Hexane Isomerization and Cracking Activity and Intrinsic Acidity of H-Zeolites and Sulfated Zirconia-Titania

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Adsorption of N₂ was studied on zeolite H–Y, ultrastabilized H–Y (H–USY), H–mordenite, H–ZSM-5, H– β , and on sulfated zirconia–titania (SZT) mixed oxide by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) at 298 K and at N₂ pressures up to 9 bar. The adsorption-induced $\Delta \nu_{OH}$ red-shift of the ν_{OH} bands was used as a measure of the intrinsic acid strength of the Brnønsted acid sites. The intrinsic acid strength of the solids follows the order of H–ZSM-5 \approx H–mordenite \approx H– β > H–USY > SZT \approx H–Y. The solids were characterized by their hexane conversion activities at 553 K and 6.1 kPa hexane partial pressure. The reaction was shown to proceed predominantly by a bimolecular mechanism, while the reaction was first order in hexane and zero order in alkenes. The site-specific apparent rate constant of the bimolecular hexane conversion was shown to parallel the intrinsic acid strength of the samples, suggesting that the ratio of the apparent and the intrinsic activity, that is, the K_A' equilibrium constant of alkane adsorption on the hydrocarbon-covered sorption sites, is hardly dependent on the catalyst structure.

1. Introduction

Provided that the energy of all interactions between a weak base adsorbate molecule and its adsorption environment is negligible relative to the energy of its H-bonding to the hydroxyls of a solid acid, any parameter that characterizes the interaction parallels the OH deprotonation energy (DE) and, thereby, the intrinsic acid strength of the sites.¹⁻¹⁷ For instance. the adsorption-induced ¹H NMR chemical shift of the protons, $\delta_{\rm H}$, or the $\Delta \nu_{\rm OH}$ shift of the $\nu_{\rm OH}$ infrared (IR) band is related to the strength of H-bonding. Studies using adsorptives, such as CO, benzene, or CD₃CN, for probing the acid strength suggested that H-zeolites, including H–ZSM-5, H–mordenite, H– β , and H-Y, were much stronger Brønsted acids than sulfated zirconia (SZ).^{13–19} As far as zeolites and SZ are concerned, this result contradicted the found activities of the solids in the conversion of alkanes.^{16–19} Moreover, the adsorption heat of strong bases such as ammonia showed better correlation with the catalytic activity than $\delta_{\rm H}$ or $\Delta \nu_{\rm OH}$.¹⁹⁻²¹ These results inferred that catalytic activity was not determined solely by the acidity of the catalysts. Another plausible explanation is that the measured parameters were inappropriate to characterize the acidity, effective under the reaction conditions.

One important aspect of probing intrinsic Brønsted acidity is that the adsorptive base should have insignificant interaction with the solid except for the H-bonding to the OH groups.^{6,7} Spatial hindrance of adsorption must be also avoided.²² For the examination of microporous materials, the application of small diatomic molecules, such as CO, N₂, O₂, or H₂, are preferred because these adsorptives comply best with above requirements.^{2–12} The nitrogen has the advantage that it does not go through chemical changes on most catalysts. It is also preferable for IR spectroscopic examination because the N₂ gas is IR inactive, and therefore, it does not contribute to the spectrum.^{3–7,12}

Recently, significant progress was achieved in understanding the relationship between the alkane conversion activity and the acidity of H-zeolites.²³⁻²⁷ It was shown that adsorption of reactant alkane contributes to the apparent kinetics of alkane isomerization and cracking. Thus, the apparent rate constant, related to a single active site, cannot be expected to correlate with the intrinsic acid strength of the Brønsted acid sites. Attempts to determine intrinsic catalytic activities and to relate them to the intrinsic acid strengths led to conflicting results.²³⁻²⁶ Lunsford et al. ^{23,24} found that intrinsic activation energies of unimolecular hexane cracking were different for H-zeolites, having different structure and composition. However, this variation was not fully consistent with the variation of the intrinsic acidities of the catalysts, determined by the mentioned IR spectroscopic method. In contrast, Williams et al.^{25,27} claimed that the intrinsic acid strength of the active Brønsted sites were similar in different zeolites, and the different activities in the unimolecular alkane cracking could be accounted primarily for the differences in the alkane adsorption properties of the catalysts.

In most previous IR works, the spectra of the surface species, obtained from adsorption of said diatomic molecular probes, were recorded at low-temperature (<100 K) in order to get detectable coverage of the sorption sites. This temperature was far lower than that of the catalytic alkane conversions. At lower temperature, the mobility of the protons is lower and their acid strength is higher than at higher temperature.²⁸ In the present study, high-pressure DRIFT spectroscopy was used to study N2 adsorption over acid catalysts at 298 K. The obtained Δv_{OH} values were taken as a measure of the intrinsic acid strength of the Brønsted sites. Virtually identical Δv_{OH} values were obtained for high-silica zeolites, such as H-ZSM-5, H-mordenite, and $H-\beta$, and significantly lower for zeolite H-Y, SZ, and SZT. Unexpectedly, the apparent site-specific rate constant of bimolecular hexane cracking was found to show fair correlation with the intrinsic acidity of the catalysts.

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TABLE 1: Characterization of the Zee	lite	25
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type	composition	note		
NH ₄ -ZSM-5	(NH ₄) _{5.75} Na _{0.05} (AlO ₂) _{5.8} (SiO ₂) _{90.2}	prepared from Na, H-ZSM-5		
		(T-3ZIPC, Chem. Kombinat, VEB,		
		Bitterfeld-Wolfen, former GDR) by ion exchange		
NH_4-Y	$(NH_4)_{>54.6}Na_{<0.2}(AlO_2)_{54.8}(SiO_2)_{137.2}$	prepared from Na $-Y$ (Linde Co., I $(Z-Y62)$ by ion exchange		
NH ₄ -USY	$(NH_4) = 20.2Na = 1.7(FEA1) = 1.5(A1O_2) = 1.5(SiO_2) = 1.5$	LZ-102) by four exchange		
	(1114) <29.51 (u <1.7(21 11)24.5(110 2)51(010 2)101	EFAI = extra framework AI: the amount		
		of EFAl was taken from ref 60		
H-mordenite	H _{5.97} Na _{0.23} (AlO ₂) _{6.2} (SiO ₂) _{41.8}	LZ-M6, UOP		
$H-\beta$	$H_{4.68} Na_{0.02} (AlO_2)_{4.7} (SiO_2)_{59.3}$	Valfor CP, PQ Corp.		

2. Experimental Section

Materials. The NH₄-zeolites, used in the present study, were either commercial products or were obtained from Na-form zeolites by conventional ion exchange. The studied H-zeolites were either commercial products or were prepared from the NH₄-zeolites by in situ thermal deammoniation (Table 1).

The preparation method and the properties of the sulfated zirconia-titania (SZT) sample was described in ref 17. An equimolar mixture of Zr-*n*-propoxide/Ti-*i*-propoxide was hydrolyzed by NH₃ solution. The obtained precipitate was dried at 383 K. The dry gel was contacted with 0.25 M H₂SO₄ solution, dried again, and calcined in air at 823 K. The sulfate content and the specific surface area of the sample were 10.2 wt % and 258 m²/g, respectively. For comparison, zirconia (Z) and sulfated zirconia (SZ) samples were prepared from Zr-*n*-propoxide by following a similar preparation procedure. The SZ sample was shown to have much lower surface area than the SZT sample, but the surface-specific properties of the samples were found to be virtually the same.¹⁷

In the DRIFTS experiments, UHP grade (>99.995%) He, N₂, and O₂ were used after further purification. The helium flow was passed through a 77 K column that was filled with activated carbon. The N₂ and O₂ flows were contacted with dehydrated molecular sieve 5A adsorbent. In the catalytic experiments, analytical grade hexane (Aldrich, 99+ %) was used without purification.

DRIFT Spectroscopy. The DRIFTS measurements were carried out by using a Nicolet 5PC spectrometer equipped with a COLLECTOR II diffuse reflectance mirror system and a high-temperature/high-pressure DRIFTS cell (Spectra-Tech, Inc.). The sample cup of the cell was filled with finely powdered catalyst. The catalyst was heated to 773 K at a rate of 10 K/min in a 50 cm³/min flow of 50% O₂/N₂ at atmospheric pressure. At 773 K, the sample was contacted with the gas flow for 1 h, then the cell was flushed with a He flow for 10 min and cooled in the He flow to 293 K. In this treatment, the catalysts were dehydrated, the NH₄-form zeolites were also deammoniated and, thereby, converted into H-form.

A single-beam spectrum was determined while flushing the catalyst sample in the DRIFTS cell with pure helium. Then the He flow was switched to a flow of 50 cm³/min N₂ flow. After flushing the cell for 5 min, a second single-beam spectrum was taken up. Under identical conditions, a single-beam spectrum was recorded also with an alignment mirror in the sample cup. The spectrum of the catalyst was obtained as the ratio of the single-beam spectra recorded for the catalyst and the alignment mirror. The spectrum of the adsorbed N₂ and the adsorption-induced spectral changes were obtained by generating the ratio of the single-beam spectra of the catalyst, in contact with N₂ and He. The gas pressure was controlled between 1 and 9 bar by using a pressure regulator, downstream of the cell. All spectra

were obtained at 298 K by averaging 512 scans at a nominal resolution of 2 cm⁻¹. Because the level of the DRIFTS signal depends on the scattering coefficient, which is function of the particle size and the packing density of the sample, only qualitative comparisons of the band intensities were made for the different samples. However, the quantitative evaluation of the signals is justified for a single sample at different gas loading.

Catalytic Hexane Conversion. The catalyst powder was compressed to pellets, and the pellets were crushed and sieved. The 0.25-0.50 mm sieve fraction was used as a catalyst. Depending on the activity, 10-500 mg of catalyst particles were filled into a quartz tube microreactor (i.d. 4 mm). The catalyst was activated in situ in the reactor in an O₂ flow of 20 cm³/min at 773 K overnight. Then the reactor was flushed with a 20 cm³/min He flow and cooled to the 553 K temperature of the reaction. The reaction was started by switching the He flow to a flow of a hexane/He mixture. The mixture was prepared by saturating a He flow with hexane vapor at 273 K. Thus, the hexane partial pressure was 6.1 kPa. The hexane feed, fed on a unit mass of the catalyst (*F/W*, μ mol g⁻¹ s⁻¹), was varied to get conversions below about 20%. The reactor effluent was analyzed by gas chromatography (GC) first after 5 min time on stream (TOS) and then in about 15-min intervals. The total hexane conversion, X, was calculated from the composition of the reactor effluent with exclusion of the n-hexane as $X = (1/6) \sum_{i=1}^{6} jX_i$, where X_i and j are the mole fraction and the carbon number of the *i*th component, respectively. The activity of the catalyst on stream decreased in time. Initial conversions (X_0) , were determined by extrapolating the conversion results to zero TOS, using the empirical X vs TOS relation, applied also by Williams et al.²⁶ Assuming that the reaction is first order in the reactant hexane (vide infra) the apparent rate constant of the reaction, $k_{B,app}$, was obtained as slope of $-\ln(1$ $-X_0$) vs *W/F* plots (Figure 1)

3. Results

The N₂ adsorption coverage of the sorption sites was increased by increasing the nitrogen pressure above the catalyst. The increasing coverage was paralleled by the erosion of the original ν_{OH} bands and by the concomitant rise of new ν_{OH} bands, shifted to lower frequencies (Figures 2–7). The appearance of the shifted bands indicated that the H-bonding of N₂ weakened the O–H bonds of some hydroxyl groups. As a rule, the OH groups in a H-bond interaction have a higher absorption coefficient and give a broader IR band than the unperturbed hydroxyls. From the spectra, recorded at different N₂ pressures, it is sometimes difficult to resolve all the bands, which are diminishing and emerging due to N₂ adsorption (Figures 2A to 7A). However, if only the adsorption-induced spectral changes are presented, these bands can be clearly distinguished (Figures 2B to 7B).



Figure 1. First-order plots for *n*-hexane isomerization and cracking at 6.1 kPa *n*-hexane partial pressure and 553 K over H–ZSM-5, H– β , H–mordenite (H–MOR), H–USY, H–Y, and sulfated zirconia–titania (SZT). The insert shows an enlarged plot for the high-silica zeolites.



Figure 2. DRIFT spectra of zeolite H–ZSM-5 in the ν_{OH} frequency region. Spectra (A) were recorded at 298 K, while the sample was in equilibrium with nitrogen at 1, 2, 4, 6, and 8 bar or under He at 1 bar. Spectra (B) were obtained by subtracting the spectrum recorded in He from each spectrum recorded in N₂. An arrow points to the band of the bridging OH groups, eroding due to N₂ adsorption, and to the concomitantly developing, red-shifted ν_{OH} band.

Zeolite H–ZSM-5 and H–mordenite. Two characteristic ν_{OH} bands were observed. The band near to 3745 cm⁻¹ was assigned to the ν_{OH} mode of terminal silanol groups. Terminal silanol groups can be present either on the external surface of the zeolite crystallites or at framework defects. At about 3610 cm⁻¹, the stretching band of those OH groups appeared that are bridging between framework Al and Si atoms (Figures 2A and 3A).^{3,4,22,29} The N₂ adsorption resulted in a 19–20 cm⁻¹ red-shift of the silanol band. For silica fume (Aerosil), the corresponding shift was found to be only 11 cm⁻¹ (not shown). The adsorption-induced drop of the stretching vibration frequency was significantly higher for the bridging hydroxyls. A new band appeared in the spectrum of both zeolites at 3529 cm⁻¹, corresponding to a red-shift of 82–83 cm⁻¹ (Figures 2B and 3B).

In previous studies, the slightly asymmetrical ν_{OH} band of H-mordenite was resolved to component bands at 3616 cm⁻¹ and at about 3590 cm⁻¹, using a curve-fitting computer program.^{3a,30} The bands were assigned to the hydroxyl groups present in larger main channels, having 12-membered rings (12-MR), and in narrow 8-MR pores or at the 8-MR access to the side pockets of the main channel.^{3a,31} The integrated absorbance ratio of the high-frequency and low-frequency component bands



Figure 3. DRIFT spectra of zeolite H-mordenite (A) under N_2 at 1-8 bar pressures and under He at 1 bar, and (B) the difference of these spectra. Spectra correspond to those in Figure 2.



Figure 4. DRIFT spectra of zeolite $H-\beta$ (A) under N₂ at 1–8 bar pressures and under He at 1 bar, and (B) the difference of these spectra. Spectra correspond to those in Figure 2.

was 2:1. There is no doubt that hydroxyl groups in the main channels can H-bond nitrogen, but the participation of the 8-MR hydroxyls in the N₂ adsorption is a matter of discussion.^{3a,30} In the present study, neither the unperturbed nor the shifted stretching band of the bridging OH groups of H-mordenite, shown in Figure 3, was resolved to components.

Zeolite H–Y and H–USY. Besides the band of the silanol groups at 3743 cm⁻¹, the bridging OH groups in the α and β cages of zeolite H–Y give characteristic bands at 3640 and 3545 cm⁻¹, respectively (Figure 5A).³² The OH band structure is more complex for the ultrastabilized H–Y, referred to as H–USY because, in this zeolite, a fraction of the bridging OH groups is under the influence of cationic extraframework aluminum (EFAI) species.^{33,34} The bands at 3625 and 3604 cm⁻¹ were unequivocally assigned to OH groups in the large supercages (α cages), while those at 3545 and 3525 cm⁻¹ were assigned to hydroxyls in the small sodalite cages (β cages). The bands at 3604 and 3545 cm⁻¹ were attributed to hydroxyl groups, affected by the presence of the Lewis acid EFAI species (Figure 6).³⁵

On H-bonding N₂ the silanol stretching frequencies suffered a 15–18 cm⁻¹ red-shift (Figures 5 and 6). Generally larger redshifts were detected for the bridging OH groups, present in the α cages, than for those in the β cages. The shifts were 45 and 25 cm⁻¹, respectively, for those hydroxyls, which were not perturbed by the electronic effect of the EFAl species. Those hydroxyls, which were under the influence of cationic EFAl



Figure 5. DRIFT spectra of zeolite H-Y (A) under N_2 at 1–8 bar pressures and under He at 1 bar, and (B) the difference of these spectra. Spectra correspond to those in Figure 2.



Figure 6. DRIFT spectra of zeolite H–USY (A) under N_2 at 1–8 bar pressures and under He at 1 bar, and (B) the difference of these spectra. Spectra correspond to those in Figure 2.

species, suffered a larger frequency shift. The 3604 cm⁻¹ band shifted by about 67 cm⁻¹ to 3537 cm⁻¹, while the band of the β -cage hydroxyls at 3545 cm⁻¹ shifted by about 45 cm⁻¹ to 3500 cm⁻¹ (Figure 6). The larger shifts are in line with the higher acid strength of these hydroxyls.³⁶ The N₂ adsorption and the Brønsted acidity of H–faujasites were discussed in a recent DRIFT spectroscopic study.³⁵

Zeolite $H-\beta$. In accordance with previous reports,^{37,38} bands of silanol and bridging hydroxyl groups were observed at 3744 and 3609 cm⁻¹, respectively (Figure 4A). The additional band at 3663 cm⁻¹ was associated with the OH groups linked to EFAI species.^{32,33} A weak OH band was also detected as a shoulder at 3780 cm⁻¹ (Figure 4A, not labeled). This band was suggested by Kiricsi et al.³⁷ to stem from the intermediates of the EFAI formation process.

The adsorption of nitrogen affected all the ν_{OH} bands. The bands of the Si- and EFAI-bound hydroxyls shifted to lower frequencies by 17–18 cm⁻¹. Two shifted bands were generated from the bridging OH groups: one at about 3570 cm⁻¹ and another at 3529 cm⁻¹ (Figure 4B). Thus, the red-shifts, brought about by N₂ adsorption, were 39 cm⁻¹ and 80 cm⁻¹, respectively. The results suggest that bridging hydroxyls of the H– β zeolite can be characterized by two distinctly different acid strengths. Because the bands resemble those of the α -cage hydroxyls of H–USY, it was suggested that the acid strengths of some of hydroxyls were enhanced by Lewis acid species.³⁹



Figure 7. DRIFT spectra of sulfated zirconia–titania (A) under N_2 at 1–8 bar pressures and under He at 1 bar, and (B) the difference of these spectra. Spectra correspond to those in Figure 2.

Sulfated Zirconia–**Titania** (**SZT**). The major absorption bands, observed in the OH region, were at 3643 cm⁻¹ and at 3741 cm⁻¹ (Figure 7A).

Zirconia (Z) and sulfated zirconia (SZ) samples were also investigated for comparison (not shown). The $\nu_{\rm OH}$ bands of the Z were at 3772 cm⁻¹ and at 3668 cm⁻¹. Except for the lower band intensities, the spectrum of the SZ was similar to that of SZT. The 3643 cm⁻¹ band was assigned to acidic OH groups, while the 3741 cm⁻¹ band was assigned to nonacidic OH groups.^{13,14}

N₂ adsorption induced a 14–15 cm⁻¹ red-shift in the OH stretching frequencies of the Z sample. The small shift reflects the weak acid character of these OH groups. In contrast, the shifts of the 3643 cm⁻¹ and the 3741 cm⁻¹ bands of the SZT were 48 and 18 cm⁻¹, respectively (Figure 7). It is also important to note that the $\nu_{S=O}$ band of the SZT sample at 1391 cm⁻¹ was hardly effected by the N₂ adsorption.

Spectrum of the Adsorbed N₂. The vibration transitions of homonuclear diatomics, such as N₂, are IR inactive in the gas phase. However, adsorption in the zeolite cavities lowers the symmetry of the molecule and results in the appearance of an interaction-induced IR spectrum.^{3-10,12,40}

The integrated absorbance of $\nu_{\rm NN}$ stretching band in the 2300–2350 cm⁻¹ frequency region was found to increase parallel with the erosion of the hydroxyl bands and the appearance of the corresponding shifted OH bands, indicating that the observed changes are related to the interaction between the OH groups and the N₂ molecules. The changes were fully reversible for all the studied samples. These observations are in agreement with earlier findings.^{3,4,7–9}

Spectra of nitrogen adsorbed over H-zeolites and SZT are shown in Figure 8. The 2330 cm⁻¹ Raman frequency of the gas-phase N_2 is given as a reference value.⁴¹ The band of N_2 , weakly bound to silica (Aerosil), was at 2332 cm⁻¹ (not shown), i.e., hardly apart from the gas-phase Raman frequency.

Two $\nu_{\rm NN}$ absorption bands were distinguished (Figure 8), a weak band in the 2340–2360 cm⁻¹ region and a major band near to 2330 cm⁻¹. The weak band, which could not be traced only in the spectrum of zeolite H–MOR and SZT, has been assigned to N₂ adsorbed on Lewis acid sites. The band at about 2330 cm⁻¹ stems from N₂, adsorbed on Brønsted acid sites.^{3–6,8} From the major band, two component bands could be resolved at frequencies slightly above and below the gas-phase Raman frequency by using a curve fitting computer program (Figure 8, thin lines).



Figure 8. The DRIFT spectra of N₂ adsorbed on H–ZSM-5, H–mordenite, H– β , H–Y, H–USY, and sulfated zirconia–titania at 8 bar pressure in the ν_{NN} frequency region. Component bands were resolved by using a curve fitting computer program.

An absorption band at 2338 cm⁻¹ with a shoulder at 2328 cm⁻¹ was observed on the spectrum of SZT. Interestingly, weak $\nu_{\rm NN}$ bands were obtained at the same frequencies from N₂ adsorption on Z (not shown), while the N₂-induced $\Delta\nu_{\rm OH}$ was much smaller for Z than for SZ or SZT.

Catalytic Hexane Conversion. When in contact with the hexane flow, catalysts became saturated with species formed from hexane. Unconverted hexane appeared in the product mixture only after an initial transient period of about 2-3 min TOS. After that, each catalyst was rapidly losing activity. The comparison of the catalytic activities involves some uncertainty due to the activity change and the different time dependence of this change. An extrapolation procedure was applied to the results, obtained at different space velocities, to estimate the conversions at zero time on stream. The conversion and product distribution data, given in Table 2, were obtained at 5 min TOS. Alkene product could not be detected. Pentane was formed over each catalyst, but much less, if any, methane was found compared to pentane. Propane and butanes were the major products. Butanes were always in large excess to ethane. The high selectivity for isobutane formation indicated that isomerization and secondary cracking processes also affected the product selectivity. The complex product distribution suggests that, at the applied relatively low reaction temperature and high hexane pressure (553 K and 6.1 kPa), the bimolecular mechanism prevails.

The high-silica zeolites, namely H-ZSM-5, H-mordenite, and $H-\beta$, were more active than the rest of the studied catalysts. The hexane conversion over H-USY and SZT was comparable to that over the most active $H-\beta$, but at 10 and 25 times longer space times, respectively. Under similar reaction conditions, the activity of H-Y was hardly measurable (Table 2). The firstorder plots of the high-silica zeolites are very close to each other (Figure 1). Zeolite H-Y showed low activity. The apparent bimolecular rate constant, $k_{B,app}$, of zeolite H–USY and sample SZT was intermediate between those of the high-silica zeolites and H-Y (Table 3). Because only the 12-MR pores (0.67 nm \times 0.70 nm) of H-mordenite are accessible for alkanes, the pore system of mordenite is one-dimensional with regard to the alkane transport. Zeolite $H-\beta$ has a three-dimensional system of pores, having 12-MR apertures. The comparable activities of these catalysts (Figure 1 and Table 3) substantiate that the diffusion effect cannot reduce significantly the catalytic efficiency of the H-mordenite. Because the number of the effective active sites (S') is not known, exact site-specific

activities could not be calculated and compared. It was assumed that the number of active sites is related to the total number of Brønsted acid sites in the catalyst. The total number of Brønsted acid sites was taken as equal to the framework Al content of the zeolites and to the sulfate content of the SZT. Because the fraction of the sites, which are accessible for the reactant hexane and also active in the reaction, is not known, apparent sitespecific bimolecular rate constants were determined by relating the apparent bimolecular rate constant, $k_{B,app}$, to the aluminum content of the catalyst sample (Table 3).

4. Discussion

Understanding the relation of the acidity and the catalytic properties of catalysts helps in learning about the underlying reasons of the catalytic activity. However, it is difficult to bridge the gap between the equilibrium thermodynamic concept of acidity and the composite kinetic concept of catalytic activity.⁴²

The free energy change of the reaction between different solid acids and a base is often used to locate the acid on an acidity scale. However, this energy is determined by all the adsorption interactions. A Lewis base can coordinate to Lewis acid sites, polarize O-H bonds, or even abstract protons from OH groups. Van der Waals forces and, in some cases, additional H-bonds, contribute to the binding of the base to the surface of a solid. Latter effects, generally referred to as solvating and medium effects, are responsible for the deviation of the intrinsic and the measured acidity of the OH groups. The medium effects depend on the structure and composition of the adsorbent and the base, moreover, on the measurement conditions, such as the temperature and the coverage. For example, the effects are more pronounced in micropores than in larger pores or over open surfaces. As a result, solids can present varying relative acidities against different bases.⁴ This is particularly important to keep in mind when we compare the acidities of very different solids, such as zeolites and sulfated zirconia, on the acidity scale of a given base and want to draw conclusions about the behavior of the same solids against another base, which can be, for instance, a reactant in an acid-catalyzed reaction. In relation to a catalytic reaction, the catalyst acidities are best characterized by the interaction of the catalysts with the reactant itself. However, an acidity scale can be established that is independent of the chemical nature of any base on the bases of the deprotonation energy (DE) of Brønsted acid sites. The difficulty of using the DE scale is that the DE of a real catalyst cannot be obtained by theoretical calculation; moreover, the experimental characterization of intrinsic catalyst acidity is still a matter of discussion.

The catalytic performance can be correlated with the acidic property if the same catalytic mechanism dominates over each compared catalyst and the correlation properly includes all adsorption and diffusion effects that contribute to the activity.⁴³ Thus, usually, not the apparent, but the intrinsic parameters of the reaction, such as the intrinsic rate constant or activation energy of an acid-catalyzed reaction, are the sufficient measures of the intrinsic acid strength.

The Intrinsic Acid Strength of the Catalysts. It was suggested that the $\Delta \nu_{OH}$ shifts of the ν_{OH} IR band, induced by N₂ adsorption, was proportional with the unperturbed, intrinsic Brønsted acid strength of the hydroxyl groups.^{6,7,12} Thus, the $\Delta \nu_{OH}$ is a parameter that shows correlation with the deprotonation energy of the acid.¹ This infers that, besides the H-bonding interaction with the acidic hydroxyl groups, any adsorption interaction of the N₂ is virtually negligible. Usually, low temperature (<100 K) was used to get a detectable amount

TABLE 2: Hexane Isomerization and Cracking over H-Zeolites and Sulfated Zirconia-Titania^a

	-	,				
	H-ZSM-5	H-mordenite	$H-\beta$	H-Y	H-USY	SZT
$F/W, \mu \text{mol} \cdot \text{g}_{\text{cat.}}^{-1} \text{ s}^{-1}$	20	20	20	0.8	2.0	0.8
total conversion, mol %	5.82	8.52	12.68	0.86	16.39	15.41
cracking, mol %	4.99	6.03	7.35	0.23	6.93	11.13
isomerization, mol %	0.83	2.48	5.33	0.63	9.46	4.28
		Product Distribution	n, mol %			
CH_4	< 0.02	2.4	< 0.02	< 0.02	1.1	< 0.02
C_2H_6	0.9	< 0.02	0.4	< 0.02	< 0.02	1.0
C_3H_8	25.7	25.9	14.1	10.1	17.1	37.4
C_4H_{10}	25.9	15.8	6.2	0	3.5	3.9
$i-C_4H_{10}$	20.6	18.5	29.0	12.1	19.0	26.3
$C_{5}H_{12}$	10.9	7.2	5.7	6.1	1.8	1.7
$i-C_5H_{12}$	7.0	9.7	12.0	6.1	10.7	10.8
$i-C_6H_{14}$	9.0	20.5	32.6	65.6	46.8	18.9

^{*a*} The space velocity of hexane, F/W, was decreased for the less active catalysts in order to get measurable conversions. The reaction was carried out at a hexane partial pressure of 6.1 kPa at 553 K. The conversions in cracking and isomerization reactions, as well as the total conversion, were calculated from the effluent composition, determined at 5 min time on stream as $X = (1/6) \sum_{i=1}^{6} jX_i$, where where X_i and j are the mole fraction and carbon number of the *i*th component, respectively.

TABLE 3:	Activity of Bimolecular Hexane Conversion and
Intrinsic Ac	idity (Δv_{OH}) of Zeolite and Sulfated
Zirconia-T	itania Catalysts

	Si/Al	$k_{\text{B,app}} = k_{\text{B}}K_{\text{A}}'S',^{a}, \mu \text{mol} \cdot g_{\text{cat.}}^{-1} \text{s}^{-1}$	$k_{\mathrm{B,app}}/S' \times I0^{3,b}$ s ⁻¹	$\Delta \nu_{\rm OH}$ for acidic OH groups, ^c cm ⁻¹
$H-\beta$	12.6	7.38	6.03	39; 80
H-ZSM-5	15.5	6.11	6.06	83
H-mordenite	6.7	7.06	3.28	82
H-USY	$2.9(5.2^d)$	0.60	$0.13 (0.24^{e}) (0.29^{j})$	45;g 67h 25;i 45j
H-Y	2.5	0.025	0.005	45 ^g
SZT	n. a. ^k	1.32	1.24	48

^{*a*} Apparent bimolecular rate constant, calculated as the slope of $-\ln(1 - X_0)$ vs *W/F* plots of Figure 1. ^{*b*} Apparent site-specific bimolecular rate constant, obtained by relating the $k_{\text{B,app}}$ value to the Al content of zeolites or to the sulfate content of the SZT, expressed in μ mol·g_{cat}⁻¹. ^{*c*} Shift of the ν_{OH} frequency of the acidic hydroxyl groups, induced by N₂ adsorption at 298 K. ^{*d*} Si to framework–Al ratio. ^{*e*} The $k_{\text{B,app}}$ was related to the framework Al content. ^{*f*} The $k_{\text{B,app}}$ was related to the EFAl content. ^{*s*} $\Delta \nu_{\text{OH}}$ of α -cage hydroxyls. ^{*h*} $\Delta \nu_{\text{OH}}$ of β -cage hydroxyls under the influence of EFAl species. ^{*i*} $\Delta \nu_{\text{OH}}$ of β -cage hydroxyls under the influence of EFAL species. ^{*k*} Note: n.a. = not applicable.

of adsorbed N₂ at the applied relatively low pressure (<1 bar). In harmony with IR and ¹H NMR results, theoretical calculations suggested that the mobility of the bridging protons in H-zeolites, their H-bonding to neighboring framework oxygen atoms, and as a consequence, their acid strength, depend on temperature.²⁸ At higher temperatures, H-zeolites are weaker acids than at lower temperatures, but show more homogeneous acid strength distribution. At low temperature, the reduced mobility of the adsorbate and the proton may hinder the adsorption on the lessaccessible sites. For example, it was found that even small molecules, like N₂, O₂, or CO, did not interact with OH groups located in the small sodalite cages of Y-zeolite.^{5–7,24} In contrast, these hydroxyls protonated the much larger pyridine molecule at room temperature.^{33,36} It was argued that the higher proton affinity (PA) of the adsorbate and the higher adsorption temperature made the interaction of pyridine and the β -cage hydroxyls feasible.24,44

The temperature, that must be low to get detectable amount of adsorbed N_2 at low adsorption pressures, can be increased if the equilibrium pressure is also increased. In the present study, DRIFT spectra obtained from adsorption of nitrogen was recorded at room temperature in the 1–9 bar pressure range. The N_2 was found to coordinate to the bridging OH groups of H-zeolites and to the OH groups of zirconia. In agreement with results of low-temperature IR measurements, for instance with those in ref 7, N₂ was found to H-bond also to the very weak acid silanol groups. However, even at room temperature, the β -cage protons of zeolite H–Y were of limited accessibility for N₂. It can be understood if we consider that the nitrogen molecule has a kinetic diameter of 0.36 nm, while the diameter of six-member ring windows on the β -cage cage is 0.26 nm. Because the PA of nitrogen is only 493.8 kJ mol⁻¹, much smaller than the 928.8 kJ mol⁻¹ PA of pyridine, N₂ cannot pull out protons from the β -cages. Surprisingly, a very small fraction of the β -cage hydroxyls was found to H-bond N₂. This was attributed to the partly defected faujasite structure of the zeolite Y sample.³⁵ A relatively large number of the β -cage hydroxyl groups were accessible in the zeolite H–USY, indicating that ultrastabilization generates a strongly defected faujasite structure.^{35,45}

Lewis acid sites are easily distinguished from Brønsted acid sites in zeolite samples by analyzing the $v_{\rm NN}$ absorption bands in the 2340–2350 cm^{-1} frequency region^{3-6,8}. The dominant band around 2330 cm⁻¹ was assigned to Brønsted-bound nitrogen. The interpretation of the 2330 cm⁻¹ band, containing more than one component, is not straightforward. On adsorption, the stretching band of diatomic homonuclear molecules, like N₂, becomes IR active and shifts relative to the Raman band of the gas molecule. Cohen de Lara et al.46,47 associated the shift with the orientation of the adsorption-induced dipole moment with respect to the electric field. Accordingly, the shift is in the direction of the higher frequencies (blue-shift) if the molecular axis of the adsorbed molecule is oriented parallel with the **E** electric field, and is in the direction of lower frequencies (red-shift) if the molecule is oriented perpendicular or inclined to the direction of **E**.

From adsorption at low-temperature on H-mordenite, $\nu_{\rm NN}$ component bands were obtained at 2333 and 2330 cm⁻¹, which were assigned to adsorption on the Brønsted acid sites in the main mordenite channels and on the less-accessible acid sites in the side pockets, respectively.^{30a} At higher N₂ coverage, a third component was observed at 2325 cm⁻¹, which was assigned to N₂ bound to silanol OH groups.^{7,44,30a}

At variance with above results, we found component bands at 2330 and 2325 cm⁻¹, having an integrated absorbance ratio of about 2:1 (Figure 8). One of the v_{NN} component bands of N₂, bound to the Brønsted acid sites of H-mordenite, is near to the gas-phase Raman frequency, while the other is at a lower frequency (Figure 8). In accordance with the band assignment of Cohen de Lara et al.,^{46,47} the higher-frequency band could reflect parallel orientation of the induced N₂ dipole to the electric

TABLE 4: Adsorption-Induced Shift of the OH bands $(\Delta v_{OH}, \text{ cm}^{-1})$ Assigned to Acidic OH Groups in Different Zeolites and Sulfated Zirconia

	C ₆ H ₆ (298 K)	CO (77 K)	N ₂ (77 K)	N ₂ (298 K) ^m
H-ZSM-5	350 ^{<i>a</i>,<i>b</i>}	308-340 ^{d,e,f}	121-122 ^{e,l}	83
H-mordenite		290-389 ^{f,g}	107^{l}	82
$H-\beta$	352-365 ^c	$307 - 319^{e,h}$	$119 - 126^{e,l}$	39; 80
H-Y	$280 - 320^{a,b}$	273-296 ^{d,e,i}	93-110 ^{e,l}	45
H-USY		327-382 ^{d,e}	139 ^e	45; 67 (α-cage) 25; 45 (β-cage)
SZ or SZT	$185 - 200^{a,b}$	$140 - 220^{j,k}$	-	48

^{*a*} Reference 15. ^{*b*} Reference 17. ^{*c*} Reference 37. ^{*d*} Reference 50. ^{*e*} Reference 24. ^{*f*} Reference 61. ^{*s*} Reference 11. ^{*h*} Reference 8. ^{*i*} Reference 2. ^{*j*} Reference 14. ^{*k*} Reference 13. ^{*l*} Reference 4. ^{*m*} This work.

field in the main channels, while the lower-frequency band may correspond to adsorption in inclined orientation. The inclined orientation could appear because of precessional motion of the adsorbate molecule around the anchoring sorption center. This motion may be more intense if the interaction is weaker and concerns relatively more molecules at higher temperatures.⁴⁷ The abundance of N₂, bound inclined, can be increased also by spatial constraints around the sorption sites, for instance around the Brønsted acid sites in the side pockets of H–mordenite.

The band at 2325 cm⁻¹, observed by Zecchina et al.^{7,30a} and Corma et al.,¹⁹ was well below the 2330 cm⁻¹ gas-phase Raman frequency. Instead of considering the possibility of red-shift, the frequency of 2324 cm⁻¹ (ref 7) or 2321 cm⁻¹ (ref 30a) was selected as a reference value. The 2324 cm⁻¹ was obtained as the average of the values, calculated for the condensed state, and measured in rare gas matrixes.⁷ The 2321 cm⁻¹ is the measured Raman frequency of N2 adsorbed on silicalite, that is, a purely siliceous ZSM-5.30a All the ν_{NN} component bands were then considered as blue-shifted. We found that the $v_{\rm NN}$ band of N₂, adsorbed on SiO₂ (Aerosil) at room temperature, appeared blue-shifted by 2 cm⁻¹ relative to the 2330 cm⁻¹ reference frequency. Result show that, in the absence of spatial constraints, N₂ is bound with a molecular axis parallel to the electric field on the surface of SiO₂ and a positive shift can be observed. In our opinion, it is more rational to use the gasphase Raman frequency as a reference value and attribute any red-shift to inclined orientation of the molecule with respect to the electric field of the adsorbing surface, as suggested by Cohen de Lara.47

Downward- and upward-shifted $\nu_{\rm NN}$ component bands, similar to those found for H-mordenite, were observed on all the studied samples (Figure 8). The assignment of the component bands to different Brønsted acid sites seems to be ambiguous at present. Unexpectedly, two $\nu_{\rm NN}$ component bands were obtained from adsorption on the mesoporous sulfated zirconia-titania sample (Figure 8). Adsorption of N₂ on the nonsulfated zirconia, not containing strongly acidic OH groups, gave two similar bands. The bands below and above the Raman frequency indicate that the N₂ is adsorbed with the molecular axis having both parallel and inclined orientation relative to the electric field. For the studied solid acids having different structures, no correlation was found between the shifts of the corresponding $\nu_{\rm NN}$ and $\nu_{\rm OH}$ bands.

In Table 4, $\Delta \nu_{OH}$ data are given for different acid-base interactions. Our results are shown together with related data, collected from the literature, for adsorptives such as benzene (PA = 750.4 kJ mol⁻¹), CO (PA = 594.0 kJ mol⁻¹), and N₂ (PA = 493.8 kJ mol⁻¹). The small differences in the corresponding $\Delta \nu_{OH}$ shifts can be attributed to differences of the samples, studied in different laboratories. From the data, a

consistent picture emerges for the zeolites. The H-ZSM-5, H-mordenite, and H- β contain Brønsted acid sites, having nearly identical acid strength. These zeolites are stronger acids than zeolite H-Y. Some hydroxyls of the H-USY have significantly stronger Brønsted acidity than the bridging hydroxyls of zeolite H-Y. Studies testing the acidity of sulfated zirconia and sulfated zirconia-titania by using benzene and CO as a basic adsorptive suggest that these materials are weaker Brønsted acids than any of the mentioned zeolites. In contrast, zirconia samples showed similar acid strength against nitrogen than zeolite H-Y. The acidity of the samples against the weakest base nitrogen was compared with the activity of the catalysts in the isomerization and cracking of hexane. Higher activity was obtained for the samples, characterized by larger $\Delta v_{\rm OH}$ (Table 3). However, the apparent rate constant of the bimolecular hexane conversion showed variance for the most active high-silica H-zeolites, characterized by similar intrinsic acid strength. These differences may come from real differences in the intrinsic activities of the active sites in the different zeolites or, more probably, from the fact that the number of active sites is neither equal nor proportional with the total number of the Brønsted acid sites.

On adsorption, a Lewis base can coordinate to Lewis acid sites, polarize the O-H bonds, or even abstract protons from the OH groups. Van der Waals forces and, in some cases, additional H-bonds, contribute to the stabilization of the base on the surface. Latter effects, generally referred to as solvating and medium effects, are responsible for the deviation of the intrinsic and the measured acidities. The medium effects are more pronounced in micropores than in larger pores or on open sufaces. The adsorption of a base on a solid acid must increase the electron density on the conjugated base of the acid and, thereby, affect both the basicity of the adsorbate and the acid strength of the Brønsted acid sites. The $\nu_{S=O}$ band of the sulfate species in the sulfated zirconia samples was found to indicate these changes.^{13,17} If the electron density in the S=O bond increases, the bond loses its covalent character and becomes more ionic. As a result, the $\nu_{S=O}$ band shifts to lower wavenumbers. It has been suggested that this shift takes place on the inductive effect of the adsorbate, bound to coordinatively unsaturated Zr4+ surface sites.13,48 The extent of the shift depends on the basicity of the adsorptive. The adsorption of benzene induced a 15 cm⁻¹ $\Delta \nu_{S=O}$ red-shift.¹⁷ Upon CO adsorption, the shift was 14 cm⁻¹.¹³ In contrast, adsorption of N₂ on sulfated zirconia-titania resulted in about a 1 cm⁻¹ redshift of the $v_{S=0}$ frequency. These results unambiguously show that the basicity of the conjugate base increases during the interaction with benzene and CO, while N2 virtually does not affect the conjugate base of the Brønsted acid. From this aspect, N_2 can be considered as a good basic probe to characterize the intrinsic acid strength of the Brønsted sites.

According to the extent of the $\Delta \nu_{OH}$ shift, measured by roomtemperature adsorption of N₂ at elevated pressures (Table 4, last column), the following order of intrinsic Brønsted acidity was obtained: H–ZSM-5 \approx H–mordenite \approx H– β > H–USY > SZT \approx H–Y. For similar samples, using molecular probes of different basicity, Paze et al.⁸ obtained linear correlation between the $\Delta \nu_{OH}$ of the stretching band of the strong Brønsted acid groups and that of the silanol groups. These plots, corresponding to BHW plots,⁴⁹ suggested the same acidity order. It was also concluded that the Brønsted sites of H–ZSM-5, H–mordenite, and H– β are energetically uniform.^{4,24} However, the acid strength measurements of the present work do not support the uniformity of the H– β hydroxyls. By using the IR method and CO or N₂ as an adsorptive probe, Kotrel et al.²⁴ concluded that H–USY was a stronger Brønsted acid than any of the mentioned zeolites. However, the activity of the H–USY in the hexane isomerization and cracking was in conflict with this finding.^{24,50} The present study seems to resolve this contradiction. The $\Delta \nu_{OH}$ shift, induced by N₂ adsorption, was smaller for H–USY than for H– β , which is in agreement with the hexane conversion activities (Table 3).

The conflicting results seem to rise from the difficulty of assigning the corresponding original and shifted v_{OH} IR bands if the OH envelope is as complex as that of the H-USY (Figure 6). In this relation, it is important to notice that H-USY is a defective structure wherein the β -cage hydroxyls are accessible both for small adsorbate probe molecules and reactants.^{45,51,52} To get the right band assignment, our understanding of the v_{OH} band structure of zeolite H-Y was useful.35 In the H-USY, some of the OH groups are inductively affected by cationic EFAI species. Therefore, the spectrum shows four IR bands. Instead of the four additional bands, expected to be obtained upon N₂ adsorption, only three new bands could be resolved (Figure 5B). The band at about 3500 cm⁻¹ was attributed to the overlapping shifted bands of the β -cage hydroxyls. The band shift of β -cage hydroxyls is generally smaller than that of α -cage hydroxyls. This finding is in accordance with the conclusion of Biaglow et al. ⁵³ that the hydroxyls in the smaller β -cage are weaker Brønsted acids than those in the larger α cage. The acidity of hydroxyls can be affected by H-bonding interactions with the framework oxygen atoms. This interaction is obviously more extensive in the β than in the α cage of zeolite H–Y.^{10,54}

Activity-Acidity Relations. Recent studies of hexane conversion over H-zeolites demonstrated that products could be formed in both unimolecular and bimolecular processes. The kinetics of the reaction was described by the Langmuir rate law.²⁶ The reaction rate (r) was given as

$$r = k_{\rm U}\Theta_{\rm A} + k_{\rm B}\Theta_{\rm E}\,p_{\rm A} \tag{1}$$

where $k_{\rm U}$ and $k_{\rm B}$ are the intrinsic unimolecular and bimolecular rate constants, Θ_A and Θ_E represents the alkane and alkene coverage of the active sorption sites, respectively, while p_A is the hexane partial pressure. It was shown that, at low conversion and alkane partial pressure, the alkene coverage is low and the unimolecular mechanism dominates.²³⁻²⁷ At low coverage, the Henry rule applies and $\Theta_A = K_A p_A$, where K_A is the equilibrium constant of the hexane adsorption. Thus, in accordance with the experimental findings, the reaction is first order in the concentration of the reactant, and the reaction rate is proportional with an apparent rate constant $k_{U,app} = k_U K_A$. The appearance of methane and ethane among the alkane products and formation of some hydrogen is characteristic of the unimolecular cracking process. Also, hydrogen and alkanes are formed in an amount close to equimolar to the alkenes. Eventual alkene excess indicates significant β scission of the carbenium ion intermediate of the reaction.

The product distribution of the unimolecular cracking process can be interpreted by the protolysis of C–C and C–H bonds. The process steps are alkane adsorption (eq 2), protonation and dehydrogenation/cracking (eq 3), and alkene desorption (eq 4)

$$A \stackrel{K_A}{\longleftrightarrow} A_a \tag{2}$$

where A stands for the reactant alkane, CR_2H_2 . The reactant, adsorbed on the catalyst, is given as A_a . The protonation rate

of A_a governs the rate of carbenium ion and product formation.

$$A_{a} + H^{+} \xrightarrow{k_{U}} [A^{+}] \xrightarrow{k_{U}} E^{+} + {H_{2} \choose a}$$
(3)

Symbol A⁺ represent the transition state of the reaction that, as a comfortable convention, can be visualized as protonated alkane $CR_2H_3^+$. E⁺ stands for CR_2H^+ and CRH_2^+ carbenium ions, and *a* for product alkanes.

It is assumed here that each carbenium ion, formed in the reaction of eq 3, establishes equilibrium with the corresponding alkene (eq 4)

$$\mathbf{E}^{+} \stackrel{K_{\mathbf{E}^{-1}}}{\longleftrightarrow} \mathbf{E} + \mathbf{H}^{+} \tag{4}$$

where E is alkene and K_E is the equilibrium constant of alkene adsorption. The active site concentration *S* was assumed to remain constant during the reaction and was expressed as the sum of the carbocation and active proton concentration (eq 5).

$$S = [A^+] + [E^+] + [H^+]$$
(5)

Quantum chemical calculations showed that solid acids stabilize short alkyl chains as a covalently bound alkoxide.^{55,56} The alkoxide groups were suggested to be in equilibrium with the corresponding surface-bound carbenium ion and the H-bonded alkene. Nevertheless, the rate expressions are independent of the identity of the reactive intermediates or transition states. If, relative to the rate of the processes of eq 3, the alkane and alkene adsorption—desorption (eqs 2 and 4) are rapid processes, maintaining the equilibrium concentration of the concerned species, the rate of the unimolecular reaction, $r_{\rm U}$, can be expressed as

$$r_{\rm U} = \frac{k_{\rm U} K_{\rm A} S p_{\rm A}}{1 + K_{\rm E} p_{\rm E} + K_{\rm A} p_{\rm A}} \tag{6}$$

At low coverage, the denominator approaches to one, and the rate is

$$r_U = k_{\rm U} K_{\rm A} S p_{\rm A} \tag{7}$$

Equations 6 and 7 are identical with those derived by Williams et al. 26,27

According to the measurements of Babitz et al.,²⁵ the sitespecific apparent rate constants and the corresponding activation energies, obtained for the hexane cracking over different highsilica H-zeolites, such as H–ZSM-5, H–mordenite, H– β , and H-USY, could be largely attributed to differences in the heats of hexane adsorption, while the intrinsic activation energies were found to be nearly the same. Data suggested that either the intrinsic activation energy of the reaction is insensitive to differences in acid strength or that there is no difference in the Brønsted acid strength of the different H-zeolites. In contrast, Kotrel et al.^{23,24} reported distinctly different intrinsic activation energies for the same reaction over H-zeolite catalysts, having different structures and compositions, and except for H–USY, showed correlation between the intrinsic activity and the intrinsic acid strength of the catalysts, which was characterized by the red-shift of the v_{OH} IR bands, induced by the H-bonding of weak base adsorbates.

Under conditions of bimolecular alkane conversion, the active catalyst surface must be extensively covered by a carbenium ion/alkoxy intermediate. These surface species can be considered as sites forming activated intermediates with the reactant hexane (eq 8). The reaction is generally referred to as bimolecular,

because it proceeds with the participation of two molecular species. The product distributions obtained at the relatively high hexane pressure and conversion and the low reaction temperature, applied in this study, suggested that, over the examined solid acid catalysts, bimolecular isomerization/cracking mechanism prevailed.^{23,26} The bimolecular rate constant was found to be about 10 times higher than the unimolecular rate constant, while both processes were found to be first order in the hydrocarbon concentration.²³

A significant finding of the present work was that intrinsic acidity of the Brønsted acid sites, characterized by $\Delta \nu_{OH}$, induced by N₂ adsorption, changed parallel with the apparent site-specific rate constant of the bimolecular hexane cracking (Figure 1 and Table 3). The SZT catalyst, showing much higher activity than that corresponding to its acid strength, is an exception. It seems quite probable that the criterion of an identical reaction mechanism does not apply for the compared SZT and zeolite catalysts.^{57,58} The correlation found for the zeolites infers that the apparent rate constant hardly or similarly deviates from the intrinsic rate constant. The kinetic analysis, given below, helps to understand the above finding and points out specific features of the bimolecular cracking process. With the same symbols, used above, the elementary reactions of the catalytic cycle can be written as

$$E^{+} + A \stackrel{K_{A}^{'}}{\Longrightarrow} (EA)^{+}$$
(8)

and

$$(\text{EA})^+ \xrightarrow{k_{\rm B}} \text{E}^+ + a \tag{9}$$

where $(EA)^+$ represents the carbonium ions, formed from any alkane and any kind of E^+ surface carbonium ion, and k_B is the intrinsic rate constant of bimolecular cracking. The equilibrium of the alkenes and the carbonium ions, E and E^+ , respectively, is given again by eq 4. The condition of constant active site concentration is given as

$$S' = [EA^+] + [E^+] + [H^+]$$
(10)

From eqs 4 and 9–11, the rate of bimolecular cracking, $r_{\rm B} = k_{\rm B}$ [(EA)⁺], is obtained in the form of

$$r_{\rm B} = \frac{k_{\rm B} K_{\rm E} K_{\rm A}' S' p_{\rm E} p_{\rm A}}{1 + K_{\rm E} p_{\rm E} + K_{\rm A}' K_{\rm E} p_{\rm E} p_{\rm A}}$$
(11)

This equation seems to be at variance with the rate equation given by Williams et al.²⁶ The concentration of the transition state carbonium ions is necessarily low, i.e., $K_A'p_A \ll 1$. It is worth examining the extreme cases of low and high alkene coverage. For low alkene coverage, the denominator approaches one, and the rate, in accordance with Williams et al.,²⁶ can be given as

$$r_{\rm B} = k_{\rm B} K_{\rm E} K_{\rm A}' S' p_{\rm E} p_{\rm A} \tag{12}$$

This equation was shown to describe the dependence of the reaction rate on the alkene concentration over H–USY catalyst in the range of 0.1–6.2 kPa hexane pressure at 673 K.²⁶ It seems rational to think that, under the conditions applied in this study, i.e., at 6.1 kPa hexane pressure and 553 K, the steady-state alkene coverage of the active Brønsted acid sites is high, i.e., $K_{\rm E} p_{\rm E} \gg 1$, and thus, eq 11 can be reduced to get

$$r_{\rm B} = k_{\rm B} K_{\rm A}' S' p_{\rm A} \tag{13}$$

The reaction is zero order in alkene. Notice that formally, the same rate expression was obtained for the bimolecular cracking at high alkene coverage as for the unimolecular cracking at low coverage.

Equation 13 provides an explanation for the finding that the apparent rate constant $k_{B,app} = k_B K_A'$ changes parallel with the intrinsic acidity of the catalysts (Table 3) because the surface concentration of the transition state EA⁺ carbonium ion is low, i.e., K_A' must be small relative to k_B . Moreover, K_A' , characterizing the alkane/E⁺-zeolite interaction have, presumably, much weaker dependence on the zeolite composition and structure than the alkane/H⁺-zeolite interaction, characterized by K_A . Consequently, while the intrinsic rate constant of the unimolecular cracking, k_U , must show better correlation with intrinsic acidity than the apparent rate constant, $k_{U,app}$, both the corresponding rate constants of the bimolecular reaction, k_B and $k_{B,app}$, are expected to change parallel with the intrinsic acidity, provided that the alkene coverage is high.

In the simplified kinetic treatment, given above, *a* represent different alkane products. Therefore, E^+ must represent a number of different active site carbenium ions (eq 3). In the bimolecular reaction, the interaction of the E^+ active sites with reactant and product alkanes gives a large variety of EA⁺ and Ea⁺ transition states that are responsible for the found product distribution (Table 2).

Under conditions of unimolecular transformations, the catalyst was found to retain its activity for hours, allowing the determination of Arrhenius plots and, thereby, the apparent preexponential constant (A_{app}) and activation energy (E_{app}) of the reaction. If $k_{U,app} = k_U K_A S$, it can be easily shown that

$$\ln A_{\rm U,app} = \ln A_{\rm U,int} + (\Delta S_{\rm A}/R)$$
(14)

$$E_{\rm U,app} = E_{\rm U,int} + \Delta H_{\rm A} \tag{15}$$

where $A_{u,int}$ and $E_{U,int}$ are the intrinsic preexponential constant and activation energy, and ΔH_A and ΔS_A are the adsorption enthalpy and entropy, respectively.

The proton transfer to a base is a concerted process wherein bonds are broken and new bonds are formed. The net energy of the process is favorably calculated on the route wherein (i) the Brønsted acid site is deprotonated, (ii) the proton is added to the alkane, and (iii) the protonated alkane is adsorbed on the conjugated base of the acid. Processes (i) and (ii) involve the deprotonation energy (DE) of the acid and the proton affinity (PA) of the base, respectively. The sum of DE and PA is referred to as the proton-transfer energy, ΔH^{pt} . The DE of zeolites was determined to be about 1200 kJ mol⁻¹,⁵⁹ and the PA of hexane is 665 kJ mol⁻¹. The adsorption environment provides energy to the Brønsted acid site/alkane ensemble to facilitate proton transfer. The energies associated with process (iii) are generally referred to as stabilization energy, ΔH^{st} . The stabilization energy includes all the energies of adsorbate-adsorbate and adsorbateadsorbent interactions. The proton transfer from H-zeolites to strong bases, such as ammonia, is an exothermic process. For weak base alkanes, the energy balance gives the E^{pt} activation energy of the process.

$$E^{\rm pt} = \Delta H^{\rm pt} + \Delta H^{\rm st} \tag{16}$$

 $\Delta H^{\rm st}$ is the energy of interaction between the gas-phase carbonium ion and the oxide anion of the solid acid. For a given base, $\Delta H^{\rm pt}$ depends only on the intrinsic acidity of the solid acid, while $\Delta H^{\rm st}$ includes all the structure-dependent energy contributions.

Provided that the hexane activation occurs through full proton transfer, $E_{U,app}$ must be equal to E^{pt} . The measured activation energies of the unimolecular hexane conversion over different H-zeolites ranged from 149 to 186 kJ mol^{-1.25} Thus, the energy, $\Delta H^{\rm st}$, needed to facilitate full proton transfer to hexane, is estimated to $349-386 \text{ kJ mol}^{-1}$. ΔH^{st} is obviously much higher than the approximately 70–90 kJ mol⁻¹ value of $\Delta H_{\rm A}$.^{23,25} Comparison of eqs 15 and 16 suggests that, in case of full proton transfer, $E_{\text{U,int}}$ must include a considerable fraction of the structure-sensitive stabilization energy, and it cannot be expected to be identical for zeolites, having different structure and composition. Nevertheless, $E_{U,int}$ was found to be independent from the structure and composition of high-silica zeolites.²⁵ It seems quite probable, therefore, that alkane isomerization and cracking proceeds through a reaction route having an intrinsic activation energy much lower than ΔH^{pt} . Data substantiate that alkane activation for unimolecular cracking and dehydrogenation (eq 3) does not require full proton transfer, but alkane H-bonding to acidic hydroxyl groups. The similarity of H-bonding interaction of the weak base reactant alkane and the even weaker base adsorptive N_2 explains the good correlation between E_{Uint} and the adsorption-induced $\Delta v_{\rm OH}$ IR shifts.

Because of the rapid deactivation of the catalysts, it was not attempted to determine the Arrhenius parameters of the bimolecular hexane conversion. It would have been also dubious to assign the apparent activation energy to any specific step of the complex bimolecular catalytic chain process. It was shown by Lunsford et al.²³ that the intrinsic rate constant of the bimolecular hexane conversion was about 10 times larger than that of the unimolecular process on the same catalyst. In the present study, zeolites H–ZSM-5, H–mordenite, and H– β , having stronger intrinsic Brønsted acidity, were found to be more active than the H-Y, H-USY, and SZT catalysts having weaker Brønsted acid sites (Figure 1 and Table 3). The found correlation of $k_{\text{B,app}}$ and the intrinsic acidity may indicate that the deviation of $k_{B,app}$ and $k_{U,app}$ cannot be related exclusively to the deviation of the preexponential factors only, but also $E_{B,app}$ must be lower than $E_{U,app}$. It is to be noted that associated molecules have higher proton affinity than single molecular species. Therefore, EA⁺ transition state of the bimolecular process must have a higher stability than the A⁺ transition state of the unimolecular process (eqs 3 and 8). A decrease of the activation energy as low as about 10 kJ mol⁻¹ can already account for the found rate difference of the uni- and bimolecular processes. Theoretical calculations can support or negate this notion.

Conclusions

The aim of studying the relation between the acidity and the alkane conversion activity of solids is to gain better understanding of the catalytic mechanism. To establish meaningful correlation for catalysts having different composition and structure, intrinsic acidities and activities had to be compared. The controversial results, reported here and in earlier studies, come from the difficulty of determining intrinsic properties.

The present study shows that the $\Delta \nu_{OH}$ shift of the ν_{OH} band, induced by adsorption of N₂ at room temperature, is a good measure of the intrinsic acid strength of the Brønsted acid sites of solid acid catalysts. The intrinsic acidity of the high-silica H–ZSM-5, and H–mordenite, was found to be stronger than that of H–USY and sulfated zirconia–titania and virtually independent of the zeolite composition and structure. Zeolite H– β has two kinds of Brønsted acid sites, which are distinctly different by their intrinsic acid strengths. The stronger acid sites are similar to those in H–ZSM-5 and H–mordenite. Zeolite H–Y is a relatively weak solid acid. The intrinsic site-specific rate constant of hexane conversion is attained if the apparent rate constant is corrected by the equilibrium constant of hexane adsorption and related to the number of active sites. In the present study, intrinsic activities of hexane conversion were not obtained. First-order bimolecular apparent rate constants were determined and related to the total number of the acid sites. No correction was made for the adsorption enrichment of hexane on the catalyst surface. After all, both the apparent and the site-specific apparent rate constants showed fair correlation with the intrinsic acidity of the catalysts. The results suggest that the adsorption effect on the rate of hexane conversion cannot be strongly dependent on the catalyst composition and structure if the bimolecular transformation is the dominating reaction mechanism.

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