Solid State Nuclear Magnetic Resonance, 3 (1994) 39–42
Elsevier Science B.V., Amsterdam

Solid-state ^{27}Al and cross-polarization ^{13}C magic-angle spinning nuclear magnetic resonance characterisation of aluminas derived from basic aluminium succinate [1]

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(Received 9 September 1993; accepted 22 October 1993)

Abstract

Solid-state ^{27}Al and cross-polarization (CP) ^{13}C magic-angle spinning nuclear magnetic resonance (MAS NMR) was used to characterise aluminas obtained by calcining basic aluminium succinate at different temperatures. In basic aluminium succinate, aluminium is in the tetrahedral coordination only. However, in both X-ray amorphous and γ-aluminas aluminium is in the tetrahedral and octahedral coordination. The intensity of the aluminium peaks is at a maximum for samples calcined at 700°C. ^{13}C CP MAS NMR indicates the bonding of Al with carbon of the carboxylate group in basic aluminium succinate. Samples calcined at 400–870°C do not give ^{13}C spectra.

Keywords: ^{27}Al magic-angle spinning nuclear magnetic resonance; cross-polarization ^{13}C magic-angle spinning nuclear magnetic resonance; aluminas; aluminium succinate

Introduction

Alumina finds extensive applications in the fields of ceramics, adsorbents, catalysts and catalyst supports. The properties of aluminas vary considerably depending on the method of preparation and pretreatment [1–4]. The adsorptive and surface properties of aluminas depend on the structure, the type of crystal phase and on the chemical nature of the surface [5–8]. The bifunctional (acidic and basic) character of γ-Al_2O_3, its high surface area, mechanical strength and thermal stability make it useful as a catalyst and catalyst support [9,10].

Aluminas are variously characterised by X-ray diffraction (XRD) for crystallographic composition [6], infrared (IR) for surface hydroxyl groups [7,11] and, in some cases, ^1H MAS NMR [12,13]. More recently, solid-state ^{27}Al MAS NMR has been used to elucidate the nature of Al coordination in crystalline as well as X-ray amorphous aluminium compounds [14–16].

The γ-Al_2O_3 and other transitional aluminas are usually formed during thermal dehydration of boehmite, bayerite and pseudo-boehmite [6,17], following the transformations

$$\text{Boehmite} \xrightarrow{450°C} \gamma\text{-}Al_2O_3 \xrightarrow{600°C} \delta\text{-}Al_2O_3 \xrightarrow{1050°C} \theta\text{-} + \alpha\text{-}Al_2O_3 \xrightarrow{1200°C} \alpha\text{-}Al_2O_3$$

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SSDI 0926-2040(93)E0049-4

$$\text{Bayerite} \xrightarrow{300°\text{C}} \eta\text{-Al}_2\text{O}_3 \xrightarrow{850°\text{C}}$$
$$\theta\text{-Al}_2\text{O}_3 \xrightarrow{1200°\text{C}} \alpha\text{-Al}_2\text{O}_3$$
$$\text{Pseudo-boehmite} \xrightarrow{300°\text{C}} \gamma\text{-Al}_2\text{O}_3 \xrightarrow{900°\text{C}}$$
$$\delta\text{-Al}_2\text{O}_3 \xrightarrow{1000°\text{C}} \theta\text{-} + \alpha\text{-Al}_2\text{O}_3 \xrightarrow{1200°\text{C}} \alpha\text{-Al}_2\text{O}_3$$

Sivaraj and co-workers [18,19] have recently reported the preparation of catalytically active aluminas from basic aluminium succinate precipitated from a homogeneous solution. The transformation of basic aluminium succinate by thermal treatment can be depicted as

$$\text{basic aluminium succinate} \xrightarrow{400°\text{C}}$$
$$\text{amorphous Al}_2\text{O}_3 \xrightarrow{600\text{–}870°\text{C}}$$
$$\gamma\text{-Al}_2\text{O}_3 \xrightarrow{950°\text{C}} \gamma\text{-} + \alpha\text{-Al}_2\text{O}_3 \xrightarrow{1050°\text{C}} \alpha\text{-Al}_2\text{O}_3$$

This paper presents the results of a solid-state ^{27}Al MAS NMR study to elucidate the coordination state of aluminium in X-ray amorphous and crystalline aluminas derived through the thermal treatment of a basic aluminium succinate precursor. The basic aluminium succinate is also characterised by ^{13}C CP MAS NMR to confirm its structure and its transformation into active aluminas upon calcination.

Experimental

Preparation

Basic aluminium succinate was prepared from a solution containing 0.05 *M* aluminium chloride and 0.3 *M* succinic acid by precipitation from a homogeneous solution using urea (0.8 *M*) as hydrolysing agent at 90–95°C under stirring. After the precipitation was complete (pH 6.6), the product was filtered and washed with distilled water until free of chloride ions and dried at 110°C for 24 h [18]. The basic aluminium succinate was then calcined at temperatures ranging from 300 to 870°C for 5 h. The calcined samples were characterised by solid-state ^{27}Al MAS NMR and ^{13}C CP MAS NMR.

Solid-state ^{27}Al MAS NMR spectra have been recorded at 78.18 MHz using a Bruker CXP-300 spectrometer (magnetic field 7.05 τ) in a frequency range of 100 kHz, a $\Pi/8$ pulse duration of 1 μs and a pulse repetition frequency of 5 Hz. MAS of the sealed samples was performed in quartz rotors at a frequency of 4 kHz. Chemical shifts are given relative to $\text{Al(H}_2\text{O)}_6^{3+}$. The ^{13}C CP MAS NMR spectra of basic aluminium succinate and the products of calcination at higher temperatures have been recorded at 75.43 MHz with spinning at 1.15 kHz.

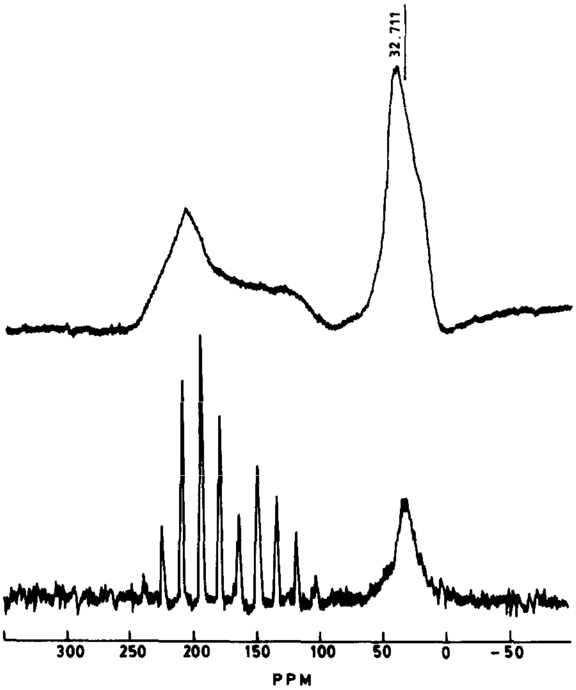

Fig. 1. ^{13}C CP static and MAS NMR spectra of basic aluminium succinate dried at 110°C.

Results and discussion

^{13}C CP MAS NMR

The ^{13}C CP MAS NMR spectrum of the precipitated basic aluminium succinate sample dried at 110°C in Fig. 1 consists of two lines from $\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-$ and $-\text{CH}_2-$ carbon atoms. The first has an axial anisotropy of σ-tensor with $\sigma_{\|}$, $\sigma_{\perp}$, which are different from those of the $\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-$

carbon atom in succinic acid which has three-fold anisotropy of σ-tensor with $\sigma_1 = 276$, $\sigma_2 = 196$ and $\sigma_3 = 123$ ppm. The line from the $-CH_2-$ carbon atom has nearly axial anisotropy with $\sigma_{iso} = 32$ ppm in both succinic acid and aluminium succinate. The difference in the chemical shift parameters for succinic acid and aluminium succinate indicates the bonding of Al to the $O{-}\overset{\overset{O}{\|}}{C}{-}$ carbon atom. This is an important observation from ^{13}C CP MAS NMR of basic aluminium succinate. Samples heated at elevated temperatures (400–870°C) did not give ^{13}C spectra. These findings are in agreement with the results of IR spectra of aluminum succinate calcined at different temperatures.

^{27}Al MAS NMR

^{27}Al NMR spectra of different thermally treated samples are given in Fig. 2. The spectra depend on the temperature of the sample treatment. The spectrum of basic aluminium succinate dried at 110°C measured without MAS is typical of second-order quadrupole splitting, which indicates a highly distorted environment of Al nuclei. Parameters of the spectra were found by comparison with the spectra calculated for a combination of the quadrupole coupling constant e^2qQ/h, asymmetry parameter η and isotropic chemical shift δ. They are $\delta = 58$ ppm, $e^2qQ/h = 4.5$ MHz and $\eta = 0.8$. The chemical shift value is typical for Al in a tetrahedral oxygen environment. This

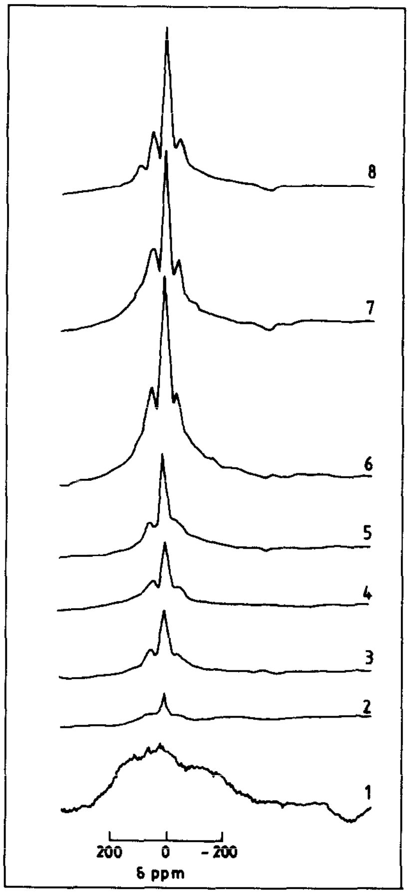

Fig. 2. Solid-state ^{27}Al MAS NMR spectra of aluminas derived from basic aluminium succinate calcined at different temperatures. (1) Basic aluminium succinate dried at 110°C and calcined at (2) 300°C, (3) 400°C, (4) 500°C, (5) 600°C, (6) 700°C, (7) 800°C, (8) 870°C (sample No. 1 was measured without MAS).

TABLE 1

Chemical shift values of samples calcined in air at various temperatures

Sample No.	Sample	XRD data	Calcination temperature (°C)	Observed chemical shift value (ppm)	
				Tetrahedral	Octahedral
1	Al-110	Basic aluminium succinate	110	58.0	–
2	Al-300	Basic aluminium succinate	300	55.1	0.60
3	Al-400	Amorphous	400	53.1	1.25
4	Al-500	Amorphous	500	58.0	1.25
5	Al-600	γ-Al_2O_3	600	60.0	2.80
6	Al-700	γ-Al_2O_3	700	60.5	3.70
7	Al-800	γ-Al_2O_3	800	56.1	3.10
8	Al-870	γ-Al_2O_3	870	55.6	1.25

indicates that all aluminium in basic aluminium succinate is four-coordinate.

An increase of the treatment temperature results in the appearance of two lines at ~ 1 ppm and at ~ 60 ppm. The first can be attributed to Al in octahedral coordination, the second to Al in a tetrahedral environment. The broad line at the background of these narrow signals can be attributed to Al in a highly distorted amorphous environment [20]. As the temperature of the treatment increases, the intensities of the lines from tetrahedral and octahedral Al increase while the intensity of a broad line from the amorphous phase decreases. After treatment at 700°C, narrow lines from octahedral and tetrahedral Al remain, while the intensity of the broad line from amorphous Al is greatly diminished.

Chemical shift values of tetrahedral and octahedral Al measured from ^{27}Al MAS NMR spectra, along with XRD data of aluminas derived through calcination of basic aluminium succinate at different temperatures are listed in Table 1.

Solid-state ^{27}Al NMR has allowed us to characterize X-ray amorphous samples of aluminas (calcined at 400 and 500°C). XRD of the sample calcined at 300°C shows the presence of basic aluminium succinate, which means that at this temperature the conversion to amorphous alumina is only partial. Octahedral coordination begins to appear in this sample. The spectra allow us to determine the coordination state of aluminium in the amorphous samples and revealed the closeness of chemical shifts in amorphous and crystalline samples.

The changes in the solid-state ^{27}Al MAS NMR spectra of samples upon variation of the treatment temperature reflect the crystallisation of alumina from the amorphous complex of Al succinate with distorted tetrahedral environment.

Acknowledgement

We thank Prof. K.I. Zamaraev, Director, Institute of Catalysis (Novosibirsk, Russia) for access to solid-state NMR facilities.

References

1 R.M. Levy, D.J. Bauer and R.F. Roth, *Ind. Eng. Chem. Process. Design. Dev.*, 7 (1968) 217.
2 H. Kanoh, T. Nishiyama and A. Ayame, *J. Catal.*, 57 (1979) 372.
3 T. Inui, T. Sezume, K. Miyaji and T. Takegami, *J. Chem. Soc. Chem. Commun.*, (1979) 873.
4 D.L. Trimm and A. Stanislaus, *Appl. Catal.*, 21 (1986) 215.
5 J.B. Peri, *J. Phys. Chem.*, 69 (1965) 211.
6 B.C. Lippens and J.J. Steggerda, in B.G. Linsen (Ed.), *Physical and Chemical Aspects of Adsorbants and Catalysts*, Academic Press, London, New York, NY, 1970.
7 H. Knozinger and P. Ratnasamy, *Catal. Rev., Sci. Eng.*, 17 (1978) 31.
8 W.C. Conner, E.L. Weist and L.A. Pedersen, in B. Delmon, P. Grange, P.A. Jacobs and G. Poncelet (Eds.), *Preparation of Catalysts, IV*, Elsevier, Amsterdam, 1987, p. 323.
9 G.H. Posner, *Angew. Chem. Int. Ed. Engl.*, 17 (1978) 487.
10 W. Kania and K. Jurczyk, *Appl. Catal.*, 34 (1987) 1.
11 M.L. Hair, *Infrared Spectroscopy in Surface Chemistry*, Marcel Dekker, New York, NY, 1967, Ch. 7.
12 V.M. Mastikhin, I.L. Mudrakovskii and K.I. Zamaraev, *React. Kinet. Catal. Lett.*, 34 (1987) 161.
13 K.I. Zamaraev and V.M. Mastikhin, *Colloid. Surf.*, 12 (1984) 401.
14 D. Muller, W. Bessner, H.J. Berens and G. Scheier, *Chem. Phys. Lett.*, 79 (1981) 59.
15 C.S. John, N.C.M. Alma and G.R. Hays, *Appl. Catal.*, 6 (1983) 341.
16 N.S. Kotsarenko, V.M. Mastikhin, I.L. Mudrakovskii and V.P. Shmactikova, *React. Kinet. Catal. Lett.*, 30 (1986) 375.
17 B.C. Lippens and J.H. de Beer, *Acta. Cryst.*, 17 (1964) 1312.
18 Ch. Sivaraj, B. Prabhakara Reddy, B. Rama Rao and P. Kanta Rao, *Appl. Catal.*, 24 (1986) 25.
19 Ch. Sivaraj, K. Hanumanlu, P.S. Sai Prasad, P. Venkateswara Rao and P. Kanta Rao, *Ind. J. Chem.*, 29A (1990) 1210.
20 V.M. Mastikhin and K.I. Zamaraev, *Z. Phys. Chem. Neue Folge*, 152 (1987) 59.