An NMR study of acid sites on sulfated-zirconia catalysts using trimethylphosphine as a probe

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Concentrations of Brønsted and Lewis acid sites on sulfated-zirconia catalysts were determined using the ^{31}P MAS NMR spectra of adsorbed trimethylphospine. A sample that had been calcined and exposed to air for a long period exhibited only Brønsted acidity; however, treatment of the sample at progressively higher temperatures resulted in the development of at least three types of Lewis acidity, along with a decrease in the concentration of Brønsted acid sites. In a related study the activity of these catalysts for the alkylation of isobutane with 2-butene was determined. The aged catalyst was inactive, but activation of the material at 100°C resulted in the most active catalyst. Thermal treatment at higher temperatures resulted in a loss in activity which paralleled the decrease in the Brønsted acid sites. These results are consistent with a model in which strong Brønsted acidity is a result of the interaction between bisulfate groups and adjacent Lewis acid sites.

Keywords: sulfated zirconia; NMR; acidity; trimethylphospine; isobutane alkylation

1. Introduction

Sulfated zirconia and related materials have received considerable attention because of their potential for replacing sulfuric acid or hydrogen fluoride as catalysts in alkylation reactions. The nature of the acidity that gives rise to the unusual activity of SO_4^{2-}/ZrO_2 catalysts is the subject of this study. Previous research using the infrared spectra of adsorbed pyridine has shown that both Lewis and Brønsted acid sites are present on SO_4^{2-}/ZrO_2 catalysts [1]. More recently, in a very thorough study, again using pyridine as a probe of acidity, Morterra et al. [2] have shown that pyridine adsorbed on Lewis acid sites dominated the spectra of samples degassed in vacuo at 400°C. The addition of water at 27°C, however, significantly increased the amount of Brønsted acidity.

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The ^{31}P solid state magic angle spinning (MAS) NMR spectroscopy of adsorbed trimethylphospine (TMP) also is an effective method for probing the acidity of heterogeneous catalysts [3,4]. The method has an advantage over the infrared spectroscopy of adsorbed pyridine in that the amount of TMP bound in a particular state can be readily quantified [5]. Moreover, the chemical shifts of TMP coordinated to different types of Lewis acid sites are often distinctly different. When aluminum is present at a Lewis acid center it sometimes is possible to observe J_{P-Al} coupling in the spectrum, which makes the assignment of the complex unequivocal [6,7]. In most cases when Brønsted acid centers are present, the spectra reflect the J_{P-H} coupling of the $[(CH_3)_3P-H]^+$ adduct [3,4]. One would hope to be able to determine Brønsted acid strengths from the chemical shifts, but, in general, the range of shifts is small and other factors, such as the extent of solvation, appear to have an effect comparable to that of acid strength.

Although most of the research on the use of TMP to determine the acidity of catalysts has been carried out on zeolites [3,6], the method has recently been extended to sulfated ZrO_2, HfO_2, TiO_2 and Al_2O_3 [8], as well as to Al_2O_3–SnO_2 [7] and silica–alumina catalysts [9]. Fripiat and co-workers [8] observed a sharp ^{31}P resonance at +26 ppm, which they attribute to TMP adsorbed on very strong Lewis acid sites. By way of comparison, the $CH_3P{:}AlCl_3$ adduct has a chemical shift of −42 ppm, and it is generally assumed that stronger Lewis acidity causes a greater downfield chemical shift. Here, we adopt the convention that a downfield shift in the spectrum corresponds to a larger (more positive) chemical shift.

In the present study the acid site distribution, as characterized by the ^{31}P NMR spectra of adsorbed TMP, was compared with the catalytic activity of SO_4^{2-}/ZrO_2 for the alkylation of isobutane with 2-butene to form C_8 isomers. The results indicate that Brønsted acid centers, perhaps in concert with Lewis acid centers, are responsible for the activity in the alkylation reaction with 2-butene.

2. Experimental

Sulfate-promoted zirconia was synthesized by using a two-step procedure. In the first step, a modified sol–gel process developed by Dosch et al. [10] was used to synthesize hydrous potassium zirconium oxide. Details of this synthesis and the subsequent sulfation with H_2SO_4 are given in a separate publication [11]. The resulting material was dried overnight at 115°C and calcined in static air at 500°C for 1 h. After calcination the tetragonal form of ZrO_2 was present. A negligible amount of K was present in the catalyst, which had a sulfur content of 3.9 wt%. An infrared spectrum of the sample revealed that sulfate was coordinated to the ZrO_2 in a bidentate mode.

For the NMR experiments TMP was introduced at 50 Torr and was allowed to equilibrate at 25°C for 2 h. The sample was then degassed at that temperature for 0.5 h. The SO_4^{2-}/ZrO_2 powder was transferred to a ceramic zirconia NMR rotor in a dry, oxygen-free glove box. The spectra were recorded immediately, using dry N_2 as the drive gas. The MAS frequency was 3.5 kHz. The ^{31}P MAS NMR spectra were acquired using a Bruker MSL-300 spectrometer. ^{31}P chemical shifts were recorded using 90° pulses (5 μs), with and without proton decoupling. Chemical shifts are reported relative to 85% H_3PO_4. A standard consisting of $NH_4H_2PO_4$ and $NaNO_3$ was used to determine the absolute concentrations of the specific forms of adsorbed TMP. The integrated proton-decoupled spectra of the samples and the standard were compared. Where necessary, the spectra of overlapping peaks were deconvoluted to obtain the concentration of a particular species. The estimated error is ±10%, except as indicated below.

Catalytic results were obtained in a constant flow stirred-tank reactor at 76°C and at 350 psi. A mixture of isobutane (Airco; 99.0%) and 2-butene (Matheson; 63% trans-2-butene and 37% cis-butene) was fed into the reaction at a total weight hourly space velocity of 49 h^{-1}. The reactor contained 4 g of catalyst. Product analysis was by gas chromatography.

3. Results

The acidity and catalytic properties of the SO_4^{2-}/ZrO_2 were remarkably altered by varying the subsequent treatment of the calcined material. In addition to the freshly calcined material, SO_4^{2-}/ZrO_2 (fresh), which had been exposed to air for only a few minutes, an aged catalyst, SO_4^{2-}/ZrO_2 (aged), was prepared by exposing the material to air in a capped glass vial for 2 weeks. Alloquats of this aged material were subsequently heated for 2 h at 100, 200 or 320°C (SO_4^{2-}/ZrO_2 (100), SO_4^{2-}/ZrO_2 (200), SO_4^{2-}/ZrO_2 (320)). For the NMR experiments the respective samples were heated in vacuo; whereas, for the catalytic experiments the samples were heated in flowing N_2. Following this in situ treatment the catalyst was cooled to 76°C before charging isobutane into the reactor.

3.1. NMR CHARACTERIZATION

The proton-decoupled and coupled spectra are shown in figs. 1 and 2, respectively. The proton-decoupled ^{31}P NMR spectrum of the SO_4^{2-}/ZrO_2 (aged) sample is characterized by a central resonance at −2.7 ppm with spinning side bands, as shown in spectrum a, fig. 1. There may also be a weak resonance at −46 ppm. The corresponding proton-coupled spectrum (spectrum a, fig. 2) exhibits much more intense spinning side bands that result from dipolar ^{31}P–^{1}H interactions. Although the isotropic J_{P-H} coupling is not evident in the central resonance, it can be found in the second, low field spinning side band. The magnitude of chemical shift, the intense spinning side bands and the evidence for J_{P-H} coupling indicate that the dominant species present on the aged sample was $[(CH_3)_3P-H]^+$. The larger line width in the coupled spectrum (see below) suggests that there also may be intermo-

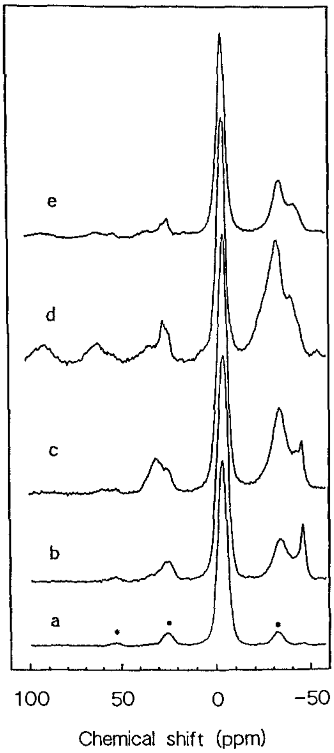


Fig. 1. Proton-decoupled ^{31}P MAS NMR spectra following adsorption of trimethylphosphine on (a) SO_4^{2-}/ZrO_2 (aged), (b) SO_4^{2-}/ZrO_2 (100), (c) SO_4^{2-}/ZrO_2 (200), (d) SO_4^{2-}/ZrO_2 (320), (e) SO_4^{2-}/ZrO_2 (fresh). Spinning sidebands are denoted by asterisks.

lecular dipole–dipole P–H interactions. Lewis acid centers, if present at all, are a very minor species. The concentrations of the two types of acid sites are summarized in table 1.

When the aged catalyst was treated in vacuo at 100°C and higher temperatures there was clear evidence for the formation of one or more types of Lewis acid centers. The spectrum of SO_4^{2-}/ZrO_2 (100) exhibited resonances at −3.4 and −45 ppm, in addition to a resonance at ca. −33 ppm which overlaps a spinning side band, as shown in fig. 1b. Because of this overlap the amount of TMP held at this site, reported in table 1, is only approximate. Again, the concentration of protonated TMP was much greater than that of the Lewis-bound form. In the coupled spectrum the 520 Hz scalar J_{P-H} coupling is clearly evident, even in the central resonance, as shown in fig. 2, spectra c–e. The unequal intensity of the doublet (the high field component is smaller in the central resonance) is a consequence of the intramolecular dipolar P–H coupling [12]. The decrease in line width that allows one to partially resolve these two lines is consistent with the loss of H_2O. The protons, for example, in hydrogen-bonded H_2O might interact with ^{31}P, and thus provide the additional broadening that is evident in fig. 2a.

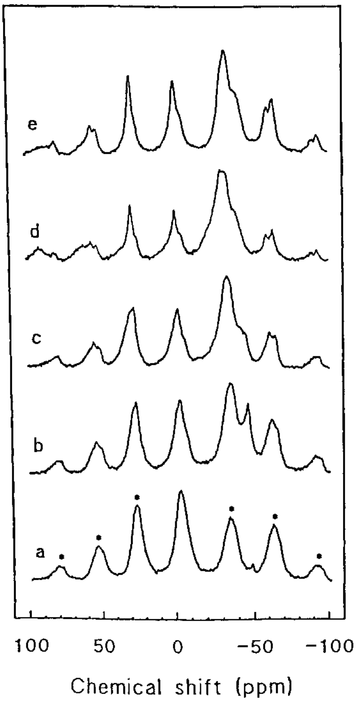


Fig. 2. Proton-coupled ^{31}P MAS NMR spectra following adsorption of trimethylphosphine on (a) SO_4^{2-}/ZrO_2 (aged), (b) SO_4^{2-}/ZrO_2 (100), (c) SO_4^{2-}/ZrO_2 (200), (d) SO_4^{2-}/ZrO_2 (320), (e) SO_4^{2-}/ZrO_2 (fresh). Spinning sidebands are denoted by asterisks.

Upon degassing the sample at 200 and 320°C the concentration of the protonated adduct decreased further, and that of the adduct with a chemical shift of −33 ppm increased. One might conclude that Brønsted acid centers are converted to Lewis acid centers, although the respective changes are not equivalent in magnitude (table 1). There was also a significant loss in the resonance at −45 ppm and a new maximum appeared at −39 ppm. The ^{31}P NMR spectrum of the SO_4^{2-}/ZrO_2 (200) sample had a rather broad resonance at +31 ppm, which is not due to a spinning side band. Moderately sharp resonances were observed at +23 and +26 ppm following TMP adsorption on the SO_4^{2-}/ZrO_2 (320) sample. In addition, broad resonances were observed at +34, +63 and +91 ppm. The origin of the resonances at +23 and +26 ppm is unknown (see below); however, the resonance at +34 ppm may be attributed to physisorbed trimethylphosphine oxide (TMPO), with the resonances at +63 and +91 ppm being its spinning sidebands. TMPO physisorbed in zeolite-Y has a chemical shift of +37 to +43 ppm, with intense spinning sidebands [13]. In fact, the first low-field spinning sideband may be more intense than the central band. Lewis-bound TMP is the most easily oxidized form, and during sample handling some of the phosphine may have contacted a small amount of air.

The spectrum obtained following calcination in air at 500°C, SO_4^{2-}/ZrO_2 (fresh) was intermediate between that of the samples degassed at 200 and 350°C.

Table 1
^{31}P chemical shift and the concentration of each type of adsorbed $(CH_3)_3P$

Sample	Chemical shift (ppm)	Concentration mmol-TMP g-cat.$^{-1}$ $\times 10^3$
SO_4^{2-}/ZrO_2 (fresh)	−4.1	160
	−33	42
	−41	20
SO_4^{2-}/ZrO_2 (aged)	−2.7	384
	−46	4
SO_4^{2-}/ZrO_2(100)	−3.4	229
	−33	34
	−45	24
SO_4^{2-}/ZrO_2(200)	−3.8	196
	−33	71
	−45	9
SO_4^{2-}/ZrO_2(320)	−3.5	126
	−33	83
	−39	5

Only one type of protonated adduct was detected (at −4.1 ppm), but there was no resonance at −45 ppm. Clearly, the distribution between types of acid centers is strongly affected by the pretreatment conditions.

3.2. CATALYTIC RESULTS

For purposes of comparison with the spectroscopic results the activities of the same set of catalysts were determined during the reaction of 2-butene with isobutane to form C_8 isomers. The results are reported in table 2. The formation of butane is believed to occur via the initiation steps

Table 2
Summary of alkylation results

Product	Catalyst				
	SO_4^{2-}/ZrO_2 (fresh)	SO_4^{2-}/ZrO_2 (aged)	SO_4^{2-}/ZrO_2 (100)	SO_4^{2-}/ZrO_2 (200)	SO_4^{2-}/ZrO_2 (320)
n-butane (wt%)	0.44	0.24	0.48	0.39	0.31
C_8 (wt%)	2.0	0.0	2.3	1.2	0.5
cum. C_8 yield (wt%)[a]	69	0	77	51	24

[a] See text for definition.

$$\text{2-butene} + H^+ \rightarrow \text{sec-butyl cation} \quad (1)$$

$$\text{sec-butyl cation} + \text{isobutane} \rightarrow \text{butane} + \text{tert-butyl cation}. \quad (2)$$

The C_8 wt% is the weight percent of C_8 products in the effluent. The dominant component was trimethylpentane. The catalyst deactivated with time on stream, therefore a cumulative C_8 yield is defined by the equation

$$C_8 \text{ yield} = \frac{\int_0^t m_8 \, dt + M_8}{m_A^f t}, \quad (3)$$

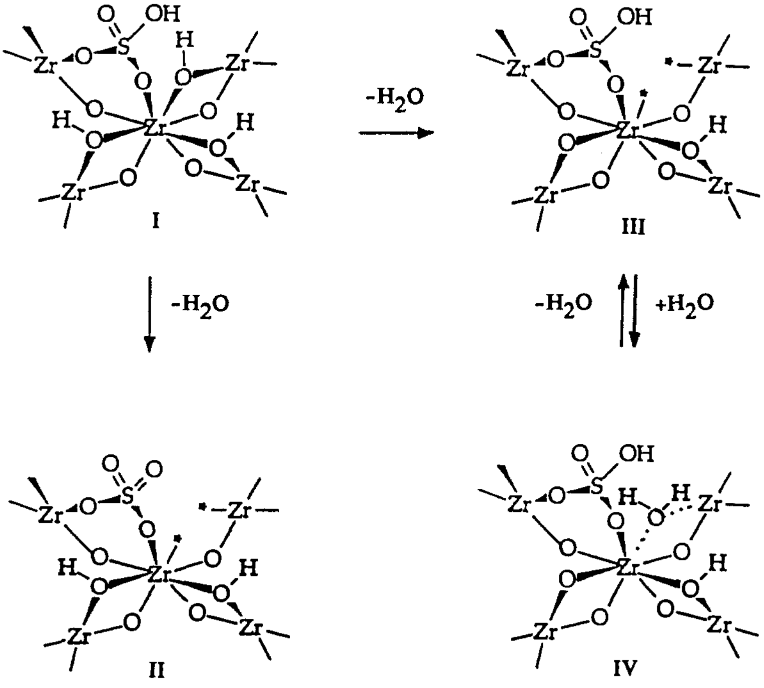
where m_A^f is the mass flow rate of butene in the feed, m_8 is the mass flow rate of C_8 compounds in the effluent, M_8 is the mass of m_8 compounds in the reactor and t is the time on stream. For the data shown in the table, t was 15 min. The cumulative wt% was greater than the wt% in the effluent, which indicates that a large amount of C_8 hydrocarbons accumulated in the reactor; i.e, the relative value of M_8 in eq. (3) was large.

It is apparent from the alkylation results that the formation of butane was rather insensitive with respect to the treatment of the catalyst, but the C_8 wt%, both in the effluent and cumulative, was strongly influenced by the activation conditions. In particular, the aged catalyst had no alkylation activity, while degassing this catalyst at 100°C resulted in maximum activity. Thermal treatment at higher temperatures resulted in a decrease in activity. The freshly calcined catalyst, SO_4^{2-}/ZrO_2 (fresh), exhibited an activity that was only slightly less than the catalyst treated at 100°C.

4. Discussion

A model of acidic sites on sulfated zirconia, recently proposed by Clearfield [14], provides a basis for the interpretation of the spectroscopic and catalytic results described here. As shown in scheme 1 the uncalcined catalyst (I) contains protons as bisulfate groups and as hydroxyl groups bridging two Zr ions. During calcination, water is lost to form II and III. In both structures Lewis acid centers are formed, but in III the bisulfate group remains intact, which results in a Lewis acid site adjacent to an S–O–H group. According to Clearfield, these bisulfate groups act as Brønsted acid centers and account for the strong acidity. As a final point with respect to the model, we suggest that water, acting as a weak Lewis base, may be non-dissociatively adsorbed via its nonbonding electrons as described in IV. As a result of this perturbation, the acidity of the bisulfate protons is diminished.

Thus, in the present study the calcined catalyst would be a mixture of II and III. The protonated form of TMP could be derived from both types of protons. Prolonged exposure to water vapor in the air results in IV, which has almost no remain-



Scheme 1.

ing Lewis acid centers. The poorly resolved $J_{P\text{-}H}$ coupling in spectrum a of fig. 1 may be attributed to interaction of ^{31}P with the additional protons from H_2O. The molecular water may be removed by heating the catalyst at 100°C in vacuo or under N_2, and the strong acidity of III is regained. Finally, thermal treatment at $T > 200°C$ results in the partial loss of bisulfate hydrogen and the corresponding Brønsted acidity.

It should be noted that just as the coordinative unsaturation on zirconium ions influences the acidity of adjacent bisulfate protons, the presence of the protons also will modify the Lewis acidity at the zirconium centers. Therefore, at least three types of Lewis acid centers are anticipated, as was observed in the NMR spectra of adsorbed TMP. We tentatively assign the resonance at −45 ppm to TMP on Lewis acid sites adjacent to the bisulfate group and the one at −33 ppm to the remaining Lewis acid sites in II. As the bisulfate proton is thermally removed, the resonance at −45 ppm is replaced by a new one at −39 ppm, which may reflect TMP adsorption on the modified Lewis acid site. One difficulty with this interpretation is the observation that the concentration of TMP molecules having a chemical shift of −45 ppm is always much less than the concentration of protonated adducts. This difference may result from the presence of two types of Brønsted acid centers, one of which is weakly acidic and is unaffected by the Lewis acid center. In addition, the disparity in concentration could be due to steric effects. That is, there is insufficient space for TMP molecules at the bisulfate proton and at the adjacent Lewis acid center. Generally, the bond strength favors the formation of the protonated adduct.

Although Fripiat and co-workers [8] attributed ^{31}P resonances in the +23 to +26 ppm range to TMP at very strong Lewis acid sites, this assignment seems unlikely for several reasons. First, ^{31}P chemical shifts as large as +24 ppm are known for Lewis-bound TMP, but they occur as a result of soft base–soft acid coordination (e.g. $(CH_3)_3P–PF_3$) [15]. Second, sharp resonances with chemical shifts of +24 and +29 ppm have been observed following adsorption of TMP in Mg-ZSM-5 and dehydroxylated zeolite-Y, respectively [16]. In the Mg-ZSM-5 catalyst the resonance was particularly strong after oxidation of the sample containing TMP in static air at 600°C. These samples were loaded into ceramic rotors as described in this paper. It is doubtful that zeolites would have strong Lewis acid centers, and as noted above, TMP coordinated to $AlCl_3$, which is a reasonably strong Al-containing Lewis acid, has a chemical shift of only −42 ppm. Third, the very narrow line width of the resonance at +26 ppm indicates that the molecule is in rapid motion or the phosphorous is present in a state of high symmetry. TMP bound strongly to a strong Lewis acid center probably would not be very mobile; therefore, we conclude that the ^{31}P exists in some molecular entity which gives rise to the high symmetry.

A cursory comparison of the spectroscopic results of table 1 and the catalytic data of table 2 might suggest that there is no correlation between Brønsted acidity and the alkylation activity. For example, the SO_4^{2-}/ZrO_2 (aged) catalyst had the largest concentration of Brønsted acid centers, but no activity for the alkylation of isobutane with 2-butene. One should keep in mind, however, that the strength of the acid centers also is an important factor, and according to the model described above, strong Brønsted acidity requires the interaction of bisulfate groups with adjacent Lewis acid centers. The SO_4^{2-}/ZrO_2 (aged) catalyst had almost no Lewis acid centers, presumably because of molecularly adsorbed water, as described in IV. Activation at 100°C would remove this water, and the resulting catalyst was active because it had a reasonable number of both Brønsted acid centers, (−3.4 ppm) and Lewis acid centers (−33 ppm). Treatment of the catalyst at progressively higher temperatures caused a decrease in the number of Brønsted acid centers, which is manifested by the decrease in catalytic activity. Under these conditions the number of Lewis centers increased, which confirms that the Lewis centers, acting alone, are not responsible for the catalytic reaction. This analysis assumes, of course, that the actual active centers are not some small subset of those detected by the NMR spectrum of adsorbed TMP.

5. Conclusions

A comparison of the solid state NMR spectra of adsorbed TMP with the activity for the alkylation of isobutane with 2-butene suggests that the strongly acidic protons on sulfated zirconia are responsible for the catalysis. But the strong acidity requires the presence of adjacent Lewis acid centers. That is, through an inductive effect electrons are withdrawn from O–H bonds by coordinatively unsaturated Zr, thus giving rise to more acidic protons.

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