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Magnetic Resonance Studies on Porous Alumina doped with Iron and Chromium

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A combined magic-angle spinning (MAS) NMR and electron paramagnetic resonance (EPR) study has been performed on Fe- and Cr-doped alumina as a function of the heat-treatment temperature. Between 300 and 600 °C large quantities of tetra- and penta-coordinated Al were produced in porous xerogels. The penta-coordinated Al species have been found to be related to the catalytic activity. It has been found that the Fe ions accelerate the transition from γ- to α-Al_2O_3 and were mainly found within the alumina granules. On the other hand, Cr ions in high oxidation states (Cr^{5+}, Cr^{6+}) hampered the transition from γ- to α-Al_2O_3 and it has been proposed that they are preferentially situated on the surfaces of the granules.

Aluminas exist in a large variety of amorphous and microcrystalline forms with high surface areas that are widely used as catalysts or catalyst supports.[1] At high treatment temperatures they all transform into α-Al_2O_3 (corundum). The transition from γ- to α-Al_2O_3 dramatically reduces the surface area and, accordingly, the catalytic potency. It is therefore of interest to investigate the influence of small quantities of other oxides on the transition temperature from γ- to α-Al_2O_3. The stability of γ-Al_2O_3 at high temperature is very important in some applications, *e.g.* catalysts for automobile emission control.[2] It is already known that Fe^{3+} and Cr^{3+} affect the $\gamma \rightarrow \alpha$ transition,[3,4] but understanding on a molecular level is lacking.

Paramagnetic doped alumina has been studied extensively by EPR,[5–7] optical[8,9] and diffuse reflectance spectroscopies.[10–11] The simultaneous use of EPR and NMR techniques for the investigation of doped alumina from starting solution up to stable α-Al_2O_3 is still unreported in the literature.

In this paper we present the results of a combined NMR and EPR investigation on Fe- and Cr-doped alumina as a function of the heat-treatment temperature. At heat-treatment temperatures between 300 and 600 °C large quantities of tetra- and penta-coordinated Al are produced in porous xerogels.[12] The penta-coordinated Al species are related to the catalytic activity.[13] It is found that Fe ions accelerate the transition from γ- to α-Al_2O_3 and are mainly found in the interior of the alumina granules. On the other hand, Cr ions in high oxidation states hamper the transition from γ- to α-Al_2O_3 and it is proposed that they are preferentially situated on the surfaces of the granules. We focus particular attention on the stability of the γ-phase of alumina because it is involved in many catalytical applications.

Experimental

Alumina samples were prepared with the composition $Al_{2(1-x)}M_{2x}O_3$ with $x = 0$ and 0.002 and M = Fe, Cr. Although the synthesis has been described in detail in the literature,[14] a short description of it is appropriate here. To a mixture of $Al(NO_3)_3 \cdot 9H_2O$ and $M(NO_3)_3 \cdot 9H_2O$, 10 wt.% glycerol was added as reducing agent along with a small amount of water, so that clear solutions were obtained. Subsequent heating of these solutions at 95 °C for 1.5 h resulted in viscous gels. Prolonged heating yielded spongy, bulky solid samples (xerogels). These solid samples were heated in the open air for 30 min at various temperatures, T_t (°C). Immediately after heating, the samples were sealed in quartz EPR tubes or placed in airtight bottles for NMR measurements. Just before the beginning of the NMR measurements the samples were rapidly transferred to the spinners in order to minimize hydration effects. The samples are denoted by AM_x-T_y, where x refers to the fraction of M and y to the treatment temperature ($y = T_t/100$).

The crystalline phases obtained at high heat-treatment temperatures were identified by X-ray diffraction (XRD) at room temperature with a Philips PW 1820 X-ray powder diffractometer. ^{27}Al NMR measurements were carried out at room temperature on a Bruker AM-500 spectrometer. For the MAS NMR experiments a home-built probehead equipped with a Jakobsen 5 mm spinning assembly was used. Excitation pulses of 1 μs and spinning speeds up to 14 kHz were typically employed. Spectra were referenced with respect to an external $Al(NO_3)_3$ solution [$Al(H_2O)_6^{3+}$].

EPR spectra were recorded on a Bruker ESP-380 X-band spectrometer at room temperature for solid samples and at 140 K for sol and gel samples. The average microwave frequency was 9.3 GHz.

Results

X-Ray Measurements

All samples remained amorphous up to 700 °C. At higher temperatures, broad lines characteristic of γ-Al_2O_3 were first observed, followed by sharp lines belonging to α-Al_2O_3. The latter was the only phase present after heating for 30 min at 1200 °C. In Table 1 the observed phases have been summarized for the undoped and doped samples after 0.5 and 24 h heat treatment at 860 °C.

^{27}Al NMR

Fig. 1 shows ^{27}Al NMR spectra of alumina (AM_0-T_y) as a function of the heat-treatment temperature. The samples labelled sol and gel were measured without spinning. As expected, below 200 °C only one resonance was observed which was due to Al hexa-coordinated to water, hydroxy

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Table 1 Crystalline phases observed for undoped and doped samples after 0.5 and 24 h heat treatment at 860 °C

	sample		
Heat-treatment time/h	undoped (AM_0-$T_{8.6}$)	iron-doped ($AFe_{0.002}$-$T_{8.6}$)	chromium-doped ($ACr_{0.002}$-$T_{8.6}$)
0.5	γ	α, γ	γ
24	γ	α	γ

groups or oxygen atoms. The linewidth of this resonance peak increases with increasing temperature as a result of network formation and accordingly decreasing mobility of the hexa-coordinated Al. At $T_t \geqslant 200$ °C three resonances developed in the ranges 0–8, 30–36 and 60–64 ppm, which were assigned previously to hexa-, penta- and tetra-coordinated Al, respectively.[15]

The small peak at *ca.* 105 ppm is from AlN, present as an impurity in the Si_3N_4 spinner. Between 200 and 300 °C rapid development of penta- and tetra-coordinated Al takes place almost simultaneously. Between 300 and 600 °C the fraction of penta-coordinated Al reaches its maximum value of *ca.* 0.5. Above 600 °C penta-coordinated Al gradually disappears until at 1200 °C only α-Al_2O_3 is present, containing hexa-coordinated Al.

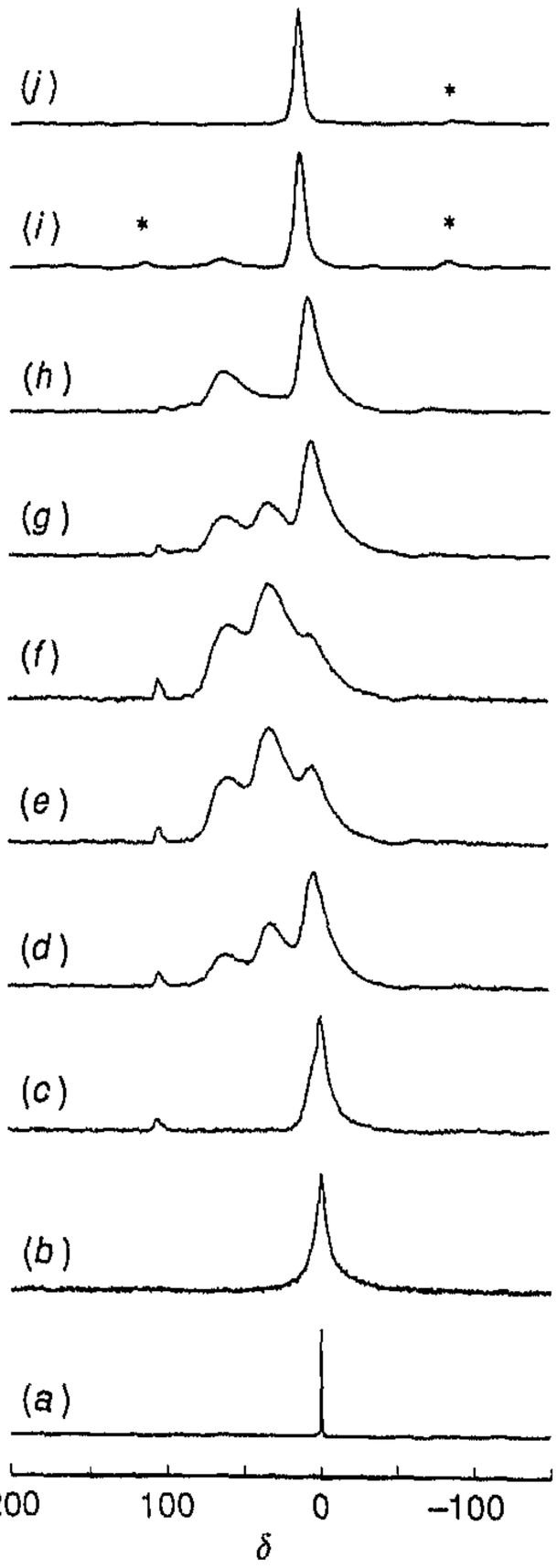

Fig. 1 ^{27}Al NMR spectra of undoped alumina samples showing the effect of heat-treatment temperature. (*a*) Sol, (*b*) gel, AM_0-T_y with y: (*c*) 1, (*d*) 2.5, (*e*) 3, (*f*) 6, (*g*) 7.5, (*h*) 8.6, (*i*) 10, (*j*) 12. All spectra were measured at room temperature and, except for sol and gel samples, with magic-angle spinning. Spinning side bands are indicated by *.

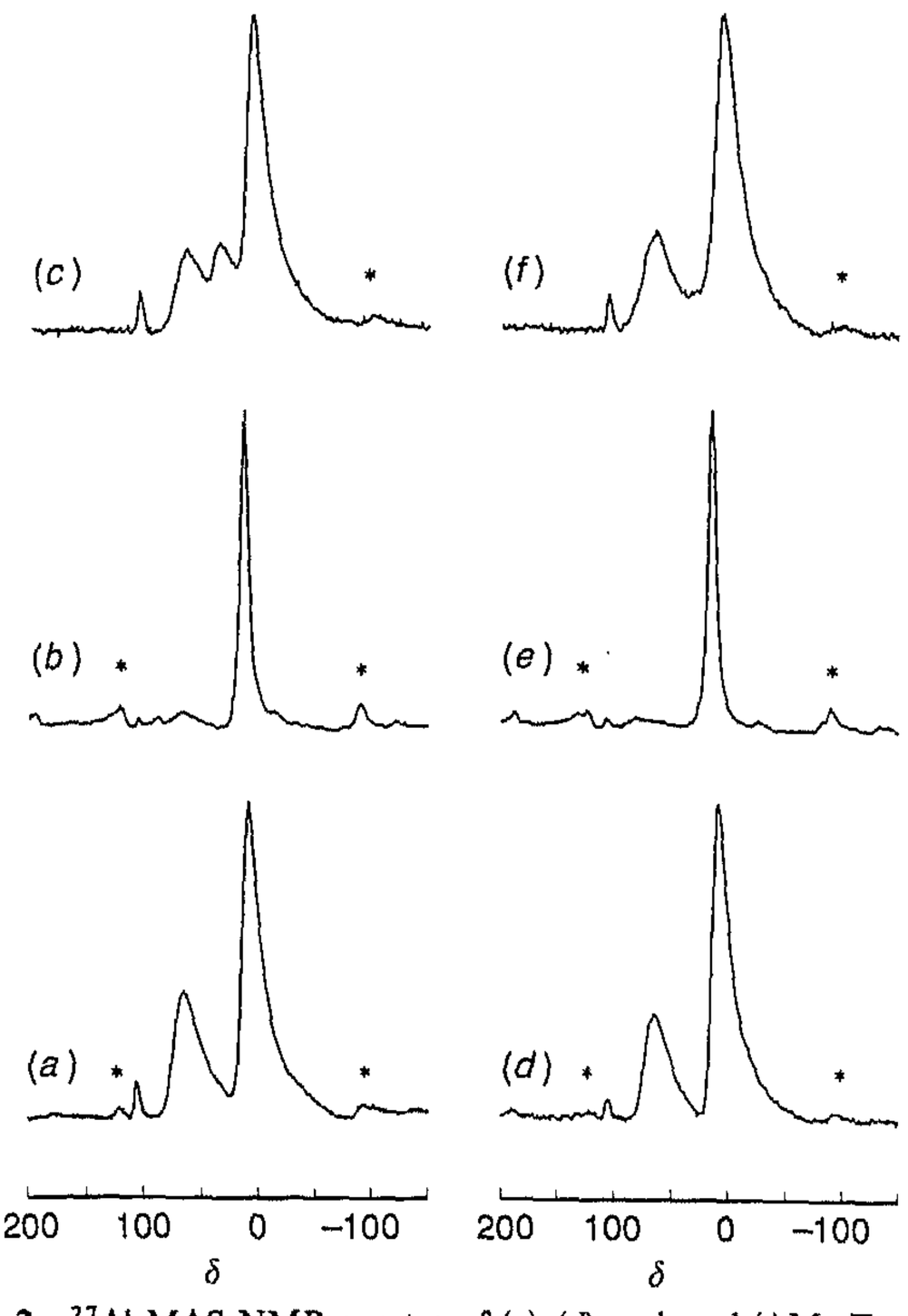

Fig. 2 ^{27}Al MAS NMR spectra of (*a*), (*d*) undoped (AM_0-$T_{8.6}$) and (*b*), (*e*) Fe- and (*c*), (*f*) Cr-doped samples ($AM_{0.002}$-$T_{8.6}$) after heat treatment at 860 °C for (*a*)–(*c*) 30 min and (*d*)–(*f*) 24 h. Spinning side bands are indicated by *.

In Fig. 2 the ^{27}Al MAS NMR spectra of undoped and doped samples, heated for 30 min [Fig. 2(*a*)] and 24 h [Fig. 2(*b*)] at 860 °C are presented. At this temperature the undoped sample, AM_0-$T_{8.6}$, consists of γ-Al_2O_3. The spectrum shows only resonances due to four- and six-coordinated Al in a ratio of 1 : 2.

Surprisingly, the presence of a small amount of iron and chromium strongly influences the thermal stability of the γ-phase. The presence of iron lowers the transition temperature from γ- to α-Al_2O_3, whereas chromium has the opposite effect. To be more specific, the small fraction of tetra-coordinated Al of the γ-phase in the undoped sample at 1000 °C [Fig. 1(*i*)] is already present in the Fe-doped sample treated at $T_t = 860$ °C. On the other hand, in the Cr-doped sample heated for 30 min at 860 °C, penta-coordinated Al can be distinguished, as is the case for the undoped samples treated at 750 °C. Even after 24 h of heating at 860 °C the NMR spectrum of the Cr-doped sample still shows features of distorted Al surroundings. Taking the AlN signal as an intensity indication, it can further be concluded that in the Cr-doped sample an appreciable fraction of Al is not detectable. This loss is probably due to the presence of paramagnetic ions[16] and the severe line broadening of a number of highly distorted surface sites.[17]

EPR

Fe-*doped Alumina*

Fig. 3 shows the EPR spectra of the Fe- doped samples as a function of the heat-treatment temperature. Up to 750 °C the main feature is the signal at $g = 4.28$, which is typical for Fe^{3+} ($S = 5/2$) in disordered systems.[18] The derivative linewidth decreases from 8 mT for the gel sample to 3 mT for the sample labelled $T_{7.5}$. A completely new spectrum develops at higher treatment temperatures at the expense of the signal at

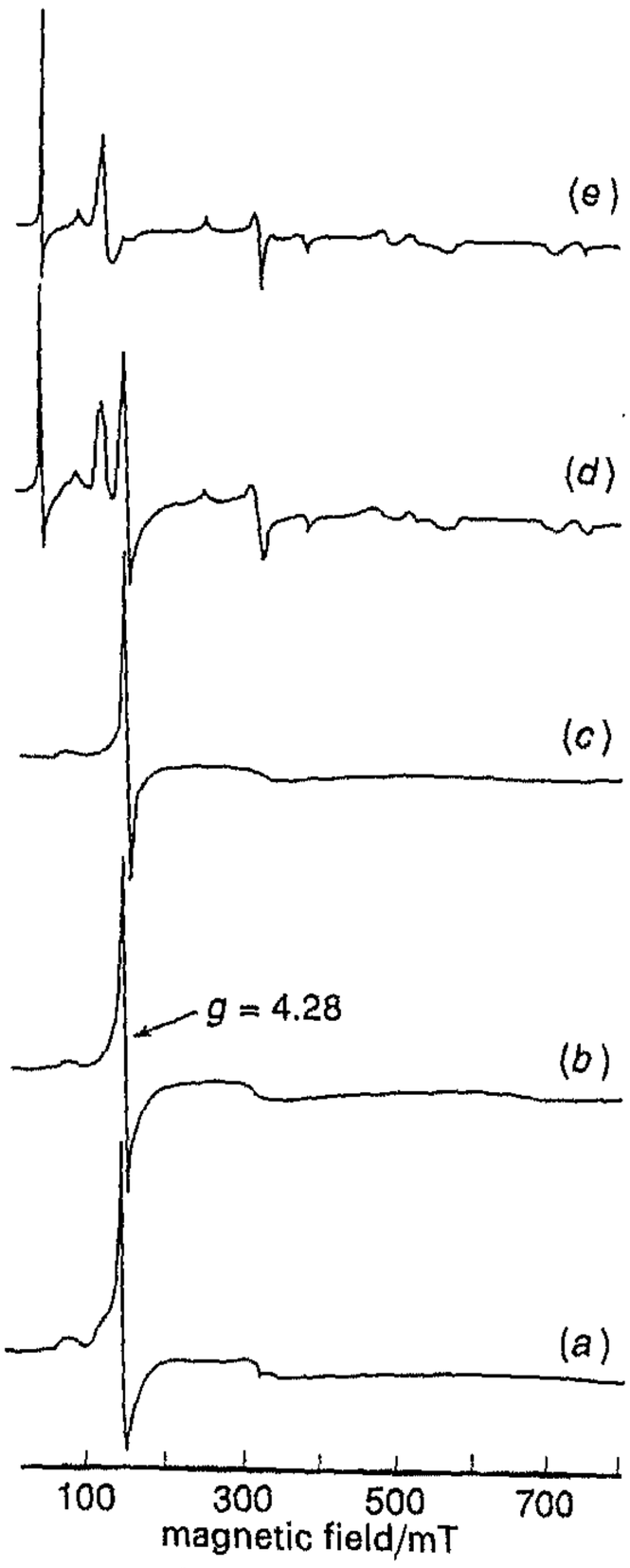

Fig. 3 EPR spectra of Fe-doped alumina as a function of heat-treatment temperature. (*a*) Gel, $AFe_{0.002}$-T_y with y: (*b*) 1, (*c*) 7.5, (*d*) 8.6 for 30 min, (*e*) 8.6 for 24 h. Spectrum (*a*) was measured at 140 K, other spectra at room temperature.

$g = 4.28$. For instance, after heat treatment for 30 min at 860 °C, the temperature at which only γ-Al_2O_3 exists in the undoped sample, the new spectrum is already well developed. After 24 h heat treatment at 860 °C the signal at $g = 4.28$ is absent and the remaining spectrum is identical to the well known powder spectrum of Fe-doped corundum.[19] This means that in the Fe-doped sample we already have α-Al_2O_3 at 860 °C, in agreement with the X-ray and NMR results (Fig. 2).

Cr-*doped Alumina*

Fig. 4 illustrates the changes in the local environment and in the oxidation state of chromium upon heating the Cr-doped sample. The signal at $g = 1.97$ of the sol sample can be ascribed to Cr^{3+} ($S = 3/2$) hexa-coordinated to H_2O in a slightly distorted octahedral configuration.[20] A new spectrum is observed for the dry gel (T_1) with dominant lines at $g = 2.0$ and $g = 5.6$, apart from the small peak at $g = 4.28$ (see Fig. 4) which is due to Fe^{3+} present as an impurity in aluminium nitrate (*ca.* 0.03%). This new spectrum was assigned to Cr^{3+} ions subjected to a strong orthorhombic crystal field arising from a slightly distorted octahedral environment.[21] The intermediate spectrum [Fig. 4(*b*)] is mainly a superposition of the sol and $ACr_{0.002}$-T_1 spectra. It is evident that in the viscous gel sample several Cr complexes are present with different six-coordinated geometries.

An important change in the spectra occurred at higher treatment temperatures. Between $T_t = 100$ and 800 °C a single, relatively narrow (derivative linewidth *ca.* 5 mT), symmetrical line was observed which is usually assigned to penta-coordinated Cr^{5+} ($S = 1/2$) ions.[22] After 24 h treatment at 860 °C a new spectrum developed (marked with asterisks) at

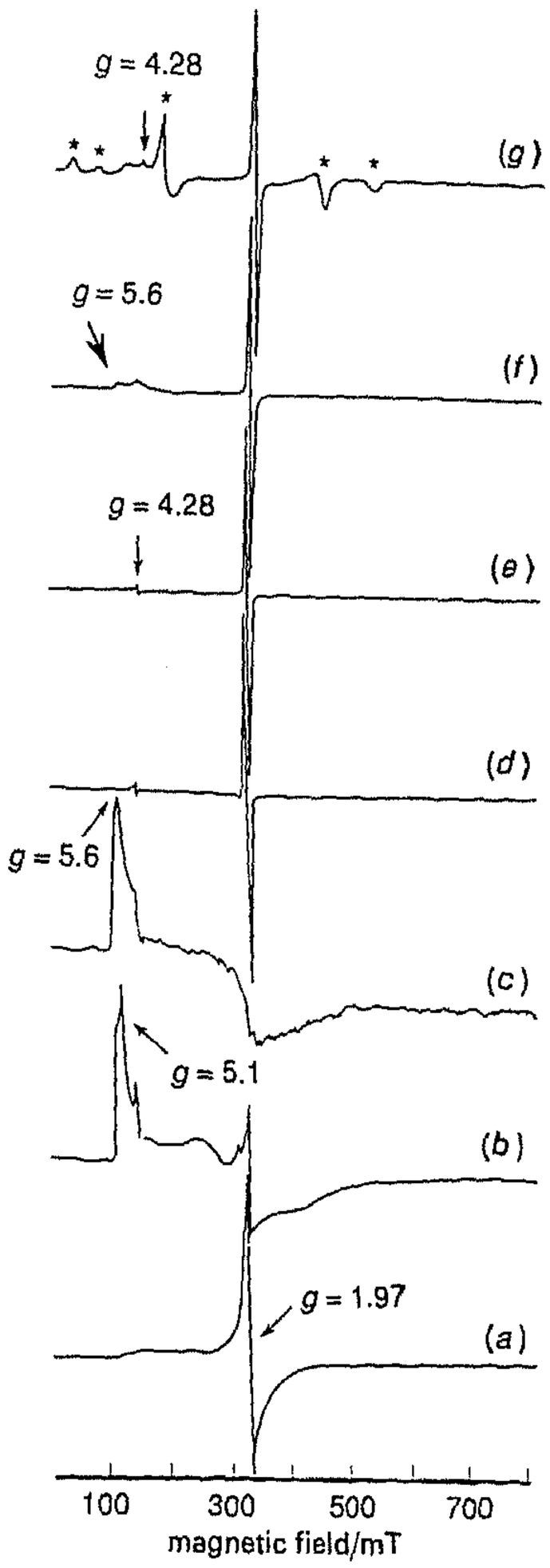

Fig. 4 EPR spectra of Cr-doped alumina as a function of heat-treatment temperature. (*a*) Sol, (*b*) gel, $ACr_{0.002}$-T_y with y: (*c*) 1, (*d*) 2, (*e*) 7.5, (*f*) 8.6 for 30 min, (*g*) 8.6 for 24 h. Spectra (*a*) and (*b*) were measured at 140 K, other spectra at room temperature.

the expense of the narrow signal at $g = 1.97$. This spectrum was identical to the well known spectrum of ruby (Cr-doped corundum). This spectrum has been simulated with the zero field splitting parameters $D = 0.193$ cm^{-1} and $E = 0$.[23] Note that the strong line due to iron at *ca.* 50 mT in the spectrum of the Fe-doped sample $T_{8.6}$ is absent in the spectrum of the Cr-doped sample $T_{8.6}$.

Discussion

To understand the opposite effects of the Fe and Cr ions on the formation of xerogels and eventually on the formation of γ- and α-Al_2O_3, we recall the molecular mechanisms occurring during the synthesis. In the starting solution small Al oligomers are produced by the interlinking of Al octahedra. The presence of water prevents extensive polymerization. During the drying and precipitation process these small oligomers agglomerate to form larger particles (granules) leading to viscous liquids and dry gels. At heating temperatures of *ca.* 200 °C dehydroxylation and pyrolysis of glycerol commence and simultaneously low-coordinated Al species are formed. The maximum fraction of these species is observed for amorphous xerogels with $3 < y < 6$ and amounts to *ca.* 0.7.

Recently we showed that a considerable part of the low-coordinated Al is situated on the surfaces of the xerogels.[12] As shown here, the presence of Fe^{3+} and Cr^{3+} in the starting solutions have opposite effects on the formation of the xerogels and on the subsequent formation of γ- and α-Al_2O_3, despite the similar electronegativity and coordination number of Fe^{3+} and Cr^{3+}. High-spin Fe^{3+} ($S = 5/2$) exhibits no crystal field stabilization in an octahedral environment. Therefore it will be easily available for incorporation into the Al oligomers by formation of M—OH—M bridges.[24] In contrast, high-spin Cr^{3+} ($S = 3/2$) is stabilized in an octahedral crystal field. This would imply a lower reactivity of Cr^{3+} towards such bridge formation. As a result of this, Cr^{3+} ions have a tendency to remain in solution. On continuing the heat treatment we therefore suggest that xerogels are produced with Fe^{3+} located mainly inside the xerogels and with Cr^{3+} located preferentially on the surfaces of the xerogels. This difference in behaviour of Fe^{3+} and Cr^{3+} during the synthesis is reflected in both the NMR and EPR spectra.

The Fe^{3+} ions inside the alumina xerogels act as sites for the formation of γ- and subsequently α-Al_2O_3. Fig. 2 shows that at $T_t = 860\,°C$ the Fe-doped sample is mainly in the α-phase, whereas the undoped sample is still in the γ-phase at this temperature. Thus Fe^{3+} ions accelerate the transformation from γ- to α-Al_2O_3. The EPR spectra of the Fe-doped sample shown in Fig. 3 support the conclusions drawn from NMR results. From the decrease in linewidth of the signal at $g = 4.28$ going from the gel to $AFe_{0.002}$-$T_{7.5}$ it may be inferred that the changes in the environments of Fe^{3+} are minor. In Fig. 3(*d*) the line at $g = 4.28$ can still be observed and therefore the α-phase in addition to the γ-phase is present at $T_t = 860\,°C$. This is in agreement with XRD and NMR results. If the heat treatment procedure is extended to 24 h only the α-phase remains.

As mentioned above, the Cr-doped sample exhibits a different behaviour. The formation of the γ-phase is hampered compared with the undoped sample. The EPR spectra in Fig. 4 give information on the kind of Cr complexes present in the gels. When the gel is formed, in addition to the Cr^{3+} species giving rise to the signal at $g = 1.97$, there are Cr^{3+} complexes attached to the surfaces of the formed granules which are responsible for the signals at $g = 2.0$ and $g = 5.6$ [see Fig. 4(*c*)]. Between $T_t = 100$ and $200\,°C$ only one signal is detected, which is generally ascribed to Cr^{5+} in a square-pyramidal configuration (*i.e.* penta-coordinated species).[22] It is known that on heating Cr gels at $200\,°C$ higher oxidation states of chromium are generated (Cr^{5+} and Cr^{6+}). The presence of an active oxidant like NO_3^- facilitates the oxidation,[25] so that below $200\,°C$ these high oxidation states are formed. In Fig. 4(*f*) a small peak at $g = 5.6$ (see arrow) can be discerned, which is definitely not present in the $T_{7.5}$ spectrum [Fig. 4(*e*)]. From this it can be concluded that chromium is partly reduced to Cr^{3+}. Prolonged heat treatment at $860\,°C$ for 24 h produces the spectrum of Cr^{3+}-doped α-Al_2O_3. Note that a strong signal from Cr^{5+}, a small peak at $g = 5.6$ from Cr^{3+} and a small signal from Fe^{3+} at $g = 4.28$ (see arrow) are still present. These facts can only be reconciled by the simultaneous presence of γ- and α-Al_2O_3. Note that the corresponding NMR spectrum and XRD pattern show only the presence of γ-Al_2O_3. A plausible explanation for this is that Cr^{3+} ions situated on the surface of the granules are in the α-phase, whereas in the inside of the granules the γ-phase still exists. This explanation is supported by the absence of an iron signal at *ca.* 50 mT, which should be easily detectable if Fe^{3+} were in α-Al_2O_3 (see Fig. 3). The lack of ^{27}Al MAS NMR signals due to α-Al_2O_3 may be caused by the relatively high concentration of paramagnetic Cr ions in the small fraction of the α phase (too small to be detected by XRD), which will broaden the ^{27}Al resonances beyond detection.

Conclusions

Porous amorphous alumina with a high fraction of penta-coordinated Al can be prepared by decomposition of aluminium nitrate solutions associated with glycerol oxidation. A fraction of the low-coordinated Al species were found on the surfaces of the xerogels.

In alumina samples doped with Fe^{3+} or Cr^{3+} ($x = 0.002$), low-coordinated Al species were also formed. Iron accelerated the transition from γ- to α-Al_2O_3, whereas chromium hampered not only this transition, but also the formation of γ-Al_2O_3. Furthermore, Fe^{3+} ions were mainly situated within the alumina granules whilst Cr^{3+} ions were preferentially located on the surface of the granules.

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References

1 H. Knözinger and P. Ratnasamy, *Catal. Rev. Sci. Eng.*, 1978, **17**, 31.
2 P. Burtin, J. P. Brunelle, M. Pijolat and M. Soustelle, *Appl. Catal.*, 1987, **34**, 225.
3 G. C. Bye and G. T. Simpkin, *J. Am. Ceram. Soc.*, 1974, **57**, 367.
4 T. Tsuchida, R. Furuichi, T. Ishii and K. Itoh, *Thermochim. Acta*, 1983, **64**, 337.
5 C. J. Carman and W. J. Kroenke, *J. Phys. Chem.*, 1968, **72**, 2562.
6 A. Ellison and K. S. W. Sing, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 2807.
7 A. S. Hare and J. C. Vickerman, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 1103.
8 Y. Hirai, T. Fukuda, Y. Kobayashi, H. Kuwahara, Y. Kido and K. Kubota, *Solid State Commun.*, 1987, **62**, 637.
9 G. Carturan, R. DiMaggio, M. Montagna, O. Pilla and P. Scardi, *J. Mat. Sci.*, 1990, **25**, 2705.
10 B. M. Weckhuysen, L. M. de Ridder and R. A. Schoonheydt, *J. Phys. Chem.*, 1993, **97**, 4756.
11 B. M. Weckhuysen, A. A. Verbeckmoes, A. L. Buttiens and R. A. Schoonheydt, *J. Phys. Chem.*, 1994, **98**, 579.
12 S. Simon, A. van der Pol, E. J. Reijerse, A. P. M. Kentgens, G. J. M. P. van Moorsel and E. de Boer, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 2663.
13 F. R. Chen, J. G. Davis and J. J. Fripiat, *J. Catal.*, 1992, **133**, 263.
14 F. Abbatista, A. Delmastro, G. Gozzelino, D. Mazza, M. Vallino, G. Busca and V. Lorenzelli, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 3653.
15 M. E. Smith, *Appl. Magn. Reson.*, 1993, **4**, 1.
16 A. P. M. Kentgens, A. Bos and P. J. Dirken, *Solid State Nucl. Magn. Reson.*, 1994, **3**, 315.
17 B. A. Huggins and P. D. Ellis, *J. Am. Chem. Soc.*, 1992, **114**, 2098.
18 D. L. Griscom, *J. Non-Cryst. Solids*, 1980, **40**, 211.
19 J. van Dijk, Ph.D. Thesis, Technical University Delft, 1976.
20 R. Karthein, H. Motschi, A. Schweiger, S. Ibric, B. Sulzberger and W. Stumm, *Inorg. Chem.*, 1991, **30**, 1606.
21 S. Doeuff, M. Henry, C. Sanchez and J. Livage, *J. Non-Cryst. Solids*, 1987, **89**, 84.
22 D. Cordischi, M. Cristina Campa, V. Indovina and M. Occhiuzzi, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 207.
23 D. E. O'Reilly and D. S. MacIver, *J. Phys. Chem.*, 1962, **66**, 276.
24 J. Livage, M. Henry and C. Sanchez, *Prog. Solid State Chem.*, 1988, **18**, 259.
25 N. E. Fouad, H. Knözinger, M. I. Zaki and S. A. A. Mansour, *Z. Phys. Chem.*, 1991, **171**, 75.

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