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The ^{27}Al State in CeO_2 - γ - Al_2O_3 Mixed Oxides Determined by Solid-State NMR Spectroscopy

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Abstract: In this work, CeO_2 - γ - Al_2O_3 mixed oxides were studied by solid-state NMR techniques to understand the interaction between CeO_2 and γ - Al_2O_3 . The ^{27}Al magic angle spinning (MAS) NMR spectra of the mixed oxides showed a sharp peak at ca. 37 ppm and a high-field shoulder, in addition to the signals from tetra- and hexa-coordinated ^{27}Al sites. It was demonstrated that the sharp peak at ca. 37 ppm originates from the ^{27}Al atoms residing in the lattice of CeO_2 with an eight-fold coordination, representing the interaction between CeO_2 and γ - Al_2O_3 ; the high-field broad shoulder peak arises from penta-coordinated Al sites originally present in γ - Al_2O_3 . It was postulated that four Al^{3+} ions have replaced the three Ce^{4+} ions in three CeO_2 crystal cells so that the overall charge balance of the system is maintained. Furthermore, it was shown that the concentration of Al substitution is limited, and only about 1% of the total CeO_2 can be replaced by Al^{3+} .

Key words: ^{27}Al MAS NMR, CeO_2 , γ - Al_2O_3 , substitution, MQMAS NMR

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Introduction

CeO_2 - γ - Al_2O_3 mixed oxides are well-known promoters in automobile three-way catalysts^[1-3]. Many investigations have shown that there is a strong interaction between

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CeO₂ and γ -Al₂O₃, but the nature of this interaction still keeps arguing^[4,5]. X-ray diffraction studies of CeO₂- γ -Al₂O₃ mixed oxides indicated that poorly crystallized γ -Al₂O₃ phase was present and only CeO₂ with fluoride structure could be detected^[4]. Based on XPS and Raman studies of this system, Shyu et al.^[5] proposed that a precursor was responsible for the formation of CeAlO₃. Eengler et al.^[6] investigated the coordination behavior of Al³⁺ in CeO₂- γ -Al₂O₃ samples by ²⁷Al NMR. For pure γ -Al₂O₃, two characteristic peaks were observed at ca. 60 ppm and 0 ppm, belonging to the tetrahedral and octahedral sites of Al³⁺ present in this structure, respectively^[6,7]. Some other authors also observed an additional peak at ca. 40 ppm and assigned it to penta-coordinated Al in γ -Al₂O₃^[8-10]. However, the assignment of the signal becomes complicated in the case of γ -Al₂O₃ containing mixed oxide. For lanthanum- and cerium-doped γ -alumina samples, a similar peak at ca. 35 ppm was also observed and was assigned to the formation of a new compound resulting from the interaction between γ -alumina and cerium/lanthanum^[6,11]. Recently, Kulshreshtha *et al.* studied the CeO₂- γ -Al₂O₃ oxides by ²⁷Al NMR. They observed a sharp peak at ca. 40 ppm and assigned it to Al³⁺ that substituted the Ce⁴⁺ sites in CeO₂ lattice, possessing cubic site symmetry with an eight-fold coordination^[12]. However, the detailed substitution mechanism is still unclear. After these samples were treated by the temperature programmed reduction (TPR), another peak at ca. 25 ppm appeared and was thought to be originated from the Al³⁺ that had Ce³⁺ in its vicinity (produced by the partial reduction of Ce⁴⁺). No evidence for the presence of the Ce³⁺ ions was given by the authors. To have a better understanding of the interaction between CeO₂ and Al₂O₃, we have prepared a series of mixed samples with different Al contents (Ce : Al = 9 : 1, 7 : 3, 5 : 5), and studied the Al states in the mixed oxides by ²⁷Al MAS and MQMAS NMR methods.

1 Experimental Section

1.1 Sample Preparation

The sample preparation follows the method in the literature^[13-16]. An appropriate amount of citric acid was added to a mixture of Ce(NO₃)₃ and Al(NO₃)₃ solution. The solution was then soaked by active carbon in equivalent volume. The impregnated mixture was dried at 373 K, pyrolyzed at 553 K and then calcined in a muffle furnace at 973 K under ambient atmosphere for 3 h. The as-synthesized samples were also steam-aged under 90% (v/v) H₂O/air flow at 1061 K for 12 h to get the steam-aged products.

1.2 NMR Spectroscopy

All of the NMR experiments were carried out at 9.4 T on a Varian Infinityplus-400 spectrometer equipped with a Chemagnetic double-resonance 4-mm probe with resonance frequency of 104.26 MHz for ²⁷Al. The excitation pulse length was adjusted to $\pi/12$ and the pulse duration was 0.5 s for ²⁷Al single-pulse experiments. The chemical shift was referenced to a 0.1 mol/L Al(NO₃)₃ solution. The MAS spinning speed was 12 kHz.

Prior to NMR measurements, the samples were packed into a ZrO_2 MAS rotor (4 mm o. d.) with a Kel-F endcap.

A three-pulse z -filtered sequence was used for ^{27}Al multiple-quantum magic angle spinning (MQMAS) experiments^[17,18]. The radio frequency (rf) pulses used to excite the three-quantum coherences (3Q) and to transfer them back to zero quantum had a field strength of 147 kHz. A selective $\pi/2$ pulse with a 10 kHz field strength was applied after the z -filter period (200 μs)^[19]. The optimized three pulse widths were 3, 1, 1, 1 and 11 μs , respectively. To produce pure absorption-mode line-shapes in the two-dimensional spectra, the hypercomplex method was applied for data collection, and all two-dimensional data were processed with a shearing transformation prior to the complex Fourier transformation. Typically 3 600 scans were acquired for each t_1 increment and two dimensional data sets consisted of 36 $t_1 \times 512 t_2$.

2 Results and Discussion

Figure 1 shows the ^{27}Al MAS NMR spectra of the series of mixed oxide samples. For the pure $\gamma\text{-Al}_2\text{O}_3$ sample (Figure 1a), besides the two distinct peaks at ca. 60 and 5 ppm, belonging to tetra- and hexa-coordinated Al sites, respectively, there is another weak signal at ca. 35 ppm, which is usually assigned to penta-coordinated aluminum site. Generally, the penta-coordinated aluminum site exists on the external surface of $\gamma\text{-Al}_2\text{O}_3$. The amount of the penta-coordinated Al is associated with the crystal size of $\gamma\text{-Al}_2\text{O}_3$. The smaller the crystal size, the more the amount of Al on the external surface, and thus the more the amount of penta-coordinated Al sites. Figure 2 gives the ^{27}Al MAS NMR spectra of $\gamma\text{-Al}_2\text{O}_3$ samples with different crystal sizes. The penta-coordinated Al signal at ca. 35 ppm can be observed only in the ^{27}Al MAS NMR spectrum of $\gamma\text{-Al}_2\text{O}_3$ with small size (30~50 nm). ^{27}Al MAS NMR spectrum (Figure 1b) of mechanically mixed CeO_2 - $\gamma\text{-Al}_2\text{O}_3$ oxide exhibits similar feature compared with that of pure $\gamma\text{-Al}_2\text{O}_3$ (Figure 1a), probably indicating that no chemical interaction exists between CeO_2 and $\gamma\text{-Al}_2\text{O}_3$ in the mechanically mixed oxides. Figures 1c~e show ^{27}Al MAS NMR spectra of the as-synthesized CeO_2 - $\gamma\text{-Al}_2\text{O}_3$ oxides with different Ce: Al ratios. The appearance of a new sharp signal at ca. 37 ppm with a broad down-field shoulder implies that a kind of interaction takes place between CeO_2 and $\gamma\text{-Al}_2\text{O}_3$. It is interesting that the intensity of the sharp peak gradually increases while that of the broad shoulder almost remains unchanged when the concentration of Al in the CeO_2 - $\gamma\text{-Al}_2\text{O}_3$ mixed oxides decreases. After steam-aged treatment on the CeO_2 - $\gamma\text{-Al}_2\text{O}_3$ oxides with different Ce: Al ratios (shown in Figures 1f~h), the broad shoulder disappears and only the sharp peak remains in the ^{27}Al MAS NMR spectra, probably indicating that they are two independent resonances. The broad shoulder peak likely belongs to the penta-coordinated Al originally present on the external surface of $\gamma\text{-Al}_2\text{O}_3$. The conversion of penta-coordinated Al sites into tetra- or hexa-coordinated Al sites by steam treatment results in the dis-

appearance of the broad shoulder. The sharp signal probably originates from the interaction between CeO_2 and $\gamma\text{-Al}_2\text{O}_3$. Obviously, the interaction is strong enough to resist the steam-aged treatment.

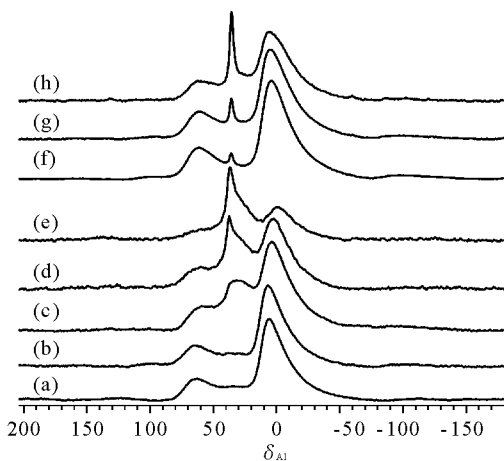


Fig. 1 ^{27}Al MAS NMR spectra of pure small-sized $\gamma\text{-Al}_2\text{O}_3$ (a); mechanical mixture of $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ (b); synthesized $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ without steam-aged treatment (c) Ce : Al = 5 : 5, (d) Ce : Al = 7 : 3, (e) Ce : Al = 9 : 1; synthesized $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ with steam-aged treatment (f) Ce : Al = 5 : 5, (g) Ce : Al = 7 : 3, (h) Ce : Al = 9 : 1.

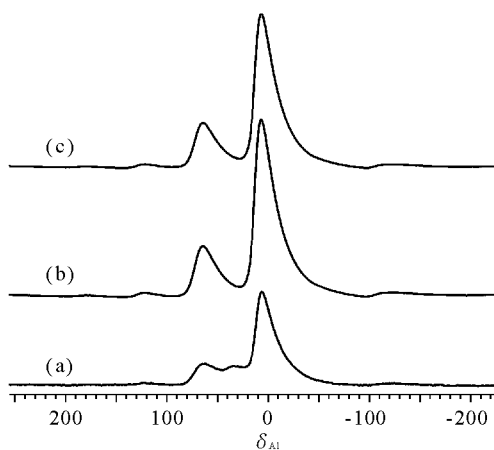


Fig. 2 ^{27}Al MAS NMR spectra of $\gamma\text{-Al}_2\text{O}_3$ samples with different crystal sizes: (a) small-size (30~50 nm), (b) medium-size (50~90 nm), (c) large-size (90~120 nm).

In order to gain more detailed information about the various Al sites in this series of samples, MQMAS method that combines MAS technique and spin manipulations and can average out the effects of second-order quadrupolar interaction was performed. In the two-dimensional (2D) MQMAS spectrum, the projection into the F_1 dimension can give rise to a spectrum in which the anisotropic effect has been removed. Meanwhile, the NMR parameters of quadrupolar nuclei such as quadrupolar product (P_Q) and isotropic chemical shift can be obtained directly from the 2D MQMAS spectrum by the following equations^[20,21].

$$\delta_{\text{iso}} = \frac{10}{27}\langle\delta_{F_2}\rangle + \frac{17}{27}\langle\delta_{F_1}\rangle \quad (1)$$

$$P_Q = \sqrt{\frac{17\nu_0^2 \times 10^6}{162000}(\langle\delta_{F_1}\rangle - \langle\delta_{F_2}\rangle)} \quad (2)$$

Where δ_{iso} is the isotropic chemical shift, P_Q is quadrupolar product, ν_0 is quadrupolar frequency, $\langle\delta_{F_2}\rangle$ and $\langle\delta_{F_1}\rangle$ are the position (ppm in unit) of the signal in the F_2 and F_1 dimension of the corresponding 2D MQMAS spectrum, respectively.

Figure 3 shows the ^{27}Al 2D MQMAS spectra of this series of samples. For pure small-size $\gamma\text{-Al}_2\text{O}_3$, three aluminum sites can be resolved, corresponding to tetra-, pen-

ta- and hexa-coordinated Al sites, respectively.

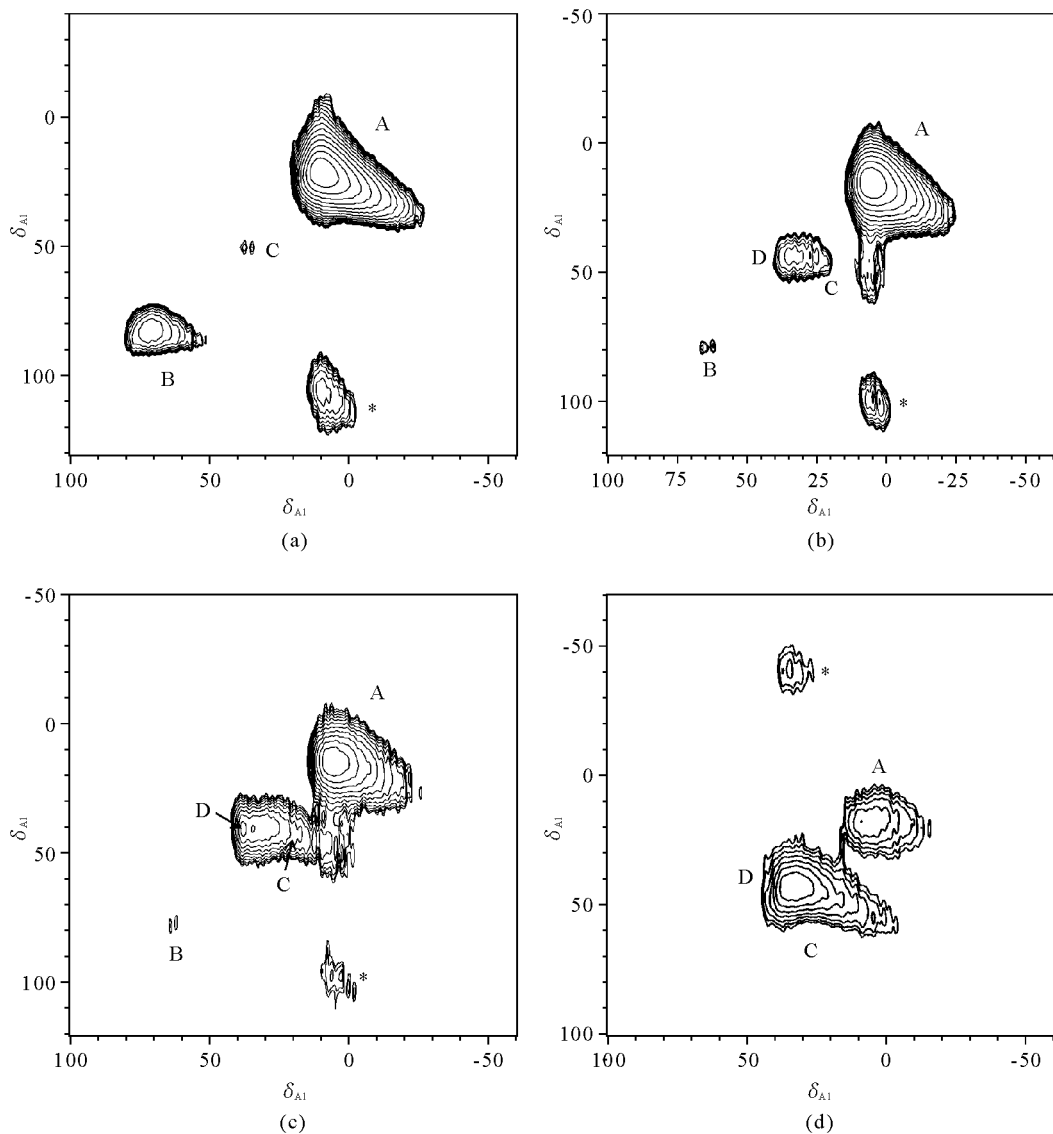


Fig. 3 ^{27}Al two-dimensional MQMAS spectra of pure small-sized $\gamma\text{-Al}_2\text{O}_3$ (a) and $\text{CeO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$ mixed oxides with different Al contents; (b) Ce : Al = 5 : 5, (c) Ce : Al = 7 : 3, (d) Ce : Al = 9 : 1. The asterisks in the spectra denote spinning sidebands.

For the $\text{CeO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$ mixed oxides containing different Al contents (Figures 3b~d), site A and site B are also observed. The intensity of the tetra-coordinated Al signal decreases with the Al concentration decreasing, and this signal is hardly observed in the MQMAS spectrum of the sample with a Ce/Al ratio of 9 : 1. In addition, two signals denoted as C and D, corresponding to the broad shoulder and the sharp signal in the ^{27}Al MAS NMR spectra, are present in the MQMAS spectra of the mixed oxides. There-

fore, the sites A, B and C are probably associated with the hexa-, tetra-, and penta-coordinated Al sites in the initial γ -Al₂O₃ though their chemical shifts move ca. 4~5 ppm to high-field due to the incorporation of CeO₂, and only the site D arises from the interaction between CeO₂ and γ -Al₂O₃. Some authors proposed that an intermediate compound with perovskite structure (CeAlO₃) was formed related to the interaction^[5], but our XPS analysis (not shown) demonstrate that no Ce³⁺ exists in our samples. The NMR parameters derived from the MQMAS spectra of the four Al sites for the sample with Ce : Al=7 : 3 are listed in Table 1 (the NMR parameters of the other two samples are similar).

Table 1 ²⁷Al NMR parameters for the different Al sites in CeO₂- γ -Al₂O₃ mixed oxide with Ce : Al=7 : 3

site	$\delta_{\text{iso}}/\text{ppm}$	P_Q/MHz
A	10.5	3.3
B	71.0	4.1
C	31.2	6.4
D	37.0	2.8

It can be seen from Table 1 that the sites C and D are indeed two independent signals with different isotropic chemical shifts. The site C arising from the penta-coordinated Al present on the external surface of γ -Al₂O₃ has the largest P_Q due to the low symmetry of its local structure, while the site D possesses the smallest P_Q , implying that its local structure is the most symmetrical. The most possible reason for the high symmetry of site D is that a portion of Al atoms incorporates into the CeO₂ lattice, possessing a cubic symmetry with an eight-fold coordination, as proposed by Kulshreshtha et al^[12]. Since the radius of Al³⁺ (0.054 nm) is much less than that of Ce⁴⁺ (0.092 nm), it is expected that the CeO₂ lattice will be distorted when an Al³⁺ ion substitutes a Ce⁴⁺ ion in one unit cell. Meanwhile, such substitution will result in a charge imbalance of the CeO₂ lattice. However, the diffractograms studies have no apparent shift for the peak positions of the CeO₂ phase. The most possible explanation is that the substitution is not limited in one CeO₂ unit cell and thus does not lead to the distortion of local lattice structure. If four Al³⁺ ions replace three Ce⁴⁺ ions in three CeO₂ crystal cells, the system can keep charge balance. Furthermore, the relatively wide range substitution can decrease the distortion of CeO₂ crystal as small as possible.

The concentrations of substituted Al sites relative to either the total amount of Al sites or the total amount of CeO₂ crystal were determined from the ²⁷Al MAS spectra, which are listed in Table 2. It is noteworthy that the concentration of substituted Al sites in CeO₂ crystal relative to the total amount of CeO₂ remains constant (around 1%), which may well explain the interesting phenomenon (see Figure 1) that the inten-

sity of the sharp peak at 37 ppm gradually increases when the concentration of Al in the CeO_2 - γ - Al_2O_3 mixed oxides decreases. Since the Al substitution into the CeO_2 crystal phase is limited, a decrease in the amount of Al in the mixed oxides corresponds to an increase of the CeO_2 crystal phase, leading to an increase in the amount of Al into CeO_2 lattice, and the relative intensities of the substituted Al sites to the non-substituted Al sites increase. Compared with pure γ - Al_2O_3 , the incorporation of Al into the CeO_2 lattice causes a slight high-field shift (ca. 4~5 ppm) of the signals of the tetra-, penta- and hexa- coordinated Al sites (shown in Figures 1c~e).

Table 2 The amount of substituted octa-coordinated Al relative to the total amount of Al and to the total CeO_2 in CeO_2 - γ - Al_2O_3 mixed oxides with different Ce : Al ratios

CeO_2 - γ - Al_2O_3 (Ce/Al molar ratio)	9 : 1	7 : 3	5 : 5
octa-coordinated Al/total Al % (molar ratio)	12%	3%	1%
octa-coordinated Al /total CeO_2 % (molar ratio)	1%	1%	1%

3 Conclusion

The present investigation demonstrates that solid state NMR is a powerful tool for clarifying the interaction between CeO_2 and Al_2O_3 , and it actually provides a more detailed information about the incorporation of Al into the CeO_2 lattice. The appearance of the sharp signal at ca. 37 ppm in ^{27}Al MAS NMR spectra is proved to be arised from the strong interaction between CeO_2 and γ - Al_2O_3 . For the CeO_2 crystal, only about 1% of total Ce^{4+} ions in cubic lattice can be substituted by Al, which remains constant with the ratio of CeO_2/γ - Al_2O_3 increasing.

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用固体核磁共振方法研究 CeO_2 - γ - Al_2O_3 混合氧化物中的 Al 状态

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摘 要: 用固体核磁共振技术研究了 CeO_2 - γ - Al_2O_3 混合体系中 CeO_2 和 γ - Al_2O_3 两相间的相互作用. 在混合物的 ^{27}Al MAS NMR 中, 除了四配位和六配位的 Al 位外, 有一个尖锐的位于 37 处的峰, 这个峰在高场处有一宽的肩峰. 实验证实: 位于高场的宽峰来自于 γ - Al_2O_3 中的五配位 Al, 而位于 37 处的尖峰则是由 CeO_2 和 γ - Al_2O_3 两相间的相互作用产生的, 即 Al 取代了 CeO_2 晶格中八配位的 Ce. 定量研究表明, 这种 Al 取代的量是极其有限的, 整个 CeO_2 晶格只有 1% 的 Ce 能被 Al 取代.

关键词: ^{27}Al MAS NMR; CeO_2 ; γ - Al_2O_3 ; 取代; MQMAS NMR

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