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An NMR study of acid sites on chlorided alumina catalysts using trimethylphosphine as a probe

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The MAS-NMR spectra of adsorbed trimethylphosphine (TMP) were used to determine the concentration of Brønsted and Lewis acid sites on pure and chlorinated γ-Al_2O_3 samples. Chlorination with $CHCl_3$, CCl_4 or $AlCl_3$ promoted the formation of Brønsted acid centers, which are characterized by the protonated adduct of TMP. This adduct has a ^{31}P chemical shift of ca. −3.8 ppm and a J_{P-H} scalar coupling of 517 Hz. Additional resonances in the −44 to −54 ppm range are attributed to Lewis acid–base pairs. In some cases a partially resolved J_{P-Al} coupling is observed, which confirms the assignment. Upon thermal treatment of a chlorinated sample at temperatures $>200°C$, the concentration of Brønsted acid centers decreased; the concentration of one type of Lewis acid increased and another remained almost constant. In a parallel set of experiments the initial conversion of *n*-hexane at 150°C and the yields of cracking and isomerization products were determined. Comparable functional relationships were observed between the loss of Brønsted acid sites and the decrease in yields of both cracking and isomerization products. These results suggest that Brønsted acidity is responsible for the cracking and isomerization of *n*-hexane over chlorided aluminas at 150°C.

Keywords: NMR; TMP; acid sites; gamma alumina; chlorine

1. Introduction

Although reforming of hydrocarbons over platinum on chlorided-alumina catalysts is a well established process, the exact roles of the platinum (or a related bimetallic phase) and the acidic support remain uncertain. It has been generally accepted that platinum promotes the dehydrogenation of the alkane, and the acidic alumina catalyzes the isomerization of the alkene. Finally, the isomerized alkene is hydrogenated on the platinum [1]. More recently it has been established, mainly through the work of Primet and co-workers [3,6], that a properly chlorided alumina is itself an effective alkane isomerization catalyst, even at relatively mild temperatures. For example, *n*-butane can be isomerized at 100°C [6]. These catalysts, however, suffer from rapid deactivation, presumably because of coke formation.

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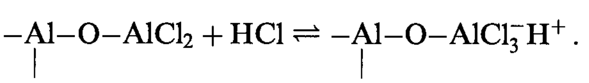
Under the more conventional conditions (450°C, 30 atm, H_2/alkane = 5), it is possible that the platinum serves to activate H_2, which in turn limits the amount of coke present on the alumina phase under steady-state conditions.

Apart from resolving the bifunctional nature of the conventional catalysts, it is important to understand the origin of the exceptional activity that is found in the chlorinated aluminas, without platinum. Bernard and Primet [6] found that their most active catalyst was obtained by first reacting γ-Al_2O_3 with CCl_4 and then with HCl. The treatment with CCl_4 alone introduced Lewis acidity, and the catalysts exhibited modest activity; however, the exposure to HCl created strong ("super") Brønsted acidity that resulted in the high initial activity for *n*-butane isomerization. The mechanism for the formation of the most active acid centers has been described as



$$-\underset{|}{Al}-O-AlCl_2 + HCl \rightleftharpoons -\underset{|}{Al}-O-AlCl_3^-H^+ . \quad (1)$$

As part of a more general study of the nature of acid sites in alkane reactions, we used the NMR spectra of adsorbed trimethylphosphine (TMP), a weak Lewis base ($pK_b = 5.35$), to determine both the types and the quantity of acid sites that are present on chlorided-alumina catalysts. The ^{31}P magic-angle-spinning (MAS) NMR spectrum of TMP has been extensively employed to probe Brønsted and Lewis acidity in zeolites [7–13] and other materials [14,15]. The identification of Brønsted acidity is unambiguous because of the splitting from J_{P-H} coupling in the spectra. In some cases with Lewis acids, one can also detect splitting from J_{P-Al} coupling [12,13,15]. Moreover, it is relatively easy to determine the number of spins; therefore, the number of acid sites can be measured provided the adsorption equilibrium is favorable and there are no limiting steric interactions, such as might occur in the cavities of a zeolite [10]. In this study, spectroscopic results are compared with the catalytic properties obtained during the initial conversion of *n*-hexane at 150°C.

2. Experimental

2.1. CATALYST PREPARATION

γ-alumina (Catapal SB) was first pretreated overnight in flowing O_2 at 500°C and then under vacuum at the same temperature for 2 h. In order to introduce Cl^- ions into most of the samples, the alumina was reacted at 300°C for 0.5 h with a flowing (5 ml min^{-1}) CH_3Cl/N_2 gas mixture. The partial pressure of chloroform was maintained at 50–60 Torr. After chlorination at 300°C, the flow of CH_3Cl/N_2 was stopped and the sample was heated or cooled to a particular temperature. The sample was maintained at this temperature under pure flowing N_2, usually for 1 h. The temperature was then decreased to 25°C. For one sample, CCl_3 was used in place of CH_3Cl; after reaction at 300°C, the sample was heated under vacuum at 200°C for 0.5 h and cooled to 25°C prior to the adsorption of TMP at that temperature.

Another type of sample was prepared by mechanically mixing γ-alumina with fresh aluminum chloride in a dry glove box. The Al_2O_3 had been degassed under flowing O_2 at 500°C. The sample contained approximately 15 wt% $AlCl_3$. After mixing, the sample was treated under vacuum at 25 or 100°C for 0.5 h.

2.2. NMR MEASUREMENT

In preparation for the NMR analyses, TMP was introduced from the vapor phase (50 Torr) and allowed to equilibrate for 2 h at 25°C. The sample was degassed under vacuum at 25 or 80°C for 0.5 h and was transferred into a ceramic zirconia NMR rotor in a dry, oxygen-free glove box. The spectra were recorded immediately using dry nitrogen as the drive gas to ensure that no oxidation took place. To simplify the presentation, the samples are identified according to the following example:

$$CHCl_3/Al_2O_3(200-25),$$

which indicates that the γ-Al_2O_3 sample was chlorided with $CHCl_3$, subsequently treated in N_2 at 200°C, exposed to TMP, and then degassed at 25°C.

The ^{31}P and ^{27}Al MAS-NMR spectra at 121.493 and 78.206 MHz, respectively, were acquired using a Bruker MSL-300 spectrometer. ^{31}P chemical shifts are reported relative to 85% H_3PO_4, while ^{27}Al shifts are referenced to an 0.1 M aqueous solution of $AlCl_3$. The 90° pulse width was 5 μs for ^{31}P and ^{1}H, and 6 μs for ^{27}Al. For ^{27}Al concentration measurements, a 30° pulse was used. ^{31}P NMR spectra were recorded with and without proton decoupling. The typical spinning rate was 3.5 kHz, but in order to distinguish spinning side bands from a resonance signal, ^{31}P NMR spectra were sometimes recorded at different spinning rates.

Suitable ^{31}P NMR spectra were normally acquired with only 15 min of signal averaging. The phosphorous T_1 was relatively short (2 s), so direct 90° pulses were used. Thus, the spectra were acquired under conditions appropriate for direct quantification of the adsorbed species. A standard consisting of $NH_4H_2PO_4$ (0.0098 g) and $NaNO_3$ (0.4300 g) was used to determine the absolute intensity.

2.3. CATALYTIC MEASUREMENTS

For the catalytic measurements 2.4 g of γ-Al_2O_3 was chlorinated in situ using $CHCl_3$. The chlorination was carried out for 0.5 h in the manner described above. The catalyst was then heated or cooled in static $CHCl_3$ to a predetermined temperature, and was maintained at that temperature in flowing N_2 for 1 h. A stream of H_2/n-hexane (n-hexane pressure ca. 45 Torr) was passed over the catalyst at a flow rate of 35 ml min^{-1} and at 150°C. The contact time was ca. 4 s. Using an 8-port sampling valve, the exit stream was sampled 5 s after the reaction, and every 10 s thereafter. The data was extrapolated back to zero time in order to obtain the initial percent conversion and the product selectivity. The products were analyzed by gas chromatography.

3. Results and discussion

3.1. CHARACTERIZATION OF ACID SITES BY ^{31}P NMR OF TMP

As hydroxyl groups are removed from the surface of alumina during the dehydroxylation process, the underlying Al^{3+} cations become exposed to the surface and form Lewis acid sites. Peri [16] has reported that for γ-Al_2O_3, 56% of the water (present as hydroxyl groups) is removed at 400°C and 84% is removed at 600°C. In principle, the remaining OH^- ions could function as proton donors, i.e. as Brønsted acid sites; however, they are so weakly acidic that they cannot, for example, protonate pyridine ($pK_b = 8.82$).

The ^{31}P NMR spectra of TMP adsorbed on γ-Al_2O_3 pretreated at 500°C are shown in fig. 1. The spectrum obtained after removal of excess TMP at 25°C (spectrum a) is characterized by a resonance at −51 ppm, which is assigned to TMP adsorbed on Lewis acid centers. A comparable resonance has been found in zeolite-Y in the range of −51 to −61 ppm, while physically adsorbed TMP has a resonance at −67 ppm [10]. On the low field side of this major peak, there is a shoulder with a chemical shift of −46 ppm and a hint of J_{P-Al} coupling (see below). The downfield shift of the shoulder suggests a site of greater acid strength. Indeed, when the TMP was removed at 80°C, the spectrum (spectrum b) was dominated by the reso-

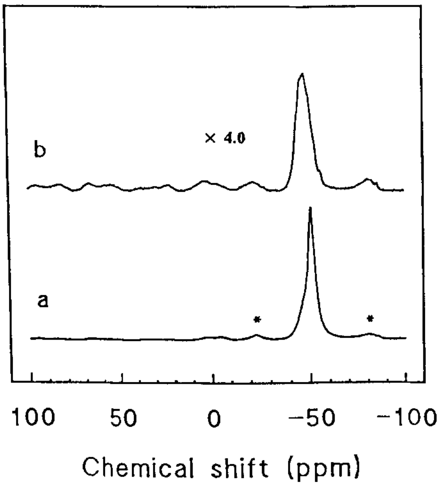


Fig. 1. ^{31}P decoupled MAS-NMR spectra of TMP on γ-Al_2O_3: (a) after TMP adsorption sample degassed at 25°C, (b) after TMP adsorption sample degassed at 80°C. Asterisks indicate spinning sidebands.

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}) $\times 10^3$
γ-Al_2O_3(25)[a]	2.7	7
	−3.9	8
	−46	52
	−51	231
γ-Al_2O_3(80)[b]	2.7	7
	−3.9	7
	−46 to −51	116
$CHCl_3/Al_2O_3$(80–25)	−3.5	207
	−44	78
$CHCl_3/Al_2O_3$(80–80)	−3.4	204
	−44	3
$CHCl_3/Al_2O_3$(200–25)	−3.3	221
	−44	78
$CHCl_3/Al_2O_3$(300–25)	−3.8	131
	−45	40
	−52	156
$CHCl_3/Al_2O_3$(400–25)	−3.9	68
	−46	42
	−53	186
$CHCl_3/Al_2O_3$(500–25)	−4.0	12
	−46	59
	−54	200
$CHCl_3/Al_2O_3$(80–25)[c]	−4.0	149
	−43	149
CCl_4/Al_2O_3(200–25)	−4.0	162
	−44	58
$AlCl_3/Al_2O_3$(25–25)	−3.4	505
	−41	125
	−53	46
$AlCl_3/Al_2O_3$(100–25)	−3.4	477
	−42	68

[a] Sample degassed at 25°C after TMP adsorption.
[b] Sample degassed at 80°C after TMP adsorption.
[c] Sample pretreated in H_2 at 600°C prior to reaction with $CHCl_3$.

nance at −46 ppm. Two weak resonances occur at −3.9 and 2.7 ppm. The resonance at −3.9 ppm is conceivably due to a small number of Brønsted acid sites and the resonance at 2.7 ppm could result from a small number of much stronger Lewis acid sites, although this assignment is speculative. The 1 : 1 CH_3P : $AlCl_3$ complex on zeolite-Y has a chemical shift of −42.5 ppm [13]. The amounts of the adsorbed species, as well as the chemical shifts, are summarized in table 1.

The NMR spectra of the $CHCl_3/Al_2O_3$(80–25) sample, shown in fig. 2, are typical of those obtained for samples chlorided with $CHCl_3$. Spectrum a is dominated by a resonance at −3.5 ppm, which results from the protonated adduct of TMP, $[(CH_3)_3P\text{–}H]^+$. The unequal intensity of the doublet (the high field component is smaller in the center resonance) is a consequence of the dipolar P–H coupling [11]. In addition to having the correct chemical shift, the proton-coupled spectrum (spectrum b) exhibits doublet features, both in the central band and the spinning side bands. This doublet indicates a J_{P-H} scalar coupling of 517 Hz. A Lewis acid adduct is represented by the resonance at −44 ppm, which clearly exhibits a J_{P-Al} coupling of ca. 300 Hz. The center of the six-line multiplet is at −50 ppm, which is up field from the peak maximum at −44 ppm. This difference in chemical shift sug-

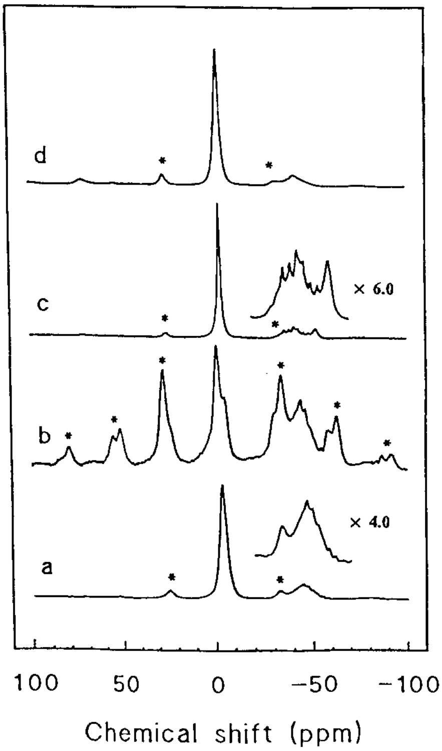


Fig. 2. ^{31}P MAS-NMR spectra of TMP on: (a) $CHCl_3/Al_2O_3$(200–80) sample, proton decoupled; (b) $CHCl_3/Al_2O_3$(200–80) sample, proton coupled; (c) $AlCl_3/Al_2O_3$(25–25) sample, proton decoupled; (d) $AlCl_3/Al_2O_3$(100–25) sample, proton decoupled. Asterisks indicate spinning sidebands.

gests that there are actually two different types of Lewis acid centers; however, because of the uncertainties introduced by the overlapping spectra, their concentrations are reported together in table 1. It is evident from the table that the concentration of Brønsted acid centers is considerably greater than that of Lewis acid centers. When the TMP was removed at 80°C, the concentration of protonated adducts remained almost constant while the concentration of Lewis acid adducts decreased remarkably.

In order to determine the effect of temperature on the acidity, the chlorinated samples were heated to progressively higher temperatures in flowing N_2 for 1 h. Changes in the ^{31}P NMR spectra are depicted in fig. 3, and the concentrations of the TMP bound at the different acid sites are given in table 1. Treatment in flowing N_2 at 80 or at 200°C produced nearly the same distribution of acid sites. The concentration of Brønsted acid centers was about 6% greater for the sample treated at 200°C, but this difference is within the experimental uncertainty. When the chlorinated sample was treated at 300°C and higher temperatures, there was a marked decrease in the signal of the protonated adduct at −3.5 ppm and the growth of a

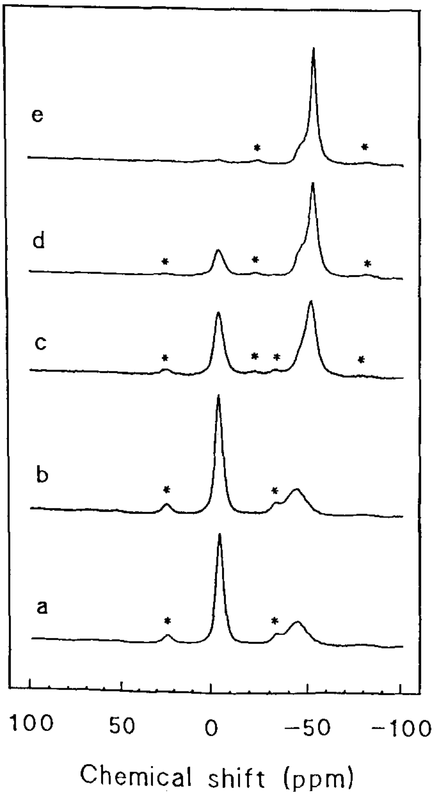


Fig. 3. ^{31}P decoupled MAS-NMR spectra of TMP on chlorided Al_2O_3 samples treated in flowing N_2 at progressively higher temperatures: (a) CH_3Cl/Al_2O_3(80–25), (b) CH_3Cl/Al_2O_3(200–25), (c) CH_3Cl/Al_2O_3(300–25), (d) CH_3Cl/Al_2O_3(400–25), (e) CH_3Cl/Al_2O_3(500–25). Asterisks indicate spinning sidebands.

new resonance at −52 to −53 ppm. Although it is difficult to resolve accurately this resonance from that at ca. −44 ppm, an attempt has been made to estimate the concentrations of the two types of Lewis acid adduct, and the results are reported in table 1. For purposes of comparison with the catalytic results (see below), the two Lewis acid concentrations, as well as the Brønsted acid concentrations, have been plotted as a function of treatment temperature in fig. 4a.

An additional experiment was carried out to determine further the effects of sample pretreatment on the acidity. In one case a $CHCl_3/Al_2O_3$(80–25) sample was pretreated 1 h in flowing H_2 at 600°C, after the usual pretreatment in flowing O_2 at 500°C. The resonance at −44 ppm almost doubled in amplitude, as indicated by the results in table 1. The use of H_2 rather than N_2 probably had a minor effect; the more significant factor was the greater degree of dehydroxylation. As expected, the number of Brønsted centers decreased by about 25%, relative to that found in the sample prepared by pretreatment at 500°C. These results confirm that chlorination at 300°C is affected by the previous history of the sample.

To elucidate the origin of the protons in the $[(CH_3)_3P{-}H]^+$ adduct, CCl_4 was substituted for $CHCl_3$ as the chlorinating agent. The spectrum of the resulting sample, CCl_4/Al_2O_3(200–25), also had a strong signal at −3.5 ppm, which was 78% as large as the one found after chlorination with $CHCl_3$. This result indicates that

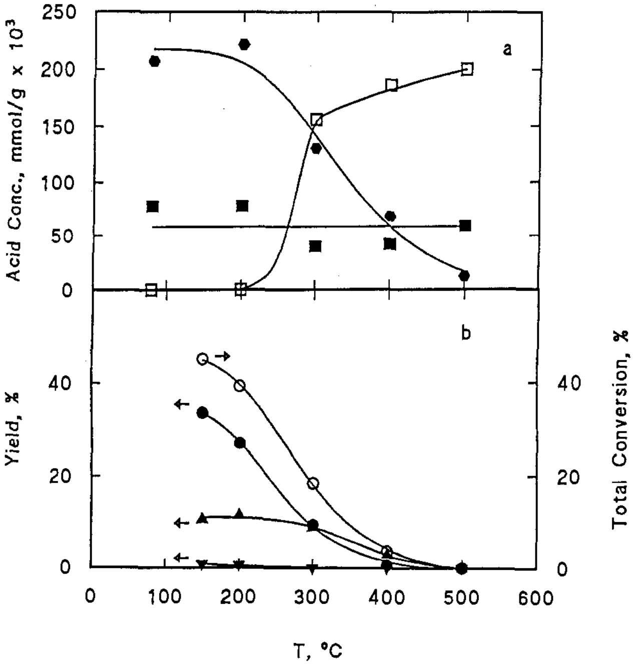


Fig. 4. Effect of thermal treatment of chlorinated Al_2O_3 on (a) acid site concentration and (b) catalytic properties for the reaction of *n*-hexane: (●) Brønsted acid concentration, −3.8 ppm; (■) Lewis acid concentration, −44 ppm; (□) Lewis acid concentration, −54 ppm; (○) total *n*-hexane conversion; (●) yield of cracking products; (▲) yield of isomerization products; (▼) yield of C_6 olefins.

the Brønsted acid centers are derived from the protons present as hydroxyl groups on the alumina, perhaps via the formation of HCl. Thomson et al. [17] reported that HCl was produced during the chlorination of γ-Al_2O_3 with CCl_4 under static conditions at 200°C.

As an alternative method of chlorination, $AlCl_3$ was first mechanically mixed with the pretreated γ-Al_2O_3 and then TMP was adsorbed. The sample, designated $AlCl_3/Al_2O_3(25)$, was characterized by the NMR spectrum shown in fig. 2c. Again, there was a sharp resonance at −3.5 ppm. More than twice as many protonated adducts were present in this sample relative to the $CHCl_3/Al_2O_3(200–25)$ sample. Moreover, in the Lewis acid region the spectrum is complicated because of the presence of two multiplets of six lines, plus another resonance with no J coupling. For purposes of counting spins the portion of the spectrum that had J coupling was integrated as a whole, and the results are reported in table 1. The J_{P-Al} coupling was 243–316 Hz. When the sample was heated to 100°C, prior to addition of TMP, part of the $AlCl_3$ was removed (see the ^{27}Al NMR spectrum). The γ-Al_2O_3 had been chlorinated so that the resulting material was similar to the sample that had been treated with $CHCl_3$, as shown by a comparison of spectra a and d in fig. 2. But again, with $AlCl_3$ as the source of Cl^- ions, the concentration of Brønsted acid sites was considerably greater.

3.2. ^{27}Al NMR SPECTRA

The ^{27}Al spectra of γ-Al_2O_3 with $AlCl_3$, chlorided γ-Al_2O_3 and pure γ-Al_2O_3 are shown in fig. 5. γ-Al_2O is composed of tetrahedrally (Al_{IV}) and octahedrally (Al_{VI}) coordinated alumina with chemical shifts of 67.2 and 5.2 ppm, respectively, as shown in spectrum d. The addition of $AlCl_3$ introduced another sharp resonance at −1.8 ppm, with the accompanying spinning side bands (spectrum a). Pure $AlCl_3$ exhibited a sharp resonance at −2.1 ppm with a similar set of spinning side bands (spectrum not shown). Thus, spectrum a is attributed to crystalline $AlCl_3$ on γ-Al_2O_3. Upon treating the $AlCl_3/Al_2O_3$ sample at 100°C, spectrum c was observed. No detectable amount of $AlCl_3$ remained, and it is evident from the TMP spectrum (see above) that the Al_2O_3 was chlorinated. A very similar spectrum (spectrum b) was observed after chlorination with $CHCl_3$ at 300°C.

Since ^{27}Al is a quadrupolar nucleus with $I > \frac{1}{2}$, special care must be taken in order to quantitatively compare resonances. Following the analysis of Fenzke et al. [18], a 2 μs, 30° excitation pulse was used to obtain accurate Al_{IV}/Al_{VI} intensity ratios. The relative ratio of $Al_{IV}/Al_{VI} = 0.39$ for γ-Al_2O_3 was within experimental error of the value of 0.34 ± 0.06 reported by Rohner et al. [19]. We found that the Al_{IV}/Al_{VI} ratio decreased to 0.32 upon chlorination, which agrees with their observation. This suggests that chlorination removes part of the tetrahedral aluminum from the sample, perhaps by converting it to volatile $AlCl_3$. Indeed a white powder, presumably $AlCl_3$, was detected at the exit of the reaction tube after the samples had been heated to 400 or 500°C in flowing N_2.

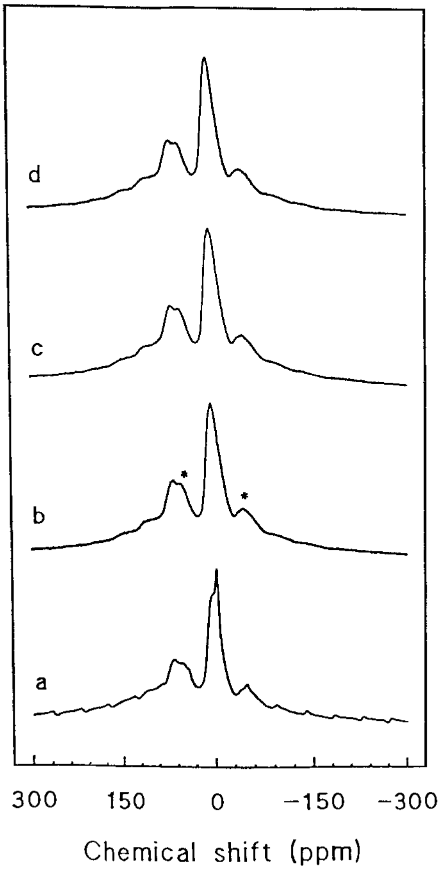


Fig. 5. ^{27}Al MAS-NMR spectra of pure and chlorided γ-Al_2O_3: (a) $AlCl_3/Al_2O_3(25)$, (b) $CH_3Cl/Al_2O_3(80)$, (c) $AlCl_3/Al_2O_3(100)$, (d) γ-Al_2O_3. Asterisks indicate spinning sidebands.

3.3. SURFACE ANALYSIS BY XPS

The results of fig. 4 show the dramatic effect of heating the chlorinated samples to 500°C in flowing N_2. The loss of Brønsted acidity involves the depletion of surface protons, but this may be accompanied by, or induced by, the loss of Cl^- ions from the surface as HCl. The extent to which chlorine was lost from the near-surface region was determined by X-ray photoelectron spectroscopy (XPS) analysis of the chlorinated Al_2O_3 samples after thermal treatment under vacuum. The results of table 2 show that the atom percent of chlorine decreased about 26% at 100°C and 53% at 500°C. Although thermal treatment removed chlorine from the surface, it is evident that there is no quantitative correlation between the loss of this chlorine and the loss of Brønsted acidity. The data, however, can be reconciled, in part, by assuming the model for the active center described by reaction (1). Through the reverse reaction, i.e. the loss of HCl, the strong Brønsted acidity would be destroyed by thermal treatment at 500°C, yet the surface would remain partially chlorided. But a discrepancy exists in the effect of thermal treatment in the 100–

Table 2
Near surface composition of catalysts treated at different temperatures [a]

Temp. (°C)	Composition (at%)			
	O	C	Cl	Al
25	58.3	6.7	2.5	32.4
100	56.4	8.8	1.8	32.9
500	57.1	8.3	1.1	33.5

[a] Samples were chlorinated with $CHCl_3$ for 0.5 h at 300°C and then degassed under vacuum at the temperature indicated.

200°C range; no decrease in Brønsted acidity was found while the chloride level decreased considerably. This inconsistency, however, may result from the different rates of chlorine removal from the samples in the XPS chamber and in the catalyst bed.

3.4. CATALYTIC CONVERSION OF *n*-HEXANE

The initial (extrapolated) *n*-hexane conversion and yield of cracking and isomerization products as a function of treatment in flowing N_2 at progressively higher temperatures is given in fig. 4b. The principal products of the cracking reaction were isobutane, isopentane and propane, and those of the isomerization reaction were 3-methylpentane and 2-methylpentane. The cracking activity rapidly decreased, with a half-life of about 18 s. A portion of the isomerization products was undoubtedly cracked before exiting the catalyst bed, but this loss of isomerization product was not taken into account in presenting the results of fig. 4b. For the catalyst pretreated at 150°C, the initial overall activity at 150°C was 7.3×10^{-4} mol h^{-1} g-cat^{-1}. There was no measurable *n*-hexane conversion over pure γ-Al_2O_3 at 150°C.

The results of fig. 4b clearly demonstrate that the conversion of *n*-hexane, the yield from the cracking reaction, and the yield from the isomerization reaction all progressively decrease with an increase in treatment temperature after chlorination. Following treatment at 500°C, there was no measurable activity. From 200 to 500°C, where the data are comparable, the decrease in yield for both types of reactions closely follows the decrease in Brønsted acidity. By contrast, the Lewis acid center having a TMP resonance at −53 ppm first developed after treatment at 300°C (fig. 3), and increased in amplitude up to 500°C. This center clearly could not be responsible for the catalytic activity. The TMP resonance at ca. −44 ppm is more problematic because there is evidence that it may be associated with two types of Lewis acid centers. The calculated total concentration of these centers showed some variation with respect to temperature (fig. 4b), but the changes from a constant value are within experimental error. Again, the functional behavior is in disagreement with the catalytic results.

4. Conclusions

Although one cannot exclude the role of some minority Lewis acid centers in *n*-hexane conversion, it appears likely, based on the results of this study, that Brønsted acid centers are responsible for both the catalytic cracking and the isomerization of *n*-hexane. These Brønsted acid centers are developed during chlorination with $CHCl_3$ or CCl_4 at 300°C. The source of the proton appears to be the hydroxyl groups in the γ-Al_2O_3. Thermal treatment at 500°C results in the partial loss of chlorine and presumably protons, thus there is a decrease in Brønsted acidity.

Acknowledgement

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