Restructuring and Redispersion of Silver on SiO$_2$ under Oxidizing/Reducing Atmospheres and Its Activity toward CO Oxidation

Zhenping Qu,[†] Weixin Huang,[‡] Mojie Cheng, and Xinhe Bao*

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

The effects of oxygen−hydrogen pretreatments of nanosilver catalysts in cycle mode on the structure and particle size of silver particles, and subsequently the activity of the catalyst toward CO oxidation (or CO selective oxidation in the presence of H$_2$), are reported in this paper. Ag/SiO$_2$ catalyst with silver particle sizes of ca. 6∼8 nm shows relatively high activity in the present reaction system. The adopting of a cycle of oxidation/reduction pretreatment has a marked influence on the activity of the catalyst. Oxygen pretreatment at 500 °C results in the formation of subsurface oxygen and activates the catalyst. As evidenced by in-situ XRD and TEM, the following H$_2$ treatment at low temperatures (100∼300 °C) causes surface faceting and redispersing of the silver particles without destroying the subsurface oxygen species. The subsequent in-situ FTIR and catalytic reaction results show that CO oxidation occurs at −75 °C and complete CO conversion can be obtained at 40 °C over such a nanosilver catalyst pretreated with oxygen at 500 °C followed by H$_2$ at 100 °C. However, prolonged hydrogen treatment at high temperatures (>300 °C) after oxygen pretreatment at 500 °C induces the aggregation of silver particles and also depletes so much subsurface oxygen species that the pathway of CO oxidation by the subsurface oxygen species is inhibited. Meanwhile, the ability of the catalyst to adsorb reactants is greatly depressed, resulting in a 20∼30% decrease in the activity toward CO oxidation. However, the activity of the catalyst pretreated with oxygen at 500 °C followed by hydrogen treatment at high temperatures (>300 °C) is still higher than that directly pretreated with H$_2$. This kind of catalytic behavior of silver catalyst is associated with physical changes in the silver crystallites because of surface restructuring and crystallite redispersion during the course of oxygen−hydrogen pretreatment steps.

1. Introduction

Catalytic oxidation is an efficient way to convert CO to CO$_2$ at low temperature. Potential uses of high-activity low-temperature CO oxidation catalysts include air cleaning for buildings or cars, gas masks for mining applications, CO detectors, and CO selective oxidation in reformer gas for fuel cell applications.[1−3] Especially the recent progress in polymer electrolyte membrane fuel cells (PEMFCs), considered as a potential power source of electric vehicles that have the better energy efficiency than the conventional combustion engines and a zero emission of air pollutants, has motivated the search of a high efficient catalyst for the CO selective oxidation at low temperature.[4−7] In our attempt, we studied silver-based catalysts. We have shown that the silver catalysts have a relatively high activity for CO selective oxidation at low temperatures.[8−11] It was found that the activity of the Ag catalyst varies greatly with the pretreatment process. A silver catalyst deactivated remarkably after pretreatment in H$_2$ at high temperatures, whereas treatment in oxygen at high temperatures could reactivate the catalyst. Interestingly, the changes in activities are mostly reversible. It is proposed that the structures of the silver particles experience massive changes during the course of various pretreatments and that the existence of subsurface oxygen resulting from an oxygen

treatment at high temperatures is crucial for high selectivity and activity in CO selective oxidation.[10,11] Moreover, silver particles finely dispersed on the support have higher catalytic activity for CO oxidation.[10] Since CO oxidation is generally claimed to be a structure-sensitive reaction, the restructure of silver particles will definitely exert an influence on the activity of the catalyst. As a consequence, the above observations prompt further studies on the control of the structures of the silver surfaces and the sizes of the silver particles by means of various pretreatments to maximize and stabilize the dispersion of a supported silver catalyst that is of both scientific interest and technological importance. Yang and Aoyama have reported the thermal stability of uniform silver clusters supported on oxidized silicon or aluminum surfaces in both oxidizing and reducing atmospheres.[12,13] It was found that the thermal stability of the silver clusters was significantly lowered in an oxidizing condition and that heating above 350 °C in an oxidizing condition can induce a migration of the silver clusters. On the other hand, reduction will give rise to the formation of small silver particles. However, Ruckenstein et al. observed an inverse effect that H$_2$ treatment induced the sintering of the silver particles, while oxygen treatment dispersed the silver particles.[14]

Many supported metal catalysts are subjected to periodical regeneration cycles, in which the catalysts are first treated in air at high temperatures (referred to as "Condition 1") and then are treated in H$_2$ (referred to as "Condition 2") to redisperse the metal components.[15,16] The redispersion process is capable of producing smaller particles for any metal component, which

---

* Corresponding author. Fax: +86-411-84694447; tel: +86-411-84686637; e-mail: xhbao@ms.dicp.ac.cn.
† Present address: Institute of Physical Chemistry, University of Stuttgart, 70569 Stuttgart, Germany. E-mail: zqu@ipc.uni-stuttgart.de.
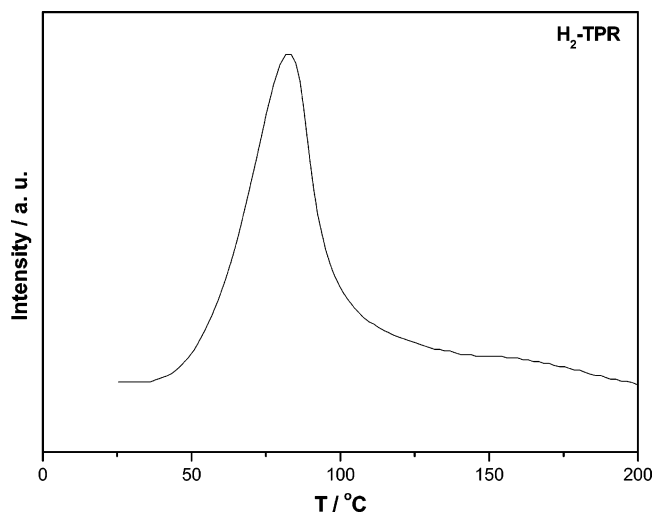‡ Present address: Department of Chemical Physics, University of Science and Technology of China, 230026 Hefei, China.

Figure 1. TPR spectra of Ag/SiO$_2$ catalyst pretreated with oxygen at 500 °C.

Figure 2. CO conversion for CO oxidation and selective oxidation over silver catalysts pretreated with oxygen at 500 °C. The square symbols refer to the oxidation of 1% CO by 0.5% O$_2$ in He, and the circle symbols refer to the oxidation of 1% CO in 1% O$_2$ in H$_2$.

can be further oxidized or reduced without sintering. Condition 1 is applicable to all metals except probably Pt. Condition 2 can only be realized when the decomposition of an oxide can be accomplished at a sufficiently low temperature, so that sintering of the resulted metal will not occur. Therefore, metals that form very stable oxides and have a high mobility are not appropriate candidates for the redispersion process. Since this redispersion phenomenon is common to many different supported noble metals, it is reasonable to propose that similar behavior may exist for silver particles on silica. It has been known that oxygen pretreatment at high temperatures (>500 °C) enhances greatly the activity of the silver catalysts for CO oxidation, which was attributed to the restructuring of silver surface and formation of subsurface oxygen species.[11] The TPR result shows that Ag/SiO$_2$ catalyst is facile to be reduced by hydrogen, as shown in Figure 1. Therefore, in this paper, we investigated the effects of pretreatments by oxidation−reduction cycles on the size and structure of the silver particles and subsequently on the catalytic activity of the silver catalysts toward the CO selective oxidation in H$_2$ and CO oxidation. A restructuring and redispersion model is proposed to correlate the observed catalysts' structure and catalytic activity.

2. Experimental Section

2.1. Catalyst Preparation. Ag/SiO$_2$ catalysts were prepared by the same method as that previously reported.[9,11] SiO$_2$ (20−40 mesh, surface area 495 m^2/g, supplied by Qingdao Chemicals Co.) was immersed with a certain amount of AgNO$_3$ precursor solution (weight loading of 16%) under stirring. The as-prepared AgNO$_3$/SiO$_2$ sample was then aged at RT and dried at 80 °C for 12 h.

2.2. Catalyst Characterization. Routine X-ray powder diffraction (XRD) experiments were carried out on a Rigaku D/max-γb X-ray diffractometer with monochromatic detector. Copper Kα radiation was used, with a power setting of 40 kV and 100 mA, and a scan rate of 5°/min. The sizes of the Ag particles were calculated from the half-width of the main peak at $2\theta = 38°$ according to Scherrer's method. In-situ XRD measurement was done on a Germany Bruker D8 Advance X-ray diffractometer.

TEM experiments were performed with a JEOL 2011 transmission electron microscope, using an accelerating voltage of 200 kV. A sample was dispersed in absolute alcohol by an ultrasonic bath and was deposited on a Formvar-coated 200
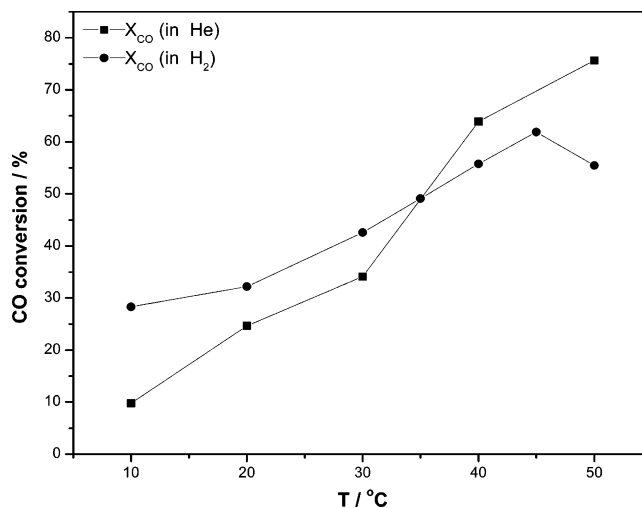
mesh Cu grid for measurements. IR spectroscopy studies were performed with a Nicolet Impact 410 Fourier transform infrared spectrometer. Self-supported pellets were directly heated in the IR cells, which were connected with a vacuum/sorption apparatus. Prior to the adsorption measurements, the samples were treated with oxygen at 500 °C followed by H$_2$ at different temperatures and then were evacuated to 10^{-5} Torr at the treatment temperature for 1 h. The temperature of CO adsorption on the silver surface was −120 °C. During the course of in-situ IR experiments of CO oxidation, the catalyst experiences such a sequence: pretreatment−evacuation−oxygen exposure−evacuation−CO exposure−evacuation−(heating)−IR measurement.

2.3. Activity Measurements. Catalytic activity measurements were conducted in a fixed-bed microreactor at atmospheric pressure and with 0.25 g of catalyst. A standard gas consisting of 98.5% H$_2$, 1% CO, and 0.5% O$_2$ passed through the catalyst bed at a flow rate of 50 mL/min. Before the reaction, the catalyst was pretreated with oxygen at 500 °C followed by H$_2$ at different temperatures (100∼500 °C). The concentration of the reacting gases in the effluent was monitored by an online GC-14B gas chromatograph equipped with a Molsieve 5Å column and a Porapak Q column ($T = 30$°C, helium as carrier gas at 30 mL/min). The conversions of CO and O$_2$, as well as the selectivity, were calculated by a method similar to that described previously.[9−11]

3. Results and Discussion

3.1. Activity Measurements. *3.1.1. The Effect of H$_2$ in the Feed Gas on CO Oxidation.* The CO oxidation activities of Ag/SiO$_2$ catalyst in the absence of H$_2$ as a function of temperature are shown in Figure 2 (square symbols). The concentration of CO in the feed was 1%, and the O$_2$ concentration in pure He was 0.5%. The silver catalyst was pretreated with oxygen at 500 °C before the reaction test. Below 10 °C, the activity is rather low, with conversions (X_{CO}) less than 10%. As the temperature is raised, X_{CO} increases first slowly and then suddenly rises sharply at ∼30 °C. This sudden increase in CO conversion at the ignition temperature, which is defined as the temperature of maximum gradient in a plot of X_{CO} versus T, is related to the onset of CO desorption. When He is replaced with H$_2$ in the above reaction mixture (circle symbols in Figure
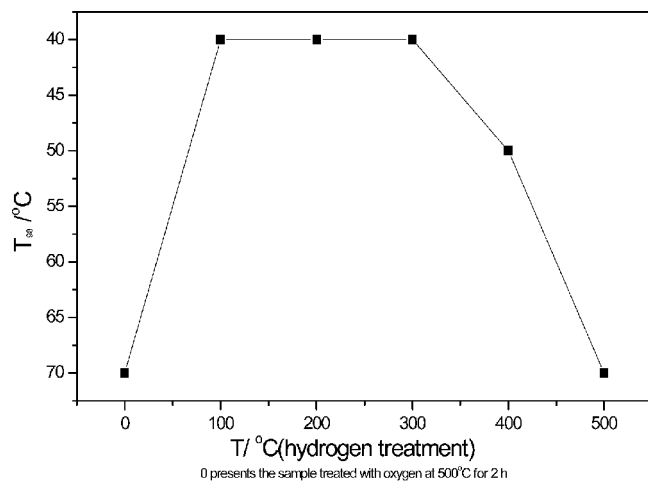
Figure 3. T_{98} for CO oxidation of silver catalysts pretreated with oxygen at 500 °C and followed by H_2 reduction at different temperatures.

2, 1% O_2 was used because of the accompanying H_2 oxidation reaction), the activity for CO oxidation at low temperatures increases obviously. The maximum CO conversion in 1% O_2 is ~60%. The decrease in the conversion of CO to CO_2 above 45 °C is again associated with the CO and O coverages on the surface of the silver catalysts.[17] At temperatures above 45 °C, the CO coverage on the surface of silver catalyst dropped. Meanwhile, hydrogen oxidation may also compete with CO oxidation.

The presence of H_2 in a CO/O_2-mixture increases the low-temperature activity of the silver catalyst toward CO oxidation, which is equivalent to a roughly 10~20% activity enhancement. Similar behavior was also observed by Muraki et al. for CO oxidation on Pt/γ-Al_2O_3, in which the reaction rate at 150 °C increased by a factor of ~3 upon the addition of ~2 Torr H_2 to 7.6 Torr CO ($\lambda = 0.9$).[18]

3.1.2. The Effect of H_2 Pretreatment on the Catalytic Activity. Figure 3 shows the catalytic activities of Ag/SiO$_2$ catalysts toward CO oxidation after pretreatment with oxygen at 500 °C followed by H_2 treatment at different temperatures. The activity of a given catalyst is expressed in terms of the temperature corresponding to the catalytic efficiency higher than 98% (T_{98}),

which was obtained from the curve of catalytic efficiency versus reaction temperature. A lower temperature for T_{98} indicates a higher catalytic activity. The silver catalyst pretreated with oxygen at 500 °C yields a T_{98} at 70 °C. The following treatment with H_2 at low temperatures (100−300 °C) increases the activity of the catalysts to give a T_{98} at 40 °C, while the activity decreases after H_2 treatment at a temperature higher than 300 °C. Similar behavior is also found in CO selective oxidation reaction. From the above results, it can be concluded that complete CO conversion can be obtained at 40 °C over the Ag/SiO$_2$, which obviously shows a better performance than other CO oxidation catalysts reported previously.[19,20]

Since the silver catalysts are highly reactive even at room temperature, it is unlikely to observe the initial reaction temperature for CO oxidation on real reaction operations over this catalyst. FTIR is well-known to be a good in-situ technique for monitoring reactions occurring on catalyst surfaces. Moreover, the IR experiments can be performed at temperatures far lower than room temperature. Figure 4 presents the in-situ FTIR spectra during the course of CO oxidation at different reaction temperatures over the Ag/SiO$_2$ catalyst pretreated with oxygen at 500 °C followed by H_2 treatment at 100, 400, and 500 °C, respectively. The catalyst was first exposed to oxygen prior to the CO exposure at −120 °C, and the sample was then heated after evacuation. All spectra were taken 10 min after the acquiring of equilibrium. The band maximum for CO absorbed on the silver catalyst reduced with hydrogen is between 2162 and 2153 cm^{-1}, which can be assigned to Ag$^{\delta+}$−CO species.[17,21] Also, the peak intensity decreases with the increasing of the reduction temperature. The amount of linearly adsorbed CO decreases with the increase of the reaction temperature for all catalysts. Most importantly, a new vibrational peak appears at 2348 cm^{-1} at −75 °C for the silver catalyst treated with H_2 at 100 °C, which is assigned to adsorbed CO_2 produced by CO oxidation. This indicates that CO oxidation can occur at very low temperatures over the active silver catalyst. The lowest temperature for CO_2 formation does not vary for the catalysts treated with hydrogen at 100−300 °C but increases to −65 °C and −50 °C when the hydrogen treatment is performed at 400 °C and 500 °C, respectively. The silver catalyst only pretreated with oxygen gives an initial reaction temperature for CO oxidation at −70 °C. These in-situ IR results are consistent with
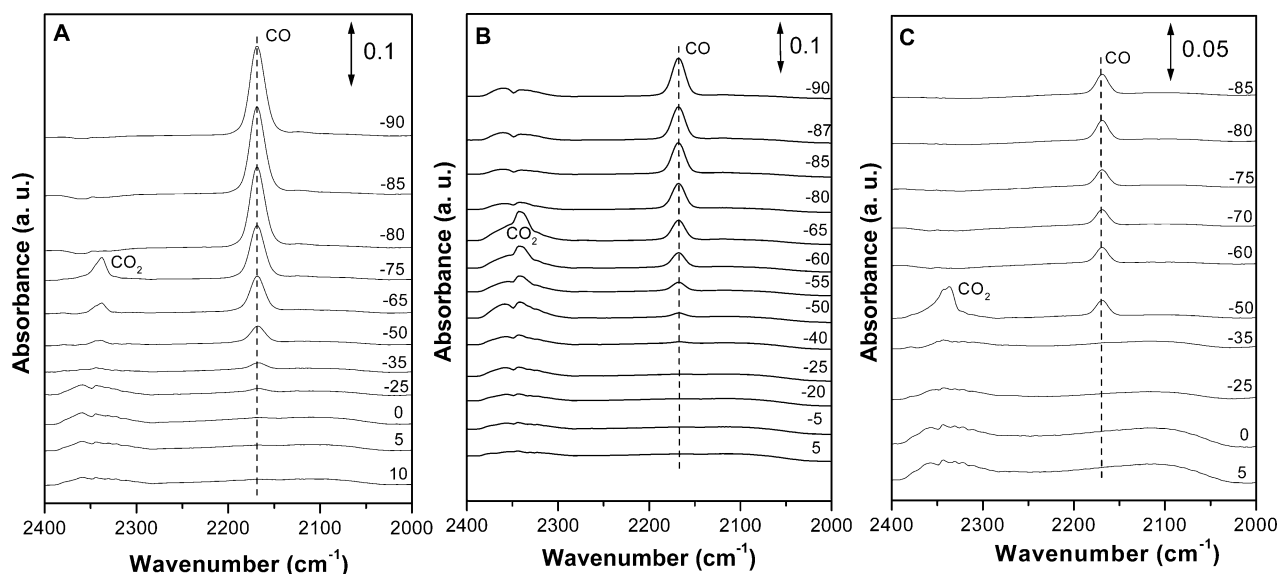

Figure 4. In-situ FTIR spectra during the course of CO oxidation at different reaction temperatures on Ag/SiO$_2$ pretreated with oxygen at 500 °C followed by H_2 reduction at 100 °C (A), 400 °C (B), and 500 °C (C), respectively.
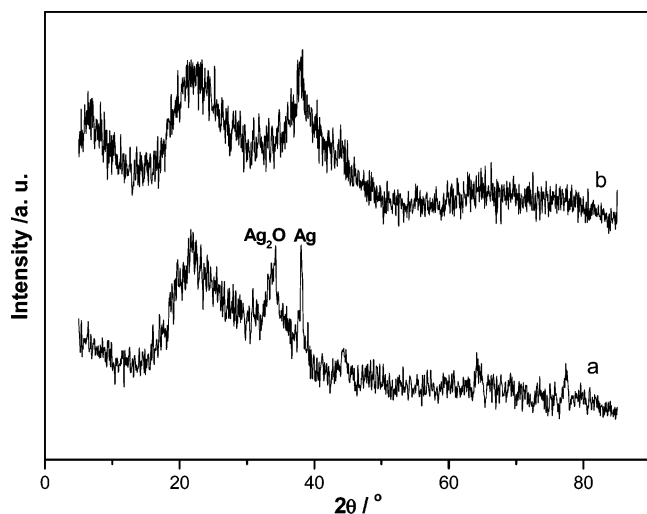
Figure 5. XRD patterns of silver catalysts after reaction for CO oxidation (a) and CO selective oxidation in H$_2$ (b).

the catalytic reaction test obtained in actual reaction operations (Figure 3): low-temperature reduction (100−300 °C) following oxygen pretreatment at 500 °C increases the catalytic activity of the catalyst, while reduction at temperatures above 400 °C decreases the activity.

3.2. Catalyst Characterization. Figure 5 shows the XRD patterns of Ag/SiO$_2$ catalysts after CO selective oxidation in H$_2$ and CO oxidation. In both cases, the catalyst was pretreated with oxygen at 500 °C before reaction, and the reaction temperature was at 100 °C. Both Ag and Ag$_2$O exist in the catalyst after pretreatment with oxygen at 500 °C.[11] The XRD pattern of the catalyst does not show obvious changes after experiencing the CO oxidation reaction (Figure 5a). However, after CO selective oxidation in H$_2$, the peak corresponding to Ag$_2$O disappears, and only metal silver particles are present on the catalysts (Figure 5b). Moreover, the silver peak at 38.2° becomes broader after CO selective oxidation, indicating the formation of smaller silver particles on the support after CO selective oxidation. It has been demonstrated that the presence of H$_2$ in a CO/O$_2$ mixture increases the low-temperature activity of silver catalyst toward CO oxidation (Figure 2). Moreover, the silver catalyst pretreated with oxygen followed by H$_2$ treatment at low temperatures has the best performance for CO oxidation (see Figure 3). Therefore, the high activity for CO oxidation may come from the reduction and dispersion of silver species resulting from the hydrogen treatment.

To get direct information about the effect of H$_2$ treatment on the structure of the silver catalyst, in-situ XRD experiments were performed and the XRD patterns of Ag/SiO$_2$ under H$_2$ atmosphere are presented in Figure 6. The silver catalyst was pretreated with oxygen at 500 °C before the in-situ XRD experiments. Again, both Ag and Ag$_2$O exist on the oxygen-pretreated catalyst. After H$_2$ is injected into the reaction system at RT for 25 min, the peaks of Ag and Ag$_2$O attenuate and the diffraction peak of the metallic silver species becomes broader. This indicates that some of Ag$_2$O is reduced by H$_2$ at RT and that smaller silver particles form. Reduction by hydrogen at 60 °C for 20 min causes the peak of the Ag$_2$O species to completely disappear, with intensifying the peak of metallic silver. This implies that Ag$_2$O has been completely reduced to Ag. This result is consistent with the TPR result (Figure 1) showing the maximum reduction peak around 80 °C. Inferred from the unchanged half-width of the peak for metallic silver, the silver particle size does not vary obviously after further reduction
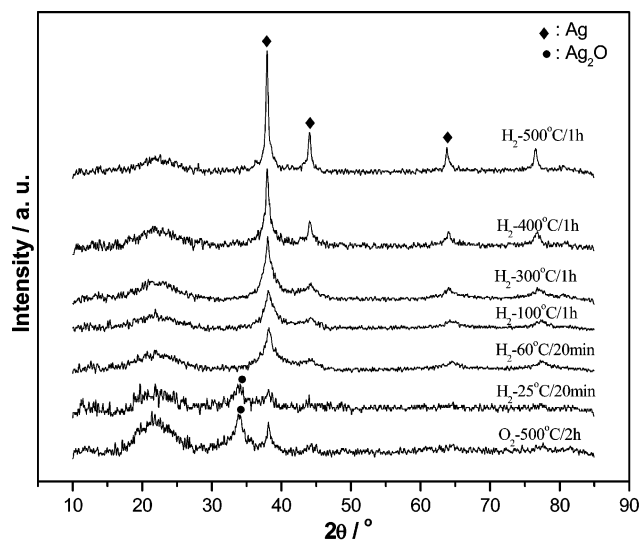

Figure 6. In-situ XRD patterns under H$_2$ atmosphere for Ag/SiO$_2$ pretreated with oxygen at 500 °C.
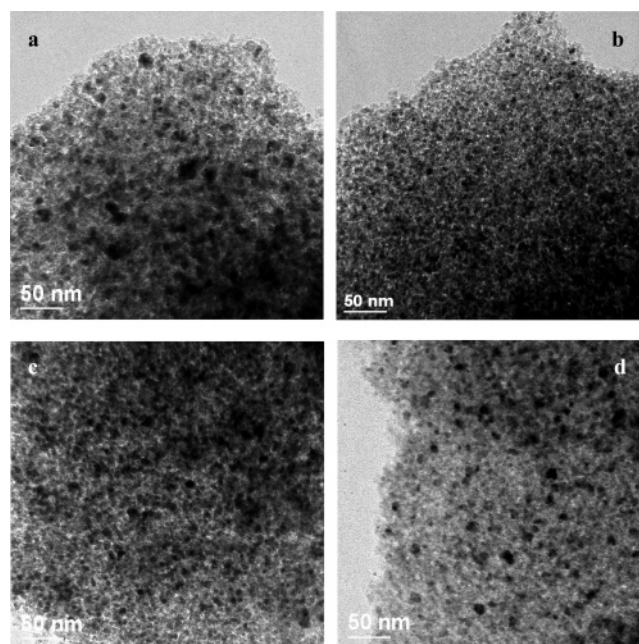

Figure 7. TEM images of Ag/SiO$_2$ pretreated with oxygen at 500 °C (a), followed by H$_2$ at 100 °C (b), 300 °C (c), and 500 °C (d).

between 100 and 300 °C. However, the peak becomes clearly narrower as the reduction temperature is above 400 °C, which suggests that some silver particles aggregate to form a larger one. From the in-situ XRD results, it can be concluded that H$_2$ pretreatment at low temperatures (100−300 °C) reduces the Ag$_2$O to Ag and disperses the metallic silver particles. A similar conclusion can also be drawn from the TEM results shown in Figure 7. Clearly, silver particles with smaller size appear after hydrogen reduction between 100 and 300 °C, whereas aggregation occurs after reduction at 500 °C.

Combining XRD and TEM results with in-situ IR results, a correlation between the initial reaction temperature for CO oxidation over the silver catalyst (IR results) and the size of the silver particles (TEM results) was obtained, as shown in Figure 8. It is interesting that the curve of the initial reaction temperature versus the particle size is "volcano-shaped" for the Ag/SiO$_2$ catalyst. Clearly, the particle size of silver has great influence on the catalytic activity of the catalyst for CO
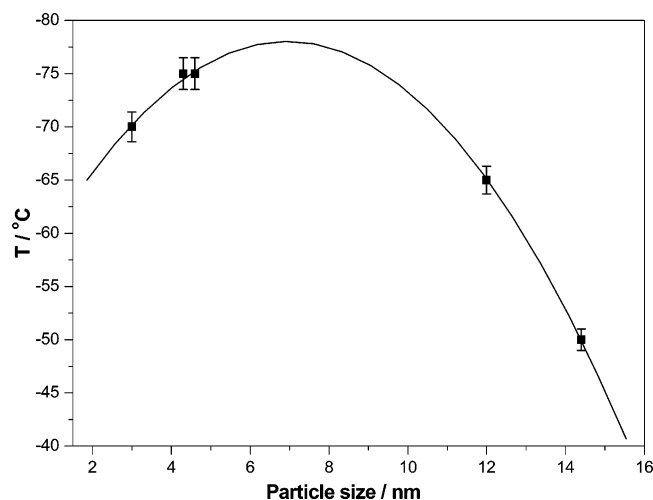
Figure 8. Correlation of the initial reaction temperature for CO oxidation over silver surface and the size of silver particles.
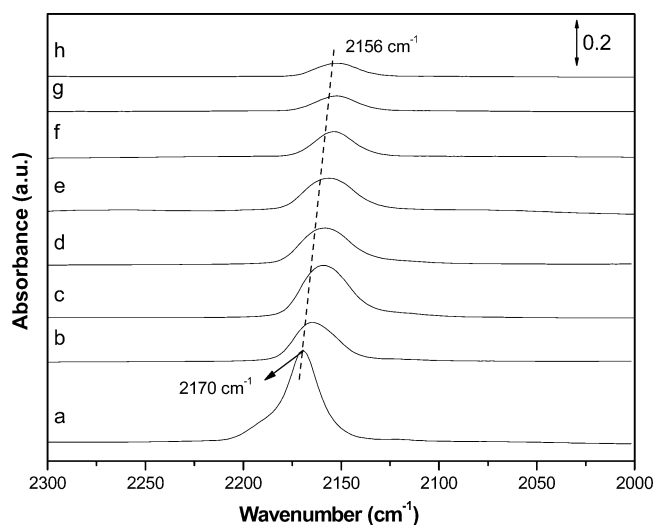

Figure 9. FTIR spectra of CO adsorbed at −120 °C over silver catalysts pretreated with oxygen at 500 °C for 2 h (a), followed by H₂ at RT for 30 min (b), 60 °C for 30 min (c), 100 °C (d), 200 °C (e), 300 °C (f), 400 °C (g), and 500 °C (h) for 1 h, respectively.

oxidation, and the maximum activity is obtained on the silver catalyst with a mean size of about 6∼8 nm.

3.3. Surface Restructuring and Redispersion of Silver Particles. It has been known that the silver catalyst directly pretreated with H₂, even at 300 °C, only has a very low activity for CO selective oxidation, and the subsequent oxygen treatment at high temperatures can reactivate the catalyst.[11] However, in the present paper, it is found that H₂ treatment at low temperatures (100−300 °C) following oxygen pretreatment at high temperatures (>500 °C) can result in the fine dispersion of the silver particles on the support and a further increase of the catalytic activity. A further H₂ reduction at high temperatures (>300 °C) decreases the activity of the silver catalyst again, for example, the maximum CO conversion of 22% for CO selective oxidation is obtained after reduction at 500 °C, which, however, is still higher than that directly pretreated with H₂ (the maximum CO conversion of 15%). These results clearly demonstrate that a cycle of oxidation−reduction pretreatment is crucial to obtain a higher activity for CO oxidation. We have known that oxygen pretreatment at high temperatures results in the formation of subsurface oxygen species that plays a crucial role during the course of CO oxidation, and the formation of subsurface oxygen is accompanied by the restructure of the silver surface, which enhances the ability of the catalyst to adsorb CO and oxygen. Thus, the higher activity of the silver catalyst pretreated with oxygen followed by H₂ treatment at 500 °C than that directly pretreated with H₂ may be related to the resulting structure of the silver catalyst during the course of the oxidation−reduction cycle pretreatment.

Figure 9 shows the FTIR spectra of CO adsorbed at −120 °C on silver catalysts pretreated with oxygen at 500 °C followed by H₂ at different temperatures. The spectrum for the catalyst without further hydrogen shows a band centering around 2170 cm⁻¹, which can be assigned to CO linearly bonded to Ag⁺ species.[22−24] The vibrational peak of CO adsorbed on the Ag/SiO₂ catalysts reduced by H₂ shifts to lower frequencies, which can be attributed to the formation of the $Ag^{\delta+}-CO$ ($0 < \delta < 1$). The shift is more obvious with higher reduction temperature, which is due to the increasing of the electron density of silver. The vibrational frequency of CO adsorbed on the catalyst reduced at 500 °C is located at 2153 cm⁻¹. It has been known that linearly adsorbed CO on metallic silver sites gives rise to the vibrational band between 2030 and 2050 cm⁻¹.[21] This means that silver species is not completely in the metallic state even after reduction at 500 °C. Although TPR and XRD experiments

have shown that Ag₂O species already disappears after reduction, a large amount of subsurface oxygen species, formed by pretreatment with oxygen at high temperatures, may still remain after the catalyst is treated by hydrogen. The IR results shown in Figure 9 clearly prove that some subsurface oxygen species is retained on the silver even after hydrogen pretreatment at high temperatures (e.g., 500 °C). However, IR experiments observed no CO adsorption on the silver catalyst without calcinations before pretreatment with hydrogen.[24]

A surface restructuring and redispersion model, illustrated schematically in Figure 10, can readily explain the correlation between the structure and activity resulting from the oxidation/reduction treatments at different temperatures. A close-packed structure forms after the silver catalyst is directly treated with H₂ at high temperatures. It is proposed that the high-temperature oxygen treatment induces faceting of silver surface to high index planes with lower average coordination numbers, and thus more silver atoms are exposed on the surface. These high-index planes are composed of more steps and kinks, which facilitate the formation of subsurface oxygen species and the migration between surface oxygen and bulk oxygen on silver catalysts. This model is consistent with previous studies of oxygen treatment effect on the surface structure of the silver catalyst, in which surface faceting has been observed for thin films, single crystals, and supported catalysts.[25−27] Nagy et al. reported that silver underwent pronounced morphological changes following a high-temperature treatment in oxygen, which led to faceting of the silver surface, as directly observed by SEM.[28]

When the silver catalyst is further treated by hydrogen, the treatment temperatures between 100 and 300 °C reduces Ag₂O species, and some subsurface oxygen reacts off, however, the high-index planes consisting of step and kink sites formed during the previous oxygen treatment mostly remain unchanged. It has been shown that metal particles annealed in a hydrogen-containing atmosphere, including silver particles, exhibit a morphology having rounded edges and corners.[29,30] Auroux and Gravelle observed that the reduced silver catalyst liberates high heats when interacting with oxygen, and they postulated that the surface of a freshly reduced silver particle contains a large number of lattice defects.[31] Furthermore, water vapor was also reported to be capable of increasing the surface roughness of a silver particle.[32]
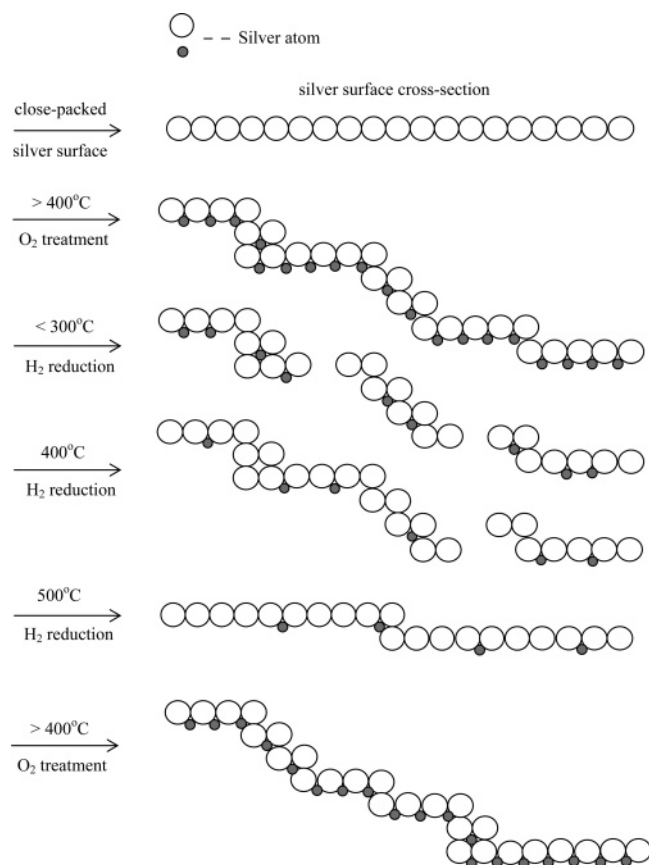
Figure 10. Surface restructuring (refacetting), subsurface oxygen formation, and redispersion model of silver crystallites under oxidation/reduction cyclic treatment.

On the other hand, the reduction by hydrogen between 100 and 300 °C following oxygen treatment at 500 °C redisperses the silver particles and results in more silver particles with smaller sizes, as evidenced by the XRD and TEM results. Thus, a supported silver catalyst experiencing such a pretreatment of O₂/500 °C followed by hydrogen/100−300 °C will show high activity to adsorb CO and O₂ and, eventually, will show high activity toward CO oxidation. Moreover, it has been found in our experiments that the amount of oxygen chemisorbed on the silver catalyst increased from 8.32 μmol/g to 33.35 μmol/g after the catalyst was reduced by hydrogen at 300 °C following oxygen pretreatment at 500 °C. A similar redispersion model has been proposed by Wang and Schmidt, to explain that a silver catalyst after calcinations and reduction at 400 °C has the maximum ability of oxygen adsorption and that reduction at 500 °C decreases the chemisorption capacity.[16] Many supported metal catalysts have to be subjected to periodic regeneration cycles, in which they are first treated in air at high temperatures, and then with H₂, to redisperse the metal component.[16,33,34] Comparable behaviors of Group VIII metals have been reported when experiencing oxygen/hydrogen treatment cycles, and the results have been interpreted in terms of metal redispersion.

Redispersion, a process that increases the surface areas of metals, is thought to proceed mainly through volatilization of the metals as oxides, which are then redeposited as smaller particles at various sites on the porous oxide support. In general, oxidation induces a spreading of the oxide phase on the support, while a subsequent reduction at lower temperatures splits this oxide phase into smaller metal particles.[34] This can be attributed to the formation of a small number of metal nuclei. Cracks of the particles can also be caused by elastic stresses when the oxides are being reduced. As the reduction progresses, the

density of the particles increases, and a tensile stress would develop in the oxide because the metal oxides are adhering strongly to the support. This could lead to more cracks, most likely forming preferentially at grain boundaries of the oxide particles where reduction rates are highest and fracture stresses are lowest. The mechanism for the formation of small silver particles on the SiO₂ support after H₂ reduction at low temperatures following the oxygen pretreatment needs further investigation. Redispersion involves the formation of small particles from larger ones, and this process will counteract the increase in free energy, which occurs with an increase in surface area.[34] The irregular shapes of the small particles after reduction should result in an even larger increase of surface area than predicted. However, the subsurface oxygen species remaining within the silver particles may act to stabilize the small particles.

High-temperature oxygen treatment prior to hydrogen reduction is necessary for the silver catalyst to show high activities. High-temperature oxygen treatment may act as "cleaning" the catalyst surface or stabilizing an active catalyst structure. Usually, the reduction treatment alone, even at high temperatures, is considered to be insufficient to completely clean the possible carbon species on the silver surfaces. However, silver nitrate used as the precursor salt in our experiments for the preparation of silver catalyst is carbon-free. In our previous paper, we have proved that the lack of activity for CO oxidation over the initial Ag−SiO₂ physical mixture catalyst is not due to the existing carbon species.[10] It was reported that low uptakes in oxygen chemisorption were observed for the silver samples without any calcination steps prior to reduction.[35] Therefore, the role of the oxygen treatment at high temperature for the silver catalyst in the current study should be the latter one, stabilizing an active catalyst structure. We have reported that the formation of subsurface oxygen accompanied by the surface structure during high-temperature oxygen treatment plays a key role in the high catalytic activity of silver catalyst for CO oxidation.[11] Therefore, we propose that hydrogen reduction at 100−300 °C following oxygen treatment at 500 °C redisperses the silver particles but does not destroy the active structure and subsurface oxygen species resulting from oxygen treatment at 500 °C. The redispersion process results in the silver particles with smaller sizes, which, comparing the catalyst without redispersion, improves the performance of the catalyst. One likely explanation is that the exchange and diffusion between surface oxygen and the subsurface oxygen might be more facile on smaller silver particles. The relevant theoretical calculations are undergoing in our group.

Hydrogen treatment temperature is crucial for the catalytic performance. Hydrogen reduction at 100−300 °C increases the activity, while reduction at higher temperatures (>300 °C) leads to the reverse effect. The activity decreasing can be apparently attributed to the agglomeration of silver particles and the depletion of more subsurface oxygen species. Although the CO−FTIR experiments indicate the existence of more or less subsurface oxygen species after reduction at high temperatures (Figure 9), these subsurface oxygens can't sustain all the active structure of the catalyst. Rovida et al. have proposed that the restructured silver surface is stable only in the presence of adsorbed oxygen.[36] Consequently, as more subsurface oxygen is removed at higher reduction temperatures, the silver surface will tend to show the close-packed plane with lowest surface energy. Again, reduction temperature determines the extent to which the silver catalyst will deactivate. Previous reports showed that strongly bound oxygen species is not very easy to be removed via the hydrogen reduction at high temperatures.[37] Our

results also show that the catalyst reduced by hydrogen at 400 °C, and even at reduction at 500 °C, still has catalytic activity, which indicates the presence of active catalyst structure and subsurface oxygen species. This can explain the experimental results that the silver catalyst reduced by hydrogen at higher temperatures (>300 °C) following oxygen treatment shows a higher catalytic activity for CO oxidation than that directly treated with H_2.

The change of surface structure and particle sizes of silver catalyst is reversible upon oxidation and reduction. This may also be because all the changes are determined by the formation and depletion of subsurface oxygen. Therefore, a high activity for CO oxidation is obtained again after another oxidation at 500 °C is applied on the deactivated silver catalyst.

4. Conclusions

In summary, silver catalysts with a proper size as well as subsurface oxygen species are active for CO oxidation. The employing of an oxidation/reduction cycle has a marked influence on the activity of silver catalyst for CO oxidation, and the low-temperature catalytic activity of the silver catalyst experienced various pretreatment procedures as follows: O_2/500 °C$-H_2$/100$-$300 °C > O_2/500 °C > O_2/500 °C$-H_2$/ (>300 °C) > H_2/(>300 °C). Oxygen pretreatment at high temperature results in the formation of subsurface oxygen and in the catalyst restructure, leading to the high activity for CO oxidation. Following reduction at 100$-$300 °C can redisperse the silver particles without destroying the active structure, which thus increases remarkably the CO oxidation activity of the catalyst. Further reduction at high temperature causes the depletion of subsurface oxygen and the aggregation of the silver particles and eventually the deactivation of the catalyst. The effect of oxygen/reduction cycle on the activity of the silver catalyst is reversible.

References and Notes

(1) Wright, P. A.; Natarajan, S.; Thomas, J. M.; Gai-Boyes, P. L. *Chem. Mater.* **1992**, *4*, 1053.

(2) Gardner, S. D.; Hoflund, G. B.; Upchurch, B. T.; Schryer, D. R.; Kielin, E. J.; Schryer, J. *J. Catal.* **1991**, *129*, 114.

(3) Igarashi, H.; Fujino, T.; Watanabe, M. *J. Electrochem. Soc.* **1988**, *135*, 2651.

(4) Kim, D. H.; Lim, M. S. *Appl. Catal., A* **2002**, *224*, 27.

(5) Grisel, R. J. H.; Nieuwenhuys, B. E. *J. Catal.* **2001**, *199*, 48.

(6) Igarashi, H.; Uchida, H.; Watanabe, M. *Chem. Lett.* **2000**, 1262.

(7) Manasilp, A.; Gulari, E. *Appl. Catal., B* **2002**, *37*, 17.

(8) Güldür, C.; Balikci, F. *Int. J. Hydrogen Energy* **2002**, *27*, 219.

(9) Qu, Z. P.; Cheng, M. J.; Shi, C.; Bao, X. H. *Chin. J. Catal.* **2002**, *23*, 460.

(10) Qu, Z. P.; Cheng, M. J.; Dong, X. L.; Bao, X. H. *Catal. Today* **2004**, *93*, 247.

(11) Qu, Z. P.; Cheng, M. J.; Huang, W. X.; Bao, X. H. *J. Catal.* **2005**, *229*, 446.

(12) Yang, M. X.; Jacobs, P. W.; Yoon, C.; Muray, L.; Anderson, E.; Attwood, D.; Somorfai, G. A. *Catal. Lett.* **1997**, *45*, 5.

(13) Aoyama, N.; Yoshida, K.; Abe, A.; Miyadera, T. *Catal. Lett.* **1997**, *43*, 249.

(14) Ruckenstein, E.; Lee, S. H. *J. Catal.* **1984**, *86*, 457.

(15) Stulga, J. E.; Wynblatt, P.; Tien, J. K. *J. Catal.* **1980**, *62*, 59.

(16) Wang, T.; Schmidt, L. D. *J. Catal.* **1980**, *66*, 301.

(17) Qu, Z. P.; Zhou, S. T.; Wu, W. C.; Li, C.; Bao, X. H. *Catal. Lett.* **2005**, *101*, 21.

(18) Muraki, H.; Matunaga, S.-I.; Shinjoh, H.; Wainwright, M. S.; Trimm, D. L. *J. Chem. Technol. Biotechnol.* **1991**, *52*, 415.

(19) Sun, Q. P.; Zong, Y. J.; Luo, M. F. *J. Zhejing Normal Univ.* **2000**, *23*, 271.

(20) Xia, G. G.; Yin, Y. G.; Willis, W. S.; Wang, J. Y.; Suib, S. L. *J. Catal.* **1999**, *185*, 91.

(21) Müslehiddinoõlu, J.; Vannice, M. A. *J. Catal.* **2003**, *213*, 320.

(22) Pestryakov, A.; Davydov, A.; Kurina, A. *Russ. J. Phys. Chem.* **1988**, *62*, 1813.

(23) Baumann, J.; Beer, R.; Calzaferri, B.; Waldeck, B. *J. Phys. Chem.* **1989**, *93*, 2292.

(24) Huang, Y. Y. *J. Catal.* **1974**, *32*, 482.

(25) Smith, A. W. *J. Phys. Chem.* **1964**, *68*, 1465.

(26) Marbrow, R. A.; Lamber, R. M. *Surf. Sci.* **1978**, *71*, 107.

(27) Herein, D.; Nagy, A.; Schubert, H.; Weinberg, G.; Kitzelmann, E.; Schlögl, R. *Z. Phys. Chem.* **1996**, *197*, 67.

(28) Nagy, A. J.; Mestl, G.; Herein, D.; Weinberg, G.; Kitzelmann, E.; Schlögl, R. *J. Catal.* **1999**, 182, 417.

(29) Merma, G. R.; Knijf, L. M.; van Dillen, A. J.; Geus, J. W.; Nongaarts, J. E.; van Buren, F. R.; Delcour, K. *Catal. Today* **1987**, *1*, 117.

(30) Sundquist, B. E. *Acta Metall.* **1964**, *12*, 67.

(31) Auroux, A.; Gravelle, P. C. *Thermochim. Acta* **1981**, *47*, 333.

(32) O'Handley, R. C.; Burge, D. K.; Jasperson, S. N.; Ashley, E. J. *Surf. Sci.* **1975**, *50*, 407.

(33) Wang, T.; Schmidt, L. D. *J. Catal.* **1981**, *70*, 187.

(34) Anderson, J. R. *Structure of Metallic Catalysts*; Academic Press: London, 1975.

(35) Czanderna, A. W. *J. Phys. Chem.* **1966**, *70*, 2120.

(36) Rovida, G.; Pratesi, F.; Maglietta, M.; Ferroni, E. *Surf. Sci.* **1974**, *43*, 230.

(37) Kagawa, S.; Iwamoto, M.; Morita, S.; Seiyama, T. *J. Chem. Soc., Faraday Trans.* **1982**, *78*, 143.