

ANL/IPNS/CP-90668 CONF-961133--3

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

RECEIVED

JAN 16 1997

Masakuni Ozawa and Suguru Suzuki

OSTI

CRL, Nagoya Institute of Technology, Tajimi, Gifu 507, Japan

C.-K. Loong, J. W. Richardson, Jr., and R. R. Thomas

IPNS, Argonne National Laboratory, Argonne, IL 60439, USA

A paper (Ref No.P52)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

submitted to Proceedings of International Symposium on Surface Nano-control of
Environmental Catalysts and Related Materials (6th Iketani Conference) at Nov.25-27,
1996, Japan

Corresponding author and address:

Masakuni Ozawa
Nagoya Institute of Technology,
CRL, Asahigaoka, Tajimi, Gifu 507, Japan
Phone 81-572-27-6811,
FAX 81-572-27-6812,
email ozawa@crl.nitech.ac.jp

MASTER

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

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 γ -Al₂O₃ and CuO, and electron spin resonance (ESR) data showed well-dispersed Cu²⁺ 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 δ' -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-NO_x 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

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

1 Introduction

Alumina-supported base-metals such as copper instead of expensive precious metals are alternative catalysts in practical lean-burn NO_x 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 NO_x 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 NO_x removal activity for copper-modified alumina catalyst.

2 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 Al_2O_3 and 10mol%Cu- Al_2O_3 samples using neutron diffraction method. Neutron diffraction experiments were carried out using General Purpose Powder Diffractometer (GPPD) at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. The in-situ diffraction experiments were performed on pelletized samples of pure Al_2O_3 , 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 $\Delta d/d=0.49\%$ can be achieved (d is the atomic plane spacing). In the case of 10mol%Cu- Al_2O_3 , 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 $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ transitions with increasing temperature. Mixed $\delta + \theta$ -phases at 1000°C, and $\theta + \alpha$ -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 $\gamma + \text{CuO} \rightarrow \delta' \rightarrow \alpha + \text{CuAl}_2\text{O}_4$, 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, Al_{1.95}Cu_{0.5}O_{3-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, $g_{\perp}=2.05$ and $g_{\parallel}=2.3$, 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 $70\text{m}^2/\text{g}$ and $62\text{m}^2/\text{g}$ for the pure Al_2O_3 and $\text{Cu-Al}_2\text{O}_3$ 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 0.70ml/g and 0.68ml/g for pure Al_2O_3 and $\text{Cu-Al}_2\text{O}_3$ powders (900°C), respectively. The results suggest good heat-stability of this Cu-modified Al_2O_3 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 C_3H_6 removal conversion efficiencies at several gas-inlet temperatures for $10\text{mol}\%\text{Cu-Al}_2\text{O}_3$ subjected to heat treatment at 900°C for 3h in air. The $\text{Cu-Al}_2\text{O}_3$ (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 $\text{Cu-Al}_2\text{O}_3$. Therefore, this Cu-modified alumina is one of the possible catalytic compounds for lean NO_x 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 γ -Al₂O₃ and CuO, and electron spin resonance data showed well-dispersed Cu²⁺ 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 δ' -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-NO_x removal efficiency in a test using a model exhaust gas mixture of space velocity = 100,000 h⁻¹.

Acknowledgement

One of the authors (M.Ozawa) would like to thank Mr.S.Matsumoto (Toyota Motor Co.) and many coworkers for useful discussions on automotive catalysts. Work in Argonne is supported by the U.S.Government DOE-BES under Contact No.W-31-109-ENG-38. Also work in Japan is supported by the foundation on advanced research and education program in Nagoya Institute of Technology.

References

- [1]M.Iwamoto and H.Hamada, Catal.Today 10(1991)57
- [2]H.Hamada, Y.Kintaichi,M.Sasaki, and T.Ito, Appl.Catal. 70(1991) L15
- [3]H.Hamada, Y.Kintaichi,M.Sasaki, and T.Ito, Appl.Catal. 75(1991) L1

- [4]Y.Kintaichi,H.Hamada,M.Tabata,M.Sasaki,and T.Ito, Catal.Lett.6(1991) 239
- [5]M.Iwamoto, S.Yokoo, K.Sasaki and S.Kagawa, J.Chem.Soc.Faraday Trans. I
77(1981) 1929
- [6]M.Iwamoto, N.Mizuno and H.Yahiro, Sekiyu Gakkaishi 34(1991)375
- [7]W.Held, A.Konig, T.Richter and L.Puppe, SAE paper No.900496 (Soc.Automotive
Engn., 1990) p1
- [8]K.C.C.Kharas, Appl.Catal.B.2(1993)207
- [9]S.Matsumoto, K.Yokota, H.Doi, M.Kimura, M.Sekikawa and H.Kasahara,
Catal.Today 22(1994)127
- [10]M.Ozawa, H.Toda, O.Kato and S.Suzuki, Appl.Catal.B 8(1996)123
- [11]P.A.Berger and J.F.Roth, J.Phys.Chem. 71(1967) 4307

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 10mol%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 10mol%Cu-Al₂O₃ heated at 1000°C, and (b) pure γ -Al₂O₃ measured at 500°C in vaccum.

(a)		(b)		
d (Å)	I	d (Å)	I	(hkl)
2.286	38	2.288	59	(222)
1.993	46	1.981	77	(400)
1.956	30			
1.533	12	1.515	10	(511)
1.510	8			
1.407	100	1.402	100	(440)
1.395	100			
1.200	43	1.195	32	-
1.184	23			
1.143	46	1.144	19	(444)
0.997	26	0.991	10	(800)
0.978	12			
0.910	12	0.908	6	-
0.891	35	0.885	15	(840)
0.880	16			

Table 2 NO and C₃H₆ removal conversion efficiencies at various gas-inlet temperatures for the Cu(10mol%)-Al₂O₃ catalysts subjected to heat treatment at (a)900°C and (b)1000°C for 3h in air.

Temperature(°C)	200	250	300	350	400	450
NO conversion(%)	6	14	20	16	12	8
C ₃ H ₆ conversion(%)	8	43	83	96	99	100

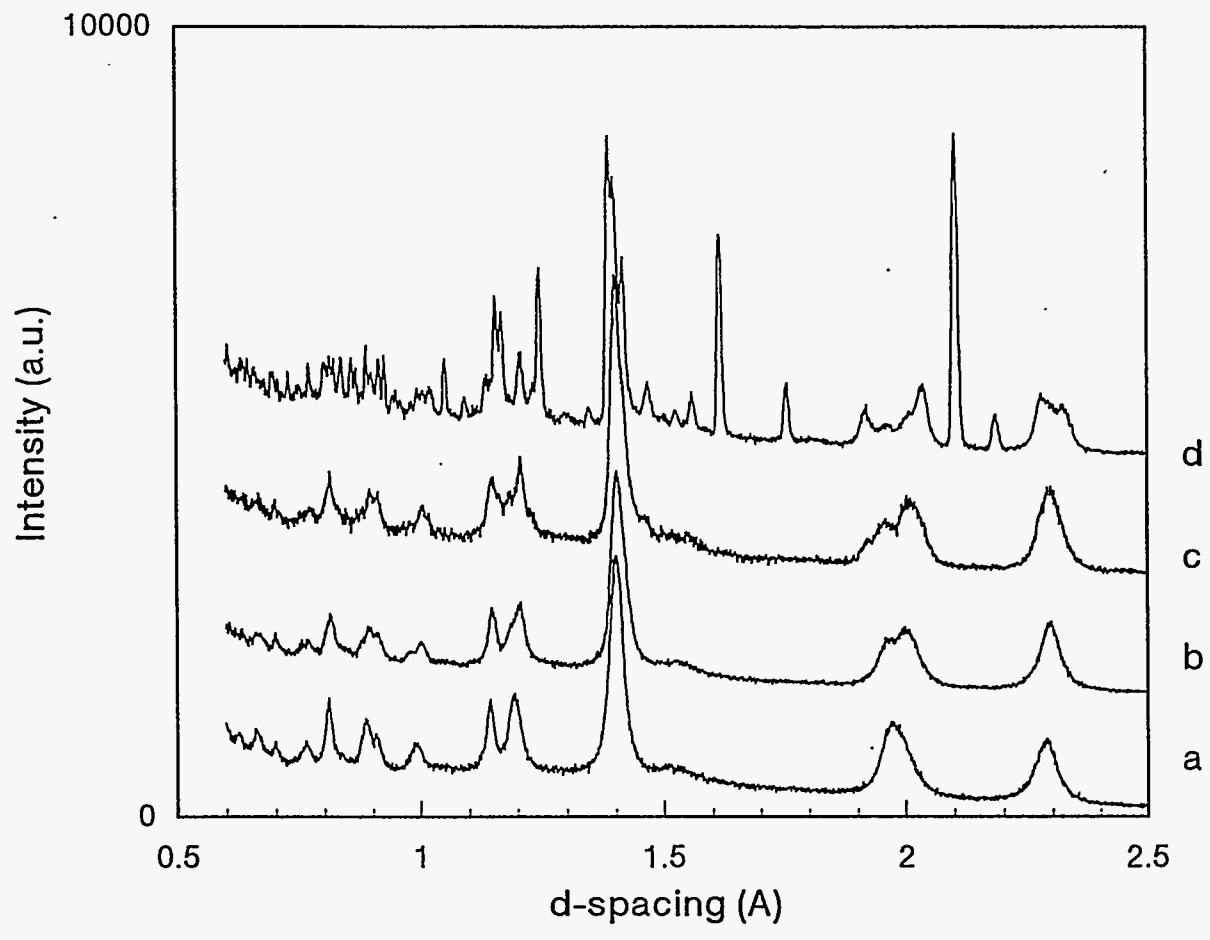


Fig 1

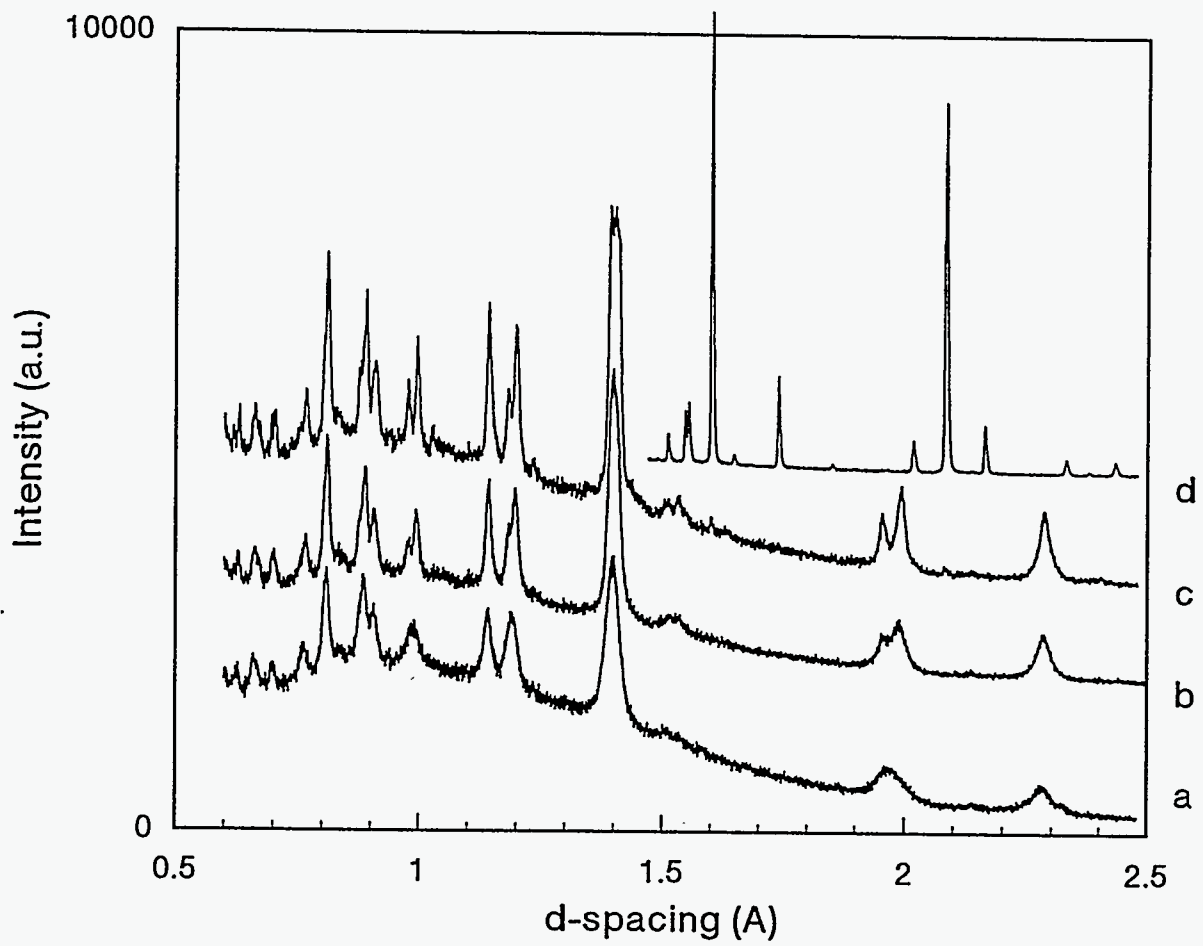


Fig 2