On the promotional effect of Sn in Co–Sn/Al_2O_3 catalyst for NO selective reduction

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NO reduction with propylene over Co/Al_2O_3 and Co–Sn/Al_2O_3 catalysts has been investigated. For the Co/Al_2O_3 catalyst, a calcination temperature exceeding 800 °C led to a decrease of NO conversion. Calcination of the Co/Al_2O_3 catalyst at 1000 °C resulted in the formation of α-Al_2O_3 and Co_3O_4. The presence of 20% water vapor showed a significant shift for the maximum NO reduction temperature from 450 to 600 °C over Co/Al_2O_3. It has been found that modification of 6 wt% Co/Al_2O_3 with 2 wt% Sn significantly enhanced the catalyst thermal stability and improved the inhibitory effect of water on NO conversion and reaction temperature. The promotional effect of Sn on the catalyst thermal stability was attributed to the suppression of the phase transformation from highly dispersed Co^{2+} species on γ-Al_2O_3 to α-Al_2O_3 and Co_3O_4. The smaller influence of water vapor on NO reduction conversion and temperature over Co–Sn/Al_2O_3, compared to Co/Al_2O_3, was attributed to the dispersion effect of Sn species on Co^{2+} species as well as the involvement of Sn species in NO reduction at a relatively lower temperature. The synergetic effect between the octahedral Co^{2+} species and γ-alumina plays a significant role in the catalysis of NO selective reduction by C_3H_6.

KEY WORDS: NO selective reduction; cobalt/alumina; cobalt–tin/alumina

1. Introduction

The catalytic selective reduction of NO with hydrocarbons in the presence of excess oxygen and water vapor is still a challenging problem in the area of catalysis [1,2]. It has been shown that alumina-based catalysts, such as Co/Al_2O_3 [3–5], Ag/Al_2O_3 [6], Ga_2O_3/Al_2O_3 [7,8], Cu/Al_2O_3 [9–11], Sn/Al_2O_3 [12,13] and Au/Al_2O_3 [14,15], are efficient catalysts to NO reduction with C_3H_6. Among them, Co/Al_2O_3 has attracted much recent attention. The Co loading, calcination temperature and source of alumina are recognized to be the crucial factors for the catalyst activity. A 2 wt% Co/Al_2O_3 catalyst shows a maximum NO reduction rate as high as 6.4 μmol/g min, and it has been shown to be stable in the presence of SO_2 and water [4]. Thus, it seems that Co/Al_2O_3 is a very promising catalyst for NO selective reduction with hydrocarbons.

However, in this study, it has been found that the catalytic activity of Co/Al_2O_3 decreased when it was calcined at a temperature higher than 800 °C. In addition, the presence of water vapor in the reaction stream also showed a significant influence on the catalyst performance. Interestingly, modification of Co/Al_2O_3 with a small amount of Sn significantly enhanced the catalyst thermal stability, improved the negative effect of water vapour on NO conversion and decreased the reaction temperature.

2. Experimental

2.1. Catalysts preparation

All catalysts were prepared by a sol–gel method similar to that of our previous report [16]. The preparation procedures for the Co/Al_2O_3 catalyst are as follows. First, a clear boehmite solution was obtained by hydrolyzing aluminum tri-isopropoxide in a diluted nitric acid solution at 95 °C. Then, an ethylene glycol solution of cobalt acetate was added to the boehmite solution. The mixture was stirred until a pink gel was formed. Then the gel was dried at 120 °C overnight, and finally calcined in air at 800 °C for 10 h. The Co/Al_2O_3 catalyst with a nominal Co metal loading of 6 wt% was denoted as Co6.

Modified 6 wt% Co/Al_2O_3 catalysts were prepared by adding a second metal salt into the ethylene glycol solution of cobalt acetate during preparation. This mixed solution was added into the boehmite solution and stirred until a gel formed. The gel was then dried and calcined as above. The tin oxide modified 6 wt% Co/Al_2O_3 catalysts with nominal tin metal contents of 2, 5, 10 and 15 wt% were prepared and denoted as Co6–Sn2, Co6–Sn5, Co6–Sn10 and Co6–Sn15, respectively.

2.2. Catalysts characterization

BET surface area, pore size and pore volume were obtained from N_2 adsorption isotherms measured at -196 °C using a Bellsorp36 (Nippon Bel Inc.) instrument. The BET surface areas, average pore diameters and pore volumes of

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Table 1
BET surface area, average pore diameter and pore volume of alumina and alumina-supported catalysts.

Catalyst	BET surface area (m^2/g)	Average pore diameter (nm)	Pore volume (ml/g)
Al_2O_3	175.8	8.2	0.535
Co6	163.9	8.0	0.488
Co6–Sn2	164.1	7.6	0.456
Co6–Sn5	159.3	6.2	0.399
Co6–Sn10	144.5	5.8	0.366
Co6–Sn15	138.9	4.8	0.321

the above prepared catalysts are given in table 1. XRD spectra were recorded using an MXP powder diffractometer (MAC Science Inc.) with a Cu Kα radiation and operated at 40 kV and 20 mA. The scan range was 10°–70° and the scan speed was 2°/min. UV-vis absorption spectra were recorded using a U-3000 spectrophotometer (Hitachi, Japan) in the similar way as that reported previously for a solid sample [17]. γ-Al_2O_3, which was prepared by the same sol–gel method as used for the Co/Al_2O_3 catalyst, was used as a reference.

2.3. NO reduction with C_3H_6

NO reduction with propylene in the presence of an excess amount of O_2 was performed with a fixed bed flow-type quartz reactor (inner diameter ∅ 8 mm). Prior to reaction, the catalyst (0.3 g, 30–60 mesh) was pretreated with flowing pure O_2 at 500 °C for 1 h, or treated in an oxygen flow containing 20% water at 500 °C for 1 h when the catalyst was to be evaluated in the presence of water. The feed mixture consisted of 665 ppm NO, 605 ppm C_3H_6, 3% O_2, with or without 20% water, and N_2 as a balance gas. The total gas flow rate was 165 ml/min, corresponding to a space velocity of about 21000 h^{-1}. NO and NO_2 concentrations were analyzed with a Horiba CLA-510SS NO_x analyzer. Other products were analyzed using a Shimadzu 8A GC equipped with a TCD. The concentrations of C_3H_6, CO_2 and N_2O were analyzed by a Parapak Q column. Over all the catalysts tested in this study, NO was converted mainly to N_2 with a small amount of NO_2. No other N-containing compound was detected. In the presence of water vapour, however, trace NH_3 was detected. All reaction data were taken after the reaction started for half an hour.

3. Results and discussion

3.1. Influence of catalyst calcination temperature and the presence of water vapor on the reaction performance of Co/Al_2O_3

Figure 1 shows that calcination of Co/Al_2O_3 catalyst at a high temperature led to a decrease in catalyst activity. With the increase of catalyst calcination temperature from 800 to 900 °C, the maximum NO conversion decreased from 84.6 to 68.8%. When the catalyst was calcined at 1000 °C, NO reduction conversion dropped greatly to 38.8%, and the temperature at the maximum NO reduction shifted from 450 to 550 °C. The low NO conversion over the 1000 °C calcined 6 wt% Co/Al_2O_3 catalyst possibly is a result of the structure deterioration of the catalyst from the high-temperature calcination. This will be discussed later. The influence of water vapor on NO conversion is significant. It is seen from figure 1 that the presence of 20% water vapor greatly shifted the maximum NO conversion temperature from 450 to 600 °C, while the maximum NO conversion decreased from 84.6 to 72.1%. A noticeable NO conversion was observed only at temperatures higher than 500 °C, which was 150 °C higher than that in the absence of water vapor. The significant influence of water vapor can be attributed to the impedance of water on NO and C_3H_6 adsorption, as reported for Co-ZSM-5 [18].

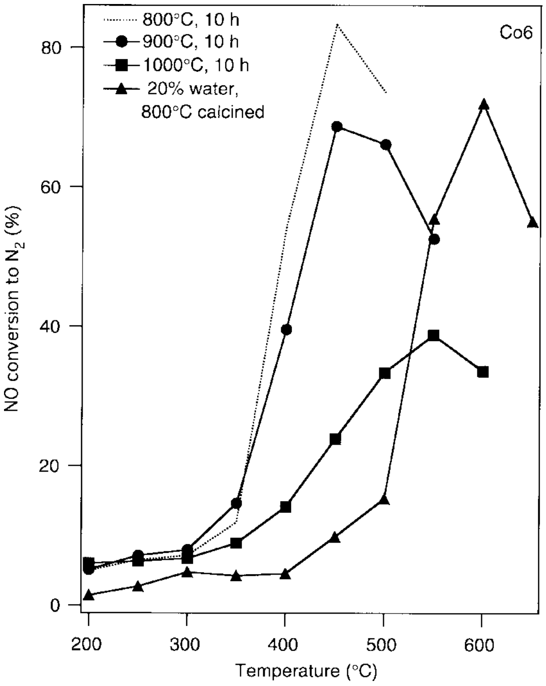

Figure 1. Influences of high calcination temperature and the presence of 20% water vapor on the catalytic performance of the Co6 catalyst. The influence of calcination temperature was investigated in the absence of water. Feed composition: 665 ppm NO, 605 ppm C_3H_6, 3% O_2, N_2 as balance gas. Catalyst weight 0.3 g. GHSV = 21000 h^{-1}. The influence of water vapor was tested over the 800 °C calcined sample and the feed composition was the same as above but with the presence of 20% water vapor.

From the above results, it may be concluded that the low thermal stability at high temperature and the significant prohibiting effect of water vapor on the Co/Al_2O_3 catalyst are the critical problems for the practical use of this type of catalyst in automobiles. Therefore, further efforts to improve the thermal stability and water resistance capability of the Co/Al_2O_3 catalyst are necessary.

3.2. Promotional effect of Sn oxide

In an attempt to improve the catalyst activity of Co/Al_2O_3 and lower the NO conversion temperature, a small amount of

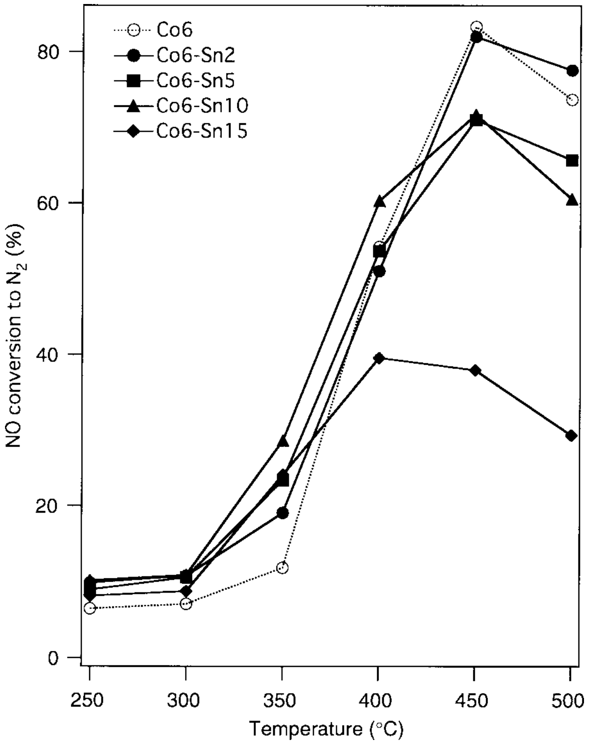

Figure 2. NO reduction conversion over Sn oxide modified 6 wt% Co/Al_2O_3 catalysts. Reaction conditions were the same as those in figure 1.

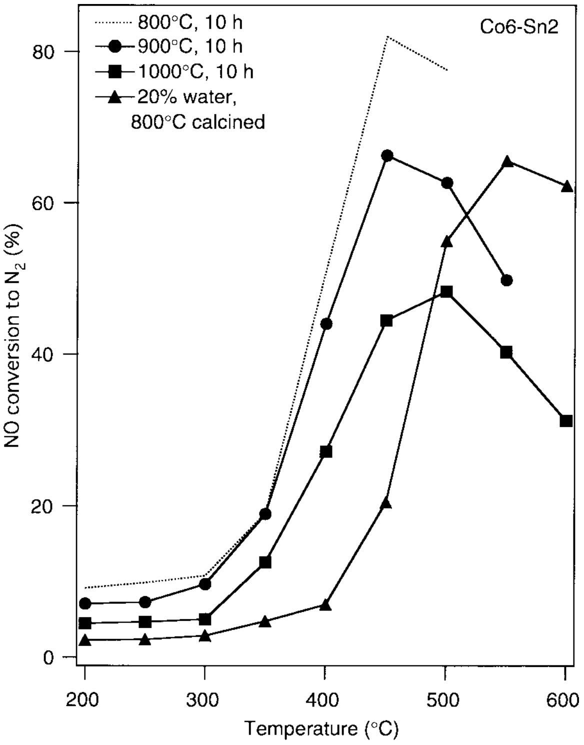

Figure 3. Influences of high calcination temperature and the presence of 20% water vapor on the catalytic performance of the Co6–Sn2 catalyst. Reaction conditions were the same as those in figure 1.

oxide of Ce, Cu, Mn, Pt or Pd was separately introduced into the 6 wt% Co/Al_2O_3 catalyst. Reaction results over these modified catalysts indicate that introduction of any of the above metal or metal oxides to the 6 wt% Co/Al_2O_3 catalyst substantially decreased the catalyst activity. Further studies on these modified catalysts are discouraged.

The NO reduction results over several Sn-modified 6 wt% Co/Al_2O_3 catalysts are given in figure 2. It is seen that addition of 2 wt% Sn did not cause much change in the activity of 6 wt% Co/Al_2O_3. With the increase of tin content, the maximum NO reduction conversion decreased. Modification of 6 wt% Co/Al_2O_3 with 15 wt% Sn led to a rather low catalyst activity, a maximum NO conversion of 37% was observed. It is interesting to note that regardless of the amount of tin oxide incorporated, addition of tin oxide slightly increased the NO reduction conversion in the temperature range of 300–400 °C.

Another advantage of introduction of Sn to Co/Al_2O_3 is the enhancement of catalyst stability. Figure 3 shows the NO reduction conversions over the 900 and 1000 °C calcined Co6–Sn2 catalyst. It is seen that a high calcination temperature also resulted in a decrease in catalyst activity. However, by comparing the results in figure 3 with those of unmodified Co/Al_2O_3 in figure 1, it can be seen that the Sn-modifed catalyst showed a much higher activity than the unmodified Co/Al_2O_3 when both were calcined at 1000 °C for 10 h. NO reduction conversions at 500 °C were 33.4 and 48.3% for the 1000 °C calcined Co6 and Co6–Sn2 catalysts, respectively. The smaller activity drop of the Sn-modified catalyst after calcination at 1000 °C indicates that the addition of 2 wt% Sn promoted the thermal stability of Co/Al_2O_3 catalyst.

The 6 wt% Co–2 wt% Sn/Al_2O_3 catalyst was also tested for NO reduction in the presence of water vapor and compared with that of unmodified Co6 catalyst. Figure 3 shows that the presence of water vapor also shifted the temperature at the maximum NO conversion to a higher temperature. However, compared with the unmodified 6 wt% Co/Al_2O_3 catalyst, the temperature shift is much less for the Sn-modified Co/Al_2O_3 catalyst. The results in figure 3 show that the Sn-modified Co/Al_2O_3 catalyst was active at temperatures above 400 °C in the presence of water, whereas unmodified Co/Al_2O_3 showed an observable NO conversion only at temperatures above 500 °C under the same reaction conditions. These results demonstrate that the modification of Co/Al_2O_3 with a proper amount of Sn enhances the catalyst thermal stability and improves the catalyst performance by showing a smaller impact of water vapor on NO reduction conversion and temperature.

3.3. Catalyst structure changes due to high-temperature calcination

Figure 4 compares the XRD spectra of Co6 and Co6–Sn2 when calcined at different temperatures. For Co6, there was not much change in structure when the calcination temperature increased from 800 to 900 °C. However, calcination at 1000 °C resulted in the formation of α-Al_2O_3 and Co_3O_4 phases. The Co6–Sn2 catalyst showed a higher thermal stability than Co6. After calcination at 900 or 1000 °C,

Table 2
Effect of high calcination temperature on the characteristics of Co6 and Co6–Sn2 catalysts.

Catalyst	Calcination temperature (°C)	BET surface area (m^2/g)	Average pore diameter (nm)	Pore volume (ml/g)
Co6	900	112.3	8.2	0.366
Co6	1000	45.8	9.0	0.241
Co6–Sn2	900	131.2	9.0	0.436
Co6–Sn2	1000	72.2	9.2	0.316

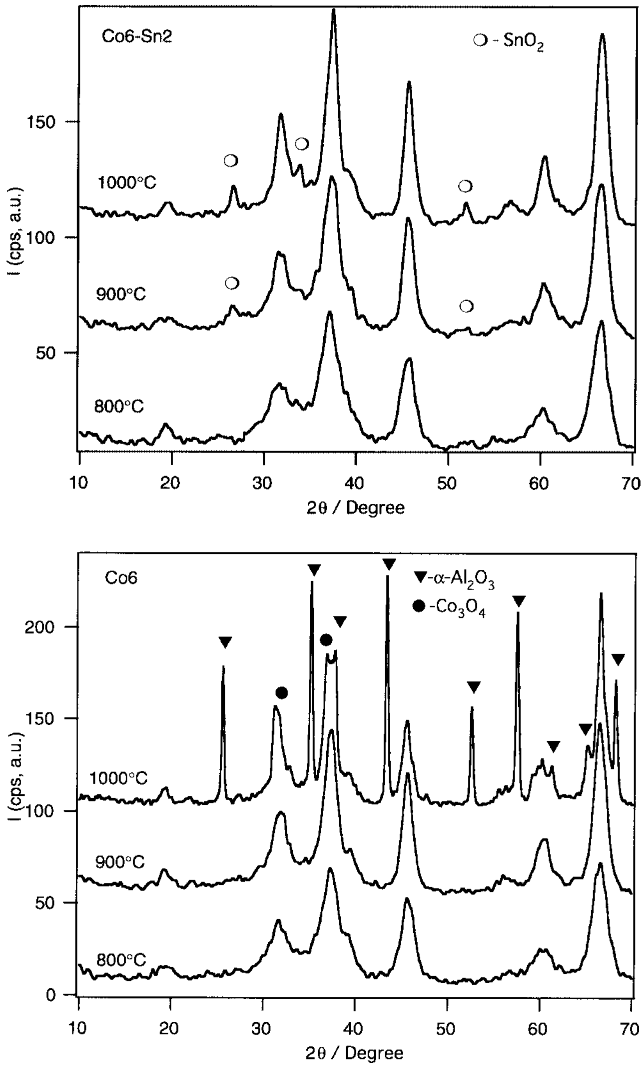

Figure 4. XRD spectra of Co6 and Co6–Sn2 catalysts calcined at different temperatures.

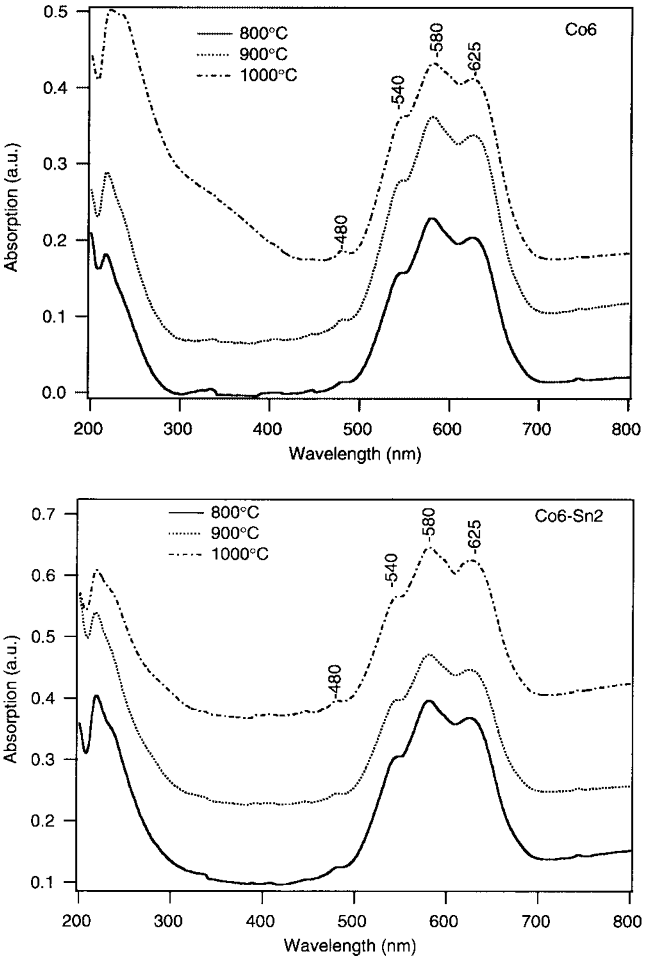

Figure 5. UV-vis spectra of Co6 and Co6–Sn2 catalysts calcined at different temperatures.

neither α-Al_2O_3 nor Co_3O_4 phase was detected; the only detectable phases were γ-Al_2O_3 and SnO_2, and no significant change in the XRD pattern was observed. This indicates that its structure was largely maintained. Therefore, it is concluded that the addition of Sn oxide to Co/Al_2O_3 enhances the catalyst thermal stability by suppression of the phase transformation at a high temperature. This conclusion can further be substantiated by the fact that Co6–Sn2 had a higher BET surface area (72.2 m^2/g) than Co6 (45.8 m^2/g) after calcination at 1000 °C for 10 h (table 2). UV-vis spectra of the above calcined catalysts are shown in figure 5. It can be seen that there is no significant change in the UV-vis spectra of Co6–Sn2 even after calcination at 1000 °C. This is further evidence to substantiate the conclusion that the 1000 °C calcination process did not lead to significant destruction to the structure of Co6–Sn2. The observed decrease of NO reduction conversion over the 1000 °C calcined Co6–Sn2 catalyst possibly is resulted from the formation of a small amount of bulk SnO_2 and the decrease of surface area as well (table 2). For Co6, calcination at 1000 °C led to the formation of Co_3O_4 phase, as confirmed by both the XRD and UV-vis results. This is an indication that the structure was largely destroyed. Nevertheless, part of its original structure, dispersed octahedral Co^{2+} species, was retained as evidenced by the presence of the triplet peak at 540, 580 and 625 nm in the UV absorption spectra [4]. The partial phase transformation is responsible for the catalyst activity drop after the high-temperature calcination, because Co_3O_4 is known to be a poor catalyst for NO selective reduction with hydrocarbons. In addition, it is also reasonable to suggest that the phase transformation of γ-Al_2O_3 to α-Al_2O_3 would also be responsible for the decrease of catalyst activity, because it is known that alumina also participates actively in the NO reduction reaction with alumina-supported catalysts [19]. The synergetic effect between the octahedral Co^{2+} and the alumina support plays an important role [20].

The inhibitory effect of water is less severe for Co6–Sn2. It is believed that this is a contribution from the dispersed Sn species, which also play an important role in the catalysis of NO selective reduction. It is reported that the temperature profiles of NO and C_3H_6 reaction over supported SnO_2 were only slightly affected by the presence of water, and the temperature for NO reduction over Sn/Al_2O_3 catalysts is lower than it is over Co/Al_2O_3 [12,13]. Therefore, the Sn-modified Co/Al_2O_3 catalyst shows a NO conversion at a relatively lower temperature as compared to the Co/Al_2O_3 catalyst when water vapor is present.

4. Conclusions

For a 6 wt% Co/Al_2O_3 catalyst, the presence of 20% water vapor greatly shifted the temperature at the maximum NO reduction from 450 to 600 °C. A high catalyst calcination temperature exceeding 800 °C resulted in a decrease in NO conversion. Calcination at 1000 °C led to the formation of α-Al_2O_3 and Co_3O_4. Modification of 6 wt% Co/Al_2O_3 with 2 wt% Sn significantly enhanced the catalyst thermal stability and improved the inhibitory effect of water on NO reduction conversion and temperature. The promotional effect of Sn on the catalyst thermal stability can be attributed to the suppression of the formation of α-Al_2O_3 and Co_3O_4. The smaller inhibitory effect of water vapor on NO reduction temperature over the Co–Sn/Al_2O_3 catalyst is a result of NO conversion over the dispersed Sn species. The synergetic effect between the octahedral Co^{2+} species and γ-alumina support plays an important role in the catalysis of NO selective reduction by C_3H_6.

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References

[1] A. Fritz and V. Pitchon, Appl. Catal. B 13 (1997) 1.
[2] V.I. Pârvulescu, P. Grange and B. Delmon, Catal. Today 46 (1998) 233.
[3] H. Hamada, Y. Kintaichi, M. Inaba, M. Tabata, T. Yoshinari and H. Tsuchida, Catal. Today 29 (1996) 53.
[4] J. Yan, M.C. Kung, W.M.H. Sachtler and H.H. Kung, J. Catal. 172 (1997) 178.
[5] N. Okazaki, Y. Yamamoto, H. Itoh and A. Tada, Chem. Lett. (1998) 807.
[6] K.A. Bethke and H.H. Kung, J. Catal. 172 (1997) 93.
[7] K. Shimizu, A. Satsuma and H. Hattori, Appl. Catal. B 319 (1998) 319.
[8] T. Maunula, Y. Kintaichi, M. Inaba, M. Haneda, K. Sato and H. Hamada, Appl. Catal. B 15 (1998) 291.
[9] J.A. Anderson, C. Márques-Alvarez, M.J. Lopez-Muñoz, I. Rodríguez-Ramos and A. Gurrero-Ruiz, Appl. Catal. B 14 (1997) 189.
[10] F. Radtke, R.A. Koeppel, E.G. Minardi and A. Baiker, J. Catal. 167 (1997) 127.
[11] L.Y. Chen, T. Horiuchi, T. Osaki and T. Mori, Appl. Catal. B 23 (1999) 259.
[12] M.C. Kung, P.W. Park, D.W. Kim and H.H. Kung, J. Catal. 181 (1999) 1.
[13] P.W. Park, H.H. Kung, D.W. Kim and M.C. Kung, J. Catal. 184 (1999) 440.
[14] A. Ueda, T. Oshima and M. Haruta, Appl. Catal. B 12 (1997) 81.
[15] A. Ueda and M. Haruta, Appl. Catal. B 18 (1998) 115.
[16] T. Osaki, T. Horiuchi, T. Sugiyama, S. Suzuki and T. Mori, Catal. Lett. 52 (1998) 171.
[17] L. Chen, S. Jaenicke, G.K. Chuah and H.G. Ang, J. Electron. Spectrosc. Relat. Phenom. 82 (1996) 203.
[18] Y. Li, P.J. Battavio and J.N. Armor, J. Catal. 142 (1993) 561.
[19] M.C. Kung and H.H. Kung, Topics Catal. 10 (2000) 21.
[20] J.Y. Yan, H.H. Kung, W.M.H. Sachtler and M.C. Kung, J. Catal. 175 (1998) 294.