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^{31}P and ^{119}Sn high resolution solid state CP/MAS NMR study of Al_2O_3–SnO_2 systems

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A series of Al_2O_3–SnO_2 catalysts with the mole ratio of Al_2O_3 to SnO_2 equal to 1 : 1, 1 : 0.5, 1 : 0.1, 1 : 0.05 and 1 : 0.01 were characterized by ^{31}P NMR of adsorbed trimethyl phosphine (TMP) and ^{119}Sn MAS NMR spectroscopy. It was found from ^{31}P NMR that no Brønsted acid sites exist in these samples. Pure SnO_2 shows two different types of Lewis acid sites; in the mixed oxide samples a Lewis peak characteristic of pure Al_2O_3 is always seen, together with either one or two other Lewis peaks, depending on the Sn concentration. ^{119}Sn CP/MAS NMR spectra of the highest Sn-content sample show one narrow line at −603 ppm superimposed on a very broad line, indicating a strong interaction between Al and Sn oxides.

Keywords: Al_2O_3–SnO_2 catalysts; acid sites; Lewis acid; trimethylphosphine; ^{31}P NMR; ^{119}Sn NMR

1. Introduction

Catalyst acidity has been found to be an important parameter in the design of catalysts for the hydrotreating of petroleum and heavy liquids, particularly shale and gas oils, as well as coal-derived liquids [1]. It is well known that increased acidity leads to increased coke formation resulting in catalyst deactivation and a shorter catalyst life [2]. Acidic sites are also thought to be responsible for cracking, isomerization and dealkylation reactions [3]. On the other hand, with supported metal catalysts, the type of surface precursor complex formed will depend on the type and strength of acidity available on the surface of the support and on the particular metal complex used as a reagent. The level of dispersity of the active metal has been found to be dependent on the nature of the binding between the metal complex and available centres of support.

In general, the aluminum hydroxides and therefore also the hydrated oxides are not strongly acidic. They are amphoteric in nature, as inferred from experience with the hydroxides in which all Al^{3+} ions are octahedral [4]. The OH^- groups attached to tetrahedral Al^{3+} ions may be more strongly acidic. Similarly Al^{3+} ions in tetrahedral positions formed during the dehydration process act as stronger Lewis acids than those in octahedral positions. Recently this was confirmed by Shimanskaya and co-workers [5] using a quantum-chemical cluster model. The calculated values for adsorption-complex stabilization energies, electron density transfer from water molecule to surface site, and optimal H_2O–Al distance clearly show that Al_s^{tet} acts as a stronger Lewis acid than Al_s^{oct}. The acidity especially of OH groups present on the surface can be markedly enhanced by the proximity of other ions. For example Cl^- develops surface acidity on alumina through the electronic asymmetry set up by the proximity of the different species drawing electrons from the O–H bond [4].

Many techniques have been used to study surface acidity, such as IR spectroscopy [6]. Solid state NMR spectroscopy has been recognized for many years as a remarkably powerful technique for investigating the structure and dynamic behaviour of molecules. Its value for studying systems of catalytic interest has become increasingly evident [7–12,16,17]. Alkyl phosphines have proven to be very useful molecular probes for investigating surface acid sites. Three different types of adsorption site, Brønsted, Lewis and physisorbed can be distinguished by ^{31}P MAS/CP NMR spectroscopy [10–12].

Alumina modified by tin ions is a promising catalyst support, which has many unique properties. One of us has investigated this system by using FTIR of adsorbed pyridine and X-ray diffraction [13,14]. It was shown in these studies that there are no strong Brønsted acid sites present in this system, and SnO_2 exists as a separate phase in preparations having a high tin content.

The objective of this study is to extend the above results by applying NMR spectroscopy. In the present report we use ^{31}P and ^{119}Sn CP/MAS NMR to further investigate these systems, and attempt to explore the surface acid sites and the interaction between Al and Sn.

2. Experimental

Samples. A series of Al_2O_3–SnO_2 samples were prepared by the co-precipitation method with Al_2O_3 to SnO_2 mole ratio of 1 : 1, 1 : 0.5, 1 : 0.1, 1 : 0.05 and 1 : 0.01. The method of preparation is described in detail in a previous paper [13].

NMR spectroscopy. Solid state NMR experiments were performed using a 3.5 T instrument on which ^{31}P and ^{119}Sn resonate at 60.46 and 55.66 MHz respectively. ^{31}P chemical shifts are referred to 85% H_3PO_4 while ^{119}Sn shifts are referred to $(CH_3)_4Sn$. A proton decoupling field strength of 45 kHz was used.

Adsorption of trimethyl phosphine (TMP) on Al_2O_3–SnO_2. For most adsorption experiments a standard pretreatment procedure 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 samples were then sealed off from the vacuum line for NMR measurements. The sealed tubes were spun at the magic angle at a speed of about 2 kHz using a spinner previously described [15].

3. Results and discussion

3.1. ^{31}P SPECTROSCOPY

The ^{31}P MAS NMR spectra of the series of Al_2O_3–SnO_2 samples together with spectra for pure SnO_2 and Al_2O_3 samples are shown in fig. 1. Fig. 1 (a) shows a spectrum of TMP adsorbed on the pure SnO_2 prepared in the same way as the Al_2O_3–SnO_2 samples. Two resonances at -14.9 and -34.8 ppm may be attributed to two different types of Lewis acid sites on SnO_2. TMP adsorbed on Al_2O_3 gave a resonance centred at -47 ppm (fig. 1 (g)) due to Lewis acid on alumina [16]. The sextet

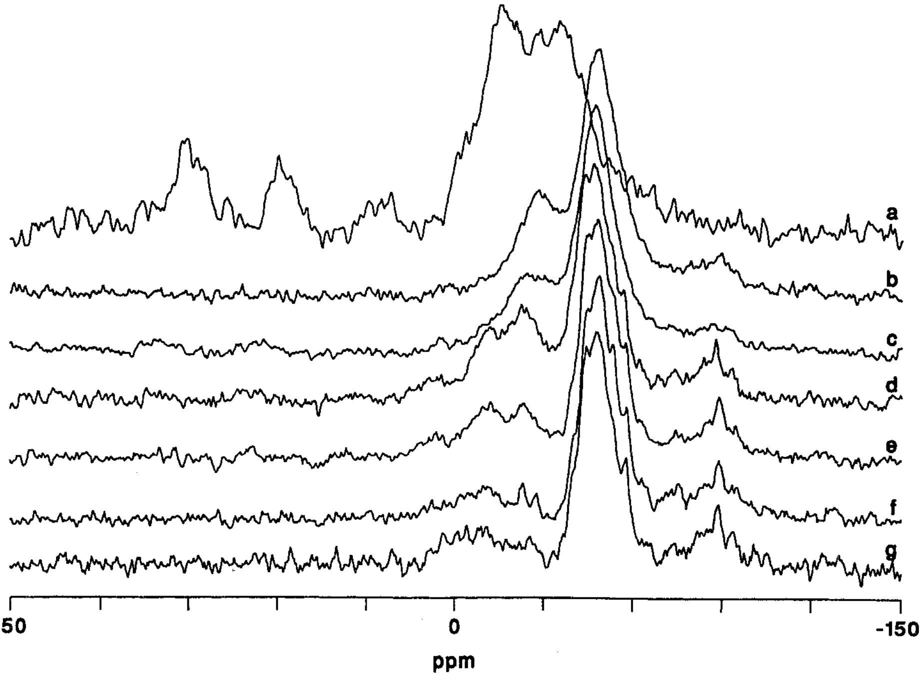

Fig. 1. ^{31}P MAS NMR spectra of PMe_3 adsorbed on (a) pure SnO_2, (b)–(f) Al_2O_3–SnO_2 with mole ratio of Al_2O_3 : SnO_2 equal to 1 : 1, 1 : 0.5, 1 : 0.1, 1 : 0.05, and 1 : 0.01 respectively, (g) pure Al_2O_3.

feature which appears is a result of the coupling of phosphorus to the ^{27}Al nucleus of spin 5/2 [17]. The peak at about −90 ppm is a spinning side band. The small peak at 57 ppm with spinning sidebands at 88, 25 and −5 ppm is likely Lewis-bound trimethyl phosphine oxide [18] arising from partial oxidation of the TMP. We see no evidence of any P–Sn scalar coupling. This is not surprising, since the abundances of ^{119}Sn and ^{117}Sn are 8.6% and 7.6% respectively. Since these have nearly the same gyromagnetic ratio, the coupling patterns would be a pair of 8% satellites symmetrically placed about the centre band. These would be unlikely to be observed at the present signal-to-noise ratio.

NMR spectra of adsorbed TMP on alumina doped with tin vary with composition of the Al_2O_3–SnO_2 system. In this respect the samples studied may be divided into two groups. One group consists of systems in which the ratio of Al_2O_3 to SnO_2 is in the range 1 : 0.01 to 1 : 0.1. For this group of samples, besides the resonance centred at −47 ppm (adsorbed TMP on alumina – fig. 1 (g)) two more resonances were detected at −22 and −12 ppm. These two resonances are similar to those found with the pure SnO_2 sample but with a minor shift to lower field. Another type of spectrum is found in mixed samples with greater than 20% of tin. For these samples only one resonance (besides −47 ppm) is seen (fig. 1 (b) and (c)) with a maximum at −28 ppm.

All of these peaks undoubtedly arise from various types of Lewis sites, generated by the interaction of the Sn- and Al-oxides. In the case of tin, the +IV oxidation state is more stable than the +II, but Sn(IV) is fairly easily reduced (the electrochemical potential for the reaction $Sn^{2+} - 2e = Sn^{4+}$ is 0.1364 V [19]). It is known from the literature, that when tin species are introduced into alumina, tin is very easily reduced to Sn(II) which is then present in a mixture with Sn(IV). Besides the presence of tin as SnO and SnO_2 some authors suggest other possible structures. Davis and coworkers [20] proposed an "egg shell" of tin aluminate stabilized by its interaction with the alumina. This oxide phase is not identical to any bulk tin oxide [21].

The ^{119}Sn NMR results (see below) indicate the absence of SnO, and suggest that, with the possible exception of the 1 : 1 sample, the catalysts are based on substitution of Sn into the Al_2O_3 lattice, rather than the reverse.

The Lewis sites may arise from any or all of (i) Sn^{4+} substituted in alumina, (ii) Sn^{2+} substitution, or (iii) modification by Sn of the surface coordination of aluminum ions, moving Al^{3+} from octahedral sites to tetrahedral ones. Al^{3+} in tetrahedral sites, acts as a stronger Lewis acid than Al^{3+} in octahedral positions. It should be noted that while we do not find a significant amount of SnO by ^{119}Sn NMR, the possibility of a low level of substituted Sn^{2+} is not excluded.

The above results are in good agreement with the FTIR investigation [14] where pyridine was used as a probe molecule; there the 1613–1625 cm^{-1} band is the most important in elucidating the quantity and strength of the Lewis sites. For samples of low tin oxide content, this band is clearly resolved into a number of components one of which is attributable to weak Lewis acid sites (1615 cm^{-1}) and one to strong

Lewis acid sites (1625 cm^{-1}). With an increase in the tin content, the band responsible for strong Lewis acid sites disappears. Clearly one feature common to all NMR spectra is that the resonance from the Lewis acid on alumina at −47 ppm does not change significantly in the series of samples with varying contents of SnO_2, as shown in fig. 1 (b)–(f). In other words, addition of SnO_2 into Al_2O_3 has no pronounced effect on the Lewis acid sites which already exist on pure alumina.

Previous studies [16,22] show that surface phosphonium ions resonating at about −4 ppm would be expected if Brønsted sites are present. Fig. 1 thus shows that there are no Brønsted acid sites on these samples. The same conclusion has been reached in the IR study using pyridine as a probing molecule [14]. Since the base strength of TMP is about 1000 times greater than pyridine ($pK_b = 5.35$ for TMP, 8.75 for pyridine) the present NMR study excludes the presence of weaker (by up to 3 orders of magnitude) Brønsted acid sites not detectable with pyridine, on the SnO_2–Al_2O_3 surface.

Two different kinds of excitation, cross polarization (CP) and single pulse were used in this study. CP excitation would favour species more rigidly bound to the surface. Fig. 2 shows the spectra obtained by the two different excitation methods, which show little difference in the relative peak intensities. This means that TMP molecules bound to the different Lewis sites have similar dynamic behaviour.

3.2. ^{119}Sn NMR SPECTROSCOPY

Some structural information on the SnO_2–Al_2O_3 system can be obtained from ^{119}Sn MAS NMR spectra. Fig. 3 (A) shows a ^{119}Sn MAS NMR spectrum for a pure

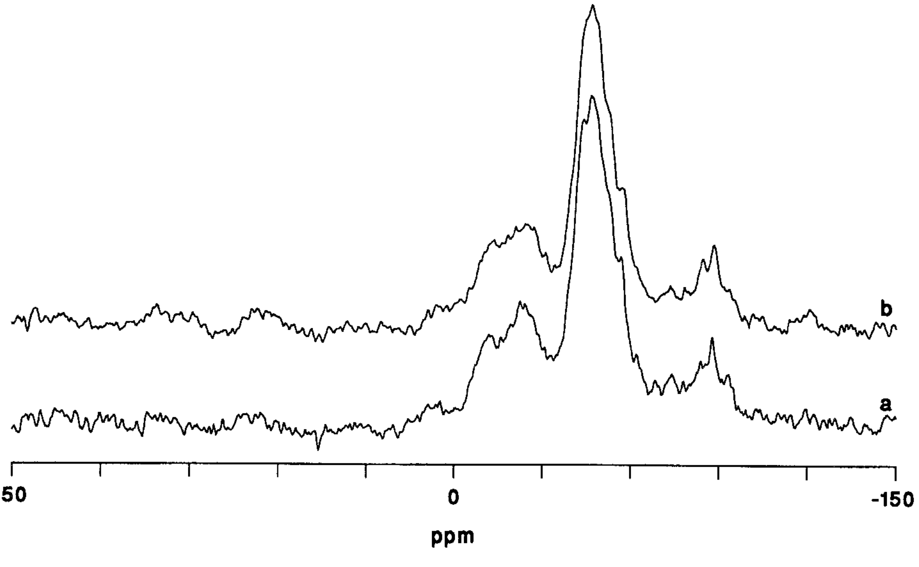

Fig. 2. ^{31}P MAS NMR spectra of PMe_3 on Al_2O_3–SnO_2 (1 : 0.1) (a) single pulse excitation, (b) cross-polarization.

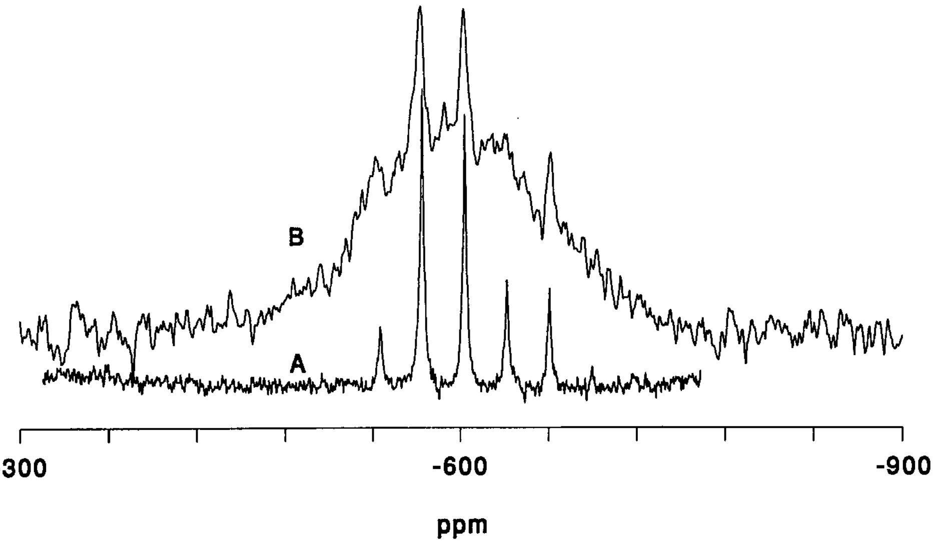

Fig. 3. ^{119}Sn MAS NMR spectrum for (A) pure SnO_2 sample and (B) Al_2O_3–SnO_2 (1 : 1) sample.

SnO_2 sample with 0.018 mM TMP adsorbed on it. Pure SnO_2 without TMP adsorbed gives the same ^{119}Sn spectrum. There is a centre band with a series of spinning sidebands. The centre band was identified by varying the spinning speed and found to be at −602.8 ppm. This agrees with the literature value of the chemical shift of SnO_2 [23].

The ^{119}Sn MAS spectrum for the SnO_2–Al_2O_3 sample (1 : 1) is shown in fig. 3 (B), and consists of a broad line near −600 ppm, and a sharp peak at −602.3 ppm together with spinning side bands of the latter. Clearly this shows unreacted SnO_2 together with a tin species giving rise to the broad band. Since SnO resonates at −208 ppm [24] the broad line is probably from Sn^{4+} rather than Sn^{2+}. The broadness might arise either from a range of chemical shifts for Sn in slightly differing environments, or from dipolar coupling to several neighbouring ^{27}Al ions. (Strong quadrupole coupling of ^{27}Al removes the effectiveness of magic angle spinning in removing dipolar couplings. Six Al atoms at a distance of 3 Å could produce a broadening of the magnitude observed.) In either case it is clear that most of the Sn is not present as crystalline SnO_2, and is in some form involving an intimate interaction with Al_2O_3.

For the samples with lower SnO_2 content, it is extremely difficult to observe a ^{119}Sn NMR signal of reasonable signal to noise ratio. For one of these samples do we observe any line from crystalline SnO_2. For the 1 : 0.5 Al to Sn sample, we observe a very weak broad line similar to the broad component of fig. 3 (B). As the Sn content decreases, the ^{119}Sn spin–lattice relaxation time (T_1) appears to increase in the more dilute samples. While we have not studied relaxation behaviour carefully, it is apparent that T_1 is several seconds in SnO_2, some tens of seconds in the 1 : 1 sample, and over 1 min in the 1 : 0.5 sample. This makes it impractical to obtain ^{119}Sn spectra of the more dilute samples in a reasonable time. Our ^{119}Sn spectra have been recorded to cover the range from +300 to −900 ppm, and no resonance has been observed apart from those discussed above.

4. Conclusions

The ^{31}P and ^{119}Sn MAS NMR study of the system of Al_2O_3–SnO_2 reveals that there are no Brønsted acid sites present; two types of Lewis acid sites exist on SnO_2 and either one or two types of Lewis site on the mixed oxide catalysts. Less conclusive results on the details of the structure and the interaction between Sn and Al can be reached at present. It is, however, safe to say from the ^{119}Sn NMR spectra that the interaction between Sn and Al is strong and formation of a surface tin aluminate or other compound is possible.

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