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Acid Sites in Sulfated and Metal-Promoted Zirconium Dioxide Catalysts

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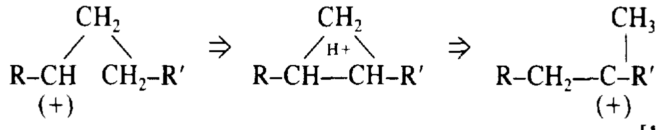
Unpromoted sulfated zirconia (SZ) and sulfated zirconia that was promoted with iron and manganese ions (FMSZ) have been tested as catalysts for the isomerization of *n*-butane to isobutane. FMSZ is the superior catalyst; its activity at 60°C is similar to that of SZ at 180°C. Both catalysts deactivate rapidly. FTIR analysis of adsorbed CO and acetonitrile reveals the presence of Lewis and Brønsted sites in both catalysts. Acetonitrile is strongly adsorbed on FMSZ. Subsequent desorption is destructive; CO_2, SO_2, and O_2 are formed, while temperature-programmed oxidation shows that no carbon-containing products are left on the surface. CO-FTIR reveals equal acidity, within experimental error, for the Lewis sites on SZ and FMSZ. Changes in proton NMR and FTIR parameters caused by adsorption of acetonitrile show that the acid strength of the Brønsted sites of SZ and FMSZ is similar to that of the lower OH-frequency protons in HY, but weaker than that of the protons in HZSM-5. The results indicate that the remarkable activity of SZ and FMSZ is not caused by exceptionally strong acid sites, but by stabilization of the transition state complex at the surface.

I. INTRODUCTION

This paper deals with a class of solid catalysts, based on sulfated zirconium dioxide, that are able to catalyze the isomerization of alkanes at comparatively low temperature (1, 2). The most active member of this family, a sulfated ZrO_2 doped with the oxides of iron and manganese, was found by Hsu *et al.* to catalyze the isomerization of *n*-butane even at room temperature (3). This discovery raises some fundamental questions on the nature of the sites responsible for this "acid-catalyzed" reaction.

This classification is based on the convention that an essential step in alkane isomerization used to be written as a skeletal rearrangement of carbenium ions. For instance, the transformation of a secondary carbenium ion to a tertiary carbenium ion was assumed to occur via a substituted cyclopropyl ion (4, 5):



$$\begin{array}{c} CH_2 \\ / \quad \backslash \\ R\text{-}\underset{(+)}{CH} \quad CH_2\text{-}R' \end{array} \Rightarrow \begin{array}{c} CH_2 \\ /_{H^+}\backslash \\ R\text{-}CH\text{—}CH\text{-}R' \end{array} \Rightarrow \begin{array}{c} CH_3 \\ | \\ R\text{-}CH_2\text{—}\underset{(+)}{C}\text{-}R' \end{array} \qquad [1]$$

As carbenium ions can be though to be in equilibrium with olefins and Brønsted acids,

$$H^+ + \text{olefin} = \text{carbenium ion}, \qquad [2]$$

it is clear that rather strong acid sites are required to maintain a high concentration of carbenium ions. Moreover, as coexistence of appreciable concentrations of olefins and carbenium ions easily leads to formation of undesired heavier molecules, a catalyst for alkane isomerization should preferably have very strong acid sites, so that equilibrium (2) is shifted far to the right; i.e., the steady-state concentration of olefins should be minimized.

In the case of paraffins as the sole reactants, formation of carbonium ions with pentacoordinated carbon atoms has been proved by Haag and Dessau (6) to occur on strong acid sites. When these intermediates lose H_2 or CH_4, they are thought to be converted into carbenium ions. Hydride ion transfer between paraffins and carbenium ions, in principle, enables an unlimited number of paraffin molecules in contact with a limited number of carbenium ions to temporarily acquire the high reactivity of this state and thus undergo skeletal isomerization as depicted in (1).

For heterogeneous catalysts this simple model is, however, only a crude approximation of the truth, as was shown by Kazansky (7). Quantum chemical calculations performed with optimization of the geometry show that the bond of protonated alkyl groups with the surface is covalent; no ion pairs of "carbenium ions" and negatively charged surface groups are formed (8, 9). The term "surface ester" is, therefore, a more adequate description of the adsorption complex. An important feature is the

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bifunctional character of the active sites in which the acid moiety acts as proton donor, while the basic moiety stabilizes the protonated species. The calculated energies for zeolite surfaces are similar to the experimental values for sulfuric acid esters. Kazansky concludes that any attempt to determine acid strength of a given surface OH group from its stretching frequency is bound to fail: "The only proper way to proceed is to follow the response of hydroxyl groups to their interaction with adsorbed bases" (7).

While the presence of strong acid sites remains a necessary condition for alkane isomerization catalysts, this does not justify the assumption that the catalytic activity for alkane isomerization will always increase with strength and/or number of acid sites. As the activation energy is determined by the enthalpy of the transition state, the most active catalyst will be the material which provides the lowest enthalpy for the transition state complex. On surface-exposed sulfate groups the intermediates are likely to be similar to alkyl sulfates or esters, as was proposed more than 60 years ago by V. N. Ipatieff (10).

In this respect the isomerization of *n*-butane is of high relevance. When applying the classical carbenium ion scheme (1) to C_4, a *primary* carbenium ion would be formed in the second step. The enthalpy difference between secondary and primary carbenium ions is, however, very large and so should be the activation energy if free carbenium ions were the intermediates. The much lower activation energy consistent with the experimentally observed high reaction rates suggests, therefore, that the crucial feature of these catalysts is the low enthalpy of the reaction intermediates, including the transition state complex.

In the present paper a quantitative comparison is attempted of the strength and concentration of acid sites at the surface of sulfated zirconia catalysts and the zeolite HZSM-5. FTIR of weak bases, such as CO and CD_3CN, and solid-state proton NMR are used to titrate the strength of exposed Brønsted and Lewis sites.

For clarity, some definitions should be recalled. A Brønsted site at a catalyst surface is a proton H^+, attached to the catalyst matrix M^-. Conceptually, the acidity of the site could be defined, in close analogy to the definition of work functions and ionization potentials, by the energy required to remove the proton and carry it to infinity:

$$M^-H^+ = M^- + H^+. \qquad [3]$$

The strength of the Brønsted site will then be given by the negative of the proton affinity of the base M^-. Unfortunately, it is difficult to do such measurements; it is more practical to use a base, B, and define the acid strength via the equilibrium constant of

$$M^-H^+ + B = BH^+ + M^-. \qquad [4]$$

In homogeneous solutions, where the concentrations and activity coefficients of H^+, B and BH^+ can be measured, the Hammett acidity function H_0 can be defined by

$$-\log K_a = pK_a = H_0 + \log C_{BH^+}/C_B \qquad [5]$$

$$K_a = (a_{H^+}\gamma_B/\gamma_{BH^+})\, C_B/C_{BH^+}. \qquad [6]$$

However, as protons, bases, and BH^+ complexes are often solvated, the validity of measured data is limited to the particular solvent in which the equilibrium (4) has been measured.

Mobile physisorbed complexes BH^+ are seldom formed on catalyst surfaces; bases B which are used as Hammett indicators are often strongly chemisorbed on the site carrying the proton and they interact with its environment. Measurements with the Hammett indicator method (11) give, therefore, not necessarily values which permit reliable comparisons between different catalysts or with liquid acids. The same holds for Lewis acid sites; while they react with Lewis bases such as pyridine or ammonia, the energy of this interaction which can be measured calorimetrically or by TPD, includes all interactions between base and catalysts surface.

Of the two methods used in this research to characterize Brønsted and Lewis sites at the surface of unmodified and modified sulfated ZrO_2 catalysts, the first is based on the shift of characteristic FTIR bands of both the surface and the probe molecule. Some authors state that the shift in the C≡N frequency of deuterated acetonitrile, CD_3CN, is characteristic for the character of the acid site, Brønsted or Lewis, whereas the perturbation by acetonitrile of the bands characteristic for surface OH groups reveals their Brønsted acid strength. This method has been described by Pelmenschikov *et al.* (12) who applied it to the zeolites HY and HZSM-5. Use of deuterated acetonitrile avoids Fermi resonance of internal molecular modes.

The second method is based on magic angle spinning (MAS) NMR of surface protons (13). It has been established that a relation exists between the acid strength of a proton in a zeolite and the chemical shift of this proton. This relation was verified by quantum chemical calculations of small clusters of zeolitic materials containing B, Al, Si, or P atoms in T positions (14). For surface OH groups of these materials a linear correlation was found between the deprotonation energy and the ^1H NMR chemical shift. No such relation could be observed for gas-phase acidity of *X*–OH groups of many molecules (14). Very recently, Haw *et al.* (15), showed that Brønsted acidities cannot simply be related to NMR chemical shifts of hydroxyl groups; the ^1H NMR chemical shift and, hence, any correlation of acid strength and chemical shift, depend on the H bonding of the proton. A well known example is the IR low-frequency (LF) proton in HY zeolite which is less acidic than the high-frequency (HF) proton, but gives a higher ^{1}H NMR chemical shift (16). This higher shift is due to H bonding of the LF proton with a neighboring oxygen atom. Therefore, we suggest to determine not only the position of the ^{1}H NMR line, but also the *additional shift* caused by adsorption of a weak base. The situation is analogous to that found for IR spectroscopy and described above. The shift of the OH-stretching frequency upon adsorption of a base of medium strength gives a reliable measure of the acidic strength of a surface proton (17).

II. EXPERIMENTAL

1. Catalyst Preparation and Nomenclature

Sulfated zirconia, SZ, catalysts were prepared from sulfated zirconium hydroxide, $Zr(OH)_4$, kindly provided by Magnesium Elektron Inc. This material was calcined at 650°C for 1 h in a flow of dry air. The sulfur content, determined by ICP analysis, was 1.1 wt%. The Fe- and Mn-promoted samples were prepared from sulfated $Zr(OH)_4$ by stepwise impregnation. A solution of about 1.1 g of $Fe(NO_3)_3 \cdot 9H_2O$ in 10 ml of water was added to 10 g of sulfated $Zr(OH)_4$; the slurry was stirred thoroughly and dried at 100°C for several hours. This procedure was repeated with a solution of 0.22 g $Mn(NO_3)_2 \cdot 6H_2O$ in 10 ml of water. The catalysts were calcined in a flow of dry air (30 ml/min) at 725°C for 1 h. The ICP analysis showed an elemental composition of 1.5 wt% Fe, 0.5 wt% Mn, and 0.9 wt% S. This catalyst will be referred to as FMSZ. This catalyst exhibits a grayish-orange color, whereas SZ was white.

2. Reaction Studies

The isomerization of *n*-butane to isobutane was carried out in a flow reactor. The catalyst (1.5 g) was pretreated in dry air (30 ml/min) at 450°C for 2 h. In order to obtain similar conversions with SZ and FMSZ, the reaction was carried out at 60°C over FMSZ catalysts and at 180°C over SZ. A mixture of 1 vol% *n*-butane in N_2 at a flow rate of 80 ml/min was used as the feed. The products were analyzed by using a HP 5890 gas chromatograph with a 50-m PONA column.

3. Temperature-Programmed Desorption (TPD) and Oxidation (TPO)

TPD/TPO experiments were conducted in a flow reactor at atmospheric pressure. For the TPD runs, the catalyst (0.4 g) was pretreated in an Ar flow (30 ml/min) at 450°C for 2 h. After cooling to room temperature the catalyst was exposed to a flow of He into which 10 μl of acetonitrile was introduced. The sample was first purged with He for 1 h 30 min to remove any physisorbed acetonitrile. The subsequent temperature-programmed desorption was carried out by raising the temperature at a rate of 8°C/min to 700°C. The desorbed products were identified with an on-line Dycor Quadrupole Gas Analyzer (MS).

The TPO experiments were conducted after TPD by heating the catalyst in a flow of 5 vol% O_2 in He at a heating rate of 8°C/min from 21 to 700°C.

4. Fourier Transform Infrared Spectroscopy

Infrared spectra were recorded by a Nicolet 60SX single-beam Fourier transform infrared spectrometer at a spectral resolution of 1 cm^{-1} in the transmission mode with the smallest aperture available. In view of the low transmittance of the samples, the use of a liquid-nitrogen-cooled MCT detector was considered absolutely necessary. In addition, each spectrum was scanned 200 times for a good signal-to-noise ratio. The samples were pressed into thin self-supported wafers (5–10 mg/cm^2) and placed into an *in situ* IR cell. The precalcined samples were activated in UHP He at a flow rate of 30 ml/min up to 450°C for 2 h with a ramp of 8°C/min. Adsorption of CH_3CN and CD_3CN at room temperature was performed with a syringe technique: 1.0 μl of CD_3CN (Aldrich Chemical Company, Inc. 99% D, from glass ampules) was introduced, immediately after opening the ampules, into the He stream via a septum by a gas-tight syringe (Hamilton, Inc.).

5. MAS NMR

The ^{1}H MAS NMR experiments were performed at room temperature on a Bruker NMR spectrometer MSL 400 with a magnetic field of 9.4 T, the MAS spinning rate was 5 kHz. About 60 FID's were accumulated by using 90° pulses (1.5 μs) with a repetition time of 5–60 s. The samples for the NMR experiments were degassed on a vacuum line at 723 K for 2 h in high vacuum (10^{-5} mbar) and cooled to room temperature. Adsorption was carried out at equilibrium pressure (1 mbar or 0.01 mbar for CCl_3CN; 0.5 mbar or <0.01 mbar for CD_3CN, at 297 K). The lower pressures correspond to about one base molecule per Brønsted site for HZSM-5 or less (HY), whereas at the higher pressure adsorption also takes place on the weakly acidic protons, such as the silanol groups. This was verified by IR measurements with different loadings including the same range of equilibrium pressures. After adsorption, the samples were kept in a sealed tube. Prior to the NMR experiment the samples were transferred into tightly closed rotors (standard 4-mm ZrO_2 rotors) in a glove box.

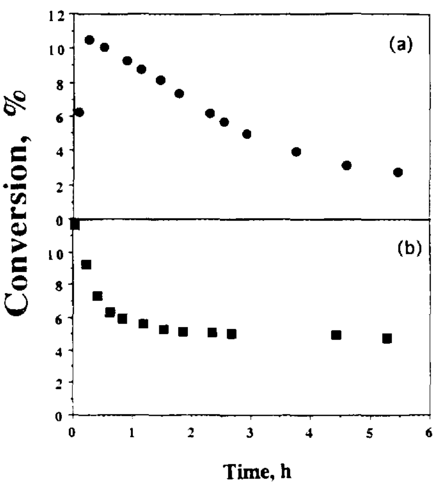

FIG. 1. Formation of isobutane from n-butane. (a) Catalyst, metal promoted sulfated zirconia, FMSZ; temperature, 60°C. (b) Catalyst, unpromoted sulfated zirconia, SZ; temperature, 180°C.

III. RESULTS

1. Catalytic n-Butane Isomerization

The catalytic data of the conversion of *n*-butane to i-butane are shown in Fig. 1 for SZ and FMSZ. The FMSZ catalyst showed an induction period the activity passes through a maximum with time on stream, followed by severe deactivation. Similar induction period have also been reported by Jatia *et al.* (18). The maximum activity is strongly enhanced by promoting SZ with Fe and Mn ions. While keeping all other parameters constant, a reaction temperature of 180°C was required to obtain a reaction rate over the SZ catalyst similar to that observed for FMSZ at 60°C. No induction period is observed with SZ. This catalytic signature of both catalysts is similar to that described by previous authors (2, 3). Over both catalysts minor amounts of propane and i-pentane were detected. Reaction rates were calculated by taking the conversions at the observed maxima and normalized by the sulfur content; this leads to 1.2 × 10^{-4} molecules of *n*-butane converted per sulfur per second for SZ at 180°C as well as for FMSZ at 60°C. The physical causes of the induction period and of the catalyst deactivation will be discussed in a separate paper.

2. Temperature-Programmed (Destructive) Desorption and Oxidation

The TPD studies showed no detectable desorption of acetonitrile or its fragments (*m/e* ratios 41, 39, 38, 32, 29). Large desorption peaks were, however, observed for O_2, CO_2, and SO_2 with *m/e* ratios of 32, 44, and 64, respectively. The same products were observed in TPD of benzene from FMSZ and SZ (18). The O_2 and SO_2 peaks appeared at almost the same temperature and were of similar area. In Fig. 2, the TPD profiles are shown for *m/e* 44 corresponding to CO_2. This peak is much larger for the FMSZ catalyst, which indicates that FMSZ has more sites capable of strongly adsorbing and oxidizing acetonitrile, at least under the present TPD conditions. The desorption temperature of CO_2 is slightly lower than that reported by Jatia *et al.*, which is likely due to a slower temperature ramp (8°C/min) in this study.

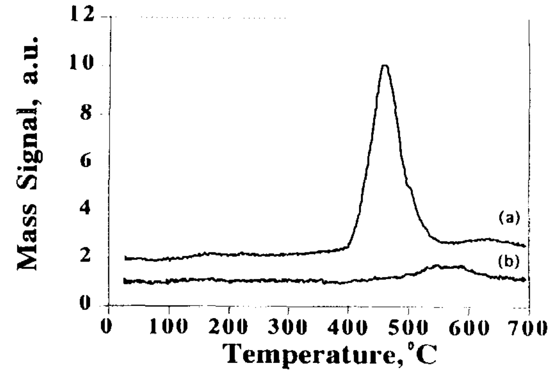

FIG. 2. Temperature-programmed "desorption" of acetonitrile from (a) FMSZ and (b) SZ catalysts. Product with *m/e* = 44 is plotted vs *T*.

The TPO analysis conducted after the TPD run showed that the surface was completely clean; no carbon- or sulfur-containing species were detected.

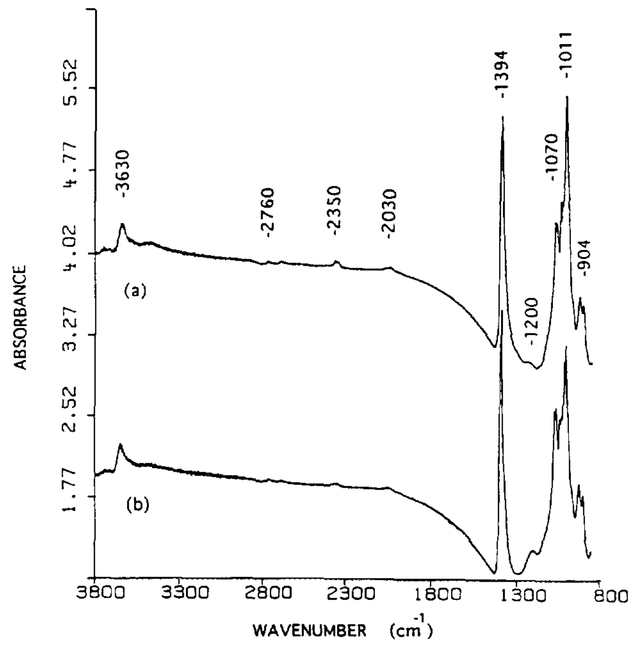

FIG. 3. IR-spectra of sulfated zirconia catalysts after activation in He up to 450°C: (a) unpromoted SZ; (b) metal promoted FMSZ.

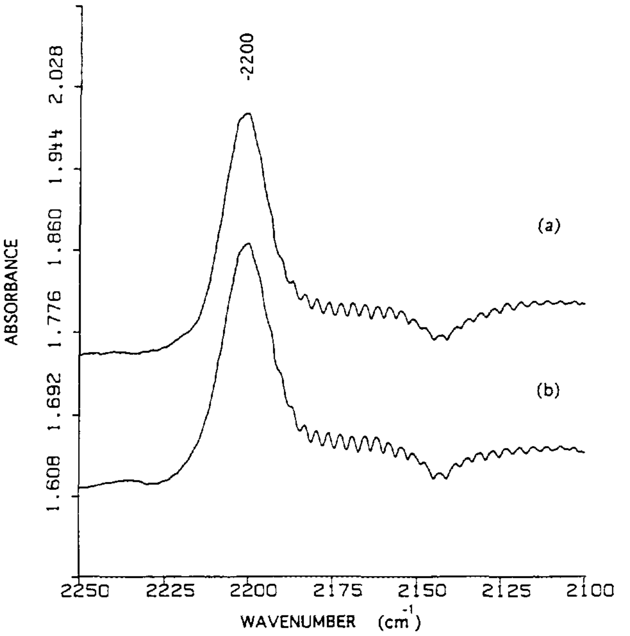

FIG. 4. FTIR spectra of CO-stretching region after adsorption at room temperature: (a) SZ; (b) FMSZ.

3. FTIR spectra

A. After activation. Figure 3a shows the FTIR spectrum of SZ after activation of the precalcined sample in He up to 450°C. The spectrum exhibits a band in the OH-stretching region at 3630 cm^{-1}, which is attributed to acidic OH groups, as will be discussed in more detail below.

Furthermore, characteristic sulfate bands are observed, the two most intense ones at 1394 and 1011 cm^{-1} with overtones at 2760 and 2030 cm^{-1}. The band at 2350 cm^{-1} is likely to be caused by residues of CO_2 in the gas lines. Additional peaks appear at 1200, 1070, 928, and 904 cm^{-1}. Jin *et al.* (19) observed similar, but less resolved spectra of sulfated ZrO_2. They assigned bands at 1390 and 1190 cm^{-1} to the asymmetric and symmetric stretching modes of sulfate groups binding via two oxygens to the zirconium of the support. Bands at 1020 and 930 cm^{-1} were assigned to the asymmetric and symmetric stretching modes of the oxygens binding to the sulfur of the sulfate groups. Bensitel *et al.* (20) reported spectra of sulfated ZrO_2 similar to ours and concluded that at least three sulfur species with only single S=O oscillators were present.

Figure 3b shows the spectrum of the metal-modified sample FMSZ after He activation. No peak shifts are observed with respect to SZ. Both the OH-stretching region and the sulfate region look the same. It should be mentioned here that comparisons of peak intensities are of limited value in view of the poor reproducibility of wafer thickness and the high optical density of the samples.

B. After CO adsorption. Figure 4 shows the spectra of (a) SZ after CO adsorption and purging in He for 1 min. A band at 2200 cm^{-1} appears, indicating CO adsorption on Lewis acid sites (21). Likewise, CO adsorption on FMSZ (trace b) gives rise to the same bands. The presence of Fe and Mn ions does not cause observable peak shifts. It should also be noted that the OH region is negligibly affected by CO adsorption.

C. After CD_3CN adsorption. Figure 5a shows the spectrum of SZ after adsorption of CH_3CN. The OH band at 3630 cm^{-1} disappears and a broad band is observed in the 3630–2800 cm^{-1} region indicating that at least part of the CH_3CN has been bound to the proton of the OH groups exhibiting the band at 3630 cm^{-1} after activation. The disappearance of the OH band indicates Brønsted acidity. The bands at 3001 and 2937 cm^{-1} are due to CH-stretching modes. The CN-stretching region with peaks at 2314, 2285, and 2250 cm^{-1} is strongly complicated by Fermi resonance between the CN and the combination of the symmetric CH_3- and the CC-stretching modes (12).

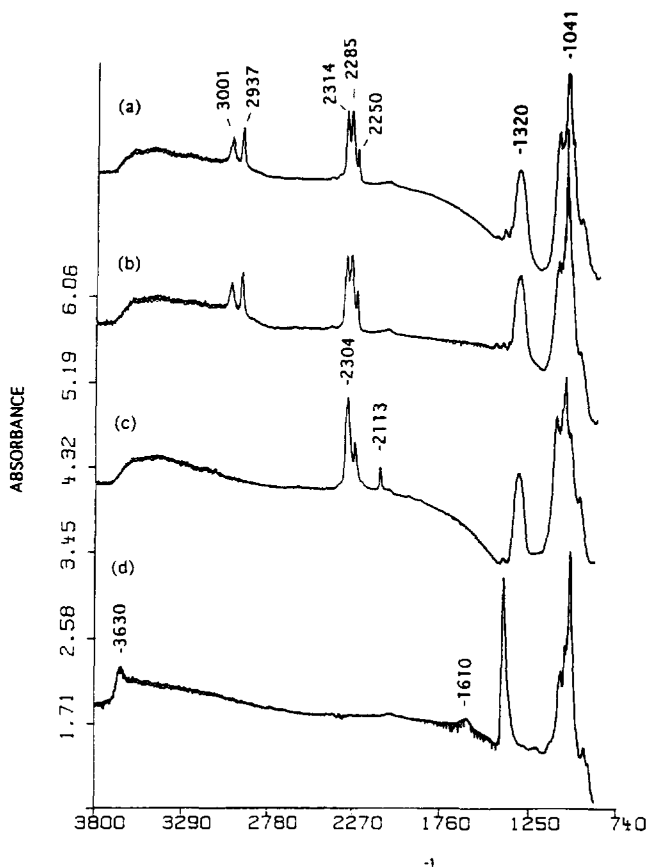

FIG. 5. IR-spectra of: (a) SZ after adsorption of 1 μl CH_3CN; (b) FMSZ after adsorption of 1 μl CH_3CN; (c) FMSZ after adsorption of 1 μl CD_3CN; (d) FMSZ after adsorption of 0.05 μl H_2O.

The sulfate region is strongly affected by the adsorption of CH_3CN; the band at 1394 cm^{-1} has shifted to 1320 cm^{-1}, whereas the band at 1011 cm^{-1} is shifted toward higher wavenumbers (1041 cm^{-1}). Similar shifts in the sulfate region have been reported by Jin *et al.* (19) for pyridine adsorption on sulfated ZrO_2.

Figure 5b shows the spectrum of FMSZ after CH_3CN adsorption. The spectrum looks essentially the same as that of the CH_3CN-loaded SZ (Fig. 5a). Again, the disappearance of the OH stretching at 3630 cm^{-1} and the generation of a broad band from 3630–2800 cm^{-1} indicates interaction of the base CH_3CN with the acidic protons present in FMSZ. Identical shifts of the OH band upon acetonitrile adsorption indicate comparable strength of Brønsted acid sites on SZ and FMSZ.

Interpretation of the bands in the CN region is difficult, as discussed above. To resolve this complication, CD_3CN was used as a probe molecule. The spectrum of FMSZ after adsorption of CD_3CN is shown in Fig. 5c. The same broad feature in the OH region indicating Brønsted acidity is observed. The bands at 2112 and 2251 cm^{-1} are due to CD stretching modes. The CN-stretching frequency of Brønsted acid bonded acetonitrile can be expected between 2290 and 2300 cm^{-1} (12); such a complex might contribute to the band at 2304 cm^{-1}. A second conceivable origin of this band is interaction of the CN vibration with Lewis acid sites. It is known that bonding of the CN group to Al^{3+} sites in alumina exhibits a vibration band in the 2332–2323 cm^{-1} region, which is not observed here; a lower frequency for the CN-stretching mode is, however, to be expected for bonding to Zr^{4+}, because the position of this band is determined by the nature of the cation, in particular, its ionization potential and its radius (22). Therefore, the perturbation of the CN vibration by acid sites cannot be definitely assigned at this stage.

The effect of traces of water on the spectrum of FMSZ is shown in Fig. 5d: adsorption of 0.05 μl H_2O leads also to a broad band in the region from 3630 to 2600 cm^{-1} representing the OH stretching of physisorbed H_2O, but in addition a bending mode at 1610 cm^{-1} is clearly visible. The fact that this band is absent in the spectra discussed above eliminates the possibility that traces of water during the adsorption of acetonitrile caused the observed disappearance of the OH stretching at 3630 cm^{-1}. It is thus concluded that at least part of the acetonitrile is bonded to Brønsted sites of SZ and FMSZ.

4. *MAS NMR*

The ^1H MAS NMR spectrum of the sulfated zirconium dioxide, SZ (spectrum c in Fig. 6), differs from that of the nonmodified sample (spectrum b); a strong band at a chemical shift of about 6 ppm appears upon modification, whereas the band at 4.5 ppm (spectrum b) disappears. This is very similar to the findings of Riemer *et al.* (23). The band between about 0 and 2 ppm is partially due to protons of the spinner material itself (compare spectrum a with b) and a contribution of the basic OH of the zirconia at approximately 1.7 ppm. The signal at 4.5 ppm could be due to a very small amount of acidic protons of the zirconia. The 6 ppm band of spectrum c can be assigned to acidic protons of the modified zirconia in accordance with the assignment for zeolites (24). In comparison to zeolites, this shift is quite large.

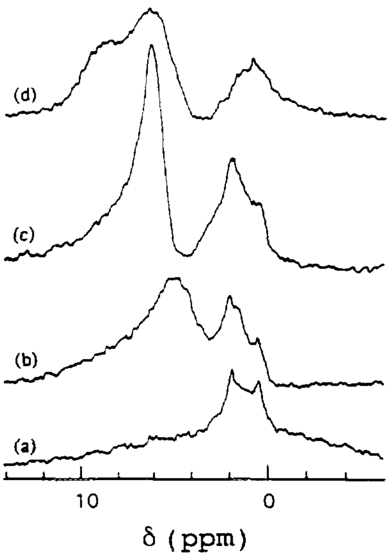

FIG. 6. ^1H NMR spectra of: (a) spinner spectrum blank; (b) zirconia; (c) SZ; (d) SZ after adsorption of CCl_3CN at 1 mbar.

For comparison, Fig. 7 shows the ^1H MAS NMR spectra of HZSM-5 and HY zeolite. As can be seen the bands for the acidic protons (spectra a, HY; b, HZSM-5) appear at a chemical shift of approximately 4–5 ppm. The silanol protons give a line at 2 ppm. An additional line at 2.8 ppm is found for the slightly dealuminated HY due to OH on extraframework Al (25). The acidic protons in HY pointing into the large cavities show a band at 4.1 ppm, the same value as found for protons in HZSM-5, and the less acidic protons in HY, pointing into the 6-ring, reveal a shift of 4.7 ppm (17). Figure 7 displays the ^1H MAS NMR spectra of the loaded zeolites as well. Upon adsorption of CCl_3CN the bands for the acidic protons at 4–5 ppm shift to 7–9 ppm. The band at 6.5 ppm in spectrum d cannot yet be assigned.

Adsorption of the base CCl_3CN on SZ gives a shifted band at approximately 8.5 ppm (Fig. 6, spectrum c), which corresponds to a band shift of $\Delta\delta_H = 2.3$; this is in contrast to the case of adsorption on zeolites where shifts of 3–6 ppm have been observed (Table 1). The stronger base, acetronitrile, shifts the band by 3.8 ppm as it does in the case of the less acidic "LF proton" in HY.

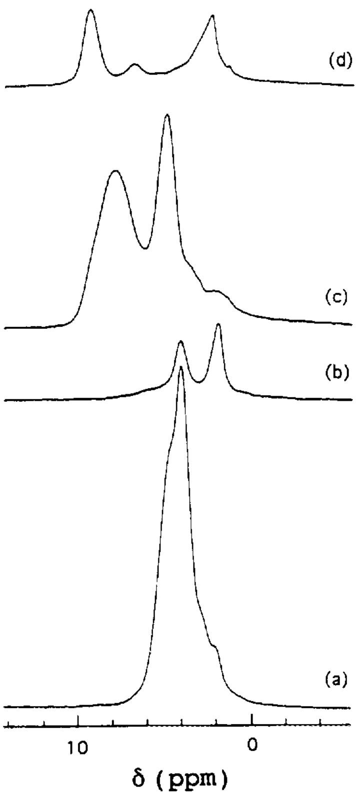

FIG. 7. ^1H NMR spectra of: (a) HY, Si/Al = 5; (b) HZSM-5, Si/Al = 50; (c) HY after adsorption of CCl_3CN at 1 mbar; (d) HZSM-5 after adsorption of CCl_3CN at 1 mbar.

Table 1 summarizes the results of the NMR measurements on the samples loaded with different bases. It can be seen that on adsorption of a base the chemical shifts of the acidic protons increase with increasing basicity of the probe. No influence of the adsorbed amount on the chemical shift measured was found except the fact that at the lower equilibrium pressure of the bases the LF proton of HY does not absorb any base. Consequently, the band at 4.7 ppm does not shift because of the low acidity and the band at 7.7 ppm (CCl_3CN) or 9 ppm (CD_3CN) disappears. The shoulder at 8.5 or 10.5 ppm becomes a single peak due to the shifted band of the HF proton of the HY. The result obtained for HZSM-5/CD_3CN are very close to findings of Haw *et al.* (compare lines 4 and 5 in Table 1). Surprisingly, the chemical shift of the proton in SZ upon adsorption shows a value which is not very different from that found for acidic protons in zeolites. The acid strength of the Brønsted sites in SZ is about the same as in zeolite Y (LF band) and less than in HZSM-5. Consequently, the proton of SZ does not adsorb the bases at the lower pressure as well. The weak signal of the acidic proton on the pure zirconia (spectrum b in Fig. 6) is shifted after adsorption by approximately 4 ppm. Brønsted acidic properties of ZrO_2 have been characterized by Nakano *et al.* (26). The larger shift of the proton NMR signal upon acetonitrile adsorption indicates stronger Brønsted sites in ZrO_2 than in SZ.

TABLE 1

^1H MAS NMR shifts, δ_H (in ppm), of Sulfated Zirconia and Zeolites and Their Shifts, $\Delta\delta_H$, upon Adsorption of Bases

Sample	δ_H before ads.	δ_H after CCl_3CN ads.	$\Delta\delta_H(CCl_3CN)$	δ_H after CD_3CN ads.	$\Delta\delta_H(CD_3CN)$
ZrO_2	4.5	8.5	4	—	—
ZrO_2/SO_4	6.2	8.5	2.3	10	3.8
HY	4.7	7.7	3	9	4.3
	4.1	8.5[a]	4.4	10.5[a]	6.4
HZSM-5	4.1	9	4.9	11	6.9
HZSM-5[b]	4.3	—	—	11.5	7.2

[a] Shoulder.

[b] Ref. (15).

IV. DISCUSSION

The catalytic data presented here are in agreement with previous reports: sulfated zirconia is an active catalyst for *n*-butane isomerization, a reaction conventionally classified as "acid-catalyzed," but the catalytic activity of this material is strongly enhanced by "promoting" it with Fe and Mn. Isomerization of *n*-butane is known to require a high temperature with all conventional acid catalysts; the present result, confirming earlier findings by Hsu *et al.* (3) shows that this catalyst has a higher activity, during its short life, than any other known catalyst for *n*-butane isomerization.

An extremely active catalyst for an "acid-catalyzed" reaction need not be an extremely strong acid. Indeed, the spectroscopic data reveal that the acid sites of this material are not unusually strong acids in comparison to, e.g., the sites in zeolites HY or HZSM-5. The FTIR fact after CO adsorption indicate the presence of Lewis acid sites on both SZ and FMSZ. The fact that the CO stretching frequency has the same value (2200 cm^{-1}) on both samples indicates roughly equal strengths of these Lewis acid sites. If one correlates the shift of the CO-stretching frequency with the Lewis acid strength of the adsorbing site, it appears that the sites of the present catalyst are weaker acids than trigonal coordinated Al^{3+} ions at the surface of γ-Al_30_3; CO adsorption on the latter sites give rise to a stretching frequency of 2215–2220 cm^{-1} (27). Bensitel *et al.* have compared the Lewis acidity of SZ and ZrO_2 and conclude that the increase of the Lewis acidity observed is not sufficient to explain the superacidic properties of SZ samples (28).

TABLE 2

Shifts of the OH Stretching Modes, ν_{OH}, of Some Zeolites and FMSZ upon Adsorption of CD_3CN

Samples	ν_{OH} (cm^{-1}) before ads.	Subband A after ads.	Subband B after ads.	Center of broad band
HZSM-5	3610	2770	2400	2500
HY	HF 3630 LF 3550	2950	2450	2750
HNaY	HF 3647 LF —	2980	2430	2800
CsHY	HF — LF 3554	—	—	3200
SZ[a]	3630	—	—	3200
FMSZ	3630	—	—	3200

[a] Adsorption of CH_3CN.

The FTIR data after adsorption of acetonitrile clearly indicate the presence of Brønsted acid sites by the shift of the OH band. A distinction between Lewis and Brønsted acidity based on the CN vibration is not possible in this case. It is known, that CO is able to probe for strong Brønsted sites at low temperature (typically 80 K). As the present spectra were obtained at room temperature, no bands of CO bonded to Brønsted acid sites may be expected.

We conclude, therefore, that Brønsted and Lewis acid sites are both present in this catalyst and the strength of the Brønsted and Lewis sites are comparable between SZ and FMSZ. In order to estimate the strength of the Brønsted sites present on FMSZ, it is useful to compare the shift of the OH bands, *after CD_3CN adsorption*, for the present catalysts with that for well known zeolites (see Table 2). For the OH bands of the zeolite HZSM-5 after CD_3CN adsorption, Pelmenschikov *et al.* (12) reported peak shifts of the bridging OH groups in HZSM-5 and HY from 3610 and 3630 cm^{-1} to broad bands at 2890 and 2400 cm^{-1} after the adsorption of CD_3CN. These bands are part of an even broader band, that are divided into subbands by an Evans window (12). Taking into account the position of the center of gravity, such shifts of about 1000 cm^{-1} are considered typical for OH groups with medium or fair acid strength. In the present case, we observe a broad band from 3600 to 2800 cm^{-1} with a maximum near 3200 cm^{-1}, which corresponds to a shift of 300–400 cm^{-1} (Table 2). This is very close to the shift of the remaining protons in a CsHY zeolite, which shows only the LF band, because no protons are present in supercages. No bands indicating ultrastrong acid sites have been observed for SZ or FMSZ. The shifts of the OH bands after adsorption of undeuterated acetonitrile are the same for SZ and FMSZ, indicating the same Brønsted acid strength for both catalysts. We therefore conclude that the Brønsted acid sites at the surface of SZ and FMSZ are weaker, at any rate not stronger, than those of HZSM-5 and HY.

This is confirmed by the results of the ^1H NMR measurements. Comparison of the shifts of the acidic protons of SZ and the zeolites upon adsorption of CD_3CN and CCl_3CN shows that the Brønsted acid strength of modified zirconia is quite moderate and far from that of "superacidity." The fact that ZrO_2 has a larger shift than SZ upon acetonitrile adsorption further demonstrates the moderate Brønsted acidity of SZ. The concentration of these protons in SZ is also rather low, amounting to roughly 1/8 of that in ZSM-5. We do not support an interpretation based solely on the chemical shift in the absence of an adsorbed base; the comparatively large chemical shift of the ^1H NMR line of SZ (6 ppm) to that of the zeolite (4–5 ppm) is attributed to hydrogen bonding rather than to superacidity.

Apparently the impressive catalytic behavior of metal-modified sulfated ZrO_2 cannot be rationalized in terms of "superacidity." As mentioned in the Introduction, the extraordinary activity of these catalysts is likely to be caused by a good stabilzation of the surface intermediates. An obvious candidate for a site stabilizing adsorbed moieties is the surface sulfate. In Fig. 8, a model is sketched of a plausible surface complex which combines Lewis and Brønsted acid sites in close proximity. We also suggest that the OH group is hydrogen bonded to a surface oxygen of the zirconia, similar to the LF proton of zeolite HY.

The crucial point is that reactions which are catalyzed by solid acids do not proceed via free carbenium ions but the intermediates are better described as alkylsulfates or alkoxy groups, as proposed by Kazansky (7) and more recently by Ponec for the case of adsorbed three-carbon-membered ring intermediates (29). The spectroscopic identification of surface alkoxy groups clearly proves, in full agreement with quantum chemical calculations, that zeolite framework oxygen is involved in the stabilization of the chemisorption complex, which has conventionally been described as "adsorbed carbenium ion" (30–33). While it has been pointed out by previous authors that "chemisorbed carbenium ions" are strongly different

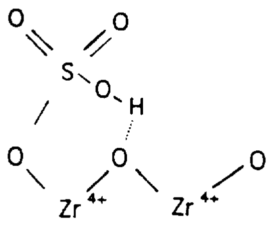

FIG. 8. Proposed model of site combining Lewis and Brønsted acidity.

from free carbenium ions, the present results show that at a certain level of acid strength the activity of a catalyst is no longer controlled by its acidity but by the nature of the intermediates, providing an energetically facile path from reactants to products.

This conclusion does not give a concrete answer to the question why the metal-promoted SZ catalysts are so much more active than their unpromoted counterparts, even though their acid sites are identical within experimental error. Greater stabilization of the highest transition state on FMSZ than on SZ is one possiblity; the corresponding difference in activation energy has not been found experimentally, but measurements of activation energies are known to be problematic for rapidly deactivating catalysts. An alternative possibility is that the presence of reducible oxides leads to the intermediate formation of olefins. In this case the isomerization of C_4 could proceed via C_8 intermediates which are known to easily undergo β-fission yielding fragments with iso-C_4 skeletons. Recent results at Northwestern University with ^{13}C-labeled C_4H_{10} lend support to this mechanism (34).

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