Structural phase transitions and lean NO removal activity of
copper-modified alumina

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Abstract

Copper-modified alumina catalysts, designed for NO removal under lean-burn engine conditions, have been investigated from the viewpoint of the structural phase transition and thermal stability. The structural changes of crystalline components heat-treated at temperatures from 500°C to 1100°C were characterized by neutron diffraction (ND) method. In the as-prepared materials, powder-diffraction patterns revealed a mixture of crystalline \( \gamma \)-\( \text{Al}_2\text{O}_3 \) and \( \text{CuO} \), and electron spin resonance (ESR) data showed well-dispersed \( \text{Cu}^{2+} \) cations coordinated by O atoms in an open-octahedron geometry. ND measurements confirmed the elimination of the CuO phase above 800°C, and suggested the stabilization of a \( \delta' \)-phase of alumina by 10mol% CuO-doping at 900-1000°C. This Cu-alumina catalyst which was subjected to heat treatment at 900°C in air showed a 20% lean de-NOx removal efficiency in a test using a model exhaust gas mixture of space velocity =100,000 h\(^{-1}\).

Keywords:

alumina; catalyst; neutron diffraction; copper; nitrogen oxides; automotive exhaust

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Introduction

Alumina-supported base-metals such as copper instead of expensive precious metals are alternative catalysts in practical lean-burn NOx removal application. In the study on the activity of Al2O3 for the selective reduction of NO with C3H6, Hamada and coworkers reported the effect of small amount of 3d-transition-metal promoters to NO removal reaction[1-4]. Copper ion-exchanged ZSM-5 zeolite was reported to be very effective for the selective reduction of NO in the presence of some reductants despite an excess of oxygen and large space velocity as well as NOx decomposition in non-oxygen atmosphere[1,5-9]. However, the thermal durability of zeolite is inadequate for practical use in high-performance gasoline-engine systems.

Detailed studies on structural phase transition of copper-aluminas at elevated temperatures are rarely reported. Considering the importance on oxygen atoms and their displacements in defective aluminas during phase transitions, we applied neutron diffraction method to characterize crystal phases of a pure alumina support and an alumina catalyst impregnated with copper. Unlike X-rays, neutrons are sensitive to light atoms such oxygen in crystals, and capable of detailed crystal-structural analyses of oxides. In this paper, we describe the structural characterization using neutron diffraction and lean-burn NOx removal activity for copper-modified alumina catalyst.

Experimental

The starting γ-Al2O3 powder (surface area 180 m²/g, purity 99.9%; Nikki-Universal Co.) was first impregnated with aqueous copper nitrate, followed by
agitation of the suspension, and drying at 110°C. The products were heated at 500°C for 3 hours in air, re-ground and further heated at selected temperatures up to 1100°C in air.

This study focuses the detailed comparison of the crystal phases between pure Al₂O₃ and 10mol%Cu-Al₂O₃ samples using neutron diffraction method. Neutron diffraction experiments were carried out using General Purpose Powder Diffractmeter (GPPD) at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. The in-situ diffraction experiments were performed on pelletized samples of pure Al₂O₃, heated under vacuum within a sample tube of a furnace. The sample temperature, monitored by thermocouples above and below the sample, were controlled to within 15°C at a selected temperature in all the runs. A 30-minute wait prior to the data collection was allowed for thermal equilibration in samples. The data were collected by the detectors situated at mean scattering angles of ±90 degree for which a resolution of Δd/d=0.49% can be achieved (d is the atomic plane spacing). In the case of 10mol%Cu-Al₂O₃, diffraction experiments were carried out on GPPD at room temperature using powders heated (ex-situ) at various temperatures in air for 3 hours.

Electron spin resonance (ESR) spectra for Cu(2+) in samples (heated in air) were measured using a JEOL-3MX (Japan) spectrometer at room temperature in X-band with a modulation frequency of 100kHz.

Steady-state catalytic activity of catalysts, subjected to heat treatment at 900°C in air for 3 hours, was examined using gas mixtures with a large space velocity of 100,000h⁻¹, simulating an automotive exhaust of a fuel-lean condition at an air/fuel ratio (A/F) of 18. The typical gas-composition is the following; CO 1000ppm, C₃H₆
800ppm, NO 700ppm, O₂ 4%, CO₂ 12.7%, H₂O 10%, and N₂ balance. The analyses of NO and C₃H₆ at both the inlet and outlet of a catalyst sample bed were performed using chemiluminescence and flame ionization detectors, respectively.

3 Results and discussion

3.1 Structural phase transition and sintering of pure and Cu-modified alumina

Figures 1 and 2 show neutron diffraction patterns for pure and 10mol%Cu-impregnated-Al₂O₃, which were heated at temperatures from 500°C to 1100°C. Fig 1 indicates the typical phase transitions for pure Al₂O₃, as usually γ → δ → θ → α transitions with increasing temperature. Mixed δ + θ-phases at 1000°C, and θ + α-phases at 1100°C (of Al₂O₃) can be seen in Fig 1c and 1d, respectively. In Fig 2, the strong background intensities in a-c suggest a large amount of hydrogen or hydroxyl groups in these Cu-Al₂O₃ samples even after heat treatments. A series of diffraction profiles for 10mol%Cu-Al₂O₃ have been identified as γ +CuO → δ' → α + CuAl₂O₄, which are different from the corresponding transitions for pure Al₂O₃. The notation, δ' denotes a diffraction pattern similar to δ-Al₂O₃ but with different d-spacing. Here, it should be noted that this phase transition sequence lacks the intermediate monoclinic θ-Al₂O₃, and that the novel δ'-phase is unique to Cu-Al₂O₃. At 1000°C, pure Al₂O₃ have partially transformed to θ-Al₂O₃, whereas Cu-Al₂O₃ retained the δ'-phase (then directly transformed to α-Al₂O₃ at 1100°C). Table 1 shows a list of d-spacing vs. neutron diffraction intensity of the δ'-phase for Cu-Al₂O₃ (a), as compared to that for pure γ-Al₂O₃ at 500°C (b). The δ'-phase is
considered to be a novel phase observed at 900-1000°C in the present and previous x-ray diffraction experiments[10]. Since the atom (Al and O) positions in δ-Al2O3 have been not reported in the literature, the present data are not sufficient to warrant to the Rietveld refinement of the structure. From a qualitative comparison with the structures of γ-Al2O3, we may assume a tetragonally distorted spinel (defective) structure for the δ'-Al2O3. Therefore, this phase should have the distorted cation sites of lower symmetries than those in γ-Al2O3 (γ-phase is cubic), as well as a large amount of oxygen defects on the surface. Since crystalline Cu-clusters are not observed in samples heated at 900-1000°C, Cu cations appear to diffuse in to the lattice and may form a solid solution, Al1.95Cu0.5O3-x during heat treatment. Thus, we expect the formation of uniquely coordinated Cu cations in present Cu-Al2O3 system (δ'-phase). The ESR of starting Cu-Al2O3 showed the polycrystalline agglomerates having Cu2+ in sites of axial symmetry. The line parameters, g⊥=2.05 and g∥=2.3, seem to be characterized with Cu2+ coordinated with open-octahedron oxygens, as discussed previously [11]. As the heat-treatment temperature increased, the line width broadened and an additional ESR signal at around g=2.1 intensified. However, even in samples heated at 900-1000°C, Cu2+ is considered to retain partially the initial octahedron site. The neutron diffraction data indicate that the surface-Cu cations should be coordinated with more distorted open-octahedron oxygens after heat treatment at 900-1000°C. In other words, the results suggest the possibility of controlling the distortion of octahedron around surface-Cu cations in a series of transition aluminas (having defective spinel structures) induced by heat treatments.
The BET surface area was 70 m²/g and 62 m²/g for the pure Al₂O₃ and Cu-Al₂O₃ powders heated at 900°C in air for 3 hours, respectively. The pore-diameter analysis indicated a broad distribution of pores at around 20 nm in diameter, and the pore volume of 0.70 ml/g and 0.68 ml/g for pure Al₂O₃ and Cu-Al₂O₃ powders (900°C), respectively. The results suggest good heat-stability of this Cu-modified Al₂O₃ powder even if it is used at around 900°C, although slight acceleration of sintering is evident.

3.2 Lean NO removal activity of Cu-modified alumina

Table 2 summarizes the data of NO and C₃H₆ removal conversion efficiencies at several gas-inlet temperatures for 10 mol% Cu-Al₂O₃ subjected to heat treatment at 900°C for 3h in air. The Cu-Al₂O₃ (δ'-phase) showed the maximum NO removal efficiency of 20% at 300°C. The NO removal efficiency has the maximum at a certain temperature and then decreases with increasing temperature, as reported before repeatedly for copper/zeolite catalysts and 3d-transition-metal doped aluminas[1-10]. It should be noted that the present performance is comparable to that of Cu/ZSM-5 subjected to heat condition at 800°C[8]. The ESR and neutron-diffraction results suggest that active Cu species remain on the stabilized surface sites in Cu-Al₂O₃. Therefore, this Cu-modified alumina is one of the possible catalytic compounds for lean NOx removal, which is characterized with distorted structures modified from pure alumina.

4 Summary

The alumina-supported copper catalysts designed for NO removal under lean-
burn engine conditions have been investigated. In the as-prepared materials, neutron powder-diffraction patterns revealed a mixture of crystalline $\gamma$-Al$_2$O$_3$ and CuO, and electron spin resonance data showed well-dispersed Cu$^{2+}$ cations coordinated by O atoms in an open-octahedron geometry. Neutron diffraction measurements confirmed the elimination of the CuO phase above 800°C, and the stabilization of a $\delta'$-phase of alumina by 10mol% Cu-doping at 900-1000°C. The structural phase transitions were compared with those in pure alumina. The NO removal activity was measured using model exhaust gas mixtures with 7 compositions and high space velocities in a temperature range of 200°C-450°C. This Cu-alumina catalyst which was subjected to heat treatment at 900°C in air showed a 20% lean de-NOx removal efficiency in a test using a model exhaust gas mixture of space velocity = 100,000 h$^{-1}$.

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References


Figure captions

Fig 1
A series of neutron diffraction patterns for pure alumina, taken from in-situ heating in vacuum.  (a)500°C, (b)900°C, (c)1000°C, (d)1100°C.

Fig 2
A series of neutron diffraction patterns for 10 mol% Cu-alumina, subjected to ex-situ heat treatment in air.  (a)500°C, (b)900°C, (c)1000°C, (d)1100°C.
Table 1  Data of d-spacing vs. intensity (I) from neutron diffraction patterns for (a) the δ' phase of 10 mol% Cu-Al₂O₃ heated at 1000°C, and (b) pure γ-Al₂O₃ measured at 500°C in vacuum.

<table>
<thead>
<tr>
<th>(a) d (Å)</th>
<th>I</th>
<th>(b) d (Å)</th>
<th>I</th>
<th>(hkl)</th>
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<tr>
<td>2.286</td>
<td>38</td>
<td>2.288</td>
<td>59</td>
<td>(222)</td>
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<tr>
<td>1.993</td>
<td>46</td>
<td>1.981</td>
<td>77</td>
<td>(400)</td>
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<td>1.956</td>
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<tr>
<td>1.523</td>
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<td>1.515</td>
<td>10</td>
<td>(511)</td>
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<td>(440)</td>
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<td>1.395</td>
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<td></td>
<td></td>
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<tr>
<td>1.200</td>
<td>43</td>
<td>1.195</td>
<td>32</td>
<td></td>
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<td>1.184</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1.143</td>
<td>46</td>
<td>1.144</td>
<td>19</td>
<td>(444)</td>
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<tr>
<td>0.997</td>
<td>26</td>
<td>0.991</td>
<td>10</td>
<td>(800)</td>
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<tr>
<td>0.978</td>
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<td></td>
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<td>0.941</td>
<td>12</td>
<td>0.908</td>
<td>6</td>
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<tr>
<td>0.891</td>
<td>35</td>
<td>0.885</td>
<td>15</td>
<td>(840)</td>
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<tr>
<td>0.880</td>
<td>16</td>
<td></td>
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</table>


Table 2 NO and C\textsubscript{3}H\textsubscript{6} removal conversion efficiencies at various gas-inlet temperatures for the Cu(10mol\%)-Al\textsubscript{2}O\textsubscript{3} catalysts subjected to heat treatment at (a) 900°C and (b) 1000°C for 3h in air.

<table>
<thead>
<tr>
<th>Temperature(°C)</th>
<th>200</th>
<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
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<tbody>
<tr>
<td>NO conversion(%)</td>
<td>6</td>
<td>14</td>
<td>20</td>
<td>16</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6} conversion(%)</td>
<td>8</td>
<td>43</td>
<td>83</td>
<td>96</td>
<td>99</td>
<td>100</td>
</tr>
</tbody>
</table>
Fig 1
Fig 2

![Graph showing intensity vs. d-spacing (A) for samples a, b, c, and d.](image)