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Penta-coordinated Al^{3+} ions as preferential nucleation sites for BaO on γ-Al_2O_3: An ultra-high-magnetic field ^{27}Al MAS NMR study

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Abstract

We report the first observation of preferential anchoring of an impregnated catalytic phase onto penta-coordinated Al^{3+} sites on the surface of γ-Al_2O_3. The interaction of barium oxide with a γ-alumina support was investigated by high resolution solid state ^{27}Al magic angle spinning NMR at an ultra-high magnetic field of 21.1 T and at sample spinning rates of up to 23 kHz. Under these experimental conditions, a peak in the NMR spectrum at ~23 ppm with relatively low intensity, assigned to 5-coordinated Al^{3+} ions, is clearly distinguished from the two other peaks representing Al^{3+} ions in tetra-, and octahedral coordination. Spin-lattice ^{27}Al relaxation time measurements clearly show that these penta-coordinated Al^{3+} sites are located on the surface of the γ-alumina support. BaO deposition onto this γ-alumina sample resulted in the loss of intensity of the 23 ppm peak. The intensity loss observed was linearly proportional to the amount of BaO deposited. The results of this study strongly suggest that, at least for BaO, these penta-coordinated Al^{3+} ions are the nucleation sites.

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1. Introduction

γ-Alumina, one of the metastable "transition" alumina structural polymorphs, is an important catalytic material both as an active phase and as a support for catalytically active phases. The widespread catalytic applications of this material range from petroleum refining to automotive emission control. As such, the bulk and surface structure of γ-alumina and its formation and thermal stability have been and continue to be subjects of an enormous amount of research [1–3]. However, due to the low crystallinity and very fine particle size of γ-alumina, applying well-established analytical techniques for determining its surface structures is very difficult. Notably, single-crystal X-ray diffraction is not feasible due to the poorly ordered structure of γ-alumina [1].

Of particular importance for understanding the catalytic properties of γ-alumina, relating its surface structure to the origin of Lewis acidity has been of considerable interest and has been studied by solid-state NMR [4–8], FTIR [9,10], and theoretical calculations [3,11–13]. For example, Fripiat and coworkers identified ^{27}Al NMR peaks due to 4-, 5-, and 6-coordinated aluminum ions in the spectra of transition aluminas [6,7]. On the basis of proton-aluminum cross-polarization (CP-MAS) spectra, these authors also reported that the tetra- and penta-coordinated Al^{3+} species are at least partially located at the γ-alumina surface and, thus, are suggested as potential Lewis acid sites [7]. Liu and Truitt differentiated three different types of Lewis acid sites on γ-alumina surfaces based on diffuse reflectance-FTIR spectra obtained following pyridine adsorption [9], where the three Lewis acid sites are assigned to three-, four-, and five-coordinated Al^{3+} ions. Ab initio studies [3] and molecular dynamic simulations [12] also support the existence of stable penta-coordinated Al^{3+} ions on alumina surfaces.

Solid-state magic-angle spinning (MAS) ^{27}Al-NMR has long been recognized as a powerful technique for the identification of Al ions in different coordination environments [4,5,7,8]. Furthermore, cross-polarization ^1H-^{27}Al MAS NMR (CP/MAS) experiments, combined with specific adsorbent

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treatments, such as ammonia, pyridine and water, have been used for probing the surface distribution of various aluminum and acid sites based on the distance between the protons and the aluminum ions under investigation. However, these studies could not answer the specific question of whether penta-coordinated aluminum ions reside exclusively on the γ-alumina surface [7]. This is due in part to the fact that ^{27}Al is a quadrupolar nucleus with a spin quantum $I = 5/2$ and thus is subject to quadrupolar line broadening and other limitations. Because such line broadening is inversely proportional to the external magnetic field strength [14], the resolution in MAS ^{27}Al spectra of γ-alumina obtained at low to medium magnetic fields is relatively poor, hindering clear separation of the peak corresponding to the penta-coordinated aluminum ions from those corresponding to the tetrahedral and octahedral aluminum. As such, the use of MAS NMR to study the relationship of γ-alumina surface structure to catalytic behavior has been correspondingly limited.

The multiple-quantum magic-angle spinning (MQMAS) technique, developed in 1995 [15,16], allows the use of standard MAS probes to obtain well-resolved two-dimensional NMR spectra that contain an isotropic dimension unperturbed by quadrupolar broadening. The application of this technique to clearly resolve and assign spectral features to Al in tetrahedral, pentahedral, and octahedral coordination has been nicely demonstrated [17–19]. Despite its remarkably rapid acceptance as an important technique for structural studies of a broad range of solid materials, especially microporous solids, glasses, and novel metal oxides, the MQMAS experiment has aspects that still require further development. Notably, the sensitivity of the technique needs to be improved, particularly for nuclei with very large quadrupolar coupling constants. Equally important, to simplify the quantification of the technique, the excitation and detection of multiple-quantum coherence as a function of the magnitude of the quadrupolar coupling needs to be made more uniform. Finally, much still remains to be understood about the theory of the MQMAS experiment and interpretation of the resulting data, particularly concerning some of the more subtle effects of the second-order quadrupolar interaction. In contrast, MAS spectra obtained at ultra-high fields and high spinning rates are by nature quantitative and very sensitive experiments. In these cases, the second-order line broadening is not eliminated but rather progressively narrowed at increasing magnetic fields.

In this contribution, we describe studies aimed at the identification of the location (i.e., surface vs bulk) of penta-coordinated Al^{3+} ions in γ-alumina. We show that in fact these Al ions are located exclusively at the γ-alumina surface, thereby enabling a specific interaction of a catalytically active phase, BaO, with these species. We believe this result may be generally applicable to understanding the initial deposition of catalytically active phases onto the surface of γ-alumina during catalyst material preparation, perhaps explaining why this support material is able to readily disperse such phases. Throughout the investigations described here, we applied ultra-high-field solid-state MAS ^{27}Al-NMR and demonstrate the unique advantages of acquiring MAS ^{27}Al MAS spectra of γ-alumina and alumina-supported BaO at the highest magnetic field studied to date (21.1 T).

The catalytically active phase chosen for the present study was motivated because γ-alumina-supported alkali and alkaline earth oxide-based NO_x storage/reduction catalysts (especially Pt-Rh/BaO/Al_2O_3) provide a promising approach for the control of NO_x (NO and NO_2) emissions from vehicle engines that operate at high air-to-fuel ratios (so-called "lean" combustion) [20]. Although there have been extensive studies on the NO_x storage/reduction mechanism, questions remain concerning the interaction of barium oxide with alumina surfaces, which fundamentally determines the properties of these materials. For example, our group has identified surface nitrates adsorbed on monolayer BaO supported on γ-alumina, as well as bulk nitrate species associated with multilayer BaO on alumina [21]. We have also reported that the morphology of Ba-related species dynamically changes during NO_x adsorption and nitrate decomposition processes [22]. However, detailed information on the interaction of BaO with γ-alumina supports, important for designing improved catalysts, is not available due to the limitations of resolution and sensitivity of characterization techniques used in previous studies, such as low-field NMR, XRD, and others.

2. Experimental

The BaO/Al_2O_3 samples were prepared by the incipient wetness method, using aqueous $Ba(NO_3)_2$ solutions and a γ-alumina support (200 m^2/g, Condea). After impregnation, the samples were dried at 120 °C and then activated via calcination at 500 °C in 20% O_2 in nitrogen for 2 h. Barium loading was varied from 0.5 to 20 wt% [21–24]. For a 2 wt% BaO loading, the amount of Ba is equivalent to 0.68 mol% of the total amount of aluminum in the γ-alumina support material.

All ^{27}Al NMR experiments were performed at room temperature on a Varian-Inova 900.52 MHz NMR spectrometer, operating at a magnetic field of 21.1 T. The corresponding ^{27}Al Larmor frequency is 234.669 MHz. All of the spectra were acquired at sample spinning rates of either 15 or 23 kHz ($\pm$5 Hz). A commercial MAS probe with a 3.2-mm-o.d. zirconium pencil-type spinner system was used for the 23-kHz experiments. Unfortunately, this probe failed during these studies, so they were completed with a homemade system of similar design at the safer spinning rate of 15 kHz. A single pulse sequence with a pulse width of about 77° was used, corresponding to a pulse width of 3 µs. Note that the solid 90° pulse was about 3.5 µs. Each spectrum was acquired using a total of 512 scans with a recycle delay time of 1 s and an acquisition time of 66 ms. All of the spectra are externally referenced (i.e., the 0 ppm position) to the NMR peak for octahedral Al^{3+} in γ-alumina. The approximate spectrometer dead time, including the probe ring-down, was only a couple of µs. All of the spinning sidebands were acquired without difficulty, including the center band, phased after the single excitation pulse. Therefore, spectrometer dead time was not an issue in our experiments, due also in part to the high sensitivity associated with the ^{27}Al MAS experiment.

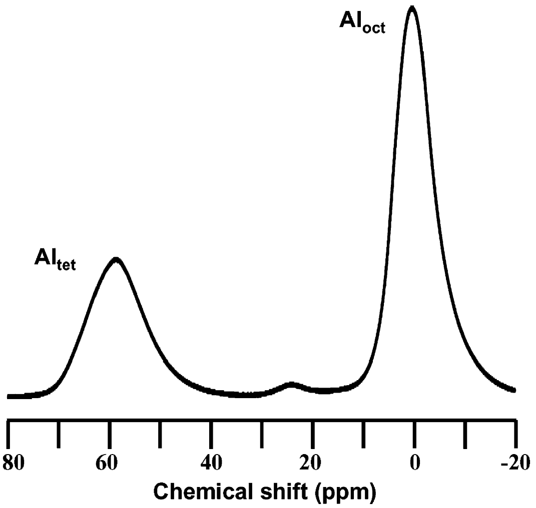


Fig. 1. Solid state ^{27}Al MAS NMR spectrum of γ-alumina, activated at 500 °C for 2 h, collected at 21.1 T and a 23 kHz spinning rate.

The ^{27}Al T_1 measurements were carried out using a single-pulse excitation (solid 90°) sequence, but the acquisition time was set to be 3 ms, which was still longer than the effective length of the free induction decay (FID). By varying the recycle delay time from 5 ms to 4 s, the relaxation time can be measured. Thus, the minimal measurable recovery time was 8 ms. A total of 512 scans were used for acquiring each spectrum in the array. The first spectrum at a recovery time of 5 ms was acquired twice, to ensure that a steady state was reached by the time the second spectrum was acquired. The first spectrum was omitted during the data-fitting process.

3. Results and discussion

Fig. 1 shows the high-resolution solid-state center band ^{27}Al MAS NMR spectrum of γ-alumina—to the best of our knowledge, the highest resolution spectrum of this material obtained to date. The spectrum contains the well-known peaks at 0 (by definition in this paper) and ~59 ppm, which are assigned to octahedral and tetrahedral Al^{3+} ions, respectively. Interestingly, an additional clearly resolved peak at ~23 ppm with relatively low intensity was also observed when the sample was spun at 23 kHz, consistent with an assignment to penta-coordinated Al^{3+} ions [6–8] as discussed above. Note, however, that this peak is not readily observable for typical γ-alumina samples in conventional low-field (7.05 T), low-sample spinning rate (~5 kHz) MAS experiments [24,25], and is only poorly resolved at intermediate fields and spinning rates [26,27]. Nonetheless, Pecharroman et al. [27] quantified the presence of a small amount (~5%) of penta-coordinated Al^{3+} ions in γ-alumina that gave a peak at ~30 ppm in the ^{27}Al MAS spectrum. (The chemical shifts were referenced to an aqueous $AlCl_3$ solution and acquired at a magnetic field of 9.4 T, using a sample spinning rate of 12 kHz; in their spectra, the chemical shifts of the tetra- and octa-coordinated Al^{3+} were observed at 65 ppm and 10 ppm, respectively). These authors also reported that the NMR signal of the penta-coordinated aluminum ions was completely eliminated when the alumina was heated above 950 °C. However, the difficulty of quantifying populations of Al-coordination types with ^{27}Al NMR at even moderate magnetic fields and sample spinning rates has been discussed recently [17,26,28].

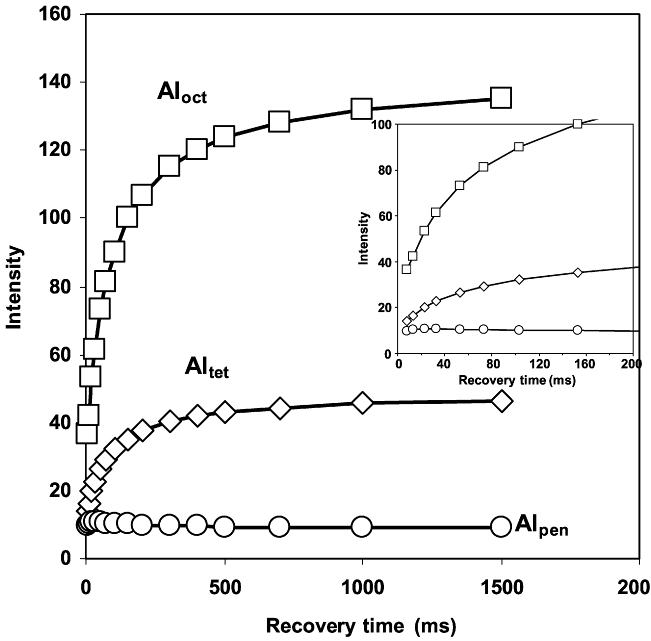


Fig. 2. Relative intensity changes of tetra- (diamond symbols), penta- (circles), and octa-coordinated (squares) aluminum with recovery time for a spin-lattice relaxation measurement of γ-alumina.

Having again spectroscopically established the presence of penta-coordinated Al^{3+} ions in the γ-Al_2O_3 support material, we sought to identify where these penta-coordinated Al^{3+} ions are located—specifically, whether these are solely alumina surface sites, as has been proposed by some [7,27], or are also located in the bulk of the oxide structure as defects. To answer this question regarding the location of penta-coordinated Al^{3+} ions, we measured the spin-lattice relaxation time, T_1, of each peak in the high-field NMR spectrum of γ-alumina. Fig. 2 shows the integrated intensity of each peak as a function of recovery time in the saturation-recovery experiment. Interestingly, the spin-lattice relaxation times of tetrahedral and octahedral alumina are almost identical, with fitted values around 120 ms. The similar relaxation times for the tetra- and octa-coordinated Al^{3+} ions indicate that most of these ions are located in the crystalline γ-alumina framework. However, penta-coordinated Al^{3+} ions relax extremely rapidly with T_1 values much less than 8 ms. These results strongly support the assignment of this NMR peak to penta-coordinated Al^{3+} ions located on the surface of the alumina support. The extremely rapid relaxation time might be due to the effective quadrupolar relaxation mechanism of the surface penta-coordinated Al^{3+} ions, arising from an enhanced molecular motion at the surface. Furthermore, early work by Huggins and Ellis [5] clearly points to a role for protons in enhancing relaxation times for Al species at the surface of γ-alumina.

Fig. 3 shows the 23-kHz center band ^{27}Al MAS NMR spectra obtained from γ-alumina samples loaded with BaO to varying levels via wet impregnation, and then activated at 500 °C.

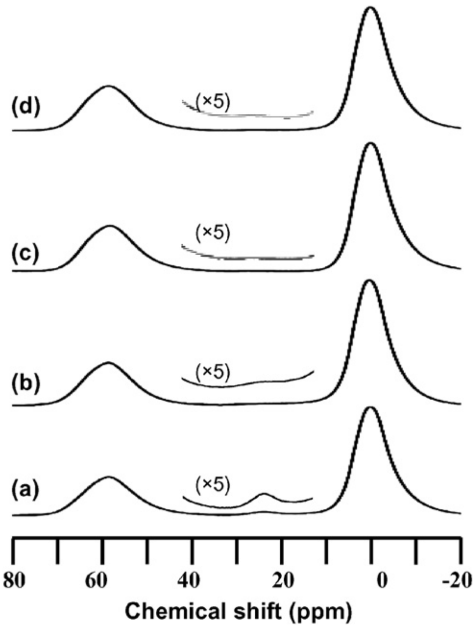
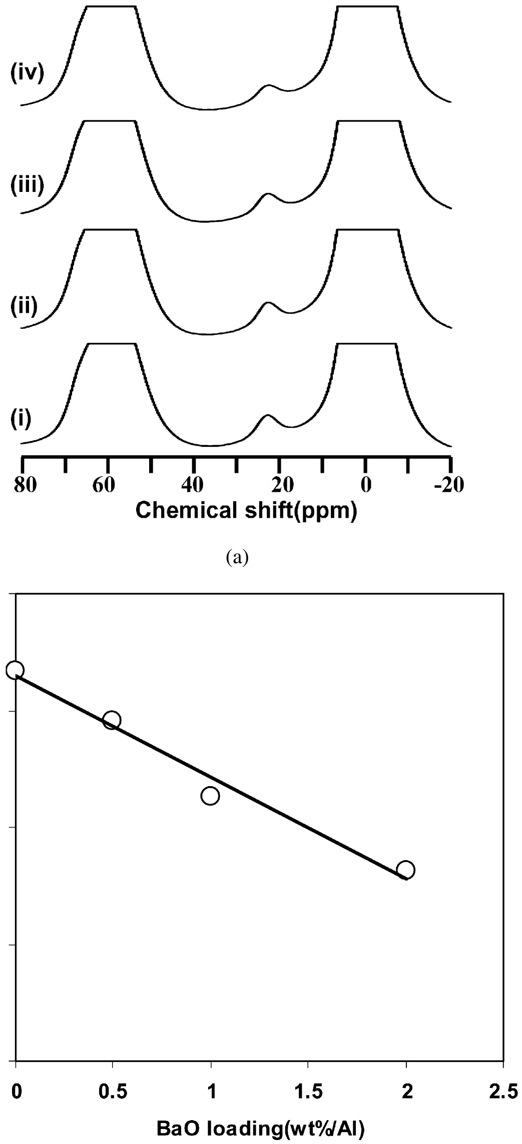


Fig. 3. Solid state ^{27}Al MAS NMR spectra, collected at 21.1 T and 23 kHz spinning rate, as a function of BaO loading: (a) γ-Al_2O_3; (b) 2% BaO/Al_2O_3; (c) 8% BaO/Al_2O_3; and (d) 20% BaO/Al_2O_3.

Neither the peak positions nor the line shapes of the tetrahedral or octahedral Al^{3+} ions changed as a function of barium loading. However, the intensity of the ∼23 ppm peak decreased significantly for 2% BaO/Al_2O_3 relative to that of the BaO-free γ-alumina. Furthermore, essentially no intensity is observed at 23 ppm for the 8 and 20% BaO/Al_2O_3 samples. These results suggest that initially BaO preferentially occupied the penta-coordinated Al^{3+} sites during the impregnation and subsequent calcination (500 °C) processes. The decrease and eventual disappearance of the 23-ppm NMR peak on BaO loading also strongly supports the assignment of this peak to Al^{3+} ions located on the surface of the alumina support and not distributed homogeneously as crystalline defect sites in the bulk.

To further clarify the interaction of BaO with penta-coordinated Al^{3+} ions, a series of BaO/Al_2O_3 samples with low BaO loadings (0.5, 1, and 2%) were prepared and activated by the same method as discussed above. ^{27}Al MAS NMR spectra were acquired for these samples along with the BaO-free γ-alumina at a spinning rate of 15 kHz. Fig. 4a displays the center band spectra, and Fig. 4b shows the relative integrated intensity of the 23-ppm peak as a function of BaO loading. Although a sample spinning rate of 15 kHz is not high enough to shift the first spinning sideband of the octahedral Al^{3+} (0 ppm) completely outside the peak of the tetrahedral Al^{3+} (59 ppm) and vice versa, the well-resolved peak at 23 ppm is clearly visible. Fig. 4b indicates that the intensity of the peak at 23 ppm decreases linearly with increasing BaO loading. These results again strongly support our conclusion that BaO, formed by the decomposition of $Ba(NO_3)_2$, interacts with the alumina by preferentially anchoring to these penta-coordinated Al^{3+} surface sites.

It is known that a certain amount of Al^{3+} ions in alumina are not detectable by ^{27}Al-MAS NMR when the spectra are acquired at low sample spinning rates [5,17,28]. The relationship between the visibility of Al^{3+} in/on γ-alumina and sample spinning rate was first reported by Kraus et al. [28], who concluded that all of the aluminum ions were visible in the NMR spectra acquired at spinning rates exceeding 20 kHz. To strengthen our argument for the special role of penta-coordinated Al^{3+} sites in the initial anchoring of BaO to the γ-Al_2O_3 surface, we estimated the number of penta-coordinated Al^{3+} sites and the number of BaO molecules loaded onto the alumina sample. Toward this end, the intensity of the NMR peak at 23 ppm (obtained at a spinning rate of 23 kHz [Fig. 2]) was integrated for the BaO-free and BaO-loaded γ-Al_2O_3 samples. For the BaO-free alumina, the mol% of penta-coordinated Al^{3+} ions was estimated as 1.56%. The amount of free penta-coordinated Al^{3+} ions over the 2% BaO/Al_2O_3 sample dropped to 0.92%, indicating that 0.64 mol% interacted with BaO and



(a)

(b)

Fig. 4. (a) Solid state ^{27}Al MAS NMR spectra for: (i) γ-Al_2O_3; (ii) 0.5% BaO/Al_2O_3; (iii) 1.0% BaO/Al_2O_3; (iv) 2.0% BaO/Al_2O_3. (b) Relative intensity change of the ∼23 ppm NMR peak, due to penta-coordinated aluminum, with BaO loading.

thus were no longer coordinatively unsaturated (i.e., penta-coordinated). The agreement between the amount of penta-coordinated Al^{3+} sites consumed (0.64 mol%) and the amount of BaO deposited (0.68 mol%) is remarkable. These results strongly suggest that at low BaO loadings, there is a one-to-one correspondence between the number of penta-coordinated Al^{3+} ions that become coordinatively saturated and the number of BaO molecules deposited.

We also should mention that at a sample spinning rate of 15 kHz, the mol% of pentahedral Al^{3+} ions, determined from the center band spectrum of γ-alumina (Fig. 4), is about 3.3%, considerably larger than that determined from the spectrum obtained at 23 kHz. This observation, however, is consistent with the results of a previous report by Pecharroman et al. [27], who estimated 5% penta-coordinated Al^{3+} ions for a γ-Al_2O_3 sample at a spinning rate of 12 kHz. The decreased molar fraction of the penta-coordinated Al^{3+} ions at increased sample spinning rate indicates that the width of the anisotropy interaction for the penta-coordinated Al^{3+} is less than those of the tetrahedral and octahedral Al^{3+} sites. The smaller anisotropy width associated with the penta-coordinated Al^{3+} suggests a considerable degree of motional flexibility, because fast molecular or segmental motion can partially or completely average the anisotropy [29]. This result is in a good agreement with the relaxation measurement results given in Fig. 2 and again supports our conclusion that penta-coordinated Al^{3+} ions are located at the surface of the γ-Al_2O_3 sample.

On the basis of the results reported here, the possibility that penta-coordinated Al^{3+} ions on the γ-Al_2O_3 surface generally serve as anchoring sites for catalytically important materials (possibly both oxides and metals) is intriguing. One of the main reasons that γ-Al_2O_3 is used so commonly as a catalyst support material is its ability to form and stabilize active centers (metal and metal oxide particles) with high dispersion. Here we have shown that BaO, the active NO_x storage phase in the LNT technology, initially anchors to these coordinatively unsaturated, pentahedral Al^{3+} sites. This is in excellent agreement with our previous observation that well-dispersed BaO nanoparticles formed on the thermal decomposition of a $Ba(NO_3)_2$ precursor loaded onto the γ-Al_2O_3 surface [22]. We believe that for the BaO/Al_2O_3 system discussed in this work, this correlation holds. However, the generality of this phenomenon is not yet established. As such, in our ongoing research efforts we are studying the impregnation of other catalytically interesting metal and metal oxide particles onto γ-Al_2O_3 to determine whether these penta-coordinated Al^{3+} sites are the anchoring points (nucleation sites) for other catalytically active species. If this correlation holds for all active-phase/γ-Al_2O_3 systems, it could open up the possibility of systematically varying the number of penta-coordinated Al^{3+} sites, and thereby provide good control of dispersion of the catalytically active phase.

4. Conclusion

We have presented the first observation of the preferential anchoring of barium oxide onto penta-coordinated Al^{3+} sites of γ-Al_2O_3 in BaO/Al_2O_3 catalysts using the results of high-field (21 T), high-resolution solid-state ^{27}Al MAS NMR at sample spinning rates between 15 and 23 kHz. The ^{27}Al MAS NMR spectroscopic results along with the results of spin-lattice relaxation time measurements clearly showed that the peak at ~23 ppm, assigned to penta-coordinated Al^{3+} ions, is located exclusively on the surface of γ-Al_2O_3. Quantitative analysis of the integrated peak intensities in the ^{27}Al NMR spectra revealed a one-to-one correlation between the number of BaO molecules deposited and the number of penta-coordinated Al^{3+} ions consumed by anchoring BaO onto the γ-Al_2O_3 surface.

Note added in proof

Recently, we obtained an NMR spectrum of aluminum nitrate, a compound commonly used as a standard chemical shift reference. Using this compound as reference, the octahedral Al^{3+} peak would appear at 11.7 ppm.

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