



Novel Pd promoted Ag/Al₂O₃ catalyst for the selective reduction of NO_x

Hong He*, Jin Wang, Qingcai Feng, Yunbo Yu, Kiyohide Yoshida

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Received 4 April 2003; received in revised form 28 May 2003; accepted 28 May 2003

Abstract

A novel palladium promoted Ag/Al₂O₃ catalyst (denoted Ag-Pd/Al₂O₃) has been developed for the selective catalytic reduction of NO by C₃H₆. The Ag-Pd/Al₂O₃ shows a higher NO_x conversion than Ag/Al₂O₃, especially at the temperatures ranging from 300 to 450 °C. The addition of a small amount of Pd (0.01 wt.%) to Ag/Al₂O₃ is considered to be favorable for the partial oxidation of C₃H₆. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) suggest that the presence of Pd catalyzes the formation of enolic species which is converted from C₃H₆. The enolic species is very active towards NO₂ and NO₃⁻, resulting in the formation of -NCO species which is the key reaction intermediate in the selective catalytic reduction of NO.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Ag-Pd/Al₂O₃; Selective catalytic reduction of NO_x; Enolic species; In situ DRIFTS; Catalytic reaction mechanism

1. Introduction

Since Iwamoto and co-workers [1,2] and Held et al. [3] first reported that Cu-ZSM-5 is an effective catalyst for the selective catalytic reduction (SCR) of NO by hydrocarbons in the presence of excess oxygen, the SCR of NO_x has received much attention as a kind of potential technology for cleaning NO_x in various oxygen-rich exhausts of diesel engine, lean burn gasoline engine and gas engine. In the recent studies [4–12], alumina-supported silver catalysts (denoted Ag/Al₂O₃), which are relatively durable and inexpensive, are considered to be a candidate for practical use. However, the NO_x conversion over Ag/Al₂O₃ is quite low at low temperature range of 300–400 °C, which is a major disadvantage. On

the other hand, catalysts based on platinum-group metals, such as well-known three-way catalysts, can eliminate NO_x, CO and unburned hydrocarbons all together in an exhaust of gasoline engines which operate close to stoichiometric condition. Unfortunately, those catalysts are almost all ineffective for the selective reduction of NO_x in the presence of excess oxygen when the temperature is over 400 °C [13,14].

We first reported on 69th Annual Meeting of JCS [15] that the selective reduction of NO with C₃H₆ over Ag/Al₂O₃ catalyst was effectively enhanced by co-impregnating a small amount of Pd, and the negative additive effect of Pt and Au. The additive effect of Pd on Ag/mordenite was also reported by Masuda et al. [16] using (CH₃)₂O as a reductant although the durability of Ag/Pd/mordenite was decreased in the presence of water vapor. Seker et al. [17] showed the negative effect of Au on Ag/Al₂O₃ for the NO_x reduction with C₃H₆. However, the mechanism of additive

* Corresponding author. Tel.: +86-10-62849123;

fax: +86-10-62923563.

E-mail address: honghe@mail.rcees.ac.cn (H. He).

effect of platinum-group metals on Ag based catalysts is still unclear.

In this study, we prepared and investigated a novel Ag-Pd/Al₂O₃ for the SCR of NO by C₃H₆. We have made in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) observation of surface species formed on Ag-Pd/Al₂O₃ and Ag/Al₂O₃ to investigate the mechanism of Pd additive effect during the SCR of NO.

2. Experimental

2.1. Catalyst preparation

The Ag/Al₂O₃ (Ag metal loading: 5 wt.%) and Pd-Ag/Al₂O₃ catalysts were prepared by an impregnation method. The γ -Al₂O₃ powder (200 m² g⁻¹) was dissolved in an appropriate amount of silver nitrate or silver nitrate and palladium nitrate mixed in aqueous solution. This was followed by evaporation to dryness in a rotary evaporator at 60 °C under reduced pressure. The resulting paste was dried at 120 °C overnight, and then calcined in air at 600 °C for 3 h. Before catalytic test, the catalysts were sieved into 20–40 meshes.

2.2. Catalytic tests

The catalytic test was measured with a fixed-bed quartz flow reactor (10 mm i.d.) by passing a mixture of 800 ppm NO, 1714 ppm C₃H₆, and 10 vol.% O₂ in high pure N₂ at a rate of 4000 cm³ min⁻¹ over 1.2 g catalyst ($W/F = 0.018 \text{ g s cm}^{-3}$, GHSV = $\sim 50,000 \text{ h}^{-1}$). H₂O vapor (10 vol.%) was supplied with a syringe pump and vaporized by a coiled heater set at inlet of the reactor. Water was removed from the reactor effluent gas by passing a condenser instrument before reaching on line analyzers. After reaching steady state, the effluent gas was analyzed by AVL Di Gas, 4000 light for HC conversion analyses and a chemiluminescence NO/NO₂/NO_x analyzer (42C-HL, Thermo Environmental) for NO_x conversion analyses.

2.3. In situ diffuse reflectance infrared Fourier transform spectroscopy procedure

In situ DRIFTS spectra were recorded in a NEXUS 670-FTIR equipped with a smart collector and a

MCT/A detector cooled by liquid N₂. The sample for studies (ca. 30 mg) was finely ground and placed in a ceramic crucible. Prior to each experiment, the catalyst was firstly heated in the flow of 10 vol.% O₂ + N₂ for 60 min at 300 and 600 °C, respectively, then cooled to 400 °C and exposed to 10 vol.% O₂ + N₂ for 30 min, and a spectrum of the catalyst in the flow of N₂ + O₂ served as the background was recorded. All spectra were measured under real reaction conditions with a resolution of 4 cm⁻¹ and accumulation of 100 scans.

3. Results and discussion

3.1. Activity measurements

Fig. 1(a) shows the NO_x reduction activity of Ag/Al₂O₃ and Ag-Pd/Al₂O₃ catalysts, respectively, at various temperatures. Both NO_x conversions increased with the increase of reaction temperature and reached a maximum at 437 °C for Ag-Pd/Al₂O₃ and at 470 °C for Ag/Al₂O₃, then decreased with the further increase of reaction temperature. The highest rate of NO_x conversion was 82% over Pd-Ag/Al₂O₃, higher than that of 73% over Ag/Al₂O₃. Obviously, a trace amount of Pd added into Ag/Al₂O₃ could enhance the NO_x conversion in the presence of excess oxygen and water vapor. This metal additive effect is considered to be favorable for activating reductant molecule; for example, scission of a C–C bond and partial oxidation.

Fig. 1(b) shows the conversions of propene into CO_x over Pd-Ag/Al₂O₃ and Ag/Al₂O₃. Similar to the NO_x conversion, the curve of C₃H₆ conversion for Ag/Al₂O₃ was shifted to lower temperature by Pd addition. This result suggests that Ag-Pd/Al₂O₃ can activate C₃H₆ to react with NO + O₂.

3.2. In situ steady-state DRIFTS of the NO_x reduction over Ag-Pd/Al₂O₃ and Ag/Al₂O₃

For directly investigating the effect of Pd addition under real catalytic reaction conditions, we carried out experiments using in situ DRIFTS. Conditions for in situ DRIFTS are the same as those in Fig. 1, namely, 800 ppm NO + 10 vol.% O₂ + 1714 ppm C₃H₆. All in situ DRIFTS spectra shown in Fig. 2 are recorded in the steady state at various temperatures of 200,

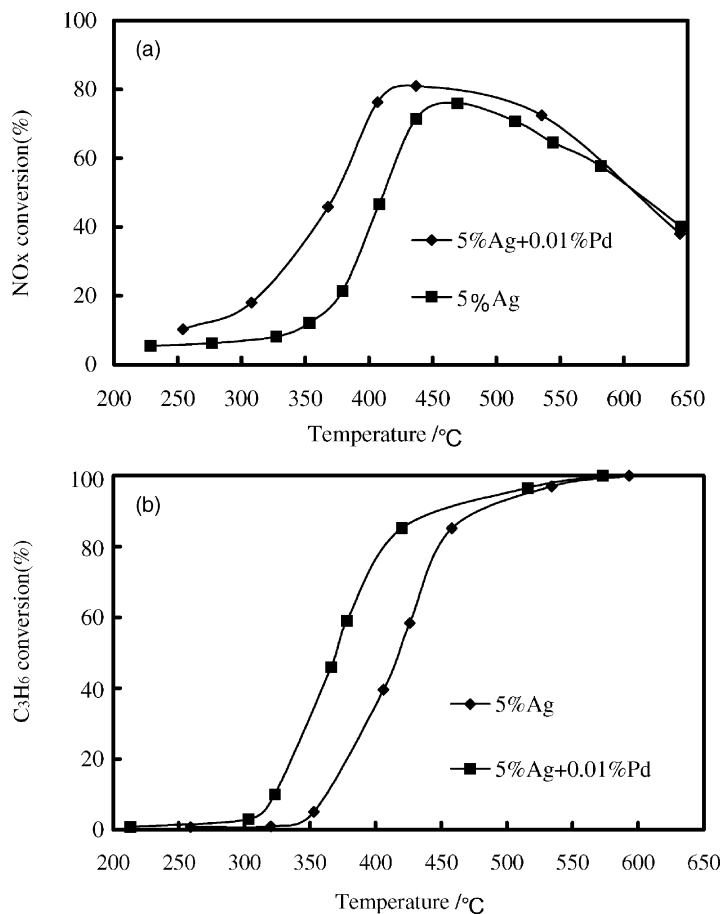


Fig. 1. (a) The catalytic activity for NO_x reduction by C₃H₆ over Ag/Al₂O₃ and Ag-Pd/Al₂O₃ catalyst, respectively, at various temperatures in the presence of water vapor. Reaction conditions: 800 ppm NO, 1714 ppm C₃H₆, 10 vol.% O₂, 10 vol.% water vapor, W/F = 0.018 g s cm⁻³, GHSV = ~50,000 h⁻¹, N₂ balance, total flow rate = 4000 ml/min. (b) Conversions of propene into CO_x over Ag-Pd/Al₂O₃ and Ag/Al₂O₃, respectively, at various temperatures in the presence of water vapor. Reaction conditions: the same as in (a).

250, 300, 350, 400 and 450 °C. After an exposure of the catalyst to NO + C₃H₆ + O₂ mixture gas for 60 min at 200 °C, as shown in Fig. 2, many IR peaks appeared in the region between 1700 and 1300 cm⁻¹. According to the previous literatures [12,18,19], the strong bands at 1651, 1591, and 1392 cm⁻¹ were attributed to ν(-ONO), ν(-NO₂) and δ(-CH₃), respectively, which suggested that the organic compounds C_xH_yNO_z (R-ONO and R-NO₂) were largely formed on the catalyst surface at 200 °C. The peaks at 1300 and 1580 cm⁻¹ were assigned to the bidentate nitrates and monodentate nitrates, respectively [7,12,20]. The peaks at 1562 and 1454 cm⁻¹ are assigned to ν_{as}(COO) and ν_s(COO) of the adsorbed

acetate [20–23]. When we increased the reaction temperature, as shown in Fig. 2, the strong band at 1651 cm⁻¹ disappeared gradually, while the weak band at 2239 cm⁻¹ can still be observed. This feature has been observed in our previous works [11,12] and assigned to isocyanate (-NCO) species, which is a key intermediate species, reported by many researchers [7–9,14].

Fig. 3 shows the IR spectra of Ag-Pd/Al₂O₃ catalyst in the flow of NO + C₃H₆ + O₂ in the steady state at various temperatures. Based on the comparison between Figs. 2 and 3, the bands at 1300, 1580, 1572, 1460 (1460–1475), 1597 and 1394 cm⁻¹ are similarly assigned to bands of adsorbed nitrates, acetate and

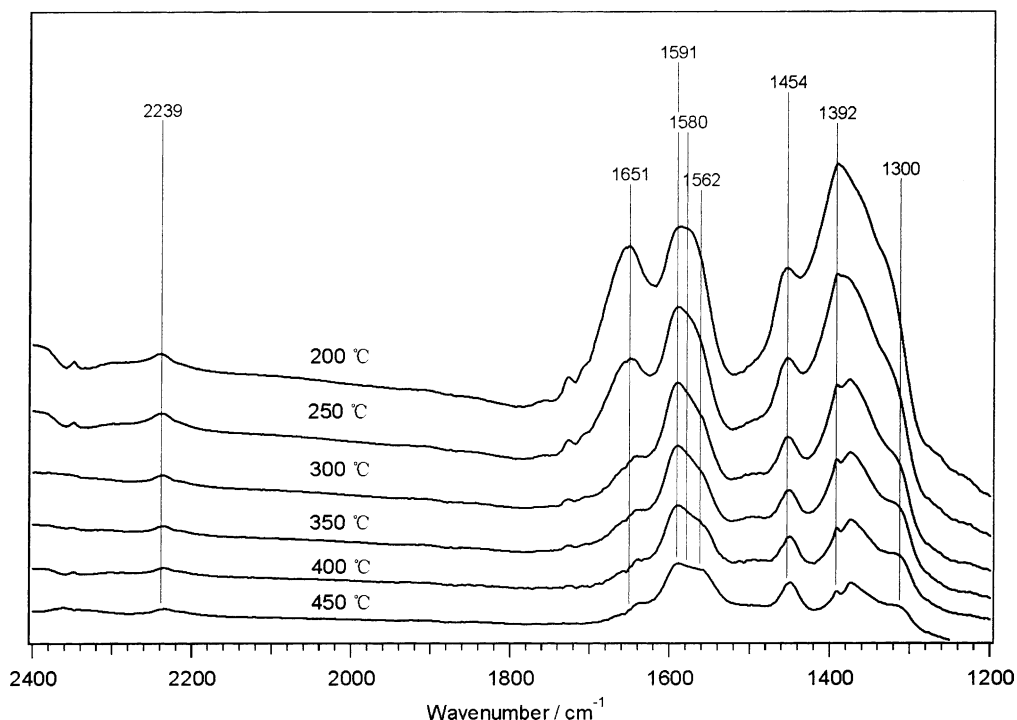


Fig. 2. In situ DRIFTS spectra of Ag/Al₂O₃ in a steady state at various temperatures in a flow of C₃H₆ + O₂ + NO. Feed: the same as in Fig. 1.

R-NO₂ species. The principle difference between Figs. 2 and 3 is the new peak on Ag-Pd/Al₂O₃ catalyst at 1637 cm⁻¹, along with the missing peak at 1651 cm⁻¹ which has been assigned to the band of R-ONO in Fig. 2. Another new band at 2158 cm⁻¹ can be assigned to -CN surface species [12,24]. Similar peak at 1630 cm⁻¹ was also observed on Ag/Al₂O₃ in the flow of *n*-hexane + NO + O₂ and assigned to carbonate species [20]. Turek et al. [25] reported that when CO₂ chemisorbed on the surface of γ-Al₂O₃, main adsorbed species was carbonate. We studied the adsorption of CO₂ on Ag-Pd/Al₂O₃ at 200 °C, but no peak at 1630 cm⁻¹ was observed. The peak at 1637 cm⁻¹ in Fig. 3 may be associated with the frequency of double bond stretching vibration, such as ν(C=C), ν(C=O). In general, the stretching vibration frequencies of isolate C=C and C=O should both be higher than 1637 cm⁻¹. When exposing Ag/Al₂O₃ to the flow of C₃H₆ + O₂, it is possible to form a surface enolic structure (H₂C=CH-O...M⁺) on the surface by partial oxidation of C₃H₆. The

conjugation of H₂C=CH-O⁻ group may induce the vibrational mode of C-C-O to shift to a frequency which is lower than ν(C=C) and higher than ν(C-O) [26]. As a consequence, the peak at 1637 cm⁻¹ in Fig. 3 could be tentatively assigned to stretching vibration mode of C=CH-O⁻. With increasing temperature, the bands of nitrate (1300 cm⁻¹) and enolic species (1637 cm⁻¹) decreased promptly, while the -NCO band (2233 cm⁻¹) progressively appeared. This indicates that the enolic surface species is reactive towards nitrate to form -NCO species. As a result, Ag-Pd/Al₂O₃ has a higher -NCO surface concentration than Ag/Al₂O₃ during the SCR of NO by C₃H₆. This result is in good agreement with activity of Ag/Al₂O₃ and Ag-Pd/Al₂O₃.

3.3. Reaction mechanism on Ag-Pd/Al₂O₃

The reaction mechanism of the SCR of NO by C₃H₆ over Ag/Al₂O₃ has been proposed with R-ONO, R-NO₂ and -NCO as the key intermediates

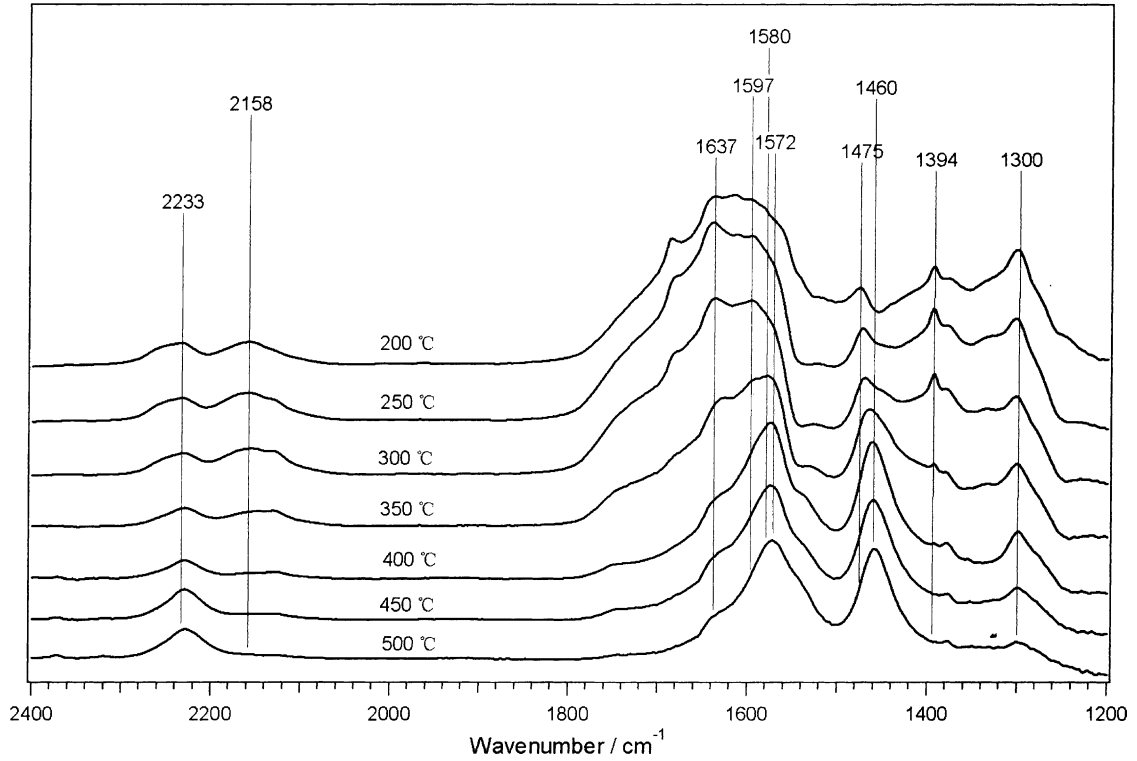
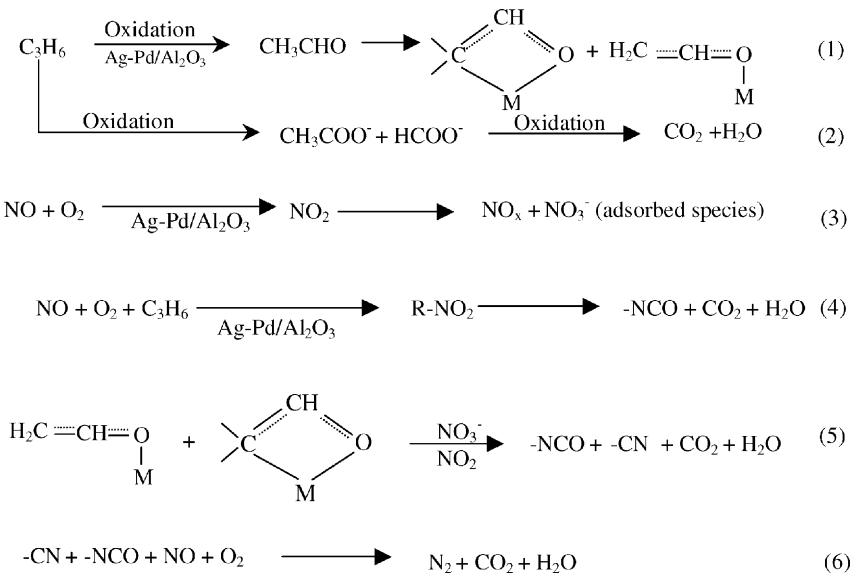


Fig. 3. In situ DRIFTS spectra of Ag-Pd/Al₂O₃ in a steady state at various temperatures in a flow of C₃H₆ + O₂ + NO. Feed: the same as in Fig. 1.



Scheme 1. The proposed reaction mechanism for the SCR of NO by C₃H₆ over Ag-Pd/Al₂O₃.

[10,12,20]. Burch et al. [14] extended a similar reaction mechanism to all oxide catalysts in a review, approximately, $\text{NO} + \text{O}_2 + \text{C}_3\text{H}_6 \rightarrow \text{NO}_x + \text{C}_x\text{H}_y\text{O}_z \rightarrow \text{R-NO}_2 + \text{R-ONO} \rightarrow \text{R-NCO} + \text{R-CN} + \text{NO} + \text{O}_2 \rightarrow \text{N}_2$. Our in situ DRIFTS in Fig. 2 also support this mechanism. R-ONO, R-NO₂ and -NCO are observed on Ag/Al₂O₃ during reaction, and high coverage R-ONO formed at a low temperature of 200 °C. However, the mechanism is dramatically altered with adding a trace quantity of Pd to Ag/Al₂O₃. In the case of Ag-Pd/Al₂O₃, R-ONO band at 1651 cm⁻¹ cannot be observed at all reaction temperatures, replaced with the enolic species band at 1637 cm⁻¹ (Fig. 3). It can be considered that the presence of Pd catalyzes the formation of enolic species, which undergoes a reaction with NO₂ and NO₃⁻ to convert into -NCO and -CN, and subsequently into N₂. Summarizing the mentioned discussion, the proposed reaction pathway of the SCR of NO by C₃H₆ over Ag-Pd/Al₂O₃ is illustrated in Scheme 1.

Much additional knowledge will be required before reliable reaction mechanism can be made. Further studies are under way in order to test some of the hypotheses made above.

4. Conclusion

We have developed a novel Ag-Pd/Al₂O₃ catalyst for the NO_x reduction by C₃H₆ under lean burning conditions. According to catalytic tests over Ag-Pd/Al₂O₃ and contrastive Ag/Al₂O₃, we find that loading trace amounts of Pd on Ag/Al₂O₃ leads to a significant improvement of NO_x conversion during the SCR of NO by C₃H₆, especially at low reaction temperature. In situ DRIFTS results suggest that Pd addition catalyzes the partial oxidation of C₃H₆ into surface enolic species, and the surface enolic species is quite reactive towards NO₃⁻ and NO₂ to form surface NCO species. Based on these results, a new reaction mechanism is proposed with enolic species and NCO species as the key reaction intermediates.

Acknowledgements

This work was financially supported by State Hi-tech Research and Development Project of the

Ministry of Science and Technology, PR China (Grant 2001AA643040) and the Chinese Academy of Sciences Program for Attracting Overseas Professionals.

References

- [1] M. Iwamoto, in: Proceedings of the Symposium on Catalytic Technology for the Removal of Nitrogen Oxides, Catalytic Society of Japan, 1990, p. 19.
- [2] M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu, N. Mizuno, Appl. Catal. 69 (1991) L15.
- [3] W. Held, A. Koenig, T. Richiter, L. Puppe, SAE Paper 900496, 1990.
- [4] T. Miyadera, K. Yoshida, Chem. Lett. 3 (1993) 1483; T. Miyadera, Appl. Catal. B 2 (1993) 199.
- [5] K.A. Bethke, H.H. Kung, J. Catal. 172 (1997) 93.
- [6] K. Shimizu, H. Maeshima, A. Satsuma, T. Hattori, Appl. Catal. B 18 (1998) 163.
- [7] F.C. Meunier, J.P. Breen, V. Zuzaniuk, M. Olsson, J.R.H. Ross, J. Catal. 187 (1999) 493.
- [8] K. Shimizu, A. Satsuma, T. Hattori, Appl. Catal. B 25 (2000) 239.
- [9] S. Kameoka, Y. Ukisu, T. Miyadera, Phys. Chem. Chem. Phys. 2 (2000) 367.
- [10] F.C. Meunier, V. Zuzaniuk, J.P. Breen, M. Olsson, J.R.H. Ross, Catal. Today 59 (2000) 287.
- [11] S. Sumiya, M. Saito, H. He, Q.-C. Feng, N. Takezawa, Catal. Lett. 50 (1998) 87.
- [12] S. Sumiya, H. He, A. Abe, N. Takezawa, K.J. Yoshida, J. Chem. Soc., Faraday Trans. 94 (1998) 2217.
- [13] A. Obuchi, A. Ohi, M. Nakamura, A. Ogata, K. Mizuno, H. Ohuchi, Appl. Catal. B 2 (1993) 71.
- [14] R. Burch, J.P. Breen, F.C. Meunier, Appl. Catal. B 39 (2002) 283.
- [15] H. He, N. Irite, K. Onai, K. Yoshida, in: Proceedings of the 69th Annual Meeting of Chemical Society of Japan, 1995, p. A314.
- [16] K. Masuda, K. Shinoda, T. Kato, K. Tsujimura, Appl. Catal. B 15 (1998) 29.
- [17] E. Seker, J. Cavataio, E. Gulari, P. Lorphongpaiboon, S. Osuwan, Appl. Catal. A 183 (1999) 121.
- [18] M. Haneda, Y. Kintaichi, M. Inaba, H. Hamada, Appl. Surf. Sci. 121–122 (1997) 391.
- [19] T. Tanaka, T. Okuhara, M. Misono, Appl. Catal. B 4 (1994) L1.
- [20] K. Shimizu, J. Shibata, H. Yoshida, A. Satsuma, T. Hattori, Appl. Catal. B 30 (2001) 151.
- [21] K. Shimizu, H. Kawabata, A. Satsuma, T. Hattori, Appl. Catal. B 19 (1998) L87.
- [22] K. Shimizu, A. Satsuma, T. Hattori, Appl. Catal. B 25 (2000) 239.
- [23] A. Martínez-Ariza, M. Fernández-García, A. Glesias-Juez, J.A. Anderson, J.C. Conesa, J. Soria, Appl. Catal. B 28 (2000) 29.
- [24] K. Shimizu, H. Kawabata, H. Maeshima, A. Satsuma, T. Hattori, J. Phys. Chem. B 104 (2000) 2885.
- [25] A.M. Turek, I.E. Wachs, E. DeCanio, J. Phys. Chem. 96 (1992) 5000.
- [26] Standard IR Spectra, Sadtler Research Labs.