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High-temperature structural change of CrOx-LaOx-Al_2O_3 catalyst for lean-burn exhaust treatment

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Solid-state reaction in the system of CrOx-Al_2O_3 and CrOx-LaOx-Al_2O_3 and their sintering at 500–1100°C were examined by X-ray diffraction, electron spin resonance (ESR) and surface area measurement for the development of heat-stable catalytic ceramic in lean-burn exhaust treatment. CrOx-LaOx-Al_2O_3 catalyst, even heated at 1000°C in air, showed the removal conversion of 100% for C_3H_6, 95% for CO and 7% for NO at 500°C for high velocity automotive lean-burn exhaust with A/F = 18 and S.V. = $10^5 h^{-1}$. La-modification of catalyst was effective to high surface area stabilization and the improvement of complete oxidation activity of CO and hydrocarbons. © *2003 Kluwer Academic Publishers*

1. Introduction

The exhaust emission of automobile is the major source of carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NOx) resulting in environmental problem [1]. Lean-burn engine is an effective system to resolve both problems of NOx removal and the reduction of CO_2 emission in practical automobiles. Since ordinary three-way catalyst using precious metals is not active for reduction of NOx under deep and steady state lean-burn conditions, exhaust treatment needs the complex management of engine, which results in large cost of system [2, 3].

Many workers have studied alternative catalytic materials including zeolite-based or alumina-based catalysts [4–16]. 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 [4, 5]. Although there are actual trials of its application to automotive NOx removal for the exhaust having oxygen and hydrocarbons [10–13], it unfortunately seems to have low stability under hydrothermal and thermal condition. Since practical engine-operation varies in the wide range of A/F and temperatures in the range of 100–1000°C, the thermal durability of an automotive catalyst is seriously required. Gamma alumina (γ-Al_2O_3) is well known as a stable catalyst support, and has been applied to coatlayer having various promoters in an automotive three-way catalyst converter. Hamada and coworkers reported the activity of Al_2O_3 catalyst for the selective reduction of NO with hydrocarbons [6–8]. They also reported that 3d-transition-metal promoters to Al_2O_3 were effective for NO removal reaction, and suggested a reaction mechanism to remove NO over these alumina catalysts.

In the development of practical alumina catalysts, the solid-sate stability for active species in composite powders is an important problem when exhaust becomes to be heated at high temperatures. In this paper, we report CrOx-LaOx-Al_2O_3 composite toward possible lean-burn catalyst with respect of high-temperature structural change of materials as well as catalytic performance.

2. Experimental

In this study, the fraction of added La and Cr in Al_2O_3 was fixed with the molar ratio for Al_2O_3:La:Cr = 100:0.5,10:0.10. The preparation of CrOx-Al_2O_3 catalyst was done as following. Powder of γ-Al_2O_3 (surface area 135 m^2/g and purity 99.9%) was used as a support. First, an aqueous solution (80 cm^3) of chromium nitrate was prepared by adding a starting powder of $Cr(NO_3)_3 9H_2O$ to distilled water, followed by stirring a solution for 1 h. Then, the suspension was prepared by adding the alumina powder (100 g) to this solution by stirring for 1 h. It was dried at 110°C (with often stirring) for 8 h, and heated at 500°C for 3 h in air. The mixture was then ground to fine powder. For CrOx-LaOx-Al_2O_3, La-added γ-Al_2O_3 powder was prepared by a mixing process of pure alumina and aqueous lanthanum nitrate ($La(NO_3)_3 6H_2O$), followed by drying at 110°C and heat treatment at 500°C for 3 h in air, and ground. After then, for the addition of chromium, the same process as in CrOx-Al_2O_3, by replacing pure alumina with La-added alumina, was applied. The prepared powders (catalysts) were heated at various temperatures up to 1100°C in air in order to examine solid-state reactions and sintering.

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Powder X-ray diffraction (XRD) apparatus (Rigaku, Rint2000, Japan) with Cu K_α source (20 kV–30 mA) was used for the characterization of phases formed in samples after heat treatment at various temperatures. The surface areas of powders were measured by BET method using nitrogen adsorption at 77 K. Samples were pelletized and pre-heated at 200°C for 3 h in flowing nitrogen before the BET measurement. Electron spin resonance (ESR) spectra of Cr ion in samples were measured using an ESR spectrometer (JEOL, JM-ME3X, Japan) at room temperature in X-band with a modulation frequency of 100 kHz and powder of 1 mW.

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 gas-composition is carbon monoxide (CO) 1000 ppm, propene (C_3H_6) 800 ppm, nitrogen monoxide (NO) 700 ppm, oxygen (O_2) 4%, carbon dioxide (CO_2) 12.7%, water gas (H_2O) 10% and nitrogen (N_2) balance [14–17]. The samples were pressed into pellets of diameter of ca. 1 mm, and set in a quartz tube reactor. 3.5 g catalyst sample was used with total gas flow rate of 7 dm^3 per minute. Space velocity (S.V.), which was defined by gas volume flow-rate per catalyst volume, was as high as ca. 10^5 h^{-1}.

3. Results and discussion

3.1. Solid state reaction and phase transformation

The structural change of CrOx-Al_2O_3 powders via heat treatment at temperatures up to 1100°C (XRD observation) was the same as in pure Al_2O_3.

$$\begin{aligned}&\gamma\text{-Al}_2\text{O}_3(500^\circ\text{C}) \rightarrow \gamma\text{-Al}_2\text{O}_3 + \delta\text{-Al}_2\text{O}_3\ (800^\circ\text{C})\\&\rightarrow \delta\text{-Al}_2\text{O}_3 + \theta\text{-Al}_2\text{O}_3\ (900^\circ\text{C}) \rightarrow \theta\text{-Al}_2\text{O}_3\\&+ \alpha\text{-Al}_2\text{O}_3\ (1000^\circ\text{C}) \rightarrow \alpha\text{-Al}_2\text{O}_3\ (1100^\circ\text{C}) \qquad (1)\end{aligned}$$

The XRD indicates no CrOx-related phase in heat-treatment at these temperatures. The solid-state reaction between amorphous CrOx (impregnated on surface) and Al_2O_3 results in solid solutions of metastable and α-Al_2O_3 at each temperature [19]. The samples heated at 900–1000°C consist of major θ-Al_2O_3 with CrOx on surface or in bulk state.

La-modification of pure alumina support resulted in the prevention of α-transformation below 1100°C and the formation of $LaAlO_3$ above 850°C [18]. In this experiment, the surface area of alumina powder after heat-treatment at 1000°C for 3 h in air was improved; 50 m^2/g for 5 mol%La-alumina and 46 m^2/g for 10 mol% La-alumina than 14 m^2/g for unmodified support.

Fig. 1 shows the change of the XRD patterns for 10 mol%Cr-5 mol%La-Al_2O_3 heated at temperatures up to 1100°C. In CrOx-LaOx-Al_2O_3, the crystallites of $LaAlO_3$ (or $LaCrO_3$) formed at elevated temperatures. The temperature to form $LaAlO_3$ depended on La-concentration (at 1000°C for 5 mol%La and at 800°C for 10 mol%La). The sequence of structural change is as following,

$$\begin{aligned}&\gamma\text{-Al}_2\text{O}_3\ (500^\circ\text{C}) \rightarrow \gamma\text{-Al}_2\text{O}_3 + \delta\text{-Al}_2\text{O}_3\\&+ \text{LaAlO}_3\ (800\text{–}1000^\circ\text{C}) \rightarrow \delta\text{-Al}_2\text{O}_3\\&+ \theta\text{-Al}_2\text{O}_3 + \text{LaAlO}_3\ (1000\text{–}1100^\circ\text{C}) \qquad (2)\end{aligned}$$

The relationship of BET surface area vs. temperature for composite powders was illustrated in Fig. 2. La-modified catalyst had lower surface area than CrOx-Al_2O_3 after calcination at 500–900°C. At 1000–1100°C, the surface area of CrOx-LaOx-Al_2O_3 was the same or higher than that of CrOx-Al_2O_3. Thus, La-modification should be effective to stabilize solid-state of a catalyst (with less sintering), even if the catalyst is subjected to exhaust at the temperatures of 1000–1100°C.

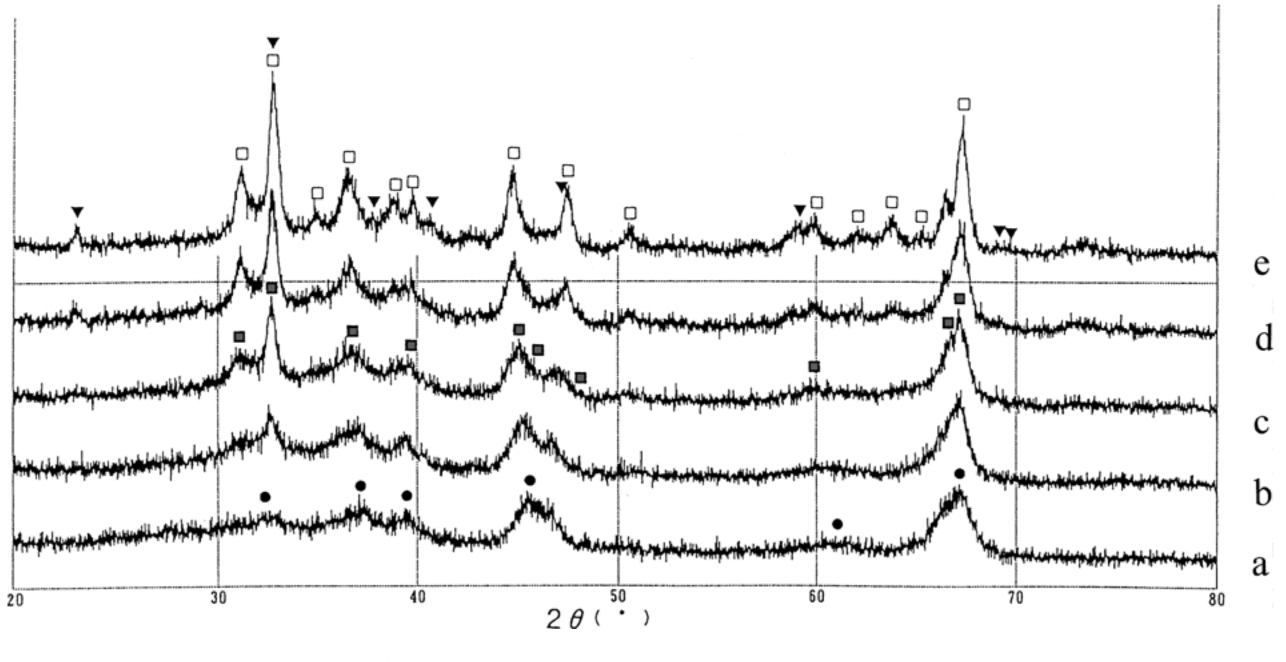

Figure 1 XRD patterns for 10 mol%CrOx-5 mol%LaOx-Al_2O_3 heated at various temperatures of (a) 500°C, (b) 800°C, (c) 900°C, (d) 1000°C, and (e) 1100°C. (●) γ-Al_2O_3; (■) δ-Al_2O_3; (□) θ-Al_2O_3; (▼) $LaAlO_3$ ($LaCrO_3$).

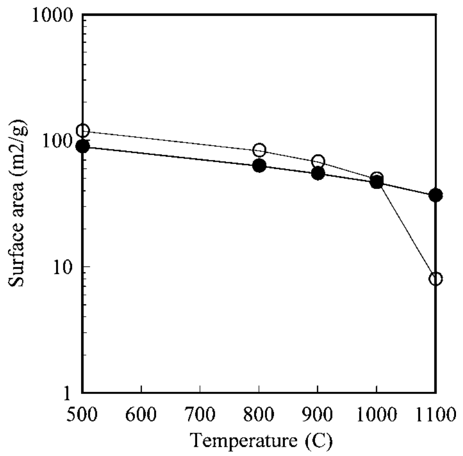

Figure 2 BET surface area versus heat-treatment temperature for (○) 10 mol%CrOx-Al_2O_3 and (●) 10 mol%CrOx-5 mol%LaOx-Al_2O_3.

3.2. Electron spin resonance spectra and Cr species

Figs 3 and 4 show the ESR spectra for the catalysts heated at various temperatures. For 10 mol%CrOx-Al_2O_3 heated at 500°C (Fig. 3a), there appeared a symmetrical resonance at magnetic field (H) of 3430 gauss, in the addition of a small signal at $H = 1370$ gauss. The samples heated at 800°C, 900°C and 1000°C had the same ESR features consisting of three resonances at $H = 1430$, 2770 and 3430 gauss. After heat-treatment at 1100°C, the ESR spectrum changed to a large broad resonance at $H = 3410$ gauss and small signals at $H = 2010$ and 4500 gauss.

Several workers [20–22] have studied the ESR absorption of chromia-alumina catalyst. They characterized the ESR of 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 $H = 1370$ gauss 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 of amorphous Cr oxide impregnated to an alumina support. The ESR spectra of CrOx-Al_2O_3, shown as (b), (c) and (d) in Fig. 3, are interpreted as due to Cr(3+) in relatively strong axial crystal field with some distortion of low symmetry. The small change of the ESR spectra of (a) to (b), (c) and (d) in Fig. 3 corresponds to the loss of a symmetrical coordination field for Cr(3+) after heat-treatment at 800–1000°C. Thus, the development of ESR spectra suggests the formation of Cr(3+)-doped θ-Al_2O_3, where is heavily defective spinel-structure with distorted anion sites, at temperatures of 800–1000°C. The ESR spectrum in Fig. 3e is the same as that observed for a Cr(3+)-doped corundum crystal agglomerate, because α-transformation of CrOx-Al_2O_3 occur at 1100°C.

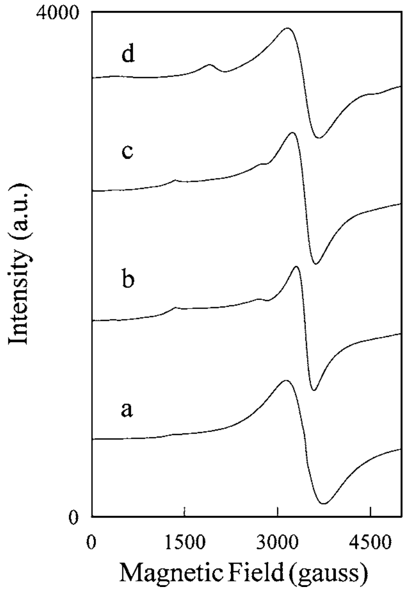

Figure 3 ESR spectra of 10 mol%CrOx-Al_2O_3 heated at (a) 500°C, (b) 900°C, (c) 1000°C, and (d) 1100°C for 3 h in air.

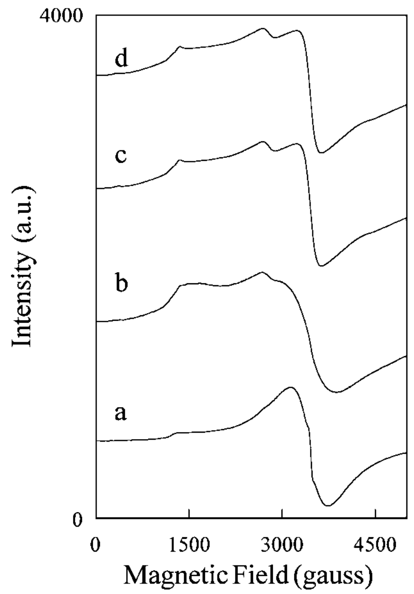

Figure 4 ESR spectra of 10 mol%CrOx-5 mol%LaOx-Al_2O_3 heated at (a) 500°C, (b) 900°C, (c) 1000°C, and (d) 1100°C for 3 h in air.

The ESR of La-modified catalyst (CrOx-LaOx-Al_2O_3) has the same absorption as in CrOx-Al_2O_3 after heat-treatment at 500°C. In samples heated at 900–1000°C, the spectra changed to strongly asymmetrical absorption. The ratio of intensities was different from those of CrOx-Al_2O_3. They suggest the existence of strongly asymmetrical sites of Cr(3+) with more distortion of alumina lattice. The XRD indicates that major phase is θ-Al_2O_3 at 900–1100°C, however that should be modified with La. Since La(3+) is larger than Al(3+), a resultant solid solution of alumina has locally distorted site in the lattice or surface. Furthermore, La-segregation on surface can form a local phase or micro domains such as La-β-Al_2O_3. In this case, the site of Cr(3+) near La-O clusters becomes different axial field, so that the ESR of Cr(3+) shows possible more asymmetrical intensities. Thus, La-modification to CrOx-Al_2O_3 results in novel site for Cr(3+) which is different from CrOx-Al_2O_3 catalyst.

3.3. Catalytic activity

Figs 5 and 6 show the plots for the removal conversion efficiencies for C_3H_6, CO and NO against inlet

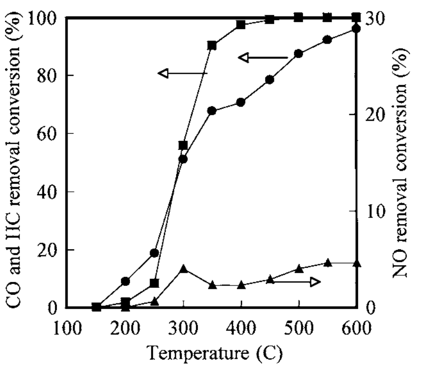

Figure 5 Removal conversion efficiencies for (■) C_3H_6, (●) CO, and (▲) NO in a model lean-burn exhaust at A/F = 18 and S.V. = 10^5 h^{-1} over 10 mol%CrOx-Al_2O_3 heat-treated at 1000°C.

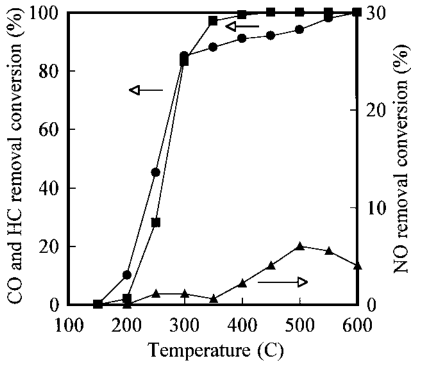

Figure 6 Removal conversion efficiencies for (■) C_3H_6, (●) CO, and (▲) NO in a model lean-burn exhaust at A/F = 18 and S.V. = 10^5 h^{-1} over 10 mol%CrOx-5 mol% LaOx-Al_2O_3 heat-treated at 1000°C.

gas temperature, which were evaluated at A/F = 18 and S.V. = 100,000 h^{-1} over 10 mol%CrOx-Al_2O_3 and 10 mol%CrOx-5 mol%LaOx-Al_2O_3 subjected to heat-treatment at 1000°C. The NO removal efficiencies for the present sample were as low as 5% and 7% at around 500–550°C, while the removal efficiencies for C_3H_6 and CO were high rate (96–100%). Torikai and coworkers [9] reported that the addition of 0.2 wt%Cr had the effect of decreasing the optimum temperature for the maximum NOx conversion (13% at ca. 300°C). However, their report deals with the experiments at a low space velocity of ca. 10,000 h^{-1}. In general, the maximum peak for activity moves to a higher temperature region and the conversion decreases with increasing a space velocity. In addition, 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.

The selective catalytic reduction (SCR) of NOx is related to the formation of partially oxidized hydrocarbons from the reaction between hydrocarbons and oxygen [2–9]. Regarding with the SCR mechanism for NO, the system of CrOx-Al_2O_3, even heated at elevated temperatures, seems to be too active for the complete oxidation reaction of hydrocarbons, as well as low activity for adsorption of NO and O_2. However, both CrOx-modified Al_2O_3 and La-modified CrOx-Al_2O_3 catalyst have the unique surface structure, where Cr ions are sited at the distorted crystal field in a defective solid solution if the heat-treatment temperature is as high as 1000°C. Especially, La-modified catalyst has a large surface area after heat treatment at 1100°C. Even if this catalyst is subjected to high temperature exhaust, statistically distributed Cr—O interactions in the defective spinel-structured matrix will be maintained to show active SCR catalysis.

On LaOx itself, the NO conversion was reported to increase with increasing temperature by Zhang *et al.* [23]. The similar relation of NO conversion efficiency vs. temperature on GdOx was described in a study of Cu-Gd-Al_2O_3 by Dziewiecka *et al.* [24]. For present CrOx-LaOx-Al_2O_3 catalysts, the contribution of LaOx to NO reduction would be assumed in the temperature range over 400°C. In contrast, the maximum conversion on CrOx-Al_2O_3 appeared at as low temperature as 300°C. However, both the removal efficiencies themselves are rather low, so that the behavior of La affecting NO removal is difficult to discuss through present reaction data. It is considered that major part of LaOx reacted with alumina support and CrOx on surface, resulting in various complex oxides or coordinated complex to influence the state of Cr cation. As the results, the active Cr species differently behave in the NO removal efficiency versus temperature, depending on the presence or absence of La. The mechanism must be examined by more detailed reaction experiments using various concentration and species. Present results, regarding solid-state thermal stability of alumina-supported La-modified CrOx-catalyst, should provide a possible exhaust-treatment catalytic composition which may be subjected to temperatures of around 1000°C.

4. Summary

The solid-state thermal behavior of CrOx-LaOx-Al_2O_3 catalyst was studied with respect to its possible high-temperature application as lean-burn exhaust catalyst. The following conclusions can be drawn:

1. La-modification lead to the stabilization of phases and surface area of CrOx-Al_2O_3 at 1000–1100°C.
2. Electron spin resonance spectra indicated the existence of Cr(3+) in an axial field, suggesting the formation of Cr(3+)-doped solid solution with the structures of θ-Al_2O_3 or La-β-Al_2O_3 at 900–1000°C.
3. CrOx-LaOx-Al_2O_3 catalyst, heat-treated at 1000°C in air, showed removal efficiencies of 100% for C_3H_6, 95% for CO and 7% for NO at 550°C for high-velocity lean-burn exhaust with A/F = 18 and S.V. = 10^5 h^{-1}.

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References

1. K. C. TAYLOR, in "Catalysis Science and Technology," Vol. 8, edited by J. R. Anderson and M. Boudart (Springer-Verlag, Berlin-NY, 1984) p. 120.
2. N. MIYOSHI, T. TANAKA and S. MATSUMOTO, *Toyota Tech. Review* **50** (2000) 28.
3. S. MATSUMOTO, *Catal. Today* **29** (1996) 43.
4. W. HELD, A. KONIG, T. RICHTER and L. PUPPE, SAE Paper No. 900496 (Soc. Automotive Engn., 1990) p. 1.
5. M. IWAMOTO and H. HAMADA, *Catal. Today* **10** (1991) 57.
6. H. HAMADA, Y. KINTAICHI, M. SASAKI and T. ITO, *Appl. Catal.* **75** (1991) L1.
7. *Idem.. ibid.* **70** (1991) L15.
8. Y. KINTAICHI, H. HAMADA, M. TABATA, M. SASAKI and T. ITO, *Catal. Lett.* **6** (1991) 239.
9. Y. TORIKAI, H. YAHIRO, N. MIZUNO and M. IWAMOTO, *ibid.* **9** (1991) 91.
10. K. C. C. KHARAS, H. J. ROBOTA and D. J. LIU, *Appl. Catal.* B **2** (1993) 225.
11. G. P. ANSELL, A. F. DIWELL, S. E. GOLUNSKI, J. W. HAYES, R. R. RAJARAM, T. J. TRUEX and A. P. WALKER, *ibid.* **2** (1993) 81.
12. R. A. GRINSTED, H.-W. JEN, C. N. MONTREUIL, M. J. ROKOSZ and M. SHELEF, *Zeolites* **13** (1993) 602.
13. S. MATSUMOTO, K. YOKOTA, H. DOI, M. KIMURA, K. SEKIKAWA and S. KASAHARA, *Catal. Today* **22** (1994) 127.
14. M. OZAWA, H. TODA, O. KATO and S. SUZUKI, *Appl. Catal.* B **8** (1996) 123.
15. M. OZAWA, S. SUZUKI and H. TODA, *J. Amer. Ceram. Soc.* **80** (1997) 1957.
16. M. OZAWA, O. KATO and S. SUZUKI, *J. Mater. Sci.* **33** (1998) 737.
17. M. OZAWA, M. KIMURA and A. ISOGAI, *J. Alloy Compd.* **193** (1993) 73.
18. *Idem., J. Less-Comon Met.* **162** (1990) 297.
19. G. C. BYE and G. T. SIMPKIN, *J. Amer. Ceram. Soc.* **57** (1974) 367.
20. D. E. O'REILLY and D. S. MACIVWE, *J. Phys. Chem.* **66** (1962) 276.
21. C. J. CARMAN and W. J. KROENKE, *ibid.* **72** (1968) 2562.
22. L. FORNI and C. OLIVA, *J. Chem. Soc. Faraday Trans.* I **84** (1988) 2477.
23. X. ZHANG, A. B. WALTERS and M. A. VANNICE, *Appl. Catal.* B **4** (1994) 237.
24. B. DZIEWIECKA and Z. DZIEWIECKI, *Catalysis Today* **17** (1993) 121.

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