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31-P NMR study of acidic sites on Al_2O_3 and Al_2O_3–SnO_2 after reaction with CCl_2F_2/H_2

P. Kirszensztejn, B. Czajka
Faculty of Chemistry, A. Mickiewicz University, 60-780, Poznan, Poland

Tai-Cheng Sheng
Department of Chemistry, Shandong University, Jinan, Shandong 250100, PR China

T.N. Bell and I.D. Gay [1]
Department of Chemistry, Simon Fraser University, Burnaby, B.C., Canada V5A 1S6

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The surface acidic properties of two series of samples, γ-Al_2O_3 and γ-Al_2O_3–SnO_2 after reaction with CCl_2F_2/H_2 (CFC12/H_2), have been investigated by solid state high resolution CP/MAS 31-P NMR, using trimethylphosphine (TMP) as a probe molecule. It was found after reaction, that Brønsted acid sites were formed on the γ-Al_2O_3 surface. The longer the reaction time, the more rigidly TMP bonded to the acid sites. For the γ-Al_2O_3–SnO_2 system, Brønsted acid sites were also found on both the Al_2O_3 and SnO_2 surfaces after reaction of the γ-Al_2O_3–SnO_2 system with CFC12/H_2. The signal intensity relevant to these sites, indicates that the SnO_2 component is attached to, and therefore covers Brønsted sites of γ-Al_2O_3. Two types of Lewis acid site initially present on SnO_2 were not observed after reaction with CFC12/H_2.

Keywords: acidic sites; alumina; reaction CF_2Cl_2/H_2

1. Introduction

Mixed oxides frequently possess unique catalytic properties in comparison to those of the pure oxide components [1–3]. For example, silica–alumina has been widely used for many acid catalyzed reactions [4,5], where the combination appears to be a stronger acid than either pure alumina or silica [6].

Tanabe [7] suggested that acidity is generated by a charge imbalance caused by substitution of a metal atom Al(III) into the structure of the host oxide SiO_2, thus, when oxides possessing different structures combine, a charge imbalance would generate new acid centers.

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[1] To whom correspondence should be addressed.

The 31-P magic-angle-spinning (MAS) NMR spectrum of TMP has been extensively employed to probe Brønsted and Lewis acidity in zeolites [8,9]. This method has recently been extended to sulfated ZrO_2, HfO_2, TiO_2 and Al_2O_3 [10] as well as to the Al_2O_3–SnO_2 system [12]. In our previous work [11,12] we found that various types of Lewis sites were generated by the interaction of Sn- and Al-oxides in the γ-Al_2O_3–SnO_2 system.

Surface acidity of the support plays an important role in the conversion of hydrocarbons on metallic catalysts. In the case of Pt/γ-Al_2O_3 catalysts, it has been commonly accepted that acidic alumina catalyses the isomerization of alkenes. Primet [13] discovered that chlorinated alumina is an effective alkane isomerization catalyst even at relatively mild temperatures.

Unfortunately the role of the support material is still not clear. Understanding the role of acidity could thus be very important, especially in the case where such a system is used as a catalyst support for the conversion of CFCs, where HCl and HF are involved in the catalytic reaction.

The goal of this study was to evaluate the acidity profile of a series of γ-Al_2O_3–SnO_2 systems as well as that of pure γ-Al_2O_3 after their use in the catalytic conversion of CFC12/H_2.

2. Experimental

2.1. SAMPLES AND REACTION WITH CFC/H_2

The method of preparation of γ-Al_2O_3–SnO_2 is described in a previous paper [14]. γ-Al_2O_3–SnO_2 samples with a molar ratio γ-Al_2O_3 : SnO_2 between 1 : 0.5 and 1 : 0.01 were synthesized by coprecipitation methods (here Sn-0.5 represents a sample with molar ratio of γ-Al_2O_3 : SnO_2 equal to 1 : 0.5, and so on). A solution of tin(IV) acetate in CCl_4 and a solution of aluminum isopropoxide in isopropanol were used as starting materials. Homogeneous mixtures of the reagents were subjected to hydrolysis at 363 K with the pH maintained between 7.0 and 7.5. Under these conditions a precipitate formed, and this was aged for one week in the solution mix. The aged precipitate was filtered, washed and dried at 373 K for 48 h, after which the product was annealed in air at 773 K for 8 h. The γ-Al_2O_3 samples were prepared from aluminum isopropoxide. To avoid small amounts of contamination (especially the presence of Na), the isopropoxide was distilled before use and the molten product hydrolyzed with doubly distilled water at 333 K. In order to convert small amounts of bayerite that might have been formed during the hydrolysis, into boehmite, the suspension was aged at room temperature for 1 week [15]. The resultant γ-Al_2O_3 was characterized by X-ray diffraction and had a surface area of 275 m^2/g and average pore size of 28 Å [11].

In order to introduce Cl^- and F^- ions into the samples, alumina and tin-modified alumina were subjected to the catalytic reaction involving CFC12/H_2 at 300°C for 1 or 6 h [16]. The volume ratio of CFC to H_2 was held constant and equal to 1 : 6. The catalytic reaction was carried out in a flow system with a contact time of ~ 13 s. The products of the catalytic conversion were determined using a Hewlett-Packard GCMS, model No. 18001A.

2.2. NMR SPECTROSCOPY

Solid state NMR experiments were carried out using a 3.5 T instrument on which 31-P resonates at 60.457 MHz. 31-P chemical shifts are referred to 85% H_3PO_4. A proton decoupling field strength of 45 kHz was used.

2.3. ADSORPTION OF TRIMETHYLPHOSPHINE (TMP)

A standard pretreatment for the catalyst after reaction involved vacuum activation for 2 h at 450°C at a base pressure of about 10^{-5} Torr. Adsorption of TMP on the samples was carried out at room temperature, and then the sample was sealed off from the vacuum line for NMR measurement. The sealed sample tubes were spun at the magic angle at a speed of about 2 kHz using a spinner previously described [17].

3. Results and discussion

3.1. USE OF DIFFERENT PULSE PROGRAMS TO DISTINGUISH AND CONFIRM THE ADSORBED SPECIES HAVING VARIOUS DYNAMIC PROPERTIES

Four different pulse sequences were used to distinguish and confirm the adsorbed species having various dynamic properties:

(1) 90° pulse program used to study weakly bound species and give uniform excitation of all 31-P resonances.

(2) CP (cross polarization) used to specifically excite 31-P nuclei with a significant dipolar coupling to protons, and hence a bias in favor of immobile species with short P–H distances.

(3) TOSS (total suppression of sidebands) used to eliminate spinning sidebands in order to simplify spectral assignments.

(4) Cross polarization with delayed decouple used to completely eliminate signals from P–H bonded species, but only partially attenuate signals from 31-P with more distant 1-H interactions.

The advantage of using these different pulse programs to distinguish adsorbed species with various dynamic properties is demonstrated in fig. 1 using one of our samples as an example. Thus, fig. 1 shows the spectra using different pulse programs for the γ-Al_2O_3 sample after reaction with CFC12/H_2 for 6 h. Peak assignments were determined from our previous studies [12,18]. The peak at −47 ppm is

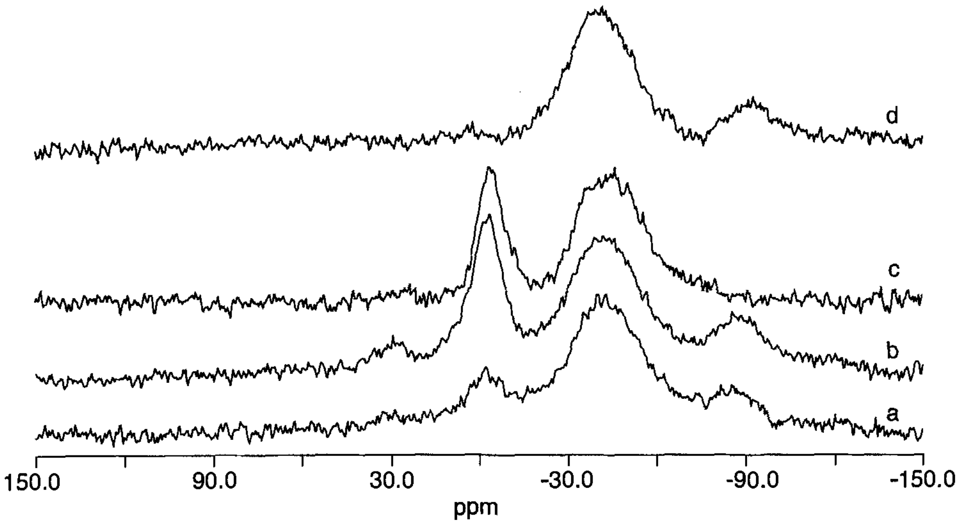

Fig. 1. 31-P NMR spectra of pure γ-Al_2O_3 after reaction with CFC12/H_2 for 6 h using different excitation pulse programs. (a) 90° pulse; (b) cross polarization (CP); (c) TOSS program; (d) delayed decouple program.

due to Lewis sites on γ-Al_2O_3 and the peak at −3 ppm to Brønsted sites. The latter peak does not occur with pure γ-Al_2O_3 samples before reaction with CFC12/H_2. The −3 ppm peak became bigger under CP excitation (fig. 1, b) compared to the peak from 90° excitation (fig. 1, a) and disappeared under delayed decoupling (fig. 1, d). These confirm the assignments made and show that the species at −3 ppm are firmly bonded to the surface. The peaks at −80 to 90 ppm (fig. 1, c) are spinning sidebands and were eliminated by using the TOSS program.

3.2. EXPERIMENTAL RESULTS FROM PURE γ-Al_2O_3 AFTER REACTION WITH CFC12/H_2 FOR 1 AND 6 H

Two γ-Al_2O_3 samples were examined, one was reacted with CFC12/H_2 for 1 h and the other for 6 h.

Lewis acid lines centered at −43.5 ppm became broader and shifted to lower field for these two samples (fig. 2, b–d), as compared with pure γ-Al_2O_3 not reacted with CFC12/H_2 (fig. 2, a).

The reason for the broadening and the slight shift could be that some Lewis acid sites on γ-Al_2O_3 had reacted with HCl or HF (resulting from the reaction with CFC12/H_2), and created new Lewis acid sites which have different chemical shifts.

No significant numbers of Brønsted acid sites were observed on the pure γ-Al_2O_3 sample, however after its reaction with CFC12/H_2, some Brønsted acid sites were observed through peaks at −3 ppm as shown in fig. 2, b–e. This assign-

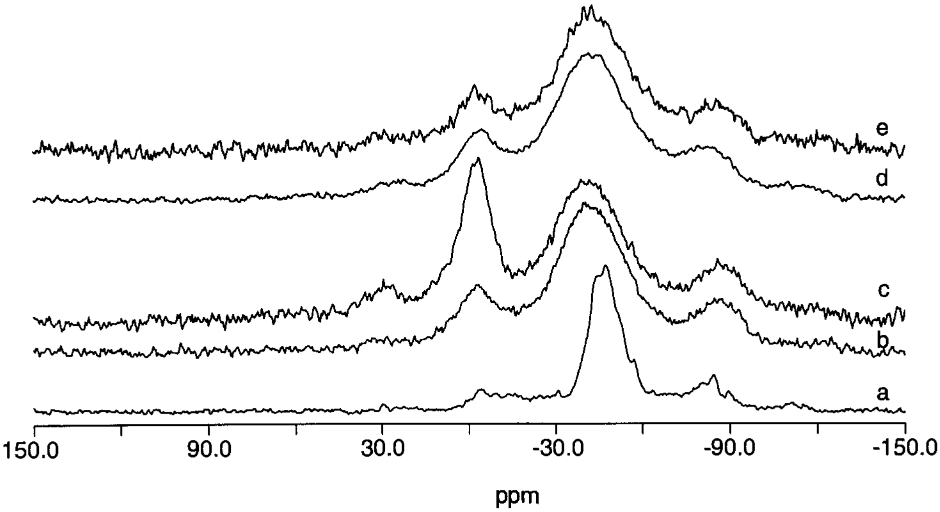

Fig. 2. 31-P NMR spectra of γ-Al_2O_3 using different excitation programs after different reaction times with $CFC12/H_2$. (a) No reaction, CP program; (b) 1 h reaction, CP; (c) 6 h reaction, CP; (d) 1 h reaction, 90° pulse; (e) 6 h reaction, 90° pulse.

ment was confirmed by the delayed decouple program under which this peak disappeared.

The mechanism of the creation of acidic sites on γ-Al_2O_3 has been fully discussed in a previous paper [12].

Fig. 2 also shows the effect of different reaction times on the amount and the rigidity of the species bonded to the Brønsted acid sites. It was found from the 90° excitation spectra (fig. 2, d and e) that the number of Brønsted acid sites on the two samples are almost the same (assuming the relaxation times of TMP on the acid sites of both samples are the same). The mobility of species held by the Brønsted acid sites, however, decreased for the sample from the 6 h reaction, as shown in spectra b and c in fig. 2. This conclusion is inferred from the cross polarization excitation program, where the species strongly bonded on the surface cause an increased spectral intensity. A mechanism for the creation of Brønsted acid sites on γ-Al_2O_3 after reaction with $CFC12/H_2$ has been proposed [11].

3.3. γ-Al_2O_3–SnO_2 AFTER REACTION WITH $CFC12/H_2$

It was found in previous studies on γ-Al_2O_3–SnO_2 catalysts [12] that there are three types of Lewis acid sites giving lines at −12, −22 and −47 ppm. No Brønsted acid sites were found. The peaks at −12 and −22 ppm are attributed to Lewis acid sites from tin oxides, and the peak at −47 ppm is from Lewis sites on γ-Al_2O_3. In the present study, the same series of γ-Al_2O_3–SnO_2 samples were used as before.

After reaction with $CFC12/H_2$, the samples with different amounts of SnO_2 demonstrate different behavior towards the formation of acid sites. The spectra for this series of samples using the TOSS program for clarity, are shown in fig. 3. For the sample with the highest SnO_2 content, the two peaks at −12 and −22 ppm disappeared and new resonances at +27.1 and −4.8 ppm appeared (fig. 3, a).

On decreasing the amount of SnO_2 (from Sn-0.5), the intensity of the peak at −4.8 ppm decreased first, and then increased with a slight shift to −3.1 ppm for the lowest SnO_2 content sample (fig. 3, b–e). The intensity of the peak at 27.1 ppm decreased continuously.

The peak at −4.8 ppm has been assigned from our previous study [18] to Brønsted acid sites. We now assign the peak at −4.8 ppm to Brønsted acid sites on the SnO_2 surface created by the reaction between SnO_2 and CFC12/H_2. The concentration of Brønsted acid sites for the Sn-0.2 and Sn-0.1 samples is so small that they are too difficult to observe (fig. 3, b and c).

The peak at −3.2 ppm created by the reaction between γ-Al_2O_3 and CFC12/H_2 for pure γ-Al_2O_3 samples, and also for Sn-0.05 and Sn-0.01 samples (fig. 3, d and e) is assigned to Brønsted acid sites on the γ-Al_2O_3 surface.

It should be noted that the peak at −3.2 ppm in sample Sn-0.01 is distinguished from the peak at −4.8 ppm in the Sn-0.5 sample. The former originates from γ-Al_2O_3, the latter from SnO_2. Their line widths are also slightly different.

It is quite possible that there is a special structural configuration available on the γ-Al_2O_3 surface which can react with CFC12/H_2 to form Brønsted acid sites. This configuration can be covered by SnO_2 leading to Brønsted acid sites on the SnO_2 surface after reaction with CFC12/H_2.

We suggest that the peak at +27 ppm is probably from phosphine oxide on the SnO_2 surface, however at this time we do not have direct evidence for this assignment. It is well known that SnO_2 is easily reducible, and could provide the oxygen to form PMe_3O.

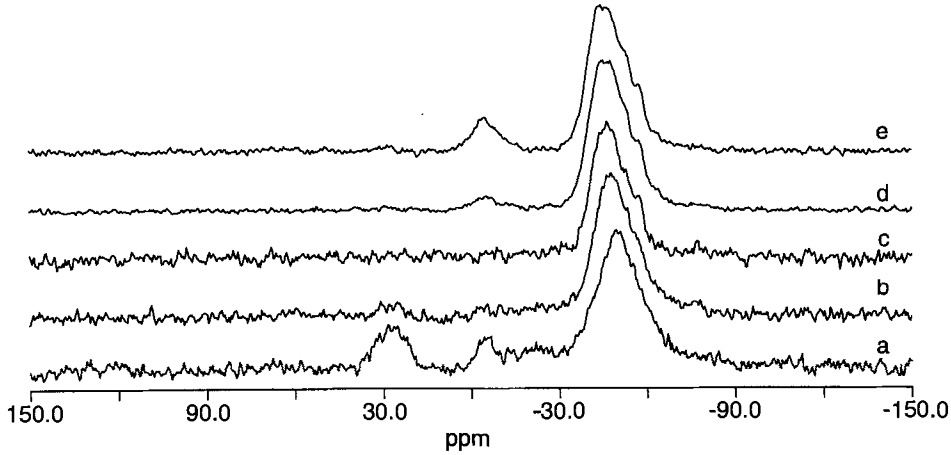

Fig. 3. 31-P NMR spectra for γ-Al_2O_3–SnO_2 with different SnO_2 content and using TOSS program. (a) Sn-0.5; (b) Sn-0.2; (c) Sn-0.1; (d) Sn-0.05; (e) Sn-0.01.

The peak at −44 ppm is assigned to Lewis acid sites on γ-Al_2O_3. It is interesting to note that the chemical shift of this peak changes from −50 to −44 ppm when the amount of Sn is decreased, moreover, the line width of the peaks at −50 to −44 ppm is narrower than that for samples without doping of SnO_2 as shown in fig. 1. These are most likely the results of interactions between the γ-Al_2O_3 and SnO_2 component.

4. Conclusions

(1) Brønsted acid sites are formed on pure γ-Al_2O_3 and γ-Al_2O_3–SnO_2 systems after reaction with CFC12/H_2.

(2) Lewis acid sites on the SnO_2 component disappeared after the reaction with CFC12/H_2.

(3) Indirect evidence is to the effect that the sites on the γ-Al_2O_3 surface which form the Brønsted acid, are the same sites that are covered up by the SnO_2 component.

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