Formation of subsurface oxygen species and its high activity toward CO oxidation over silver catalysts

Zhenping Qu [1], Mojie Cheng, Weixin Huang [2], Xinhe Bao [*]

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Science, 457 Zhongshan Road, P.O. Box 110, Dalian 116023, P.R. China

Abstract

Silver is well known to show peculiar catalytic activities in several oxidation reactions. In the present paper, we investigate the catalytic activity of silver catalysts toward CO-selective oxidation in H_2. XRD, TEM, TPD, and in situ FTIR techniques were used to characterize the catalysts. The pretreatment of the catalysts was found to have great influence on their performance. The pretreatment in O_2 improves the activity of the silver catalyst, whereas He pretreatment at 700 °C or direct hydrogen pretreatment shows an inverse effect. Silver catalysts undergo massive structural change during oxygen pretreatment at high temperatures (> 500 °C), and there is solid evidence for the formation of subsurface oxygen species. The existence of this silver-subsurface oxygen structure facilitates the formation of active sites on silver catalysts for CO oxidation, which are related to the size, morphology, and exposed crystal planes of the silver particles. Its formation requires a certain temperature, and a higher pretreatment temperature with oxygen is required for the silver catalyst with a smaller particle size. It is observed, for the first time, that adsorbed CO on the surface of silver particles can directly react with subsurface oxygen species at low temperatures (e.g., RT), and the surface oxygen can migrate into and refill these subsurface sites after the consumption of subsurface oxygen by the reaction with CO. This finding provides a new reaction pathway for CO oxidation on silver catalyst.
© 2004 Published by Elsevier Inc.

Keywords: Silver; CO-selective oxidation; Subsurface oxygen; Migration

1. Introduction

Research interest in the catalytic oxidation of carbon monoxide has surged because of the possible uses for clean air, orbiting, closed-cycle CO_2 lasers, and other remote sensing applications [1–3]. Recently, the preferential oxidation of CO in H_2 has been studied for applications in polymer electrolyte-type fuel cells (PEFCs) to reduce the CO concentration in the produced fuel gases down to 10 ppm to prevent the fuel cell electrodes from being poisoned [4,5]. The outstanding catalytic activities of Pt, Rh, and Au are widely recognized [6–11]. A high activity for CO oxidation at higher reaction temperatures (150–250 °C) can be obtained on Pt catalysts; however, the competitive adsorption of CO and O_2 decreases the low-temperature activity of the catalysts [8,10]. The reaction mechanism has also been extensively investigated over these catalysts [10,11]. For instance, a dominant reaction pathway proposed for Au catalysts supported on reducible transition metal oxides involved the adsorption of a mobile, molecular oxygen species on the support, dissociation at the interface (or lattice oxygen, which is produced by the adsorption of oxygen followed by dissociation immediately on the support), and reaction with CO adsorbed on the gold at the interface and/or on the gold particles after oxygen spillover onto the gold metal [9,10].

[*] Corresponding author. Fax: +86 411 84694447.
 E-mail address: xhbao@ms.dicp.ac.cn (X. Bao).
 [1] Present address: Institute of Physical Chemistry, University of Stuttgart, 70569 Stuttgart, Germany.
 [2] Present address: Department of Chemical Physics, University of Science and Technology of China, Hefei, 230026, China.
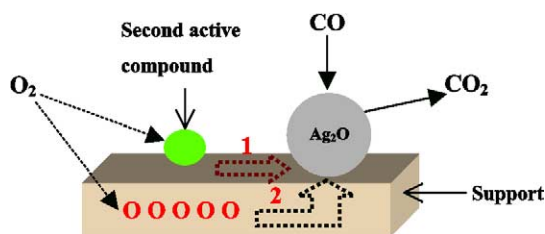
Scheme 1. Possible reaction schemes for the CO oxidation over supported silver catalysts (Ag (or Co, Mn)/Co, Mn oxides).

However, silver has rarely been considered as the catalyst for CO-selective oxidation, although it has been recognized to show a high activity in several partial oxidation reactions, such as ethylene epoxidation, formaldehyde synthesis, etc. [12,13]. Only relatively low activity of CO oxidation was observed over silver catalysts, and usually Ag_2O was considered to be the active species for CO oxidation. It is known that Ag_2O consumed by the reaction with CO is difficult to re-oxidize, and only the addition of a second active compound ((1): Co or Mn) or the use of reactive support (2) can increase the activity of the silver catalyst by the oxygen spillover from the second compound or reactive support onto the silver catalyst, as shown in Scheme 1 [14–16].

The interactions of silver with oxygen (e.g., the mechanism of oxygen activation, oxygen-induced reconstruction, and the incorporation of oxygen in the silver bulk) have been extensively studied in order to understand the catalytic behavior of silver catalysts. Various oxygen species were found on silver catalyst, for instance, the molecular, subsurface, and various forms of surface atomic oxygen [17–19]. The formation of subsurface oxygen (O_γ) was considered necessary for the activation of the silver catalysts for ethylene epoxidation and formaldehyde synthesis. Surface-bound atomic oxygen (O_α) preferentially led to the formation of complete oxidation products. The increase of the ratio of O_γ/O_α on the silver surface would result in an increase in direct dehydrogenation via the oxi-dehydrogenation pathway [20,21]. More recent studies have shown that the Ag–O interaction involving the formation of subsurface oxygen species exerts an important influence on the surface structure and, eventually, the catalytic properties of silver catalysts [22–24].

In this paper, we study the performance of Ag/SiO_2 catalysts for the selective oxidation of CO in a gas mixture (1% CO, 0.5% O_2, H_2 balance) simulating an effluent of the fuel processing and the influence of the pretreatment conditions on the catalytic activity. The formation of subsurface oxygen is found to be critical for enhancing the activity of the silver catalyst toward CO-selective oxidation.

2. Experimental

We prepared the Ag/SiO_2 catalysts by impregnating SiO_2 granules (20–40 mesh, 495 m^2/g) with an aqueous solution of silver nitrate, followed by drying at 120 °C for 12 h.

The Ag/SiO_2 catalysts were pretreated under different atmospheres at various temperatures before testing.

X-ray diffraction (XRD) measurements were made with a Rigaku D/max-rb X-ray diffractometer with a Cu-K_α X-ray source operating at 40 kV and 100 mA. The average crystallite size of silver was calculated with the Scherrer equation, $d = 0.89\lambda/B^* \cos\theta$ with Warren's correction ($B = B_M^2 - B_I^2)^{1/2}$, where B_M is the measured linewidth and B_I is the instrumental broadening. Transmission electron microscope (TEM) images were obtained with a JEOL 2011 transmission electron microscope with selected area electron diffraction (SAED), at an electron energy of 200 kV. The sample was dispersed in absolute alcohol with an ultrasonic bath and deposited on a Formvar-coated 200-mesh Cu grid for measurement. Temperature-programmed desorption (TPD) and temperature-programmed surface reaction (TPSR) experiments were carried out in a setup coupled with a quadrupole mass spectrometer. Before experiments, the catalyst was pretreated under different atmospheres and then cooled under He to room temperature (RT). CO adsorption was done at RT.

IR characterization was performed on a Fourier transform infrared spectrometer (Nicolet Impact 410) with a resolution of 4 cm^{-1} and 64 scans in the region of 4000–1000 cm^{-1}. The Ag/SiO_2 sample was pressed into a self-supporting wafer with a density of approximately 15 mg/cm^2. The wafer was placed in a quartz IR cell equipped with CaF_2 windows, in which the catalyst was pretreated in situ at different temperatures. The pretreated sample was evacuated to 10^{-5} Torr at the pretreatment temperature for 1 h, subsequently cooled to -120 °C, then exposed to about 20 Torr CO. The spectrum of the samples before adsorption was subtracted from all spectra.

The catalytic activity of Ag/SiO_2 for selective CO oxidation was evaluated with a fixed-bed flow reactor (shown in Fig. 1). A gas mixture containing 1% CO, 0.5% O_2 (volume ratio), and H_2 for the balance was fed at a rate of 50 ml/min. The composition of the effluent gas was monitored with an on-line GC-14B gas chromatograph equipped with a Molsieve 5 Å column and a Porapak Q column ($T = 30$ °C, helium as the carrier gas at 30 ml/min). The conversions of CO, oxygen, and the selectivity toward CO oxidation were calculated by a previously described method [25,26]. The CO conversion was calculated from the change in CO concentration, and selectivity toward CO oxidation was calculated from the oxygen mass balance.

3. Results and discussion

3.1. Effects of oxygen pretreatment at high temperatures

3.1.1. Activity test

During the course of our experiments, we find that the silver catalyst deactivates significantly after a direct pretreatment with H_2 at 500 °C for 2 h, whereas the treatment with
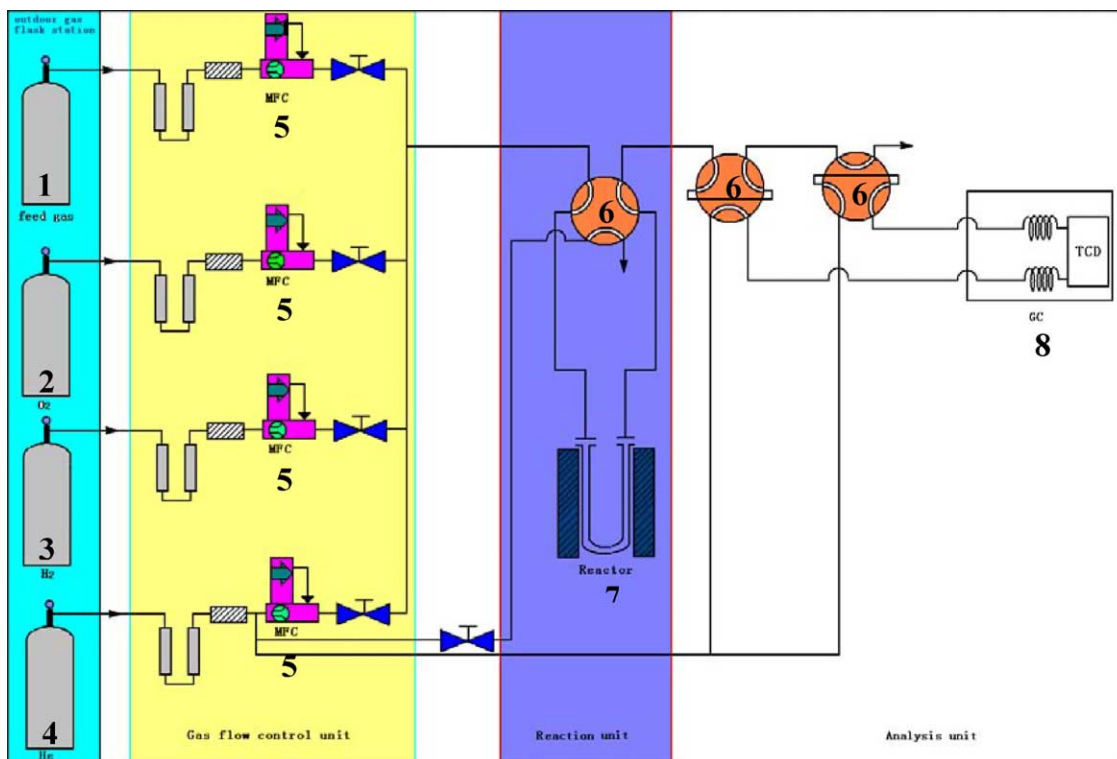
Fig. 1. Catalytic reaction system of micro-fixed bed. 1: feed gas; 2: O_2; 3: H_2; 4: He; 5: mass flow controllers; 6: six-way valve; 7: reactor; 8: gas chromatogram.
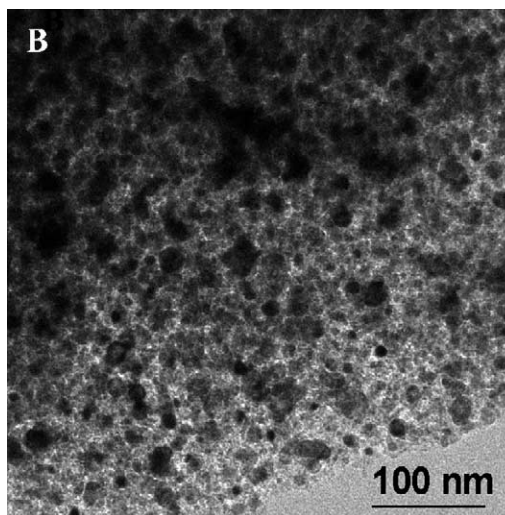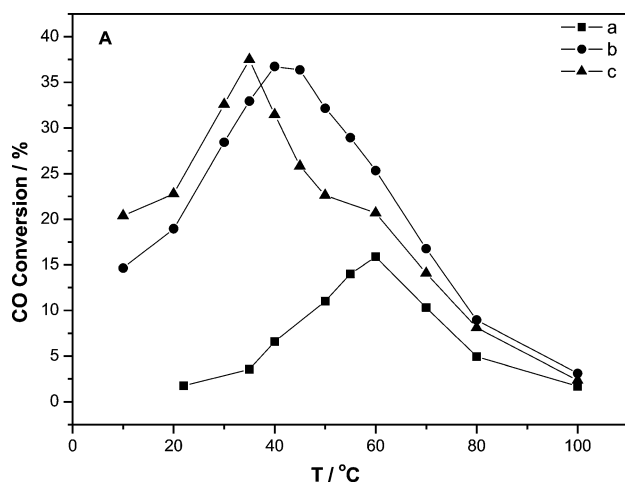

Fig. 2. (A): CO conversion as a function of the reaction temperature over Ag/SiO_2 pretreated directly treatment with H_2 at 500 °C for 2 h (a), then followed by oxygen pretreatment O_2 at 500 °C for 1 h (b), and direct pretreatment with O_2 at 500 °C for 2 h (c). (B): TEM picture of Ag/SiO_2 pretreated with H_2 at 500 °C.

oxygen (> 400 °C) (re)activates the catalyst, as shown in Fig. 2A. It can be seen from the TEM image (Fig. 2B) that silver particles do not sinter after H_2 pretreatment. It has been known that the thermal stability of the silver particles is significantly lower under oxidizing conditions, and heating at higher temperatures under oxidizing conditions will induce the migration of the silver particles [27,28]. A high catalytic activity has also been found on a physical mixture of Ag with silica powder after oxygen activation at higher temperatures [26]. These results imply that the interaction between silver and oxygen may play a crucial role in the catalytic activity of Ag/SiO_2 catalyst. The influence of the various pretreatment conditions can be further understood by the reaction performance on the catalyst pretreated with O_2 and He at 500 °C and 700 °C, respectively. The maximum conversion of CO at 35 °C on these catalysts is shown in Fig. 3. A similar value of CO conversion is obtained after pretreatment in He and O_2 at 500 °C. Increasing the pre-
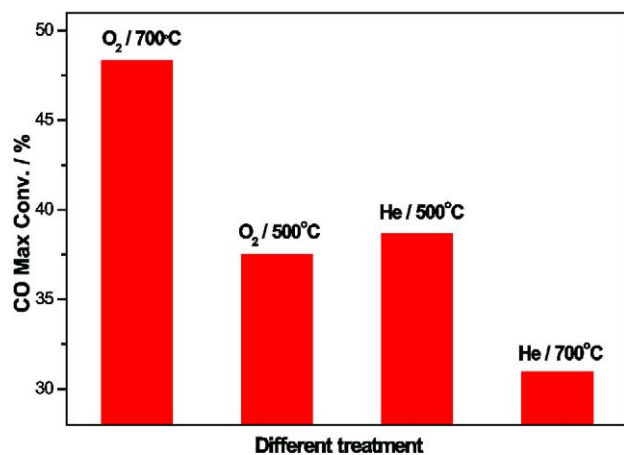
Fig. 3. Conversion of CO in excess H_2 at 35 °C over Ag/SiO$_2$ pretreated with various conditions.

treatment temperature to 700 °C with oxygen significantly increases the catalytic activity. However, the catalytic activity is greatly depressed after pretreatment in He at 700 °C. Obviously the pretreatment atmospheres greatly influence the activity of silver catalysts.

3.1.2. Catalyst characterization

Fig. 4A shows the XRD patterns of the Ag/SiO$_2$ catalysts after O$_2$ and He pretreatments at 500 °C and 700 °C, respectively. The Ag(111) surface is the main crystallographic plane on all samples. The Ag$_2$O species appears after the AgNO$_3$/SiO$_2$ catalyst is pretreated with oxygen at 500 °C. After the silver catalyst is pretreated with O$_2$ and He at 700 °C, most silver species are in the metallic state, and the silver diffraction peak at 38.2° obviously intensifies. Calculated from the half-width of the silver peak from the XRD pattern, the particle size increases from about 17 to 22 nm after pretreatment at 700 °C. TEM images in Fig. 4B show similar results. The silver particles obviously aggregated to form larger ones after O$_2$ or He pretreatment at 700 °C.

O$_2$-TPD experiments were used to study the interaction of the silver particles with oxygen and distinguish various oxygen species. Two oxygen desorption peaks appear in the TPD spectrum for the catalyst pretreated with oxygen at 500 °C (curve b in Fig. 5). The peak at the lower temperature is assigned to the desorption of the bulk-oxygen species (O$_\beta$), which diffuses via an interstitial diffusion mechanism [19,21,29]. In this case O$_\beta$ atoms jump from one interstitial site to another between the silver lattice atoms. The desorption peak at higher temperatures is attributed to subsurface oxygen (O$_\gamma$) that diffuses via an interstitial diffusion mechanism in which the subsurface oxygen atoms substitute for silver lattice atoms [19,21,30]. Oxygen pretreatment at higher temperatures (> 500 °C) enhances the formation of subsurface oxygen species, and no other oxygen species desorption but O$_\gamma$ is observed from the catalyst pretreated with oxygen at 700 °C. The O$_2$-TPD of silver catalysts pretreated with He at 500 °C (curve c in Fig. 5) is similar to that of catalyst pretreated with oxygen at 500 °C, but the oxygen desorption
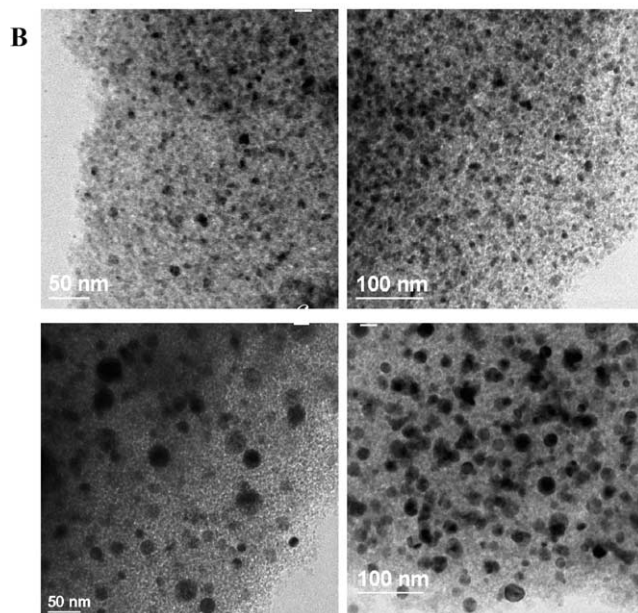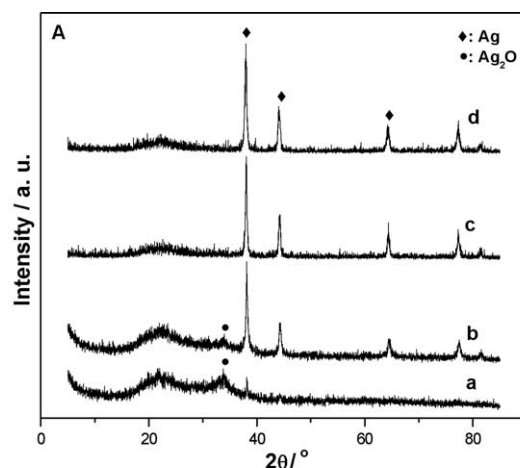

Fig. 4. XRD patterns (A) and TEM pictures (B) of silver catalysts pretreated with O$_2$ (a,c) and He (b,d) at 500 °C and 700 °C, respectively.
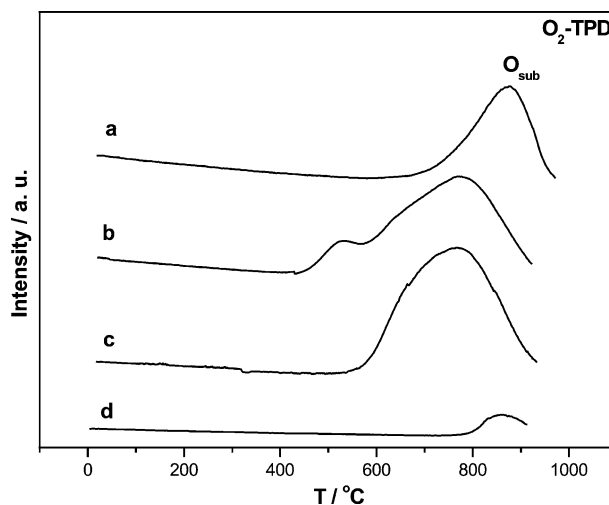

Fig. 5. O$_2$-TPD spectra of Ag/SiO$_2$ catalysts pretreated with O$_2$ at 700 (a) and 500 °C (b), and with He at 500 (c) and 700 °C (d).
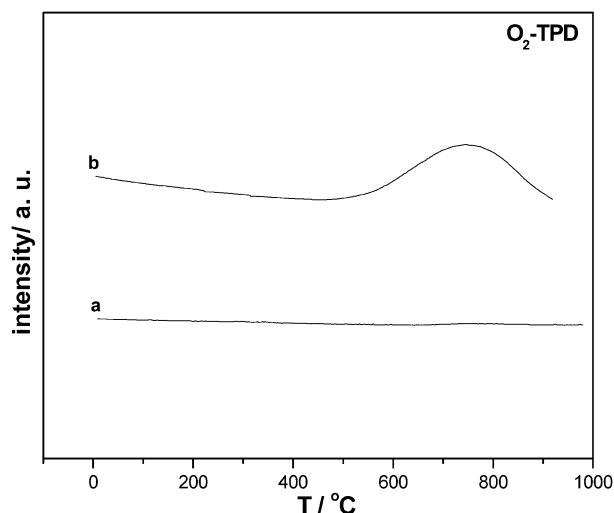
Fig. 6. O_2-TPD spectra of Ag/SiO$_2$ catalysts pretreated with H$_2$ at 500 °C (a), and followed by O$_2$ treatment at 500 °C (b).

Fig. 7. CO oxidation activity of silver catalysts with different silver loadings after hydrogen and oxygen pretreatment at various temperatures.

peak attenuates greatly after pretreatment in He at 700 °C (curve d in Fig. 5). A comparison of the reaction results (Fig. 3) and the O$_2$-TPD results (Fig. 5) clearly shows that subsurface oxygen plays an important role in CO oxidation over silver catalysts. The more subsurface oxygen species the catalyst has, the higher the catalytic activity it shows. A similar phenomenon is observed on the silver catalyst pretreated with H$_2$ at 500 °C followed by oxygen pretreatment, as shown in Fig. 6. No desorption of subsurface oxygen can be observed from the catalyst pretreated with H$_2$ at 500 °C (curve a in Fig. 6), but it appeared after the catalyst was pretreated with oxygen following H$_2$ pretreatment (curve b in Fig. 6). This observation is consistent with the reaction result that the oxygen pretreatment at high temperature can reactivate the catalyst (Fig. 2A).

3.2. Formation of subsurface oxygen species

A crystalline substance such as silver will be restricted in the formation of minimum-energy crystal structures during pretreatment [30]. Thus the silver catalyst is allowed to undergo pronounced morphological and structural changes after high-temperature treatments in various atmospheres in order to obtain the structure that is most thermodynamically favorable. These changes in morphology may be either thermally induced or reaction-induced [31]. Purely thermal-induced changes (e.g., particle size) can occur in the presence or the absence of a reacting atmosphere. Mass transport of silver atoms becomes significant at temperatures above 369 °C, the Tammann temperature of silver (calculated as $0.52T_m$, where T_m is the melting temperature of silver). Our results (Fig. 4) indicate the formation of larger silver particles on the surface of SiO$_2$ after pretreatment with O$_2$ or He at high temperatures, which reduces the surface free energy. Reaction-induced morphological changes take place in the presence of a reacting atmosphere, which results in the formation of a structure different from those formed after
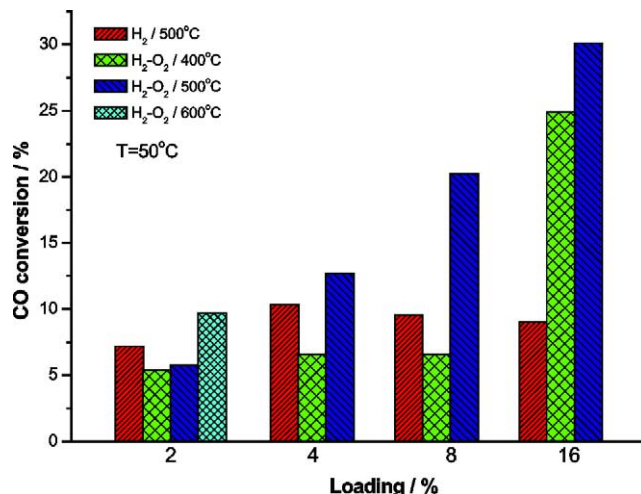
treatment in inert gas or vacuum [31,32]. Nagy et al. reported that the high-temperature treatment in oxygen led to faceting of the silver surface, as indicated by SEM analysis [30]. Waterhouse et al. also investigated oxygen chemisorption on an electrolytic silver catalyst pretreated with oxygen [33]. Oxygen diffusivity in silver increases exponentially with temperature and becomes significant at temperatures above 500 °C. Thus oxygen can be incorporated into the bulk lattice of silver when the lattice is treated with oxygen at high temperatures. And this process is usually accompanied by catalyst restructuring to form crystal facets. In other words, facet formation is observed only in the presence of oxygen and occurs at reasonable rates at temperatures above 500 °C [21,31,34]. Therefore, it is reasonable that during our experiments, the pretreatment of silver catalysts with oxygen at about atmospheric pressure and at high temperatures not only leads to the formation of a very tightly bound species, namely, the subsurface oxygen species, but also results in the faceting of silver particles, whose structure shows particularly high activity toward CO oxidation. This active structure of silver catalyst formed by oxygen–silver interaction cannot be acquired by merely thermal pretreatment, such as He pretreatment at 700 °C. Thus we attribute the higher activity of the silver catalyst pretreated with oxygen at high temperature (> 500 °C) to the surface restructuring and formation of subsurface oxygen species.

To further understand the formation of subsurface oxygen species and its effects on the silver catalyst, the catalytic activities of silver catalysts with different loadings (percentage weight ratio of silver deposited in the SiO$_2$ support) after pretreatment with hydrogen and followed by oxygen treatment at different temperatures were tested; the results of CO oxidation activities at 50 °C are shown in Fig. 7. All silver catalysts behave similarly after direct hydrogen pretreatment by showing quite low activity. However, different catalytic behaviors are observed after pretreatment with oxygen at different temperatures on these directly hydrogen-pretreated
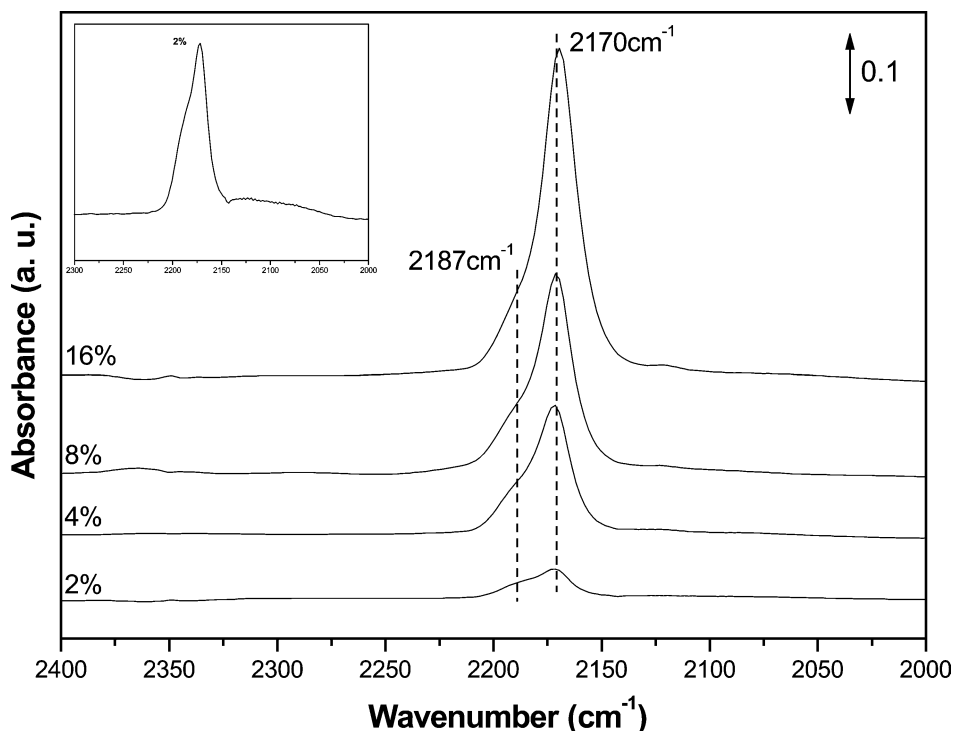
Fig. 8. FTIR spectra of CO adsorbed at $-120\,^{\circ}$C on silver catalysts with different loadings pretreated with H_2 followed by oxygen at $500\,^{\circ}$C. Inset: the catalyst with 2% silver loading.

silver catalysts. A different treatment temperature is required for the silver catalysts to show a high activity. A relatively high activity can easily be obtained on a silver catalyst with 16% silver loading after a subsequent oxygen treatment at $400\,^{\circ}$C. Only after the treatment temperature is increased to $500\,^{\circ}$C does silver catalyst with a loading of 4 or 8% show a higher activity than that pretreated with hydrogen. And to obtain a relatively better activity for 2% silver catalyst, treatment with oxygen at temperatures higher than $600\,^{\circ}$C is indispensable. Thus different activation temperatures are required for the silver catalysts with different loadings pretreated with oxygen to form active structures. This observation can be reasonably associated with the particle size and the morphology of these silver catalysts with different silver loadings.

The IR technique is very useful for probing the geometry of chemisorption sites on transitional metals. CO usually serves as the probe molecule because adsorbed CO exhibits a high extinction coefficient in infrared spectroscopy. Thus we studied CO adsorption on the silver catalysts with IR in order to understand the influence of pretreatment on the nature of adsorption sites. Fig. 8 shows the IR spectra of CO adsorbed to silver catalysts with different loadings. All silver catalysts were treated with oxygen at $500\,^{\circ}$C after hydrogen pretreatment. Exposure of CO (20 Torr) to the activated Ag/SiO$_2$ catalyst results in the appearance of a vibrational band at 2170 cm^{-1} with a higher frequency shoulder at 2187 cm^{-1}. Both bands are assigned to the linearly adsorbed Ag$^+$–CO species [35,36], but the properties of related silver sites are different. The peak intensity increases with

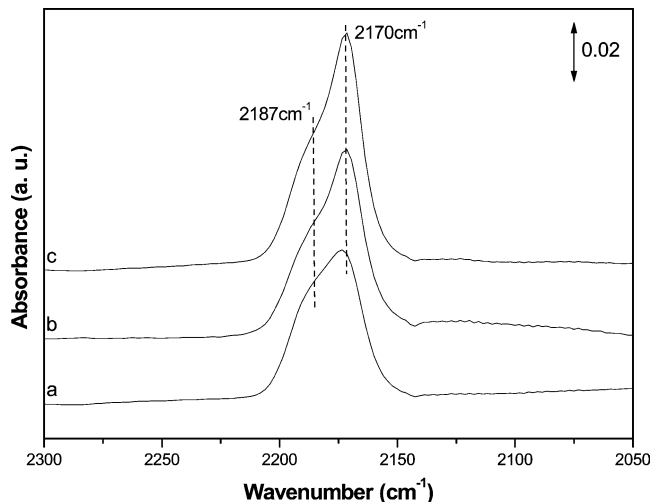Fig. 9. FTIR spectra of CO adsorbed at $-120\,^{\circ}$C over 2% Ag/SiO$_2$ catalysts pretreated with H_2 at $500\,^{\circ}$C followed by oxygen at 400 (a), 500 (b), and $600\,^{\circ}$C (c).

silver loading, which is consistent with the reaction result (Fig. 7) that higher activity is obtained on the silver catalyst with higher loading. It is interesting that the intensity ratio $I(2170$ cm$^{-1})/I(2187$ cm$^{-1})$ of adsorbed CO varies with the silver loading. With increasing silver loading, the ratio $I(2170$ cm$^{-1})/I(2187$ cm$^{-1})$ increases. Fig. 9 shows the IR spectra of the 2% silver catalyst pretreated with oxygen at different temperatures (400–600 °C). It is found that both the ratio $I(2170$ cm$^{-1})/I(2187$ cm$^{-1})$ and the overall peak intensity increase with the temperature of oxygen
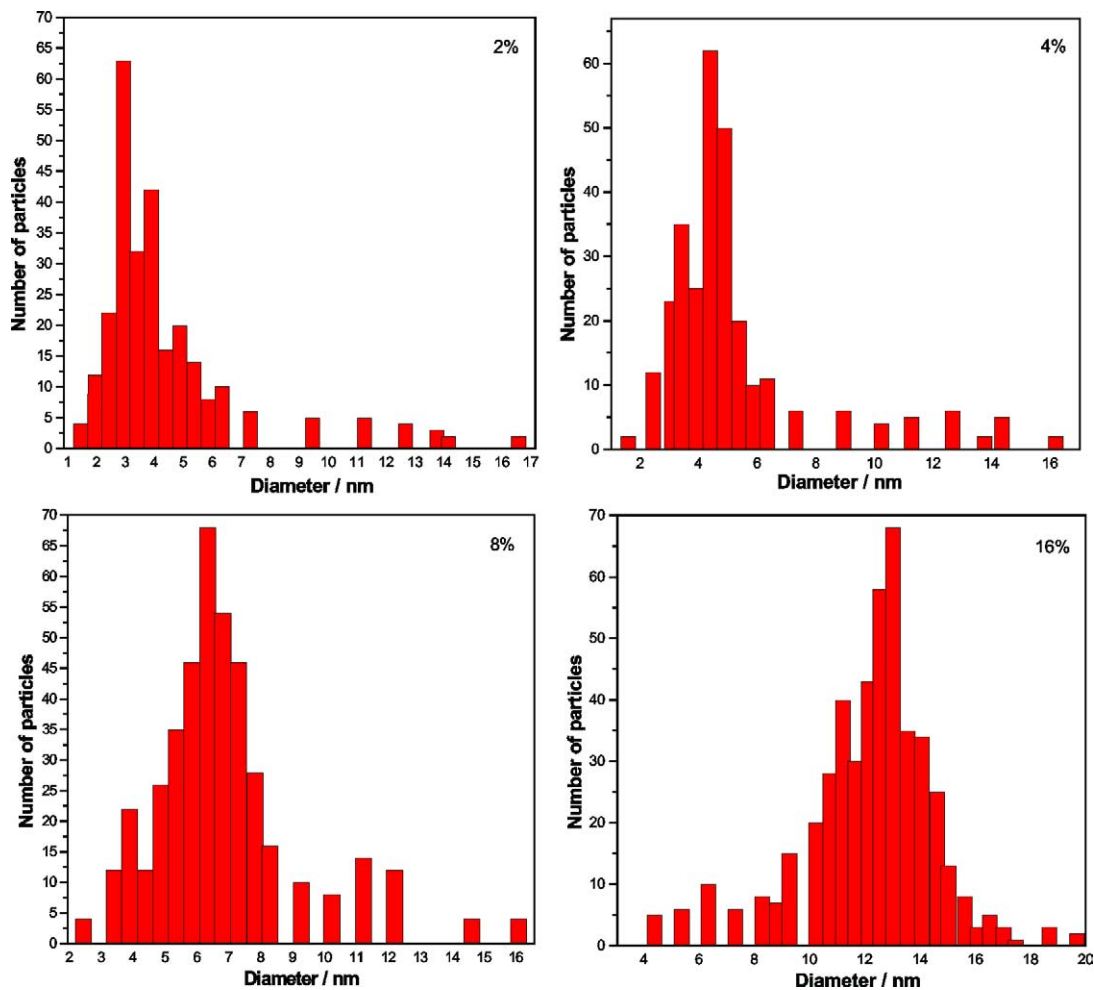
Fig. 10. Size distributions of silver particles on silver catalysts with different loadings.

pretreatment. It has been shown that larger silver particles tend to form on the silver catalyst with higher loading [25]. TEM observations were made on these catalysts with different silver loadings to obtain the distributions of particle size (Fig. 10). The results clearly show that particles with larger size form over the silver catalyst with high loading. Moreover, it is also observed that the particle size increases after the 2% silver catalyst is pretreated with oxygen at 600 °C. Thus we believe that the two observed CO vibrational bands should be related to CO adsorbed on silver particles with different particle sizes instead of CO adsorbed on different silver sites. And the variation of the intensities of these two bands actually reflects the size distribution of the silver particles. It has been known that the oxygen treatment at high temperatures will result in the surface restructuring of silver particles and the formation of the subsurface oxygen species. Here we refer to the silver catalyst with subsurface oxygen species as a special silver–oxygen compound, which is active toward CO oxidation. Reports of strongly adsorbed subsurface oxygen species associated with silver catalysts are prevalent in the literature; evidence indicates that large silver particles favor the formation of subsurface oxygen, and

oxygen can remain occluded in large silver particles after prolonged evacuation at 500 °C [37]. Therefore small silver particles have to aggregate into large ones before the formation of the special silver–oxygen compound. This is why a higher oxygen pretreatment temperature is required for the silver catalyst with low loading, which displays a smaller silver particle size. The above results suggest that the oxygen treatment at high temperatures can cause the silver particles to aggregate into larger ones, which favors the formation of a silver–oxygen active compound for CO oxidation. Moreover, from a comparison of the IR spectra with the corresponding reaction results, it can be inferred that the Ag^+–O compound responsible for adsorbed CO with a vibrational band at 2170 cm^{-1} in the silver catalyst is possibly more active for CO oxidation.

3.3. Adsorption and activation of reactants on silver catalyst

3.3.1. CO-TPD and IR spectra of CO adsorption

It is well known that CO oxidation follows the Langmuir–Hinshelwood mechanism, in that both CO and O_2 adsorb

Table 1
The integrated peak area and the temperature of maximum desorption rate of CO desorption trace from the Ag/SiO$_2$ catalysts pretreated under various conditions

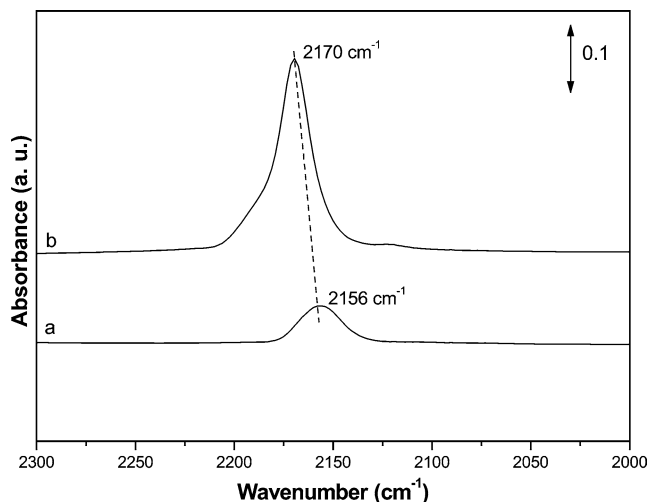|	Area (E-11)	T (°C)
He/500 °C	9.31	63.65
O$_2$/500 °C	9.15	63.93
He/700 °C	6.17	70.99
O$_2$/700 °C	10.01	61.03
H$_2$/500 °C	–	–
H$_2$–O$_2$/500 °C	9.02	65.03

Fig. 11. FTIR spectra of CO adsorbed at −120 °C on Ag/SiO$_2$ catalysts pretreated with O$_2$ at 500 °C followed by H$_2$ at 500 °C (a), and again treatment with O$_2$ at 500 °C (b).

to the catalyst surface before surface reaction [38]. Therefore, it is essential to study the adsorption of the reactants over the silver catalyst. The catalysts were pretreated with the same procedure as in O$_2$-TPD experiments, and then CO adsorption was carried out at RT for 1 h. The amounts of desorption of CO achieved with various catalysts are summarized in Table 1. Oxygen pretreatment at 700 °C results in the adsorption of more CO and the shifting of the desorption peak to a lower temperature. The silver catalyst directly pretreated with hydrogen shows no CO desorption peak, but reactivation of this catalyst by the following oxygen treatment increases its capacity for CO adsorption.

The enhancement of the effect of oxygen treatment on CO adsorption on the silver catalysts was also observed by IR. Fig. 11 presents the IR spectra after CO exposure to an oxygen-pretreated silver catalyst followed by hydrogen treatment (curve a), and then oxygen treatment (curve b). The catalyst was first pretreated with oxygen before hydrogen treatment at 500 °C because no CO adsorption was observed on the catalyst directly treated with hydrogen. It is found that the vibrational frequency of adsorbed CO shifts from 2156 cm^{-1} for the hydrogen-treated catalyst upward to 2170 cm^{-1} after oxygen treatment at 500 °C. The bonding of CO with transitional metals usually involves both the bond-

ing σ orbital and the anti-bonding π orbital of CO, although the bonding of CO to the silver surface is dominated by the σ orbital and electron donation from CO to the metal is more favorable [39]. The above results have confirmed that subsurface oxygen species forms on the silver catalysts pretreated with oxygen at high temperatures. The presence of the subsurface oxygen near the silver decreases the electron density on the silver, and therefore the back-donation from the silver to the anti-bonding π orbital of CO is decreased, resulting in a consequent insignificant increase in the CO frequency. Obviously, the vibrational peak of CO adsorbed to an oxygen-treated sample is remarkably more intense than that treated with hydrogen. Similar conclusions can also be drawn on the basis of Fig. 9, which shows that the capacity of 2% silver catalyst for CO adsorption increases with increasing oxygen treatment temperature.

The chemisorption property of the silver surface has been studied in great detail. Albers et al. found that the (111) surface of silver, the most stable crystallographic plane in silver particles, did not adsorb oxygen at all if it was free of defects [40]. Lambert et al. and Rovida et al. observed that high oxygen pressures and/or alkali-metal promoters were required to realize the adsorption of a sufficient amount of oxygen on Ag(111) [41,42]. The infrared spectroscopic results showed that no CO adsorption took place on bare silver metal [43,44]. And Krylov found it was impossible to oxidize CO on a pure silver film prepared by vapor deposition, even at elevated temperatures [45]. However, it is already known that surface morphology has a great influence on the chemisorptive properties of silver catalysts, and chemisorption on silver is sensitive to the catalyst morphology and the pretreatment history of the catalyst [33,46]. Tan et al. proposed that oxygen located very near the surface could change the adsorption properties of surface silver atoms [47]. Rocca et al. have found that the subsurface oxygen species affects the catalytic properties of the silver surface, and that CO adsorption can be stabilized up to crystal temperatures of 160 K under ultrahigh vacuum conditions [23]. Our IR results also show that CO can adsorb to an ionic silver species, Ag$^+$, after the silver catalyst is pretreated with oxygen.

Identification of active sites where adsorption and reaction occur preferentially is very important for the catalytic reaction. Defects such as steps, kinks, and vacancies are some examples of active sites [48]. The dissociation of NO on Ru(0001) takes place only at atomic step sites [49], and monoatomic steps can bind adsorbates more strongly [50]. High-temperature calcinations in oxygen induce the faceting of the silver surface to higher index planes with lower average coordination numbers, which have a more open surface structure and thus facilitate the formation of the subsurface oxygen species. Crystalline planes with a high index are usually composed of terraces, steps, and kinks, the latter two of which demonstrate a greater capacity to adsorb reactant. Meanwhile, the formation of subsurface oxygen after oxygen pretreatment at high temperatures also enhances the
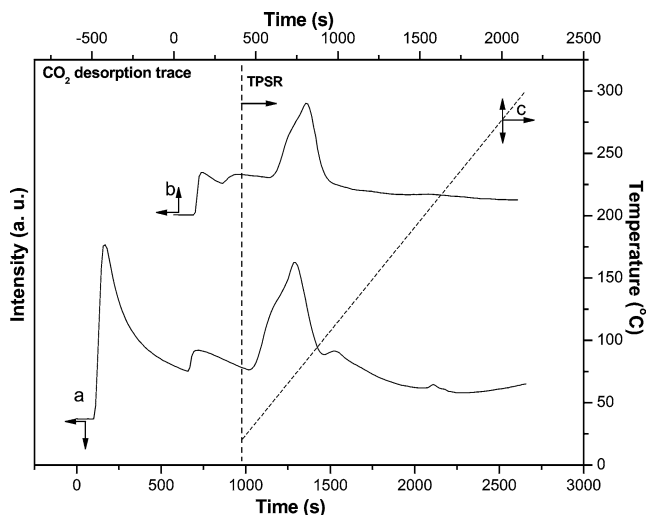
Fig. 12. CO_2 desorption trace during CO-TPSR experiments over silver catalyst pretreated with oxygen (a), and hydrogen (b) at 500 °C, and the dot line (c) shows sample temperature.

Scheme 2. Reactions of silver oxygen complexes with carbon monoxide in a solid inert gas matrix [52,53].

adsorption ability of the silver surface. Therefore CO is more prone to adsorption on the surface of silver particles with the subsurface oxygen species.

3.3.2. CO-TPSR (temperature-programmed surface reaction)

No activity was observed at low temperatures over Ag_2O/SiO_2 catalysts prepared by precipitation in our experiments. Only the addition of a second active compound or the use of a reactive support can increase the activity of the silver catalyst by the oxygen spillover from the second compound or reactive support to the silver catalyst [14–16]. However, our results show that a high activity to CO oxidation can be obtained after the precipitated catalyst is pretreated under oxygen at high temperatures. Fig. 12 shows the desorption trace of CO_2 during the CO-TPSR experiments over the silver catalyst pretreated with hydrogen and oxygen at 500 °C. After pretreatment, the silver catalyst was exposed to oxygen at RT before the CO-TPSR experiment, and CO exposure was conducted at 10 °C. The temperature ramping began from 21 °C. Obvious CO_2 formation is only observed during the course of temperature ramping for the catalyst pretreated by hydrogen, but after the silver catalyst is pretreated with oxygen, the reaction temperature for CO oxidation shifts to a lower temperature and the amount of formed CO_2 increases remarkably. Moreover, besides CO_2 formation during the course of temperature ramping, a large amount of CO_2 forms at the temperature when CO is dosed. This observation is consistent with the results of the reaction test. These results indicate that more active [O] species are formed on the silver catalyst pretreated with oxygen. We believe that the special Ag–O compound (silver catalyst with subsurface oxygen species) formed by oxygen pretreatment is more active for CO oxidation.
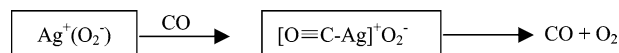
The formation of a suitable redox cycle over the surface of the catalyst is a key to obtain a high activity for CO oxidation. A high activity for CO oxidation was obtained over Au catalysts supported on reducible transition-metal oxides, in which the redox cycle is formed via the spillover of reactive oxygen from the support to gold [51]. However, the case for Ag/SiO_2 catalysts is different from a Au catalyst supported on reducible supports. As we know, SiO_2 is an inert support, and it does not adsorb CO and O_2. Therefore no oxygen spillover can take place from SiO_2 to silver, and the redox cycle of CO oxidation over the Ag/SiO_2 catalyst can occur only on the silver surface. Ag_2O was usually considered to be the active site for CO oxidation [14–16]. McIntosh and Ozin examined the reaction of silver atoms with oxygen and found that colorless $Ag^+(O_2)$ formed on the silver catalyst [52,53], which can react with CO by following the pathway shown in Scheme 2.

In our reaction system, a high activity for CO oxidation can be obtained only on the silver catalyst pretreated with oxygen at higher temperatures. Thus the resulting catalyst surface must faciliate the adsorption and activation of reactants. Many experimental and theoretical results clearly indicate that steps, kinks, and other surface imperfections play a crucial role in the surface chemistry and the activation of oxygen species. Recently Savio et al. demonstrated that the step edges present on high-index Ag surfaces are active toward O_2 dissociation and open pathways to subsurface sites [54,55]. Furthermore, theoretical calculations showed O_2 dissociation is favored on the reduced oxide surface, with a barrier of 0.40 eV as opposed to 0.64 eV on clean Ag(111) [56]. The formation of these O–Ag–O chains at step edges significantly affect both the geometrical structure and the electronic properties of the surface [57], and more active O species form through dynamic formation by thermal structural fluctuation [58]. In these processes, some oxygen atoms end up in subsurface sites. These subsurface oxygen species may either be the only reactive species or significantly affect the reactivity of surface species. It has been proposed that the interaction of oxygen with transition-metal catalysts can serve to tune the O–metal bond strength for optimum reactivity through the formation of various oxidelike species, and such atomic oxygen species actuate the reaction [24]. In the present research, oxygen pretreatment of silver catalyst at high temperatures results in surface restructuring and the formation of subsurface oxygen species. The formed silver compound with subsurface oxygen species is clearly more active for CO oxidation, for example, CO adsorption and oxygen activation. Therefore our results confirm that the formation of subsurface oxygen produces the sites on silver catalysts that are active for CO oxidation.
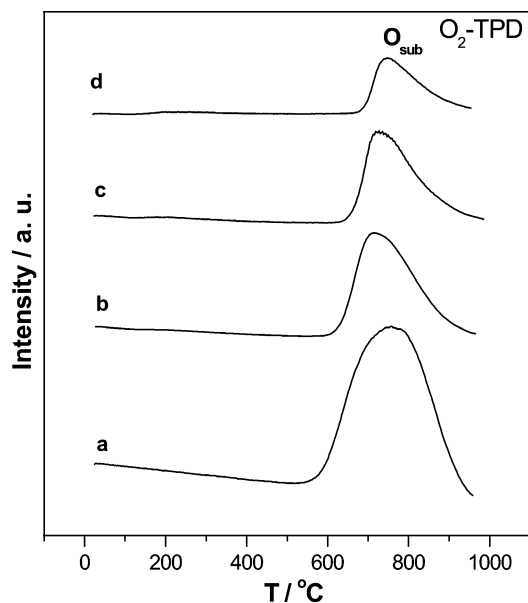
Fig. 13. O_2-TPD spectra of Ag/SiO$_2$ catalysts after pretreatment (a), and that followed by CO adsorption at RT for 1 (b), 2 (c), and 3 h (d).

3.4. Reaction of CO with subsurface oxygen species

The subsurface oxygen species (O_γ) has been considered indispensable for the activation of silver catalysts for formaldehyde synthesis from methanol. The activation temperature of the formation of subsurface oxygen is above 600 °C. In our case we observed, for the first time, that CO can react with subsurface oxygen species at RT. Fig. 13 shows the O_2 desorption trace after CO adsorption experiments were carried out on the silver catalyst at RT. The desorption trace is dominated by subsurface oxygen for the catalyst after pretreatment (curve a, Fig. 13). The amount of subsurface oxygen decreases with increasing CO exposure at RT, as shown by curves b–d in Fig. 13. Moreover, desorption of CO_2 was observed during CO adsorption at RT. These results indicate that CO can react with subsurface oxygen species on a silver catalyst to produce CO_2 at RT, which causes the observed attenuation of the desorption peak of subsurface oxygen from the catalyst.

Fig. 14 presents O_2-TPD spectra of the silver catalysts after pretreatment, followed by 1 h of CO adsorption, and finally followed by 1 h of O_2 adsorption at RT. The silver
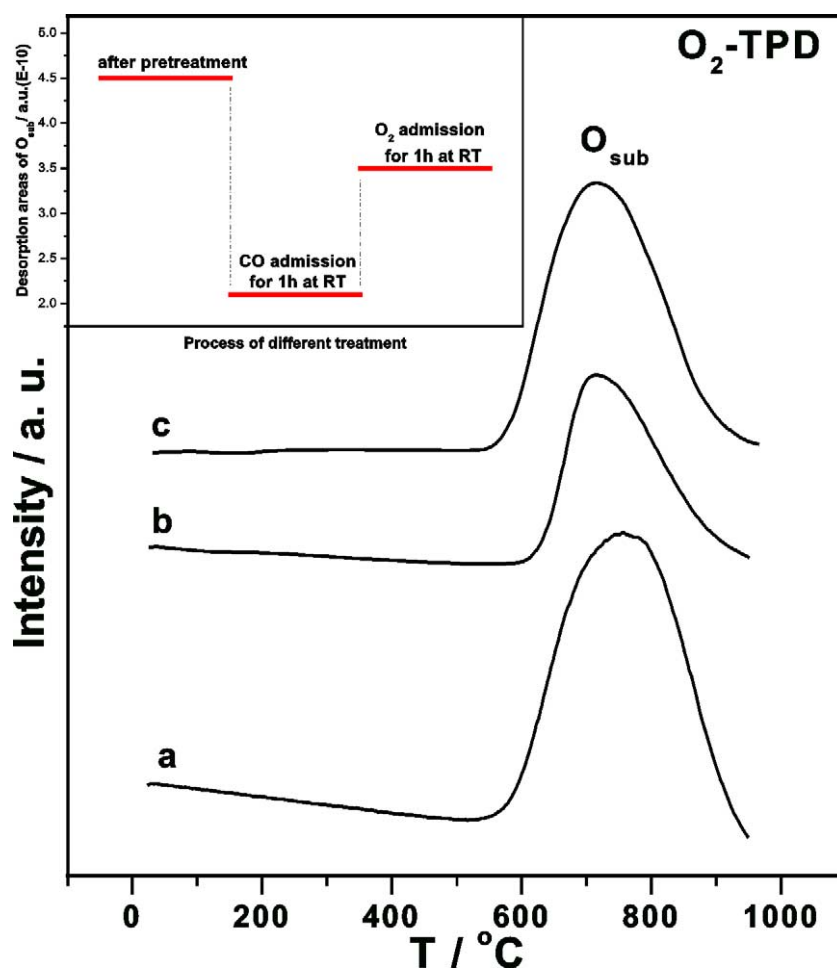

Fig. 14. O_2-TPD spectra of the silver catalysts after pretreatment (a), that followed by CO adsorption at RT for 1 h (b), and then followed by O_2 adsorption at RT for 1 h (c). Inset: the integrated desorption peak area of subsurface oxygen from the catalysts after different pretreatments.

catalyst was exposed to CO for 1 h at room temperature, followed by treatment under flowing He to eliminate the gaseous CO. Then the oxygen exposure was carried out. Interestingly, the level of desorption of subsurface oxygen from the catalyst increases after oxygen exposure at RT, whereas no desorption of surface atomic oxygen is observed. The inset in Fig. 14 shows the integration of the desorption peak of the subsurface oxygen species from the silver catalyst under different conditions. These results clearly demonstrate that the subsurface oxygen species on the Ag/SiO_2 catalyst can directly react with CO at RT and that, more importantly, the consumed subsurface oxygen can be partially restored by the following oxygen exposure at RT. This observation is very surprising because a relatively high temperature was usually necessary for the formation and reaction of subsurface oxygen [19,21].

The unique high activity for epoxidation of silver catalyst is known to be due to the formation of subsurface oxygen in silver bulk [59]. The subsurface oxygen can exchange with the surface oxygen at temperatures above 600 °C. Meanwhile it possesses a special binding strength with the surface, making it more susceptible to expoxidation. In the present work, we observed the refilling of subsurface oxygen by oxygen exposure at RT, which indicates that the exchange barrier is relatively low between surface oxygen and subsurface oxygen over the activated Ag/SiO_2 catalysts. This is possibly one of the main reasons for the observed high activity in the CO oxidation at low temperatures. Recently an increased reactivity of oxygen toward CO oxidation in the presence of subsurface oxygen was also reported for O/Ru(0001) [60].

There exists oxygen in the feed gas in the real reaction system, so it is essential to distinguish the roles of various oxygen species in the CO oxidation. Fig. 15 shows the O_2 and CO-TPD spectra of Ag/SiO_2 catalysts exposed to CO and O_2 under different conditions. All of the adsorption experiments were conducted at RT for 1 h. CO exposure at RT results in the consumption of subsurface oxygen species on the silver catalyst activated by oxygen pretreatment (curve b, Fig. 15A); meanwhile CO desorption from the silver surface is also observed (curve b, Fig. 15B). These indicate that CO can both react with subsurface oxygen and adsorb to the silver surface at RT. When the silver catalyst is exposed to oxygen before the CO adsorption, similar results are observed (curve c, Figs. 15A and 15B). However, no CO desorption is observed when the catalyst is first exposed to CO and then to oxygen (curve d, Fig. 15B), which implies that CO adsorbed to the silver surface reacts off during the following oxygen exposure. At the same time, O_2-TPD also confirms the restoration of subsurface oxygen species (curve d, Fig. 15A), but not completely back to the original one shown by curve a in Fig. 15A. These results indicate that the restoration of subsurface oxygen by oxygen exposure at RT is not influenced by the CO adsorbed to the silver surface. When CO and oxygen (1:0.5) are co-dosed onto the silver catalyst, the amount of subsurface oxygen species de-
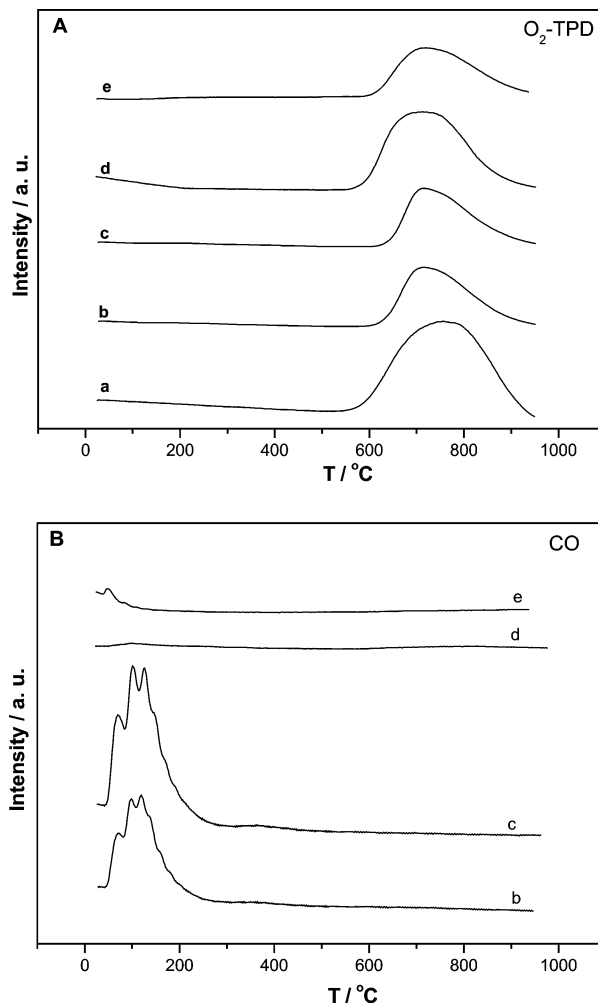

Fig. 15. O_2 (A)- and CO (B)-TPD spectra of Ag/SiO_2 catalysts after direct pretreatment (a), CO adsorption (b), oxygen adsorption followed CO adsorption (c), CO adsorption followed oxygen adsorption (d), and CO and oxygen co-adsorption (e).

creases again, and only a small amount of CO desorption is observed. Thus the following conclusions can be drawn: CO can react with both subsurface oxygen species and gas oxygen in the feed gas at room temperature over activated Ag/SiO_2 catalysts. The subsurface oxygen species can still react with CO, even though there is gas-phase oxygen in the feed gas. However, the presence of gas oxygen species in the feed gas sharply decreases the CO desorption from the silver surface, suggesting that CO adsorbed to the surface of the silver catalyst can easily be consumed by the gas-phase oxygen. And 0.5% oxygen in the feed gas is not sufficient for complete CO oxidation. It has been observed in our experiments that the activity for CO oxidation can be enhanced by increased oxygen in the feed gas. However, the details of the reaction mechanism of CO with subsurface and surface oxygen species on the silver catalyst is still unclear. Further ^{18}O isotope experiments will be required to acquire more detailed information in the future.
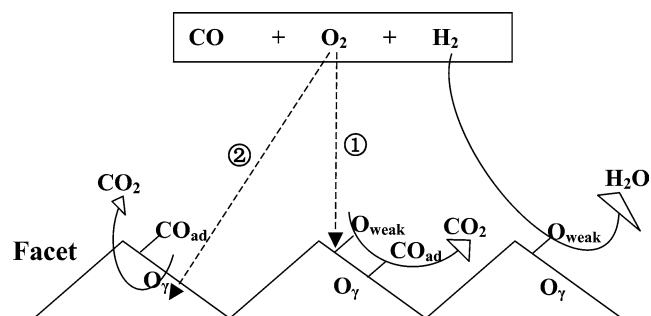
Fig. 16. A scheme of the possible reaction pathways for CO selective oxidation catalyzed by silver catalyst pretreated with oxygen at high temperatures. The possible roles of oxygen in the feed gas are also demonstrated.

No further accumulation of subsurface oxygen species occurs if no CO adsorption is conducted before further oxygen exposure to silver catalyst. The results obtained by a collaboration between Trieste, Genova, and Amsterdam showed that migration channels to subsurface oxygen were found to open up by CO oxidation of oxygen adatoms [22,23]. King et al. also investigated the transition between chemisorbed oxygen and an oxide film growth on Ag(111) with the use of atomic resolution scanning tunneling microscopy images [61]. In the case of a heterogeneous catalysis system, the reaction is driven by chemical potential gradients between involved phases. Surface oxygen does not migrate into the silver bulk when the silver catalyst is pretreated with He or oxygen at 500 °C because surface oxygen and subsurface oxygen reach equilibrium. However, the reaction of subsurface oxygen with CO decreases the potential gradient of subsurface oxygen in silver bulk, which drives the migration of surface oxygen into silver bulk. This explanation may also be applicable for the observation that the silver powders can be activated by exposure to gas mixtures containing either CO or C_2H_4 [62].

It should be noted that the formation of subsurface oxygen species is not observed on a silver catalyst pretreated with H_2, even though CO oxidation with surface oxygen species also occurs. Therefore the surface restructure accompanying the formation of subsurface oxygen during oxygen pretreatment plays a key role in the facile migration between surface oxygen and subsurface oxygen at RT. The very open surface structure and defects contained within grain boundaries resulting from oxygen pretreatment at high temperatures will definitely facilitate the migration of surface oxygen into the subsurface oxygen sites at RT. This effect can be clearly demonstrated by the catalytic activities of the silver catalyst pretreated with oxygen followed by H_2 treatment at different temperatures, which will be presented elsewhere.

On basis of the above results, we proposed a scheme for the possible reaction pathways for CO selective oxidation catalyzed by silver catalysts pretreated with oxygen and the possible roles of oxygen in the feed gas (Fig. 16). Under reaction conditions, two kinds of oxygen species exist on the silver surface: surface oxygen species formed via gas-phase oxygen adsorption and subsurface oxygen formed

during oxygen pretreatment at high temperatures. CO can react with both subsurface and surface oxygen species under reaction conditions. Gas-phase oxygen in the reaction feed gas has two functions: (1) direct reaction with CO; (2) replacing the subsurface oxygen species consumed by the reaction with CO. It is noteworthy that O_2-TPD results show no desorption peak of surface atomic oxygen from the silver surface after oxygen dosing at RT. Further experiments are needed for a full understanding of this. At the same time, hydrogen oxidation follows a pathway different from that of CO oxidation on the silver surface [63]. No hydrogen can chemisorb on either silver or an oxygen-covered silver surface, and molecular hydrogen is proposed to directly attack the adsorbed oxygen species to form water. Therefore higher reaction temperatures are usually required for H_2 oxidation, mainly because of its higher activation energy (56.3 kJ/mol) compared with that of CO oxidation (about 30 kJ/mol). The reaction temperatures chosen in the present work favor CO oxidation rather than H_2 oxidation. It is expected that an increase in reaction temperature will cause a decrease in selectivity for CO oxidation at the presence of H_2.

4. Conclusions

The catalytic activity for CO-selective oxidation over Ag/SiO_2 is reported, and details of the effect of pretreatment on the structure and chemisorption properties of the silver catalyst have been clarified by XRD, TEM, TPD, FTIR and other methods.

A high activity for CO selective oxidation in H_2 is obtained after the silver catalyst is pretreated with oxygen at high temperatures (> 500 °C), whereas a distinct reduction of the catalytic activity is observed after pretreatment with He at 700 °C or with H_2. The formation of subsurface oxygen species after pretreatment with oxygen at high temperatures is found, for the first time, to play an important role in CO oxidation. The formation of subsurface oxygen restructures the silver surface, facilitates the formation of active sites for CO oxidation, and enhances the ability of the catalyst to adsorb CO and activate oxygen. CO is found to directly react with subsurface oxygen species at RT, which may be one of the reasons for the observed high activity of the catalyst for CO oxidation. The consumed subsurface oxygen species can be partially restored by the migration of surface oxygen into the subsurface sites. This migration process can even occur at RT, demonstrating that the diffusion barrier for oxygen from the surface into subsurface sites is quite low over the activated silver catalyst. Our results show that the silver catalyst pretreated with O_2 at high temperatures is quite active for CO oxidation at low temperatures. Therefore this type of catalyst is promising for CO selective oxidation in H_2 at low temperatures because the reaction of H_2 with O_{ad} over the silver catalyst requires higher temperatures.

Acknowledgments

References

[1] P.A. Wright, S. Natarajan, J.M. Thomas, P.L. Gai-Boyes, Chem. Mater. 4 (1992) 1053.
[2] S.D. Gardner, G.B. Hoflund, B.T. Upchurch, D.R. Schryer, E.J. Kielin, J. Schryer, J. Catal. 129 (1991) 114.
[3] S.D. Gardner, G.B. Hoflund, D.R. Schryer, J. Schryer, B.T. Upchurch, E.J. Kielin, Langmuir 7 (1991) 2135.
[4] J.P. Breen, J.R.H. Ross, Catal. Today 51 (1999) 521.
[5] B. Rohland, V. Plzak, J. Power Sources 84 (1999) 183.
[6] S.H. Oh, R.M. Sinkevitch, J. Catal. 142 (1993) 254.
[7] M. Watanabe, H. Uchida, H. Igarashi, M. Suzuki, Chem. Lett. (1995) 21.
[8] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, J. Catal. 171 (1997) 93.
[9] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, J. Catal. 182 (1999) 430.
[10] M.M. Schubert, M.J. Kahlich, H.A. Gasteiger, R.J. Behm, J. Power Sources 84 (1999) 175.
[11] A. Manasilp, E. Gulari, Appl. Catal. B Environ. 37 (2002) 17.
[12] R.A. van Santen, H.P.C.E. Kuipers, Adv. Catal. 35 (1987) 265.
[13] A. Nagy, G. Mestl, T. Rühle, G. Weinberg, R. Schlögl, J. Catal. 179 (1998) 548.
[14] Q.P. Sun, Y.J. Zong, M.F. Luo, J. Zhenjing Normal University 23 (2000) 271.
[15] S. Imamura, H.R. Sawada, K. Uemura, S. Ishida, J. Catal. 109 (1988) 198.
[16] G.G. Xia, Y.G. Yin, W.S. Willis, J.Y. Wang, S.L. Suib, J. Catal. 185 (1999) 91.
[17] X.E. Verykios, F.P. Stein, R.W. Coughlin, Catal. Rev. Sci. Eng. 22 (1980) 197.
[18] W.M.H. Sachtler, C. Backex, R.A. van Santen, Catal. Rev. Sci. Eng. 23 (1981) 127.
[19] X. Bao, M. Muhler, T. Schedel-Niedrig, R. Schlögl, Phys. Rev. B 54 (1996) 2249.
[20] C. Backx, J. Moolhuysen, P. Geenen, R.A. van Santen, J. Catal. 72 (1981) 364.
[21] X.H. Bao, J. Barth, G. Lempfuhl, R. Schuster, Y. Uchida, R. Schlögl, G. Ertl, Surf. Sci. 284 (1993) 14.
[22] L. Savio, L. Vattuone, M. Rocca, F. Bauatier de Mongeot, G. Comelli, A. Baraldi, S. Lizzit, G. Paolucci, Surf. Sci. 506 (2002) 213.
[23] M. Rocca, L. Vattuone, L. Savio, F. Bauatier de Mongeot, U. Valbusa, Phys. Rev. B 63 (2001) 081404.
[24] W.X. Li, C. Stampfl, M. Scheffler, Phys. Rev. Lett. 90 (2003) 256102.
[25] Z.P. Qu, M.J. Cheng, C. Shi, X.H. Bao, Chinese J. Catal. 23 (2002) 460.
[26] Z.P. Qu, M.J. Cheng, C.X.L. Dong, X.H. Bao, Catal. Today 93–95 (2004) 247.
[27] Z.P. Qu, M.J. Cheng, C. Shi, X.H. Bao, J. Mol. Catal. A, submitted for publication.
[28] M.X. Yang, P.W. Jacobs, C. Yoon, L. Muray, E. Anderson, D. Attwood, G.A. Somorjai, Catal. Lett. 45 (1997) 5.
[29] X.H. Bao, B. Pettinger, G. Ertl, R. Schlögl, Ber. Bunsenges. Phys. Chem. 97 (1993) 97.
[30] A.J. Nagy, G. Mestl, D. Herein, G. Weinberg, E. Kitzelmann, R. Schlögl, J. Catal. 182 (1999) 417.
[31] T.C. Wei, J. Phillips, Adv. Catal. 41 (1995) 359.
[32] D. Herein, A. Nagy, H. Schubert, G. Weinberg, E. Kitzelmann, R. Schlögl, Z. Phys. Chem. 197 (1996) 67.
[33] G.I.N. Waterhouse, G.A. Bowmaker, J.B. Metson, Appl. Surf. Sci. 214 (2003) 36.
[34] Y. Uchida, X. Bao, K. Weiss, R. Schlögl, Surf. Sci. 401 (1998) 469.
[35] A. Pestryakov, A. Davydov, A. Kurina, Russ. J. Phys. Chem. 62 (1988) 1813.
[36] J. Baumann, R. Beer, B. Calzaferri, B. Waldeck, J. Phys. Chem. 93 (1989) 2292.
[37] Y.L. Sandler, W.M. Hickam, in: W.M.H. Sachtler, G.C.A. Schuit, P. Zwietering (Eds.), in: Proc. 3rd Int. Congr. Catal., Amsterdam, 1964, vol. 1, 1965, p. 227.
[38] U. Burghaus, H. Conrad, Surf. Sci. 370 (1997) 17.
[39] Q. Xu, Y. Souma, Top. Catal. 6 (1998) 17.
[40] H. Albers, J.M.M. Droog, G.A. Bootsma, Surf. Sci. 64 (1977) 1.
[41] M. Kitson, R.M. Lambert, Surf. Sci. 109 (1981) 60.
[42] G. Rovida, F. Pratesi, M. Maglietta, E. Ferroni, Surf. Sci. 43 (1974) 230.
[43] G.W. Keulks, A. Ravi, J. Phys. Chem. 74 (1970) 783.
[44] K. Kershen, H. Celio, I. Lee, J.M. White, Langmuir 17 (2001) 323.
[45] G.W. Keulks, J.F. Outlaw, in: J.W. Hightower (Ed.), Proc. 75th Int. Congr., Amsterdam, London, 1973, p. 20, paper 66.
[46] J.K. Plischke, M.A. Vannice, Appl. Catal. 42 (1988) 255.
[47] S.A. Tan, R.B. Grant, R.M. Lambert, J. Catal. 104 (1987) 156.
[48] G.A. Somorjai, Introduction to Surface Chemistry and Catalysis, Wiley, New York, 1994.
[49] T. Zambelli, J. Wintterlin, J. Trost, G. Ertl, Science 273 (1996) 1688.
[50] A. Kokalj, A. Dal Corso, S. de Gironcoli, S. Baroni, J. Phys. Chem. B 106 (2002) 9839.
[51] J.D. Grunwaldt, A. Baiker, J. Phys. Chem. 103 (1999) 1002.
[52] G.A. Ozin, Acc. Chem. Res. 21 (1977) 10.
[53] D. McIntosh, G.A. Ozin, Inorg. Chem. 15 (1976) 2869.
[54] L. Vattuone, L. Savio, M. Rocca, Phys. Rev. Lett. 90 (2003) 228302.
[55] L. Savio, L. Vattuone, M. Rocca, Phys. Rev. Lett. 87 (2001) 276101.
[56] M.L. Bocquet, A. Michaelides, D. Loffreda, P. Sautet, A. Alavi, D.A. King, J. Am. Chem. Soc. 125 (2003) 5620.
[57] N. Bonini, A. Kokalj, A. Dal Corso, S. de Gironcoli, S. Baroni, Phys. Rev. B 69 (2004) 195401.
[58] O. Nakagoe, K. Watanabe, N. Takagi, Y. Matsumoto, Phys. Rev. Lett. 90 (2003) 226105.
[59] J.B. Christopher, A.M. Charles, J. Catal. 184 (1999) 224.
[60] A. Böttcher, M. Rogozia, H. Niehus, H. Over, G. Ertl, J. Phys. Chem. 103 (1999) 6267.
[61] C.I. Carlisle, T. Fujimoto, W.S. Sim, D.A. King, Surf. Sci. 470 (2000) 15.
[62] V.I. Bukhtiyarov, A.I. Boronin, I.P. Prosvirin, V.I. Savchenko, J. Catal. 150 (1994) 268.
[63] K. Tamaru, Surf. Sci. 383 (1997) 261.