Al profile as determined by XPS, and it is clearly seen that while in the original mordenite (sample M0) there is a uniform Al profile, the other mordenites have been preferentially dealuminated at the surface. In this case the amount of protonated DTBPy should be related again to the amount of the external Brønsted acid sites which should be the same as the number of framework Al. Results from Fig. 6 indicate that there is indeed an acceptable correlation between the surface area of the 3370 cm^{-1} band and the Al/Al + Si ratio at the surface.

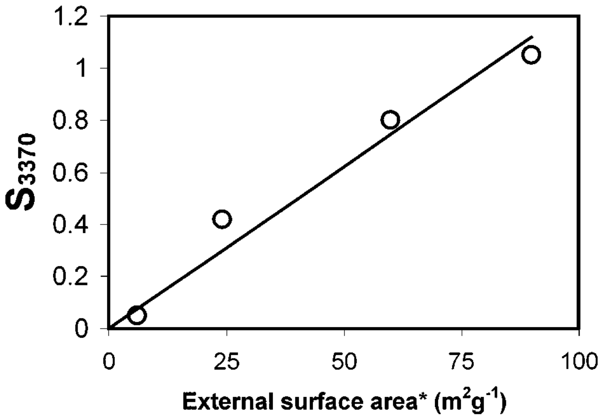

FIG. 4. Intensity of NH IR band of adsorbed DTBPy as a function of the crystal size of ZSM5 zeolite. Values calculated from crystal size considering the crystals as cubes.

Since we have a reliable probe to measure the acid sites at the external surface of 10-MR and unidirectional 12-MR zeolites, we can use these values to predict the relative activity of the samples in acid catalysis with reactants that cannot diffuse inside the pores.

Catalytic Test

We have chosen here a reactant such as triisopropylbenzene, (TIPB) whose diffusion will be strongly impeded at least in 10-MR channels of the zeolites. If this is so, then TIPB should mainly react with the acid sites located at the external surface of such zeolites.

In order to be able to correlate the catalytic activity of a sample with the number of potential active sites, it is convenient to determine a kinetic parameter whose value is directly related to the concentration of active sites. There is no doubt that the most adequate parameter is the true kinetic rate constant (k) which is related to the concentration of active sites (s_0) by means of the equation:

$$k = k_0(s_0), \tag{3}$$

where k_0 is the intrinsic rate constant. However, when the pseudo first-order kinetic rate constant equation is

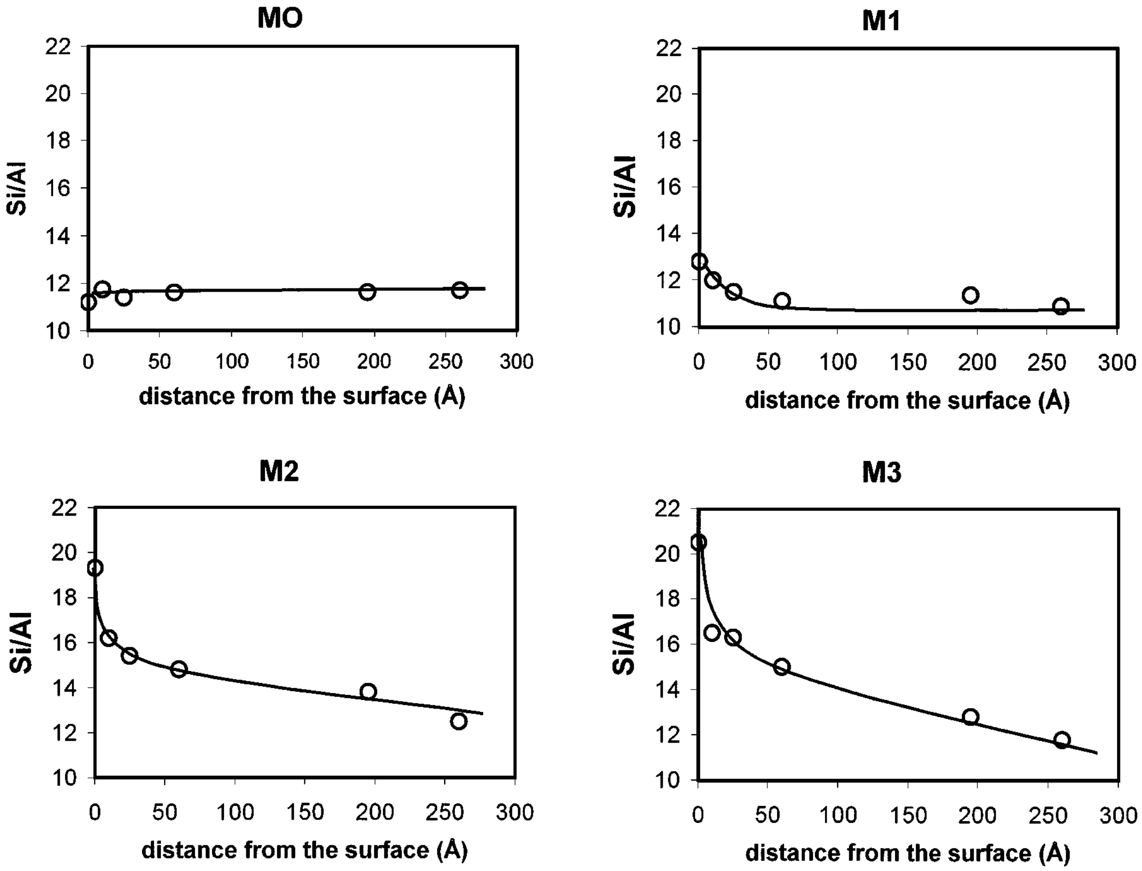

FIG. 5. Aluminum profiles in dealuminated mordenites, measured by XPS.

considered in order to fit the experimental conversion data the equation, through its integrated form, is applied,

$$\begin{aligned} r &= k' \quad \text{(reactant)} \\ \ln(1-x) &= k'\tau, \end{aligned} \tag*{[4]}$$

where r is the rate constant of the reaction, x is the level of conversion, k' is the apparent kinetic rate constant, and τ is the constant time. Working at low levels of conversion, taking into account the adsorption of the reactant, and considering a Langmuir–Hinselwood model, then the apparent kinetic rate constant is given by

$$k' = (k_0(s_0)K_a)/(1 + K_a(\text{reactant})_0) = K''(s_0). \tag*{[5]}$$

In other words, the apparent kinetic rate constant will also be directly proportional to the concentration of active sites and, therefore, it could be used to find the relative number of those when comparing catalysts of the same nature but containing a different number of acid sites.

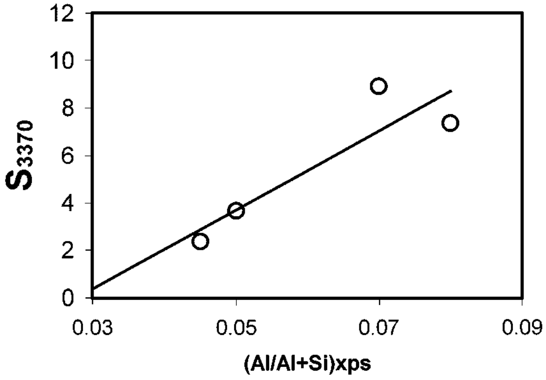

FIG. 6. Intensity of NH IR band of adsorbed DTBPy as a function of surface concentration of aluminum(XPS), in dealuminated mordenites.

The catalytic cracking of TIPB, whose size is more than 1 nm, will be strongly impeded to diffuse inside of the pores of the above zeolite topologies and, therefore, can be used as a test reaction to measure the activity of the external acid sites. In our case the apparent kinetic rate constant (k') for cracking of TIPB has been calculated by fitting the conversion data to Eq. [4] Thus, in Tables 4 and 5, the corresponding k' versus the amount of external surface acid sites as measured from the adsorption of DTBPy on mordenite whose external surface was dealuminated at different levels (Table 2) and on ZSM5 samples with different external surface areas are given. A direct correlation is

TABLE 4

Apparent Kinetic Rate Constant in the Cracking of TIPB over Mordenite Samples Dealuminated at Different Levels

Sample	$k' \cdot 10^2\ s^{-1}$	S_{3350}	$A/(Al+Si)_s$
M0	5.35	7.35	0.08
M1	6.39	8.9	0.071
M2	4.82	3.67	0.05
M3	3.95	2.36	0.045

Note. Bulk Si/Al ratio of 10.

observed between the amount of external surface acid sites as measured by the DTBPy and the amount of external acid sites reached by the TIPB. These results support the idea that DTBPy can be used as a molecular probe to measure the external acidity or even better, the more external acid sites accessible to large molecules of uni- and/or bidirectional 10-MR, as well as unidirectional 12-MR zeolites. It should be taken into account that when dividing the apparent kinetic rate constant by the surface area of the IR band associated to DTBPyH$^+$, which can be taken as a “turnover frequency” of the more external B acid sites, the value obtained for ZSM-5 is higher than for mordenites. This result is in agreement with the statement presented before indicating that DTBPy interacts also with internal sites closer to the pore mouth, besides the properly called external sites. It is also true that the same tendency in the values could be expected if one assumes that the B acid sites in ZSM-5 are stronger when interacting.

We have also performed the cracking of diisopropylbenzene (DIPB) in the mordenite M0, and the apparent kinetic rate constant obtained is three times higher than for TIPB, indicating that DIPB, with a size close to 0.8 nm can already penetrate in some pores of the mordenite.

CONCLUSIONS

The present study clearly shows that DTBPy is a good probe molecule for measuring selectively the concentration of Brønsted acid sites in zeolitic catalysts, by IR analysis of the adsorbed probe, based on the protonated N-H$^+$ stretching band at 3370 cm^{-1}. The latter proved to be much more reliable than other bands such as the ring bands previously suggested in the literature. Furthermore, this probe proved perfectly suitable for measuring selectively the surface concentration of external protonic acid sites present on the 10-MR and on unidirectional 12-MR pore channel systems where it can hardly enter.

TABLE 5

Apparent Kinetic Rate Constant in the Cracking of TIPB over ZSM-5 Samples of Different Crystal Sizes

ZSM-5 $\phi(\mu m)$	$k' \cdot 10^2\ s^{-1}$	S_{3350}
1	3.8	<0.1
0.25	5.2	.42
0.1	5.7	.8
0.05	7.4	1.05

Note. Si/Al ratio of 25.

Parallel experiments of catalytic cracking carried out on the zeolites analyzed in the present work confirm these conclusions, also, from the catalytic point of view of these materials. The cracking of TIPB, which cannot diffuse in either 10-MR nor unidirectional 12-MR pore channels, correlates well with the external surface area and Brønsted acid sites determined by DTBPy in the case of ZSM5 with the same framework Si/Al ratios and different crystal sizes. In an analogous way, it also correlates with the external concentration of acid sites present on a series of mordenite zeolites surface dealuminated at different levels. On the contrary, DIPB can partially penetrate the unidirectional 12-MR zeolites and will not be an adequate catalytic probe for measuring their most external acid sites.

ACKNOWLEDGMENTS

The financial aid of EEC (Human Capital and Mobility Program, Contract CHRX-CT94-0564) is gratefully acknowledged. L. Villaescusa is acknowledged for kindly suppling ZSM-5 samples with different crystal sizes.

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