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The effect of a Cr_2O_3-addition on the phase transformation and catalytic properties of γ-Al_2O_3 in treatment of lean-burn exhausts

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The solid-state thermal behaviour of γ-Al_2O_3 doped with 10 mol% Cr (oxide) was studied with respect to phase-transition behaviour and the co-ordination of the dopant Cr cations. A series of transformations: γ-$Al_2O_3 \rightarrow \delta$-$Al_2O_3 \rightarrow \theta$-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ was observed for Cr_2O_3-doped alumina samples between 500 °C and 1100 °C. Rapid grain growth occurred at temperatures close to 1100 °C. The electron spin resonance (ESR) spectra for the sample heat-treated at 500 °C corresponded to the resonance of β-Cr^{3+} in an amorphous Cr oxide impregnated onto the γ- and δ-alumina support. The change of ESR spectrum indicated the existence of Cr^{3+}, suggesting the formation of a solid solution with the same structures as δ-Al_2O_3 and/or θ-Al_2O_3 at 800–1000 °C. The evaluation of catalytic activities for model exhaust was performed under lean-burn (an excess of oxygen) condition of air/fuel ratio $A/F = 18$ and space velocity SV = 100 000 h^{-1}. The modified Al_2O_3 catalyst heat-treated at 1000 °C in air showed removal conversion of 100% for hydrocarbon (C_3H_6), 92% for CO and 5% for NO at 550 °C. Present results suggest that Cr-modification to Al_2O_3 leads to catalytic improvement with good thermal durability. © *1998 Chapman & Hall*

1. Introduction

Transition aluminas have been applied as catalytic supports in many chemical processes and as coating materials with various promoters in automotive three-way catalyst converters [1]. In practical conditions the thermal stability of these materials have been needed to obtain improved pollution control processes with advanced catalysts. Previously, we have examined the effect of various rare earth and transition metals on the γ to α transformation as well as their effect on the sintering of γ-Al_2O_3 at 800–1200 °C with a view to their application as automotive catalytic materials [2–5]. Although the addition of transition metals generally decreased the thermal stability of transition aluminas, chromium addition did not appear to accelerate the transformations to the α form. This effect of Cr toward transition aluminas such as δ-Al_2O_3 and θ-Al_2O_3 has been also discussed by Bye and Simpkin [6]. Their study deal with phase transition to the corundum structure by comparing the doping effects of Cr and Fe.

Recently, Hamada and coworkers [7–11] reported an excellent catalysis of aluminas for lean-burn exhaust NO_x removal in automotive engine exhaust gases and the effect of transition metals addition to promote NO_x removal activity. We have studied catalysts in the system of CuO–Al_2O_3 toward possible application to automotive exhaust NO_x removal [12]. CuO-modified Al_2O_3, even when heated at 900 °C, showed high removal activities for gas mixtures simulating practical automotive lean-burn exhaust gas with a large space velocity. However, it lost its efficiencies after heat treatment when a solid-state reaction resulted in a large decrease of surface area. In the development of automotive catalysts thermal durability is essential for practical applications with high-performance gasoline engine systems.

In this paper, we present the thermal stability of Cr_2O_3-doped γ-Al_2O_3 with respect to phase transitions for the aluminas; the co-ordination of Cr cations in the solids, and report catalytic activity in pollution controlling devices. We examine the solid-state reaction and transformation of chromia–alumina powders fabricated by an impregnation method followed by heat treatment, using X-ray diffraction (XRD), surface area measurement and electron spin resonance (ESR). Catalytic removal performance for lean-burn exhaust poison gases was evaluated at a practical level of space velocity of gas mixtures.

2. Experimental procedure

Cr-added γ-Al_2O_3 was prepared using the impregnation of an aqueous chromium nitrate for a high purity alumina powder. Starting γ-Al_2O_3 powder (Sumitomo Chemical Co., Japan) had surface area of 115 $m^2 g^{-1}$ and purity of 99.95%. This alumina as-received contained minute amounts of δ-type phase. One hundred grams of powder was used for each impregnation batch, and after agitation of the suspension dried at 110 °C for 8 h, and heated at 500 °C for 3 h in air. The product was ground again and further heated at various temperatures up to 1100 °C in air. The heating rate was 1.6 K min^{-1} with a soak period

of 3 h at each temperature. In a present paper, the fraction of added Cr in Al_2O_3 was typically fixed with the molar ratio of $Al_2O_3/Cr = 100/10$ (10 mol % of Cr) after preliminary experiments.

Powder X-ray diffraction (XRD) apparatus (Rigaku, Rint-2000, Japan) with CuK_α source (20 kV, 30 mA) and a monochromater, was used for the examination of solid phases in samples after heat treatment at various temperatures. The surface areas of powders were derived by the Brunauer Emmett–Teller (BET) method (usually single-point technique) using nitrogen adsorption at 77 K. Samples were pelletized and preheated at 200 °C for 3 h in flowing nitrogen before the measurement procedure. Electron spin resonance (ESR) spectra of Cr in the samples were measured using a Jeol-3MX (Japan) spectrometer at room temperature in X-band with a modulation frequency of 100 kHz. Pelletized samples were positioned in a quartz tube with 4 mm o.d. and 3 mm i.d.. Microwave power levels were kept as low as 10 mV enough to avoid saturation and distortion of the resonance. The g values were estimated with a 2,2-di (4-t-octylphenyl)-1-picrylhydrazyl (DPPH) tube positioned near to each sample.

Steady-state catalytic performance was tested using gas mixtures with a large space velocity, simulating automotive exhaust at fuel-lean condition when air/fuel ratio (A/F) is 18. The typical gas composition is the following: CO 1000 p.p.m., C_3H_6 800 p.p.m., NO 700 p.p.m., O_2 4%, CO_2 12.7%, H_2O 10% and N_2 balance. The samples were pressed into pellets of diameter of 0.5–1 mm, and set in a quartz tube reactor. The catalyst sample (3.5 g) was used with total gas flow rate of 7 l min^{-1}. Space velocity (SV) was *ca.* 100 000 h^{-1}, which corresponds to practice level for an automotive use. The analyses of NO, CO and C_3H_6 at both inlet and outlet of a catalyst sample bed were performed using chemiluminescence and flame ionization detectors, respectively [5]. Conversion efficiencies were plotted as a function of inlet gas temperature measured by a thermocouple.

3. Results and discussion

3.1. Phase transformation and surface area

Fig. 1 shows the XRD patterns for 10 mol % Cr (oxide)-impregnated γ-Al_2O_3 heated at various temperatures. Detected compounds were γ-Al_2O_3, δ-Al_2O_3, θ-Al_2O_3 and α-Al_2O_3, as indicated with marks in Fig. 1. Starting pure alumina consisted of γ-Al_2O_3 and minute δ-Al_2O_3. δ-Al_2O_3 was identified with broad diffraction peaks at $2\theta = 46.6°$ and 66.3° (d = 1.95 nm and 1.41 nm), which appeared near two signals of γ-Al_2O_3. The phase transformation of present alumina was observed as the usual scheme

$$\gamma\text{-}Al_2O_3 \rightarrow \delta\text{-}Al_2O_3 \rightarrow \theta\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3 \quad (1)$$

The temperature for δ-Al_2O_3 to θ-Al_2O_3-transformation was 900–1000 °C, and for θ-Al_2O_3 to α-Al_2O_3 was over 1000 °C. For 10 mol % Cr-impregnated γ-Al_2O_3 there were no lines of Cr oxides or known phases to exist in the system of Cr_2O_3–Al_2O_3. The prepared 10 mol %Cr-Al_2O_3 seemed to form the

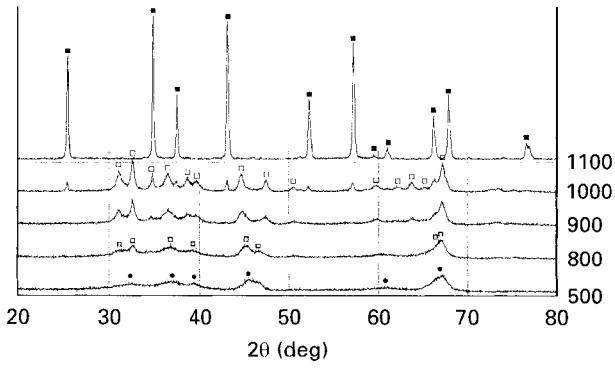

Figure 1 XRD patterns for 10 mol %Cr (oxide)-impregnated Al_2O_3 heated at various temperatures up to 1100 °C in the range of $2\theta = 20$–80° for CuK_α source. The numbers indicate heat-treatment temperatures. (●) γ-Al_2O_3; (□) δ-Al_2O_3; (□) θ-Al_2O_3; (■) α-Al_2O_3.

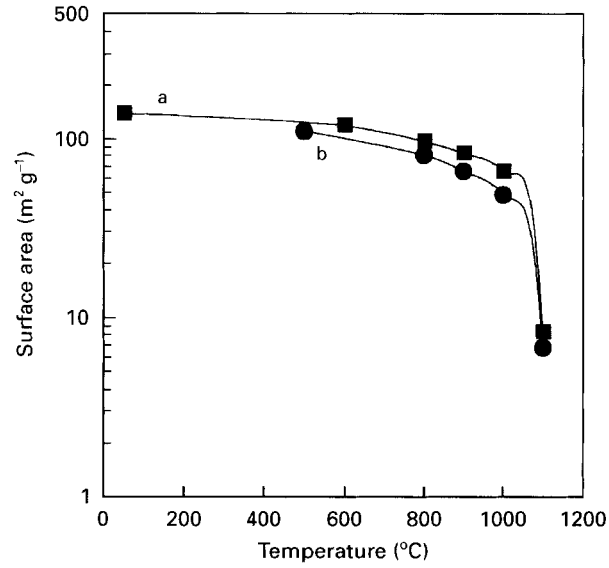

Figure 2 Plots of BET surface area versus heat-treatment temperature. (a) (■); pure Al_2O_3, (b) (●); Cr-impregnated Al_2O_3.

metastable oxide solid-solution in Al_2O_3–Cr_2O_3 system. The scheme of solid-state thermal behaviour via heat treatment at temperatures up to 1100 °C was nominally the same as in pure alumina. However, the transformation of δ-Al_2O_3 to θ-Al_2O_3 was observed in the temperatures of 800–900 °C. Small amount of α-Al_2O_3 was observed for Cr_2O_3–Al_2O_3 heated at 1000 °C. Thus, the transformation temperatures slightly decreased with Cr addition to alumina.

Fig. 2 illustrates a plot of the BET surface area against heat-treatment temperature. Cr impregnation resulted in a certain decrease of surface area of alumina in these temperatures. A large decrease was observed at temperatures of 1000–1100 °C for both aluminas. These temperatures correspond to the formation of α-Al_2O_3.

The relationship between thermal stability and the inhibition of α transformation for transition aluminas modified with impurity elements has often been considered. In the view of thermal durability of catalysts, the using condition for Cr_2O_3–Al_2O_3 seems to be limited to below 1000 °C. It should be noted that usual automotive catalysts consist of catalytic compositions

such as precious metals and promoters on oxide support, while here we present Cr_2O_3-modified alumina as a possible single phase having catalytic properties. This will be a practical advantage.

3.2. Electron spin resonance

Fig. 3 shows a series of ESR spectra of Cr_2O_3–Al_2O_3 samples heated at various temperatures. For 10 mol % Cr-Al_2O_3 heated at 500 °C (Fig. 3a), there appeared a symmetrical resonance at magnetic field (H) of 0.343 T, with the addition of a small signal at $H = 0.137$ T. The samples heated at 800, 900 and 1000 °C had the same ESR features consisting of three resonances at $H = 0.143$, 0.277 and 0.343 T. After heat-treatment at 1100 °C, the ESR spectrum changed to a large broad resonance at $H = 0.341$ T and small signals at $H = 0.201$ and 0.45 T.

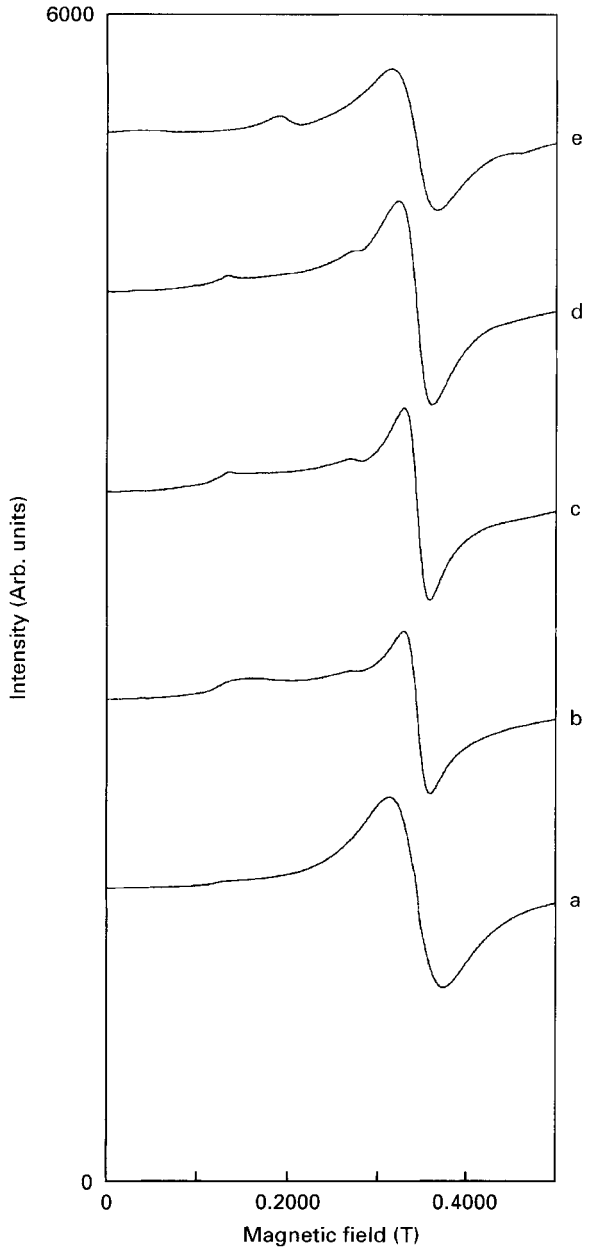

Figure 3 ESR spectra of 10 mol % Cr (oxide)-impregnated Al_2O_3 heated at (a) 500 °C, (b) 800 °C, (c) 900 °C, (d) 1000 °C and (e) 1100 °C for 3 h in air.

An ESR spectrum of pure Cr_2O_3 should be a broad line depending on temperature, since α-Cr_2O_3 is known to be antiferromagnetic with a Curie point near 30 °C [13]. Previous ESR studies on Cr-impregnated alumina have described mainly a sharp absorption at $g = 1.97$, believed to be due to Cr(5+), in the view of the solid ability to provide active sites for catalysis [14, 15]. However, present ESR in Fig. 3a shows a broad resonance the same as reported for sol–gel prepared Zn–Cr–O mixture [16]. O'Reilly and Maclvwe [17] and other workers [18, 19] have reported a detailed study on ESR absorption of chromia–alumina catalyst. They characterized the ESR for Cr ions using the symbols β, γ and δ phases. The ESR of Fig. 3a corresponds to β-Cr(3+), and additionally to γ-phase which is the same as one from Cr(5+). A weak absorption at $H = 0.137$ T is explained with a "forbidden" transition of triplet state formation in powder samples. The ESR spectrum suggests that the heat-treatment at 500 °C results in a major part of β-Cr(3+) which is a form the amorphous Cr oxide impregnated to an alumina support.

The ESR spectrum shown as (b), (c) and (d) in Fig. 3 can be interpreted as due to Cr(3+) in relatively strong axial crystal field with some distortion of low symmetry. This has been discussed in a previous paper by O'Reilly and Macivwe [17]. However, the present ESR corresponding to β-Cr(3+) is sharper than that reported by them, because of exchange-narrowing for Cr(3+) clustered in Al_2O_3 lattice. Although no detailed crystal field analysis is given in this work, it should be noted that the change of the ESR spectrum from (a) to (b), (c) and (d) in Fig. 3 corresponds to the loss of a symmetrical co-ordination field for Cr(3+) after heat-treatment at 800–1000 °C. Cr-oxide gel from both coprecipitation [17, 19] and an impregnation in this work seems to have relatively symmetrical crystal field for Cr(3+), when the heat-treatment temperature is as low as 500–600 °C. The XRD result indicated that the heat-treatment at 800–1000 °C induced the transformation of γ-Al_2O_3 to δ-Al_2O_3 and θ-Al_2O_3. The latter polymorphs are heavily defective spinel-structures in which the distorted anion sites are coordinated with cubic closed packed oxygen. Thus, the change of present ESR spectra suggests the formation of δ-Al_2O_3 or θ-Al_2O_3 doped with Cr(3+) in their crystal lattice at the temperature range of 800–1000 °C. On the other hand, the ESR spectrum in Fig. 3e can be explained as Cr(3+) in α-Al_2O_3 where is to be clustered Cr(3+) and a small amount of Cr(5+), although it is much broader spectrum than that observed for a Cr(3+)-ruby crystal agglomerate [18, 20]. The clustering of a large amount (10 mol %) of isolated Cr(3+) is assumed to result in a broad signal. Also, the ESR is an evidence indicating the formation of corundum-type solid solution in the system of Al_2O_3–Cr_2O_3 at 1100 °C.

3.3. Catalytic activity

Fig. 4 shows the plots for the removal–conversion efficiencies for (a) C_3H_6, (b) CO and (c) NO against inlet gas temperature, which were evaluated at

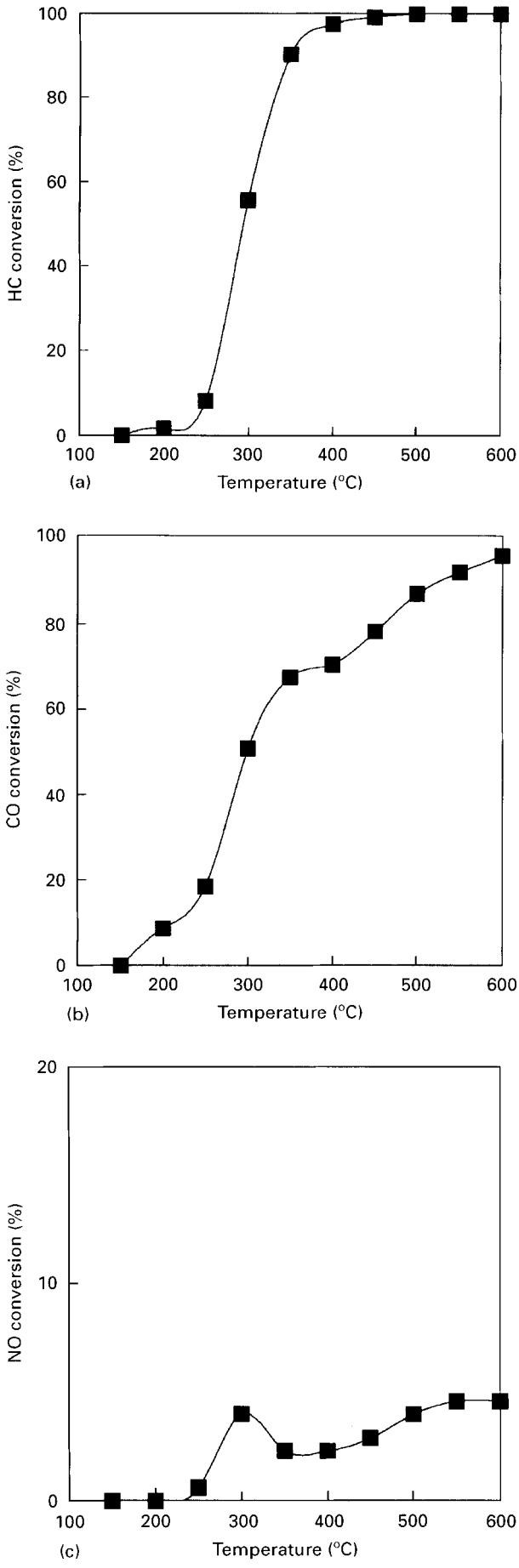

Figure 4 Removal conversion efficiencies for (a) C_3H_6, (b) CO and (c) NO in a model lean-burn exhaust at $A/F = 18$ and SV = 100 000 h^{-1} over 10 mol % Cr (oxide)–Al_2O_3 subjected to heat-treatment at 1000 °C. Gas mixture composition is described in the text.

$A/F = 18$ and SV = 100 000 h^{-1} over 10 mol %Cr–Al_2O_3 subjected to heat-treatment at 1000 °C. The NO removal–conversion efficiency for the present sample was 5% over 550 °C, while the removal–conversion for C_3H_6 and CO was 100% and 95% at 500 °C, respectively. Torikai and coworkers [11] reported the effect of various transition metals in or on a transition aluminas for the catalytic selective reduction (SCR) of NO by C_2H_4 in oxidizing atmospheres. The addition of 0.2 wt %Cr had the effect on decreasing the optimum temperature for the maximum NO_x conversion (13% at *ca.* 300 °C). However, their report deal with the experiments performed at a low space velocity of *ca.* 10 000 h^{-1}. It is known that a space velocity greatly affects the conversion of NO_x as well as the active temperature region. In general, the maximum peak for activity moves to a higher temperature region and the conversion decreases with increasing space velocity in catalysis test. The NO conversion curve in Fig. 4c seems to be explained by these tendencies for an automotive catalyst evaluation. It should be noted that present data were obtained for the powder sample subjected to heat-treatment at 1000 °C where the usual automotive catalyst would largely degenerate.

Another feature for this catalyst is high conversion for hydrocarbon (C_3H_6) at a low temperature region. It has been assumed that the selective catalytic reduction (SCR) of NO_x is related to the formation of partially oxidized hydrocarbons from the reaction between hydrocarbons and oxygen [21–27]. To achieve this scheme, it is better that the oxidation activity for hydrocarbons are at a medium level. The intermediate hydrocarbons oxidized should be able to react with NO adsorbed onto the support and/or catalyst. Regarding with the SCR mechanism for NO, present Cr Al_2O_3, even heated at elevated temperatures, seems to be too active for the complete oxidation reaction of hydrocarbons. The study by Torikai *et al.* [11] described the decrease of the maximum active region for NO conversion over Cr–Al_2O_3 compared to pure Al_2O_3; however, they did not try to explain the phenomenon. In this work, it is also difficult to discuss the detailed reaction mechanism of NO_x removal and oxidation of hydrocarbons. Present data of phase transformation, sintering and removal conversions for three poison gases in lean-burn exhaust indicate a certain potential as catalyst and/or catalytic support for the Cr_2O_3–Al_2O_3 system towards a heat-resistant automotive NO_x removal catalyst, which should be examined further.

Several workers have reported the activity of Cr_2O_3 catalyst for the SCR of NO_x with NH_3 in stationary NO_x sources [28–32]. Duffy and coworkers [31] described the effect of O_2 and water on the reduction of NO_x with NH_3; in conjunction with their previous paper [32], they concluded that amorphous chromia was shown to be a highly active material for these reactions at low temperatures (<180 °C). However, crystalline chromia (α-Cr_2O_3) gave rise to substantial amounts of nitrous oxide (N_2O). Although the reaction scheme is essentially different to the SCR with hydrocarbons and ammonia under an excess of

oxygen, it suggests that the surface state of chromia catalysts having amorphous or crystalline form affects the adsorption of reaction species. Present Cr_2O_3-modified aluminas have the unique surface structure where Cr ions are sited in the crystal lattice of a defective solid solution based on δ-Al_2O_3 and θ-Al_2O_3 if the heat-treatment temperature is between 800–1000 °C. These materials also have moderate large surface areas, and statistically distributed Cr–O interactions in the defective spinel-structured matrix, which should lead to other possible catalytic compound for a series of automotive catalysis.

4. Summary

The solid-state thermal behaviour of Cr_2O_3-doped γ-Al_2O_3 was studied with respect to its possible high-temperature application and an automotive lean-burn exhaust catalyst. The following conclusions can be drawn:

1. Cr_2O_3 doping has only a small effect on the usual transformation of γ- to α-Al_2O_3. Grain growth at elevated temperatures up to 1100 °C is moderately affected.
2. Electron spin resonance spectra for Cr_2O_3-doped Al_2O_3 indicated the existence of Cr(3+) in an axial field, suggesting the formation of Cr(3+)-doped solid solution having the structures of δ-Al_2O_3 and/or θ-Al_2O_3 at 800–1000 °C.
3. Cr_2O_3-doped Al_2O_3 catalyst heat-treated at 1000 °C in air showed removal–conversion efficiencies of 100% for C_3H_6, 92% for CO and 5% for NO at 550 °C under the lean-burn condition of $A/F = 18$ and SV = 100 000 h^{-1}.

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