Available online at www.sciencedirect.com
ScienceDirect
Journal of Catalysis 248 (2007) 137–141
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

Research Note

Anchoring highly active gold nanoparticles on SiO_2 by CoO_x additive

Kun Qian, Weixin Huang *, Zhiquan Jiang, Huaxing Sun

Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemical Physics, MPG-CAS Partner Group of Fritz-Haber-Institut der MPG, University of Science and Technology of China, Jinzhai Road 96, Hefei 230026, China

Received 24 December 2006; revised 11 February 2007; accepted 12 February 2007

Abstract

We report an easy method of using SiO_2 as the support and $HAuCl_4$ as the precursor for synthesizing a $Au/CoO_x/SiO_2$ catalyst that is highly active in low-temperature CO oxidation. The surface of SiO_2 was modified with a small amount of highly dispersed CoO_x (6 wt%) before the loading of gold. A 78% conversion of CO was achieved at room temperature and 100% at temperatures above 333 K over the $Au/CoO_x/SiO_2$ catalyst in CO oxidation. Compared with Au/SiO_2, the existence of CoO_x greatly enhances the dispersion of gold nanoparticles in $Au/CoO_x/SiO_2$, which is responsible for the excellent catalytic performance.

Keywords: Gold nanoparticles; SiO_2; CoO_x; Low-temperature CO oxidation

1. Introduction

Low-temperature CO oxidation catalyzed by supported gold nanoparticles has been extensively investigated [1–10]. Since the discovery of the activity–size relation [1–3], tremendous effort has been devoted to preparing supported highly dispersive gold nanoparticles, which play a decisive role in catalyzing the oxidation of CO at low temperature. The literature classifies various oxide supports into "active" (or reducible) supports, such as TiO_2, Fe_2O_3, CeO_2, and Co_3O_4, and "inert" supports, such as SiO_2 and Al_2O_3 [11]. With the most common Au compound ($HAuCl_4$) as the precursor, highly dispersive gold nanoparticles can be easily prepared on "active" oxides by the most traditional methods of catalyst preparation (coprecipitation and deposition–precipitation [DP]), which thus are highly active in low-temperature CO oxidation [2,11,12]. However, the same approach usually forms large gold nanoparticles on "inert" SiO_2; thus, the as-prepared Au/SiO_2 catalyst exhibits poor activity [13–17].

Because of its large surface area, high thermal stability, and mechanical strength, SiO_2 is always an attractive support, particularly for catalysts to be industrialized. Therefore, great efforts are still being devoted to developing synthetic methods to prepare highly dispersive gold nanoparticles on silica. There are several successful examples. Finely dispersed Au nanoparticles have been prepared on SiO_2 by means of chemical vapor deposition (CVD) [13], trapping Au nanoparticles in the ordered mesoporous silica [15,18], using micelle-derived Au nanoparticles [16] and cationic Au complex ($Au(PPh_3)Cl$, $[Au(en)_2]^{3+}$) [19–21] as precursors. But only some of these Au/silica catalysts exhibited satisfying activity in low-temperature CO oxidation [13,19,21]. Moreover, the above synthetic methods involve either complicated apparatus or uncommon gold compounds.

"Active" oxides have been used as additives to enhance the catalytic activity of Au/SiO_2 catalysts in CO oxidation. Dekkers et al. investigated the effect of "active" oxide additives (e.g., CoO_x, LaO_x, CeO_x) on the activity of Au/SiO_2 catalysts and found no enhancement effect in low-temperature CO oxidation under the experimental conditions used [14]. Guczi et al. investigated the $FeO_x/Au/SiO_2/Si(100)$ model catalyst and found that Au promoted the catalytic activity of FeO_x in CO oxidation [22]. Recently, Venezia et al. anchored Au nanoparticles on TiO_2/SiO_2 by the sol method and found that the $Au/TiO_2/SiO_2$ catalyst with $TiO_2 \leqslant 5$ wt% showed better catalytic performance in CO oxidation than the similarly prepared Au/TiO_2

---

[*] Corresponding author. Fax: +86 551 3601592.
E-mail address: huangwx@ustc.edu.cn (W. Huang).

0021-9517/$ – see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2007.02.010

catalyst [23]. But the $Au/TiO_2/SiO_2$ catalyst was not very active in low-temperature CO oxidation, showing the best activity of 50% CO conversion at 323 K and 100% CO conversion at ca. 380 K under the experimental conditions used [23]. The interfacial structures of various $Au/TiO_2/SiO_2$ catalysts have also been investigated in detail [24].

In this paper, by modifying the surface of SiO_2 with a small amount of highly dispersed CoO_x (6 wt%), we successfully synthesized highly active Au/SiO_2 catalysts by the routine DP method with $HAuCl_4$ as the precursor. The resulting $Au/CoO_x/SiO_2$ catalyst demonstrated excellent catalytic activity in low-temperature CO oxidation.

2. Experimental

Typically, SiO_2 (40–120 mesh, Qingdao Haiyang Chemicals Co.) was first modified with 6% CoO_x (Co/SiO_2 weight ratio) by the conventional incipient wetness impregnation method using $Co(NO_3)_2{\cdot}6H_2O$ (Sinopharm Chemical Reagent Co., Ltd., $\geqslant 99.0\%$) as the cobalt precursor, followed by drying at 60 °C. The resulting CoO_x/SiO_2 was then used directly to prepare the 2% Au/6% CoO_x/SiO_2 (Au/SiO_2 weight ratio) catalyst by the routine DP method using $HAuCl_4{\cdot}4H_2O$ (Sinopharm Chemical Reagent Co., Ltd., Au content $\geqslant 47.8\%$) as the precursor. The $HAuCl_4{\cdot}4H_2O$ aqueous solution and the ammonia water were slowly co-added into a three-necked bottle containing CoO_x/SiO_2, with pH controlled between 9 and 10. The system was stirred at 60 °C for 24 h, after which the solid was filtered and washed several times. The resulting powder was dried at 60 °C for 24 h, followed by calcination at 200 °C for 4 h. The 2% Au/SiO_2 and 6% CoO_x/SiO_2 catalysts were also prepared similarly for comparison purposes.

The catalytic activity was evaluated with a fixed-bed flow reactor. The used catalyst weight was 100 mg, and the reaction gas consisting of 1% CO and 99% dry air was fed at a rate of 20 ml/min. The composition of the effluent gas was detected with an online GC-14C gas chromatograph equipped with a TDX-01 column ($T = 80\,°C$, H_2 as the carrier gas at 30 ml/min). The conversion of CO was calculated from the change in CO concentrations in the inlet and outlet gases.

BET surface areas were acquired on a Beckman Coulter SA3100 surface area analyzer, in which the sample was degassed at 120 °C for 30 min in the nitrogen atmosphere before the measurement. X-ray diffraction (XRD) patterns were acquired on a Philips X'Pert PRO SUPER X-ray diffractometer) with a Ni-filtered Cu$K\alpha$ X-ray source operating at 40 kV and 50 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 high-performance electron spectrometer using a monochromatized Al$K\alpha$ excitation source ($h\nu = 1486.6$ eV). The binding energies in XPS spectra were referenced with respect to the C 1s binding energy of adventitious carbon in the catalysts at 285.1 eV. Transmission electron microscopy (TEM) images were obtained using a JEOL 2010 high-resolution transmission electron microscope. The gold concentrations in the catalysts were also analyzed by inductively coupled plasma atomic emission spectrometer (ICPAES).

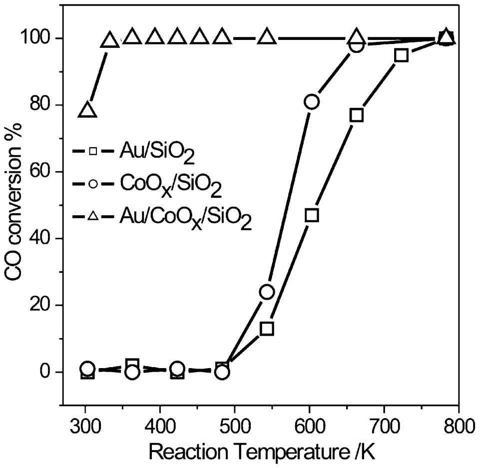

Fig. 1. Catalytic activities of 2% Au/SiO_2, 6% CoO_x/SiO_2, and 2% Au/6% CoO_x/SiO_2 catalysts in CO oxidation. The reaction gas consisted of 1% CO and 99% dry air and the feeding rate was 20 ml/min.

3. Results and discussion

Fig. 1 shows the catalytic activities of various catalysts in CO oxidation. Both 2% Au/SiO_2 and 6% CoO_x/SiO_2 catalysts exhibited poor activity, which became active only at reaction temperatures above 473 K. However, the 2% Au/6% CoO_x/SiO_2 catalyst was highly active even at low temperature. The CO conversion reached 78% at room temperature (303 K), and rose to 100% when the reaction temperature was increased to 333 K and above. The catalyst was also stable, showing no deactivation under the reaction conditions tested in our experiments. These results confirm that we succeeded in preparing highly active gold nanoparticles on CoO_x-modified SiO_2 by the traditional DP method, with the most common gold compound $HAuCl_4$ as the precursor.

The BET surface areas of these samples did not change much, being 388, 370, 353, and 331 m^2/g for bare SiO_2, 2% Au/SiO_2, 6% CoO_x/SiO_2, and 2% Au/6% CoO_x/SiO_2. The ICPAES results revealed that the Co loading was 5.58% in 2% Au/6% CoO_x/SiO_2 and that the gold loading increased from 1.02% in 2% Au/SiO_2 to 1.98% in 2% Au/6% CoO_x/SiO_2. This enhanced gold loading could be reasonably attributed to the strong interaction of the gold precursor with CoO_x on SiO_2 under the DP preparation condition. Our DP method involved the adjustment of the pH value of $HAuCl_4$ solution to 9–10 for generation of surface-reactive anionic gold hydroxide species $Au(OH)_xCl^-_{4-x}$ [25,26], which could only efficiently incorporate into a positively charged oxide surface [27]. Accordingly, the isoelectric point (IEP) of the oxide support matrix plays a key role for the successful incorporation and deposition of the gold precursors, in which the oxides with high IEP are favored in this DP synthesis route. The IEP value of CoO_x is much higher than that of SiO_2. Therefore, modifying the SiO_2 surface with CoO_x effectively enhanced the loading of gold on SiO_2.

Fig. 2 displays the XRD patterns of various catalysts. 2% Au/SiO_2 showed a single Au (111) diffraction peak at 38.4°. 2% Au/6% CoO_x/SiO_2 displayed four diffraction peaks corresponding to (111), (200), (311), and (222) crystal faces of

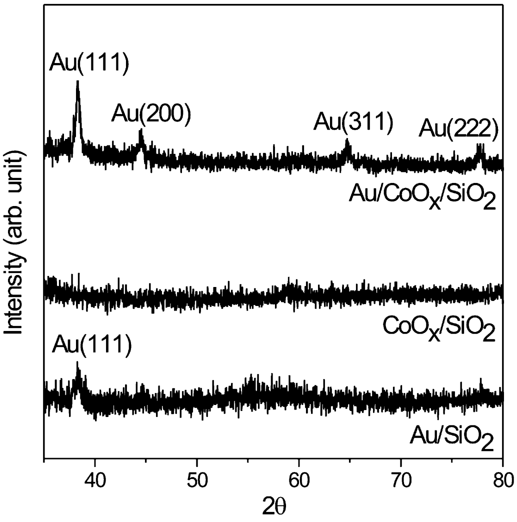

Fig. 2. XRD patterns of 2% Au/SiO_2, 6% CoO_x/SiO_2, and 2% Au/6% CoO_x/SiO_2 catalysts.

gold, respectively. Evaluated from the half-peak width of Au (111) diffraction peak, the average sizes of gold crystalline were 12 and 21 nm in 2% Au/SiO_2 and 2% Au/6% CoO_x/SiO_2, respectively. No diffraction peaks corresponding to CoO_x (CoO or Co_3O_4) was observed in 6% CoO_x/SiO_2 and 2% Au/6% CoO_x/SiO_2, indicating the high dispersion of CoO_x on SiO_2. XRD results showed that some gold nanoparticles in 2% Au/6% CoO_x/SiO_2 were larger than those in 2% Au/SiO_2. This seemed to contradict the observed catalytic performances of these two catalysts because it is generally accepted that fine gold nanoparticles are more active than large gold nanoparticles in low-temperature CO oxidation.

TEM observations (Fig. 3) give comprehensive results on the size distribution of gold nanoparticles. Fig. 3A shows a typical TEM image of 2% Au/SiO_2, giving rise mainly to gold nanoparticles with a size distribution of 7–15 nm, consistent with previous XRD results. However, gold nanoparticles in 2% Au/6% CoO_x/SiO_2 showed an interesting size distribution. Ultrafine 5–7 nm gold nanoparticles were frequently observed, as shown in Figs. 3B and 3C; meanwhile, gold aggregates as large as ~100 nm also existed on the surface (Fig. 3D), which, as inferred from their irregular shapes, likely consisted of small gold nanoparticles. We believed that these large gold aggregates were responsible for the intense and sharp diffraction peaks observed in the XRD pattern. We proposed that the ultrafine 5–7 nm gold nanoparticles were supported mostly on CoO_x-modified SiO_2, whereas those large gold aggregates on bare SiO_2. It is understandable that gold precursors on CoO_x/SiO_2 tended to eventually form ultrafine gold nanoparticles on the surface due to the strong interactions between adsorbed gold precursors and CoO_x/SiO_2. But it remained unclear why the modification of SiO_2 surface with CoO_x resulted in very large gold aggregates. A likely reason for this was that the existence of CoO_x-modified SiO_2 concentrated the gold precursors incorporated in the bare SiO_2, facilitating the aggregation of the resulting gold nanoparticles.

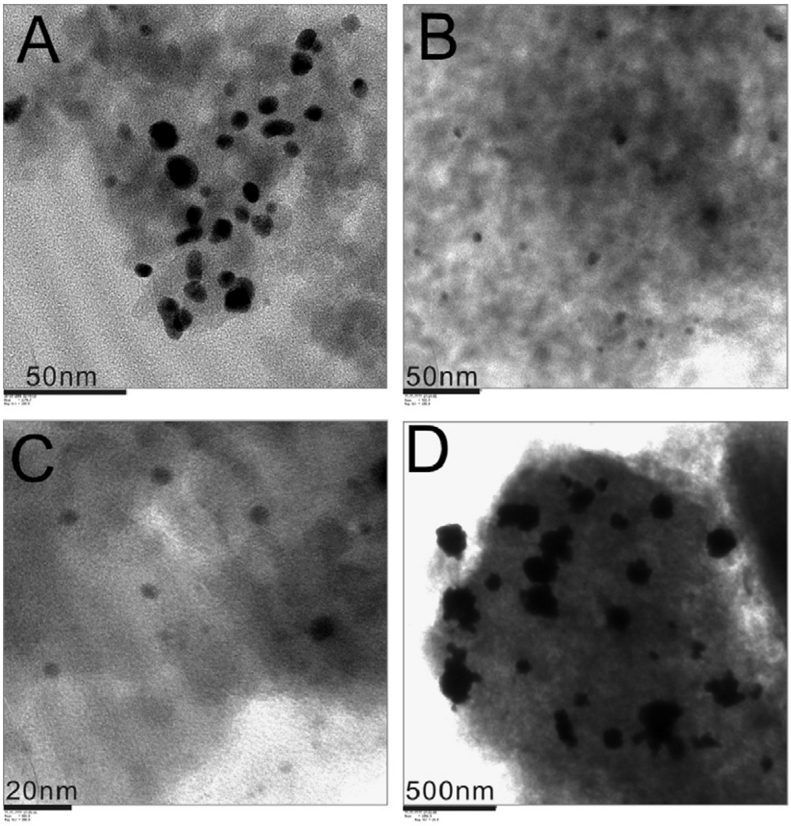

Fig. 3. TEM images of 2% Au/SiO_2 (A) and 2% Au/6% CoO_x/SiO_2 (B, C, D).

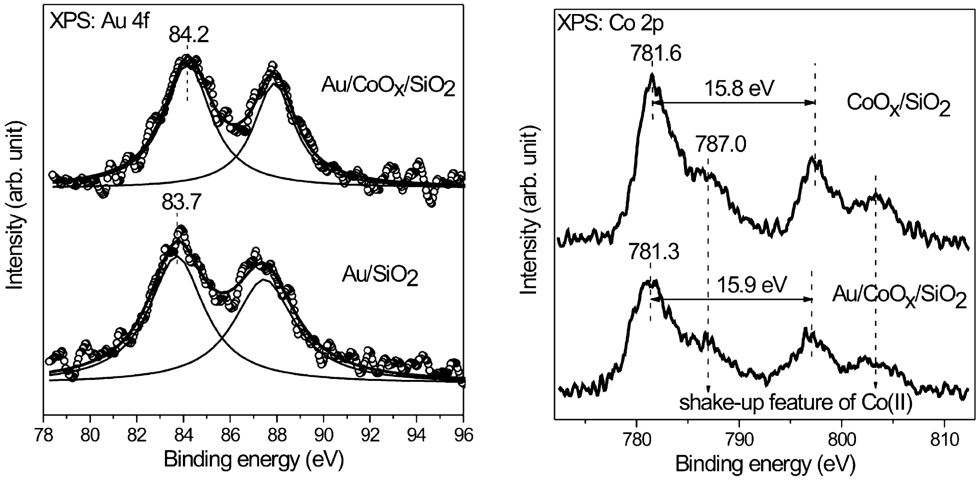

Fig. 4. Au 4f and Co 2p XPS spectra of 2% Au/SiO$_2$, 6% CoO$_x$/SiO$_2$, and 2% Au/6% CoO$_x$/SiO$_2$ catalysts.

Fig. 4 presents the Au 4f and Co 2p XPS spectra of various catalysts. The Au 4f spectra of 2% Au/SiO$_2$ and 2% Au/6% CoO$_x$/SiO$_2$ were satisfactorily fitted with one component using a Lorentzian component curve. However, their Au 4f binding energies differed greatly. Gold nanoparticles in 2% Au/SiO$_2$ demonstrated a Au 4f$_{7/2}$ binding energy at 83.7 eV, whereas those in 2% Au/6% CoO$_x$/SiO$_2$ demonstrated a Au 4f$_{7/2}$ binding energy at 84.2 eV. Both values were typical of the metallic gold. Model catalyst studies have established the size-dependent binding energy shifts in Au 4f of Au particles supported on SiO$_2$; for example, Lim et al. used STM and XPS to observe the gradual shifts of the Au 4f states to higher binding energy up to 0.8 eV with decreasing Au particle size [28]. Therefore, the experimental result that the Au 4f binding energy in 2% Au/6% CoO$_x$/SiO$_2$ was higher than that in 2% Au/SiO$_2$ indicated that the average size of the gold nanoparticles in 2% Au/6% CoO$_x$/SiO$_2$ was smaller than that in 2% Au/SiO$_2$. This finding agrees with the TEM results.

CoO$_x$ in 6% CoO$_x$/SiO$_2$ and 2% Au/6% CoO$_x$/SiO$_2$ exhibited slightly different Co 2p$_{3/2}$ binding energies at 781.6 and 781.3 eV, respectively. And both showed a 2p$_{3/2}$–2p$_{1/2}$ spin–orbit splitting (ΔE) of 15.8 eV and an obvious satellite peak at 787.0 eV. It is difficult to distinguish CoO from Co$_3$O$_4$ on basis of the Co 2p binding energy because their Co 2p binding energies show a negligible difference [29]. However, the Co 2p$_{3/2}$–2p$_{1/2}$ spin–orbit splitting (ΔE) is 15.0 eV for Co$_3$O$_4$ and 15.7 eV for CoO [30]. Moreover, a shoulder at the high-energy side, which has to be traced back to a shake-up process, can be observed only in the high-spin Co^{2+} ion, not in the diamagnetic low-spin Co^{3+} ion [31]. Thus, the XPS results unambiguously show that the Co species are essentially Co^{2+} in both 6% CoO$_x$/SiO$_2$ and 2% Au/6% CoO$_x$/SiO$_2$.

TEM and XPS results confirm the anchoring of highly dispersive gold nanoparticles in 2% Au/6% CoO$_x$/SiO$_2$, which reside mostly on the SiO$_2$ surface modified with CoO$_x$ (mainly CoO). These highly dispersive gold nanoparticles likely are responsible for the excellent catalytic performance of 2% Au/6% CoO$_x$/SiO$_2$ in low-temperature CO oxidation. Large gold nanoparticles form on bare SiO$_2$, leading to the poor catalytic performance of 2% Au/SiO$_2$. These results demonstrate that gold nanoparticles, being finer and more cationic, are more active in CO oxidation. But because the highly dispersed gold nanoparticles in 2% Au/6% CoO$_x$/SiO$_2$ are anchored mainly on the CoO$_x$-modified SiO$_2$, the participation of reducible CoO$_x$ in low-temperature CO oxidation cannot be excluded. Haruta et al. emphasized the role of the perimeter interface between Au particles and the support as a unique reaction site for low-temperature CO oxidation in the highly active Au/TiO$_2$ catalyst [5], but results of model catalyst studies reported by Goodman's group demonstrated that Au particles with a bilayer structure can exhibit a very high catalytic activity in low-temperature CO oxidation without the participation of TiO$_2$ support [8]. Further detailed investigations of the structure–activity relationship of Au/CoO$_x$/SiO$_2$ are being conducted in our laboratory.

In summary, by modifying the SiO$_2$ surface with a small amount of CoO$_x$, we successfully prepared highly active Au/CoO$_x$/SiO$_2$ catalysts in low-temperature CO oxidation by the traditional DP method using HAuCl$_4$ as the precursor. A 78% conversion of CO was achieved at room temperature and 100% at temperatures above 333 K. The modifier, CoO$_x$, greatly enhanced the deposition efficiency of gold nanoparticles on SiO$_2$ and, more importantly, led to the anchoring of highly dispersive gold nanoparticles on SiO$_2$. The method of modifying "inert" but desirable SiO$_2$ with a small amount of "active" oxides provides an easy and practical way to use SiO$_2$ as the support of highly active gold catalysts.

Acknowledgment

This work was supported by the "Hundred Talent" program of the Chinese Academy of Sciences.

References

[1] M. Haruta, M. Yamada, T. Kobayashi, S. Iijima, J. Catal. 115 (1989) 301.
[2] M. Haruta, Catal. Today 36 (1997) 153.
[3] M. Valden, X. Lai, D.W. Goodman, Science 281 (1998) 1647.
[4] G.C. Bond, D.T. Thompson, Catal. Rev. Sci. Eng. 41 (1999) 319.

[5] M. Haruta, M. Date, Appl. Catal. A 222 (2001) 427.
[6] M. Haruta, CATTECH 6 (2002) 102.
[7] H.H. Kung, M.C. Kung, C.K. Costello, J. Catal. 216 (2003) 425.
[8] M.S. Chen, D.W. Goodman, Science 306 (2004) 252.
[9] N. Lopez, T.V.W. Janssens, B.S. Clausen, Y. Xu, M. Mavrikakis, T. Bligaard, J.K. Norskov, J. Catal. 223 (2004) 232.
[10] M.S. Chen, D.W. Goodman, Catal. Today 111 (2006) 22.
[11] M.M. Schubert, S. Hackenberg, A.C. van Veen, M. Muhler, V. Plzak, R.J. Behm, J. Catal. 197 (2001) 113.
[12] M. Khoudiakov, M.C. Gupta, S. Deevi, Appl. Catal. A 291 (2005) 151.
[13] M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma, M. Haruta, Catal. Lett. 51 (1998) 53.
[14] M.A.P. Dekkers, M.J. Lippits, B.E. Nieuwenhuys, Catal. Today 54 (1999) 381.
[15] S.H. Overbury, L. Ortiz-Soto, H. Zhu, B. Lee, M.D. Amiridis, S. Dai, Catal. Lett. 95 (2004) 99.
[16] J. Chou, N.R. Franklin, S.H. Baeck, T.F. Jaramillo, E.W. McFarland, Catal. Lett. 95 (2004) 107.
[17] K. Qian, Z.Q. Jiang, W.X. Huang, J. Mol. Catal. A 264 (2007) 26.
[18] H.G. Zhu, B. Lee, S. Dai, S.H. Overbury, Langmuir 19 (2003) 3974.
[19] G. Martra, L. Prati, C. Manfredotti, S. Biella, M. Rossi, S. Coluccia, J. Phys. Chem. B 107 (2003) 5453.
[20] R. Zanella, A. Sandoval, P. Santiago, V.A. Basiuk, J.M. Saniger, J. Phys. Chem. B 110 (2006) 8559.
[21] H.G. Zhu, C.D. Liang, W.F. Yan, S.H. Overbury, S. Dai, J. Phys. Chem. B 110 (2006) 10842.
[22] L. Guczi, K. Frey, A. Beck, G. Petõ, C.S. Daróczi, N. Kruse, S. Chenakin, Appl. Catal. A 291 (2005) 116.
[23] A.M. Venezia, F.L. Liotta, G. Pantaleo, A. Beck, A. Horváth, O. Geszti, A. Kocsonya, L. Guczi, Appl. Catal. A 310 (2006) 114.
[24] A. Horváth, A. Beck, A. Sárkány, G. Stefler, Z. Varga, O. Geszti, L. Tóth, L. Guczi, J. Phys. Chem. B 110 (2006) 15417.
[25] S.J. Lee, A. Gavriilidis, J. Catal. 206 (2002) 305.
[26] F. Moreau, G.C. Bond, A.O. Taylor, J. Catal. 231 (2005) 105.
[27] S. Ivanova, C. Petit, V. Pitchon, Appl. Catal. A 267 (2004) 191.
[28] D.C. Lim, I. Lopez-Salido, R. Dietsche, M. Bubek, Y.D. Kim, Angew. Chem. Int. Ed. 45 (2006) 2413.
[29] N.S. McIntyre, M.G. Cook, Anal. Chem. 47 (1975) 2208.
[30] R. Riva, H. Miessner, R. Vitali, G. Del Piero, Appl. Catal. A 196 (2000) 111.
[31] M. Voß, D. Borgmann, G. Wedler, J. Catal. 212 (2002) 10.