A NQR Study of γ-alumina Containing Chemisorbed Cl_2*

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Cl_2 was adsorbed at 370 and 870 K on commercially available γ-alumina, with BET surface area of 180 m^2/g, after dehydration at 850 K. NQR measurements were carried out between 55 and 6 MHz. The sample containing Cl_2 chemisorbed at 870 K showed the presence of a set of quite strong NQR signals with frequencies lower than 10.6 MHz, and another set of very weak NQR signals between 18.5 and 13.0 MHz. The stronger signals have been inferred as due to ^{27}Al and have been assigned to Al in three distinct environments. The values of e^2Qq/h and η determined for the signals are (1) 35.9 MHz, 0.53; (2) 35.7 MHz, 0.74; and (3) 35.3 MHz, 0.0 respectively. These values of e^2Qq/h are found to be very high as compared to those estimated for ^{27}Al at distorted octahedral and tetrahedral sites of the alumina, viz. 3.5 and 4.0 MHz respectively, from MAS-NMR. Therefore, chemisorption causes ^{27}Al to exist in the surface region at sites with greater distortion than in the interior of the particles but much smaller than in the case of completely dehydrated samples for which no NQR signals could be observed. The weak signals have been tentatively attributed to ^{35}Cl. The present results demonstrate that the NQR technique can be used in studies of chemically bound species on heterogenous catalysts.

Key words: Nuclear Quadrupole Resonance; Chemisorption; ^{35}Cl; ^{27}Al; γ-Alumina.

Introduction

Chemisorption of chlorine may be considered a step in high temperature reductive chlorination of oxide minerals. The reductive chlorination of a number of oxides has been extensively investigated during the past decade with a view to produce metals such as Al, Zr, Ti, various lanthanides and actinides etc., by electrolysis of the chloride salts. Chlorine is known to be chemisorbed strongly on various oxides. However, presently there is no spectroscopic technique for a satisfactory detection of chemisorbed chlorine. Modern surface sensitive techniques such as XPS suffer from the complications caused by the "charging effect" on poorly conducting oxide powers. NQR suffers from inherently low sensitivity and seemed to be unsuitable for surface studies. A simple calculation based on thermodynamic and kinetic data of the system alumina-chlorine [1] showed that high surface area γ-alumina may contain a sufficient number of chemisorbed ^{35}Cl atoms for the detection of NQR. In this communication we present preliminary results of NQR measurements on a γ-alumina containing chemisorbed Cl_2. The aim is to show that NQR can be used to obtain significant information from suitable nuclei in the surface region of high surface area materials.

Experimental

Commercially available γ-alumina (Martinswerk, Bergheim, FRG) has been employed. It has a BET (Brunauer, Emmett and Teller method) surface area of 180 m^2/g, and the X-ray analysis confirmed that the material had the structure of γ-alumina. The alumina was given a heat treatment in a grease-free gas handling system to remove adsorbed water and most of the surface hydroxyl groups. The dehydration/dehydroxylation treatment consisted in increasing the temperature of alumina at a rate of 8 K/min and heating it at ca. 920 K in flowing N_2 (purity 99.995%) for 2.5 h. The alumina was allowed to cool to the adsorption temperature where Cl_2 (purity 99.9%) was adsorbed without further purification. Previous isother-

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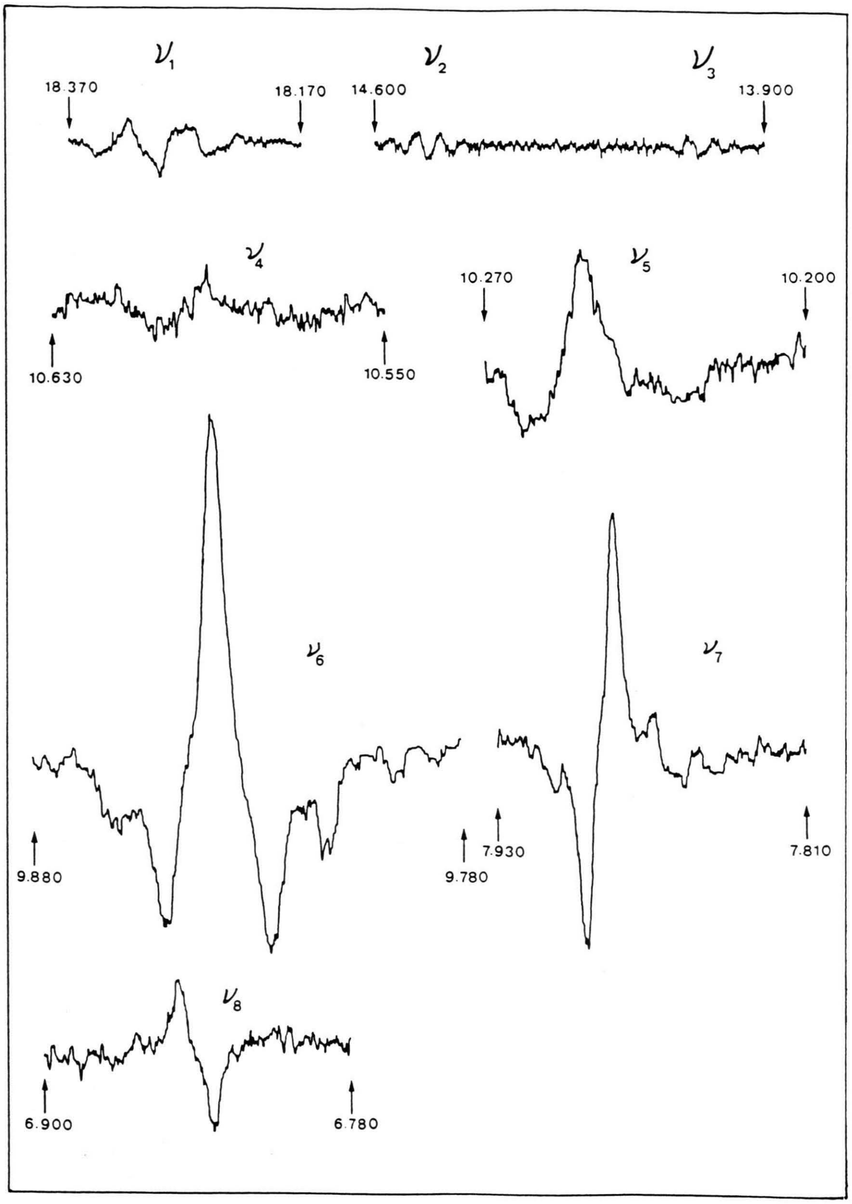

Fig. 1. NQR signals observed at 295 K from γ-alumina treated with chlorine at 870 K, i.e. sample S. The frequencies are given in MHz in the figure.

mal thermogravimetric measurements of the adsorption of Cl_2 between 370–870 K have shown [1] the existence of a strong chemisorption regime at higher temperatures and a weak chemisorption regime at lower temperatures. Therefore, different samples were prepared: sample S with chlorine adsorbed at 870 K, sample W at 370 K, the typical temperatures of the strong and the weak chemisorption regimes. A blank sample B was also prepared with the usual dehydration treatment. Samples of 2.5 g alumina were sealed in 13 mm o.d. thin walled glass tubes without exposure to air.

The NQR measurements were made with superregenerative oscillator together with a lock-in detector.

Results

On carefully scanning the frequency range from 55 to 6 MHz at room temperature, three very weak sig-

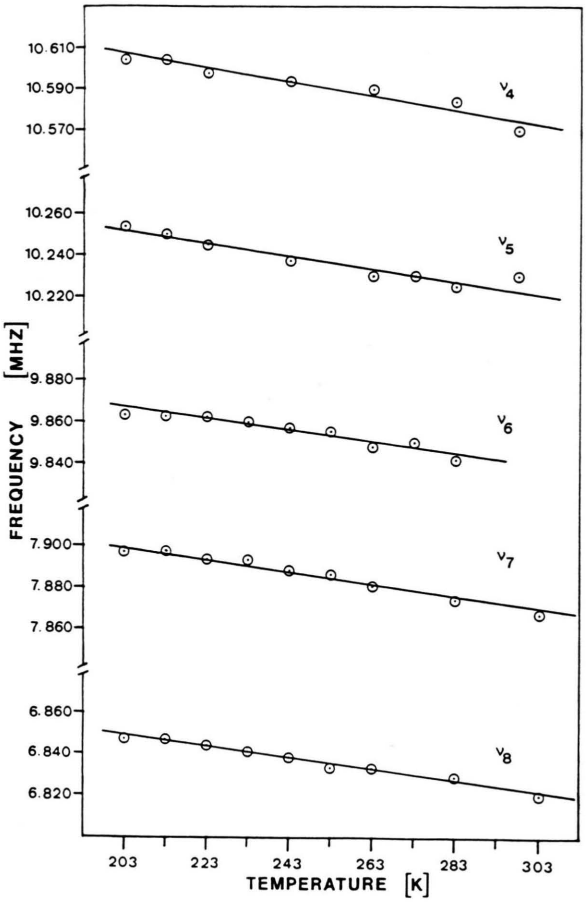

Fig. 2. Temperature dependence of the NQR frequencies of the stronger signals from γ-alumina treated with chlorine at 870 K, i.e. sample S.

Table 1. The NQR frequencies of samples of γ-alumina treated with chlorine. NQR measurements at 295 K.

Signal No.	Sample S Cl_2 adsorbed a 850 K			Sample W Cl_2 adsorbed at 370 K	
	ν MHz	"$\Delta\nu$" kHz	I a.u.	ν MHz	I a.u.
1	18.280		v.w.	17.517	v.w.
2	14.495		v.w.	17.441	v.w.
3	14.011		v.w.	13.130	v.w.
4	10.593	12.0	w.		
5	10.249	12.0	s.		
6	9.838	8.7	v.s.		
7	7.890	12.0	v.s.		
8	6.835	13.4	s.		

a.u. = arbitrary units; v.w. = very weak; w = weak; s = strong; v.s. = very strong

nals were observed on sample W at 17.517, 17.441 and 13.130 MHz. However, 8 signals were observed with sample S at frequencies lower than 18.3 MHz. Figure 1 shows the signals of S at room temperature. Table 1 contains the frequencies of the observed signals, their apparent linewidths, "$\Delta\nu$", and a qualitative indication of their strengths at room temperature. We shall refer to the various signals as ν_n (S) or ν_n (W) where n is the serial number of the signal in Table 1 and Figure 1. The temperature dependence of the stronger signals ν_4 (S) to ν_8 (S) could be studied with some difficulty. If the temperature was decreased rapidly by immersing the sample in liquid N_2, most of the signals could not be detected. In a series of measurements, the temperature of S was decreased slowly in steps of 10 K and the signals followed carefully to about 200 K. Figure 2 depicts the observed temperature dependence of the stronger signals ν_4 (S) to ν_8 (S). Finally, no signal was detected from B within the investigated frequency range at room temperature and at the higher sensitivity of the instruments used.

Discussion

The presence of impurities other than chemisorbed Cl_2 as the source of the observed NQR signals can be ruled out since no signal has been detected from B and the signals from W and S occur at quite distinct frequencies. The only NQR relevant impurity in the alumina is 0.15–0.25 wt% Na_2O. The observed signals are also not due to [2] $NaAlCl_4$ which might be thought to result from chlorination. The concentration of $NaAlCl_4$ would be too low anyway to detect an NQR signal.

No pairing of any two lines out of the observed eight signals satisfying the quadrupole moment ratio $Q(^{35}Cl)/Q(^{37}Cl)$ was found. For the very weak signals observed between 18.5 and 13.0 MHz, it is very likely that the corresponding signals from the ^{37}Cl nuclei are not observed due to a poor signal-to-noise ratio. The signals at 9.838 and 7.890 MHz have a frequency ratio of 1.2469 in disagreement with the accepted value $Q(^{35}Cl)/Q(^{37}Cl) = 1.2688$. Consequently, the stronger signals from S are assigned to ^{27}Al.

Figure 2 shows that the temperature dependences of ν_4 (S), ν_6 (S), ν_7 (S), and ν_8 (S) are practically the same while that of ν_5 (S) seems to be slightly weaker. In view of the relatively low intensity and larger apparent linewidth we believe that this difference is not

Table 2. ^{27}Al NQR coupling constants and asymmetry parameters at 295 K from γ-alumina treated with chlorine at 870 K, i.e. sample S. The NQR data pertain to aluminum nuclei believed to exist in the outermost layers of the alumina particles.

^{27}Al signals	e^2Qq/h MHz	η
ν_5(S), ν_8(S)	35.9	0.53
ν_6(S), ν_7(S)	35.7	0.74
ν_4(S), ν_4(S)/2	35.3	0.0

significant. These signals, however, may be discriminated on the basis of their relative intensities. The signals ν_6(S) and ν_7(S) have quite similar intensities and, therefore, can be assigned to ^{27}Al in one type of environment. Similarly ν_5(S) and ν_8(S) can be assigned to ^{27}Al in another type of environment. If the remaining weaker signal ν_4(S) is attributed to ^{27}Al in axially symmetric sites, then a corresponding signal is expected at 5.125 MHz. The latter would not be detected by the present spectrometer due to very low sensitivity at frequencies below ca. 6 MHz. The quadrupole coupling constants, e^2Qq/h or QCC, and the asymmetry parameters, η, for ^{27}Al in the three types of environments are given in Table 2. The parameters have been derived using the equations given by Creel et al. [3].

γ-alumina has a disordered spinel structure, where Al^{3+} ions occupy octahedral, Al_{VI}, and tetrahedral, Al_{IV}, sites [4]. A magic angle spinning nuclear magnetic resonance (MAS NMR) study of samples prepared following the same procedure as employed for the NQR samples exhibited absorption peaks due to ^{27}Al at octahedral and tetrahedral sites in the bulk of the alumina particles [5]. From the reported NMR linewidths, an upper estimate for the QCC at Al_{VI} and Al_{IV} can easily be obtained as approx. 3.5 MHz and 4.0 MHz, respectively. The values of the QCC and η obtained for ^{27}Al in this study are thus an order of magnitude higher and indicate the presence of ^{27}Al in quite asymmetric environments.

O'Reilly had shown [6] from a comparative study of ^{27}Al NMR for a number of γ-alumina samples with different BET surface areas that on the average two outermost layers of ^{27}Al nuclei must be affected by the surface. Due to the ionic nature of the Al–O bonds, the configuration of O^{2-} surrounding Al^{3+} could be easily distorted. Close to the surface of the particles, distortions of O^{2-} polyhedra could produce large changes in the EFG at the ^{27}Al nucleus even when the coordination number of aluminum remains unchanged. Thus the high values of the QCC and η given in Table 2 indicate that they belong to ^{27}Al in the outermost layers of the alumina particles.

The signals ν_1(S), ν_2(S), and ν_3(S) observed at higher frequencies are much weaker than the other signals from S. The sample W also exhibits three signals ν_1(W), ν_2(W), and ν_3(W) of similar intensity in a comparable frequency range. These weaker signals from the two samples may be attributed to ^{35}Cl, in view of their very low intensity and similar high frequencies. The corresponding ^{37}Cl signals are considered to remain undetected due to very poor S/N. The observed frequencies yield very high values of e^2Qq/h of ^{35}Cl between ca. 26 and 36 MHz as compared to the value -8.8 MHz reported [9] for gaseous AlCl. Nevertheless, the chlorine signals can be associated with Al–Cl bonds.

The QCC $= |35.5|$ MHz obtained for ^{27}Al is comparable to the QCC $= -29.2$ MHz reported [9] for gaseous AlCl. This suggests that the high values of the QCC are due to the formation of Al–Cl bonds after chemisorption of Cl_2 at higher temperatures. The presence of strong ^{27}Al signals from S but not from B clearly shows that the formation of Al–Cl bonds at 870 K induces structural reordering of O^{2-} polyhedra in the surface region so that the distortions around Al^{3+} are reduced. Since the three values of the QCC are almost the same, it seems reasonable to infer that Al^{3+} ions occupy essentially one type of sites, e.g. distorted octahedra. The axially symmetric QCC can be assigned to ^{27}Al at axially distorted octahedral sites due to the presence of an Al–Cl bond. It is difficult to attribute the sites with $\eta \neq 0$ with specific distortions of the O^{2-} polyhedra at this stage, but they appear to be associated with bond angle changes.

From S, NQR signals from both isotopic nuclei involved in Al–Cl bonds have been observed whereas only signals from ^{35}Cl nuclei have been observed from W. These facts are consistent with the conclusions of an earlier [7] in situ IR study of the adsorption of Cl_2 on alumina. In the strong chemisorption regime, adsorption of Cl_2 was inferred to occur predominantly at O^{2-} ions at sites of incomplete coordination on the surface of alumina particles by a mechanism involving electron transfer. This type of chemisorption, presumably, leads to a significant structural reordering of the surface region. It is, however, possible that greater mobility of the ions at higher temperatures also contributes to the reordering. The absence of ^{27}Al NQR signals from W shows that reactive adsorption of Cl_2 with the surface hydroxyls, which is known to occur at 370 K and above, does not produce a substantial structural reordering.

We tentatively assume that the lowest observed ^{35}Cl signal is associated with the Al–Cl bond of the axially distorted ^{27}Al. Following Townes and Dailey, $(QCC)_{Cl} = (QCC)_{atom}(1 - s_{Cl})(1 - i)$, where i is the ionic character of the bond and s_{Cl} the s character in the Cl bonding orbital. Taking s_{Cl} to be 15%, one obtains $i = 69\%$. This value of the ionic character of the bond is comparable to the results [8] on $AlCl_3$, where the ionic character of the solid has been reported as 66%. Thus, adsorption of Cl_2 leads to the formation of chemical bonds similar to those in $AlCl_3$.

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