

# Low-temperature selective oxidation of CO in H<sub>2</sub>-rich gases over Ag/SiO<sub>2</sub> catalysts

Zhenping Qu<sup>1</sup>, Mojie Cheng, Chuan Shi, 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

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## Abstract

Factors influencing basic catalytic activity of Ag/SiO<sub>2</sub> catalysts for CO selective oxidation in H<sub>2</sub>-rich gases, such as support, silver loading, oxygen concentration and reaction temperature, etc. were investigated. Among the supports used, SiO<sub>2</sub> and the pure silica zeolite are better supports for silver catalyst. Ag/SiO<sub>2</sub> catalyst has a better stabilization for CO selective oxidation at low temperatures. Carbon monoxide in the presence of large excess of hydrogen can be stoichiometrically oxidized by oxygen over Ag/SiO<sub>2</sub> catalysts at low temperatures, and the catalytic activities increase with the increase of the silver loading. Low reaction temperature favors this process of selective oxidation of CO in H<sub>2</sub>-rich gas, and the selectivity of O<sub>2</sub> to oxidize CO can reach 60–80%. The maximum conversion of CO under such selectivity levels for oxygen to oxidize CO also increases with the silver loading. XRD results show that the main species on all catalysts is crystallite silver, and the size of the silver particles increases with the silver loading. It is found that the CO conversion increases with increasing oxygen contents properly, however, CO is not consumed completely even when the overall concentration of O<sub>2</sub> is increased to 3%. Pretreatment conditions have been found to strongly influence the activity and selectivity of the catalysts. The catalysts deactivate after pretreatment with hydrogen at 500 °C, whereas a better activity is obtained after pretreatment with oxygen or He at the same temperature.

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**Keywords:** Ag/SiO<sub>2</sub>; CO selective oxidation; H<sub>2</sub>-rich gas

## 1. Introduction

Polymer electrolyte membrane fuel cells (PEFCs), operating at a relatively low-temperature (e.g. 60–80 °C) with pure hydrogen or reforming gases as fuels, have attracted much attention as power sources for electric vehicles [1,2]. However, at low-temperatures, the Pt anodes of the PEFC are extremely sensitive to and easily poisoned by traces of CO in the fuels [3]. When employing reforming gases, the CO concentration is generally ca. 1%, which is much higher than the 10 ppm level desired for the PEFC. Therefore, it is essen-

tial to develop a method that can lower effectively the CO concentration in the reforming gases.

Among the various methods available for CO removing, catalytic selective oxidation of CO seems to be a promising one and has been investigated extensively. Most catalysts employed previously are based on noble metals [4–9]. Pt/Al<sub>2</sub>O<sub>3</sub> catalysts were reported to have a high activity and selectivity for the selective oxidation of CO; however, it requires more than 2% of oxygen to oxidize 1% of CO in H<sub>2</sub>-rich gases, which might result in a wasteful consumption of H<sub>2</sub> and a risk of explosion [4,5]. Oh and Sinkevitch reported that Ru/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> catalysts exhibited high activities for the selective oxidation of CO in H<sub>2</sub>-rich gases (900 ppm CO, 800 ppm O<sub>2</sub> and 0.85 vol% H<sub>2</sub>) [6,7]. However, the reaction temperature (200–250 °C) over Pt, Rh catalysts is relatively high compared with that of PEFCs.

\* Corresponding author. Tel.: +86 411 84686637; fax: +86 411 84694447.  
E-mail address: [xhbao@dicp.ac.cn](mailto:xhbao@dicp.ac.cn) (X. Bao).

<sup>1</sup> Present address: Institute of Physical Chemistry, University of Stuttgart, 70569 Stuttgart, Germany.

Bethke has reported that selectivity of ca. 50% at 100 °C was obtained over Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts containing Au particles of about 5–10 nm in size [8]. Basic factors influencing the activity and selectivity of catalysts for CO selective oxidation in H<sub>2</sub> have also been widely investigated, which is very important for the application of the catalyst in the PEFCs and the research of the properties of the catalyst. The effect of the supports has also been investigated on the Au and Pt catalysts [9–11]. Igarashi and co-workers have shown that at high temperatures noble metal catalysts supported on mordenite and other zeolites possessed good selectivity for CO oxidation in H<sub>2</sub> [7,10]. The better activity and selectivity can be obtained on the Au catalyst supported on the reducible oxide [11]. Reaction temperature and oxygen concentration in the feed gas were found to play an important role in the activity. Manasilp and Gulari have found that the best reaction activity of Pt/Al<sub>2</sub>O<sub>3</sub> was obtained at 170 °C, and CO can be completely oxidized when the oxygen concentration was increased to 1.35%, however, the selectivity increases with the decrease of the oxygen concentration [12].

Silver has been investigated and utilized as an oxidation catalyst [13,14], and supported silver catalysts have been proved to possess a stable activity for CO oxidation at low temperatures [15–17], e.g. complete CO oxidation over Ag/Mn/perovskite can be attained below 373 K. Güldür and Balıkcı studied the Ag/Co and Ag/Mn composite oxide catalysts used in removing CO in H<sub>2</sub>-rich gases between 110 and 200 °C. However, no obvious activity for CO selective oxidation was observed at the temperatures below 100 °C [18]. Recently, we have shown that silver catalyst is a promising catalyst for the removal of CO in the fuels for PEFCs at low-temperatures [19–21]. We mainly focused on the activations of oxygen species and silver catalysts, and the effect of the formation of subsurface oxygen species on the CO oxidation. The formation of subsurface oxygen species increases the activity of the silver catalyst, and more reactant species can adsorb on the surface of silver catalyst. The presence of subsurface oxygen species supplies another way for CO oxidation. However, the basic factors influencing the activity of silver catalysts for CO selective oxidation are not carefully examined. In this paper, we concretely investigate the influence of reaction conditions, e.g. support, oxygen concentration, reaction temperature and silver loading, on the activity and selectivity.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

Silver catalysts supported on different supports were prepared by an incipient wetness impregnation method. The support was contacted with a certain amount of AgNO<sub>3</sub> precursor solution under stirring. The as prepared AgNO<sub>3</sub>/support sample was then aged at RT and dried at 80 °C for 12 h.

X-ray powder diffraction (XRD) experiments were carried out on a Rigaku D/max- $\gamma$ b X-ray diffractometer with

monochromatic detector. Copper K $\alpha$  radiation was used with power setting at 40 kV and 100 mA. Typical operation parameters were: a scan rate of 5° min<sup>-1</sup>. The size of the Ag particles was calculated from the half-width of the main peak at  $2\theta = 38^\circ$  according to the Scherrer's method [22].

Adsorption studies of CO and O<sub>2</sub> were conducted in a Chemisorption 2800 instrument. Typically, the catalyst was treated in a flow of He at 500 °C for 2 h and degassed for 1 h at the same temperature. The uptakes of CO and O<sub>2</sub> were then measured at 35 °C.

TEM experiments were performed with the JEM-2000EX microscope, using an accelerating voltage of 100 kV. For the TEM analysis, a sample was dispersed in absolute alcohol by an ultrasonic bath and deposited on a Formvar coated 200 mesh Cu grid.

### 2.2. Activity tests

The reactions of selective oxidation of CO were carried out in a conventional flow reactor. The reactants were fed with a volume ratio of H<sub>2</sub>/CO/O<sub>2</sub> = 98.5/1/0.5, which were controlled by an independent thermal mass flow controller. While in the case of experiment for the effect of oxygen concentration on the activity and selectivity of catalysts, it consisted of 1 vol% CO, 77.08 vol% H<sub>2</sub>, O<sub>2</sub> with varying O<sub>2</sub>:CO molar ratio ( $\lambda = 1-4, 6$ ) and He balance. The parameter  $\lambda$  is defined as the amount of oxygen present divided by the amount of oxygen needed to completely oxidize all of the CO in the feed gas ( $\lambda = 2[\text{O}_2]/[\text{CO}]$ ), where  $\lambda = 1$  is sufficient to provide for the complete oxidation of CO to CO<sub>2</sub> in the absence of an oxygen consuming side reaction. The total flow rate was 50 ml/min. Typically, 0.25 g of catalyst was used and pretreated under He, or 30% O<sub>2</sub> in He, or highly pure hydrogen, at 773 K for 2 h. The temperature of the catalyst bed was monitored with a thermocouple that was put on the center of the reaction bed.

On-line gas chromatograph with a TCD detector was employed to measure the reactor inlet and outlet effluent gas streams. Two columns were used: a molecular sieve 5A column (3 m  $\times$  4 mm) was used to separate hydrogen, oxygen and carbon monoxide. A Porapak Q column (3 m  $\times$  4 mm) was used to analyze carbon dioxide and H<sub>2</sub>O. Both columns were operated at a constant temperature of 30 °C.

Two parallel reactions occur in the present catalytic system:



In this paper, the CO conversion was calculated from the change of the CO concentration:

$$\text{CO conversion} = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100\%,$$

where [CO]<sub>in</sub> is the inlet CO concentration and [CO]<sub>out</sub> is the outlet CO concentration.

The O<sub>2</sub> conversion is based on oxygen consumption:

$$\text{O}_2 \text{ conversion} = \frac{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}}{[\text{O}_2]_{\text{in}}} \times 100\%,$$

where [O<sub>2</sub>]<sub>in</sub> is the inlet O<sub>2</sub> concentration and [O<sub>2</sub>]<sub>out</sub> is the outlet O<sub>2</sub> concentration.

Selectivity towards CO<sub>2</sub> was defined as the ratio of oxygen used to oxidize CO to CO<sub>2</sub> over the total amount of oxygen consumption.

$$S = \frac{\Delta\text{O}_2^{(\text{CO})}}{\Delta\text{O}_2^{(\text{CO})} + \Delta\text{O}_2^{(\text{H}_2\text{O})}}$$

The amount of oxygen not used in oxidizing CO to CO<sub>2</sub> was used to oxidize H<sub>2</sub>, which would reduce the amount of H<sub>2</sub> used to feed into fuel cell. Then the selectivity should be large enough not to reduce the fuel efficiency. Because of the large error in the quantification of H<sub>2</sub>O, the selectivity of CO oxidation was calculated from the oxygen mass balance:

$$S = \frac{0.5 \times [\text{CO}_2]}{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}} \times 100\% = \frac{0.5 \times C_{\text{CO}} \times [\text{CO}]_{\text{in}}}{C_{\text{O}_2} \times [\text{O}_2]_{\text{in}}} \\ = \frac{C_{\text{CO}}}{\lambda \times C_{\text{O}_2}}$$

where C<sub>CO</sub> is CO conversion and C<sub>O<sub>2</sub></sub> is O<sub>2</sub> conversion.

A definition comparison of λ and S demonstrates that λ and S are interrelated.

### 3. Results and discussion

#### 3.1. Catalyst characterization

Fig. 1 shows the XRD patterns of silver catalysts (weight loading of 6%) supported on different supports. All catalysts were pretreated with He at 500 °C for 2 h. No diffraction peaks of silver species are observed when the silver is sup-

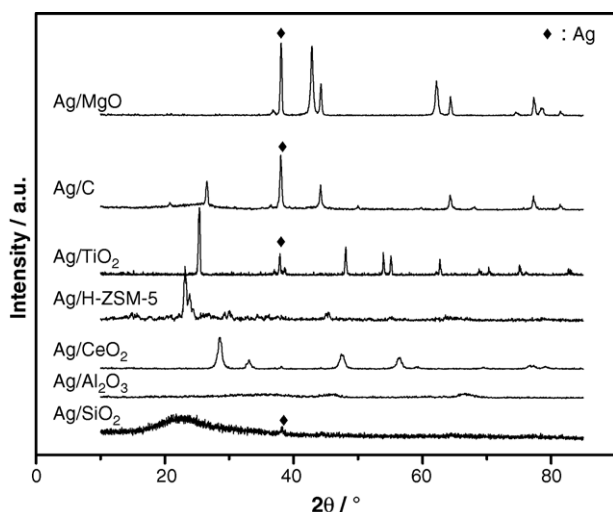


Fig. 1. XRD patterns of silver catalysts supported on different supports.

ported on the CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and H-ZSM-5, indicating the silver species are finely dispersed on the support. The peaks for metallic silver particles appear on the SiO<sub>2</sub>, MgO, C and TiO<sub>2</sub>. According to the Scherrer's method, the size of silver particles is about 8 nm for Ag/SiO<sub>2</sub> catalyst. The half-width of the diffraction peak at 2θ = 38° becomes sharp when supported on the MgO, C and TiO<sub>2</sub>, and the larger silver particles are formed. Different particle size is obtained when silver is supported on different supports. It is reasonable to think this phenomenon is related with the different properties of supports. Lower BET surface area of MgO (38.22 m<sup>2</sup>/g), C (5.49 m<sup>2</sup>/g) and TiO<sub>2</sub> (11.76 m<sup>2</sup>/g) will result in the poor dispersion of silver particles. However, a fine dispersion can still be obtained, though the BET surface area of CeO<sub>2</sub> (74.54 m<sup>2</sup>/g), Al<sub>2</sub>O<sub>3</sub> (240.23 m<sup>2</sup>/g) is lower than that of SiO<sub>2</sub> (495 m<sup>2</sup>/g). A strong interaction of silver species with CeO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> is easily formed [23,24], meanwhile the properties of silver particles are changed.

Powder XRD patterns of the Ag/SiO<sub>2</sub> catalysts with various Ag loadings and that of a reference SiO<sub>2</sub> sample are shown in Fig. 2. All samples were pretreated under He atmosphere at 500 °C. No diffraction peaks of silver or silver compounds are detected on the 2% Ag/SiO<sub>2</sub> sample, indicating that silver species are well dispersed. Metallic silver, the main peak of which is at 2θ = 38° and corresponding to the (1 1 1) plane of silver, appears in the high loading silver/silica samples. The crystallite sizes, determined by Scherrer's method from the XRD peak broadening, are 5.7, 8, 14, 16.5 and 18 nm, respectively. The particle size of silver catalyst increases with the silver loading. When the silver loading of the catalyst is higher than 16%, the average size of the Ag particles does not change obviously (not shown here). A small peak appears at 2θ = 33° for the Ag/SiO<sub>2</sub> catalysts with Ag loadings higher than 8%.

Table 1 shows the amounts of CO and O<sub>2</sub> adsorbed per gram of silver on silica-supported catalysts with different silver loadings. As can be seen, the reversible adsorption for

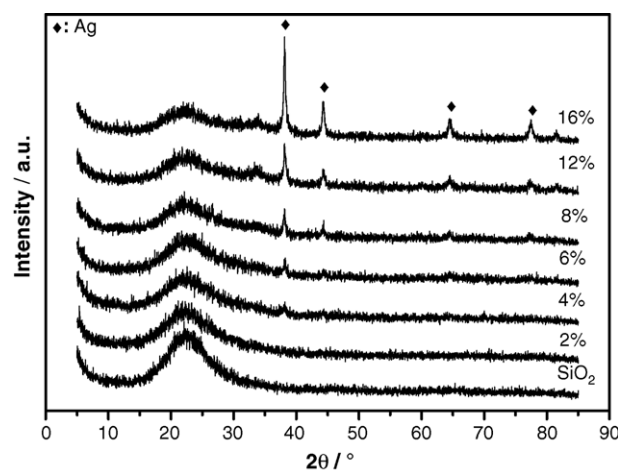


Fig. 2. XRD patterns of Ag/SiO<sub>2</sub> catalysts with different loadings pretreated with He at 500 °C for 2 h.

Table 1  
Amounts of CO and O<sub>2</sub> sorbed per gram of silver on the silica-supported silver catalysts with different loading

Extrapolation (cc/G STP)	2%	4%	6%	8%	12%
<b>CO</b>					
Total	1.4386	1.7282	2.0275	2.8596	3.1243
Reversible	1.3801	1.5765	1.8469	2.6272	2.6802
Irreversible	0.0366	0.1460	0.1845	0.2568	0.4417
<b>O<sub>2</sub></b>					
Total	0.9434	1.0106	1.1152	1.3532	1.5005
Reversible	0.9103	1.0033	1.1047	1.3428	1.4898
Irreversible	0.0366	0.0080	0.0113	0.0104	0.0107
Difference <sup>a</sup>	0.4952	0.7176	0.9123	1.5064	1.6238

<sup>a</sup> The difference between the total amounts of CO adsorbed and that of O<sub>2</sub> adsorbed.

oxygen is the dominant adsorption at this temperature. Moreover, both the total amounts of adsorption of CO and O<sub>2</sub> at 35 °C and the difference between the adsorbed amounts of CO and O<sub>2</sub> increases with the silver loading.

To understand the difference in characteristics between the Ag/SiO<sub>2</sub> catalysts treated with hydrogen and that with oxygen, the catalysts are characterized by XRD and TEM. The size distribution of silver particles after different treatment is shown in Table 2. Only a range of the mean size of the silver particles is given in Table 2, due to the limit of the particle numbers. Fig. 3 shows the XRD patterns of the 16% Ag/SiO<sub>2</sub> pretreated under oxygen and hydrogen atmospheres at 500 °C, respectively. It can be clearly seen that the atmosphere employed in the pretreatment has a great influence on the size and structure of the Ag particles. The XRD pattern of the 16% Ag/SiO<sub>2</sub> treated with oxygen at 500 °C for 2 h shows diffraction peaks corresponding to metal silver particles with average size of about 18 nm, as well as ultrafine silver oxide species ( $2\theta = 33^\circ$ ) (Fig. 3A(a)). After the sample is purged with hydrogen at the same temperature for 1 h, the diffraction peak of the silver oxide species disappears, and the average size of the silver particles decreases to about 8 nm (Fig. 3A(b)). If the 16% Ag/SiO<sub>2</sub> sample is firstly pretreated with highly pure hydrogen at 500 °C for 2 h, only metal silver particles with average size of about 12 nm are observed by XRD (Fig. 3B(c)). The average size of the metallic silver particles (about 17 nm) obviously increases after the sample (Fig. 3B(c)) is purged by oxygen at the same temperature for

Table 2  
Characteristics of silver/silver compounds on the Ag/SiO<sub>2</sub> catalyst pretreated with different gases at 500 °C analyzed with XRD and TEM

	Oxygen	Followed by H <sub>2</sub>	Hydrogen	Followed by O <sub>2</sub>
<b>TEM</b>				
Particle size (nm)	11–18		6–10	
<b>XRD</b>				
State	Metal, oxide	Metal	Metal	Metal
Particle size (nm)	18	8	12	17

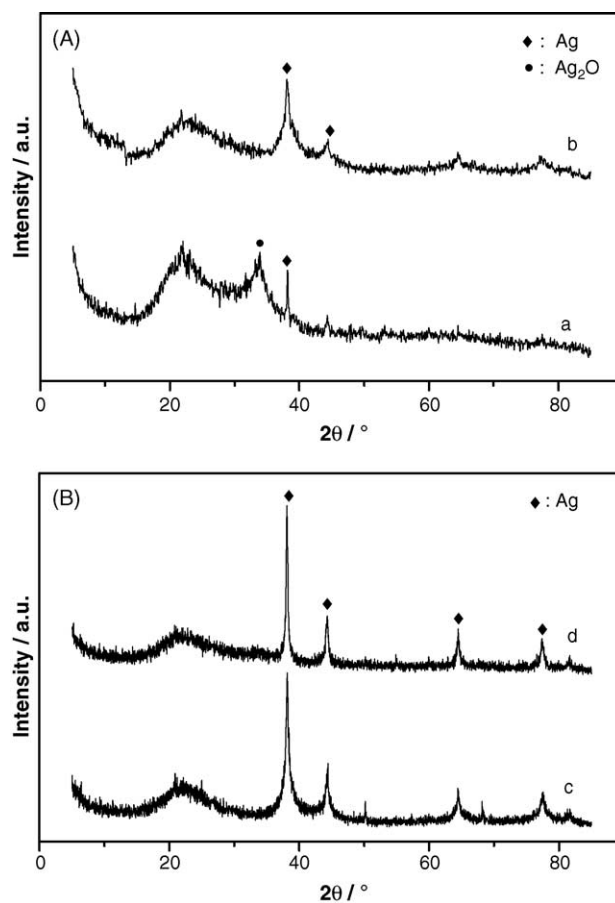


Fig. 3. XRD patterns of 16% Ag/SiO<sub>2</sub> treated with oxygen and hydrogen atmospheres at 7500 °C. (A) Firstly treated with oxygen for 2 h (a), followed by hydrogen atmosphere at the same temperature for 1 h (b). (B) Firstly treated with hydrogen for 2 h (c), followed by oxygen atmosphere at the same temperature for 1 h (d).

1 h (Fig. 3B(d)). However, in this case, no diffraction peak of silver oxide can be detected. Yang et al. have reported on the thermal stabilities of uniform silver clusters prepared on oxidized silicon and aluminum surface in oxidizing and reducing atmospheres [25]. The thermal stability of the silver cluster was significantly lower under the oxidizing conditions, and heating above 623–673 K under the oxidizing conditions induced a migration of the silver cluster. Aoyama et al. have also shown that oxidation induced a size growth of the particles. On the contrary, metallic silver particles were finely dispersed by the reduction process [26]. For the Ag/SiO<sub>2</sub> catalysts, it can also be obtained according to the characterization results that pretreatment at 500 °C in oxygen favors the migration and aggregation of metal silver particles on the support, while following pretreatment at 500 °C in hydrogen favors the dispersion of the silver particles. TEM results also confirm this conclusion. As shown in Fig. 4, the mean silver particle size of the Ag/SiO<sub>2</sub> catalyst treated with oxygen is larger than that treated with hydrogen. The detailed explanation about the aggregation of silver particle after oxygen treatment at high temperatures can be found in Ref. [20].

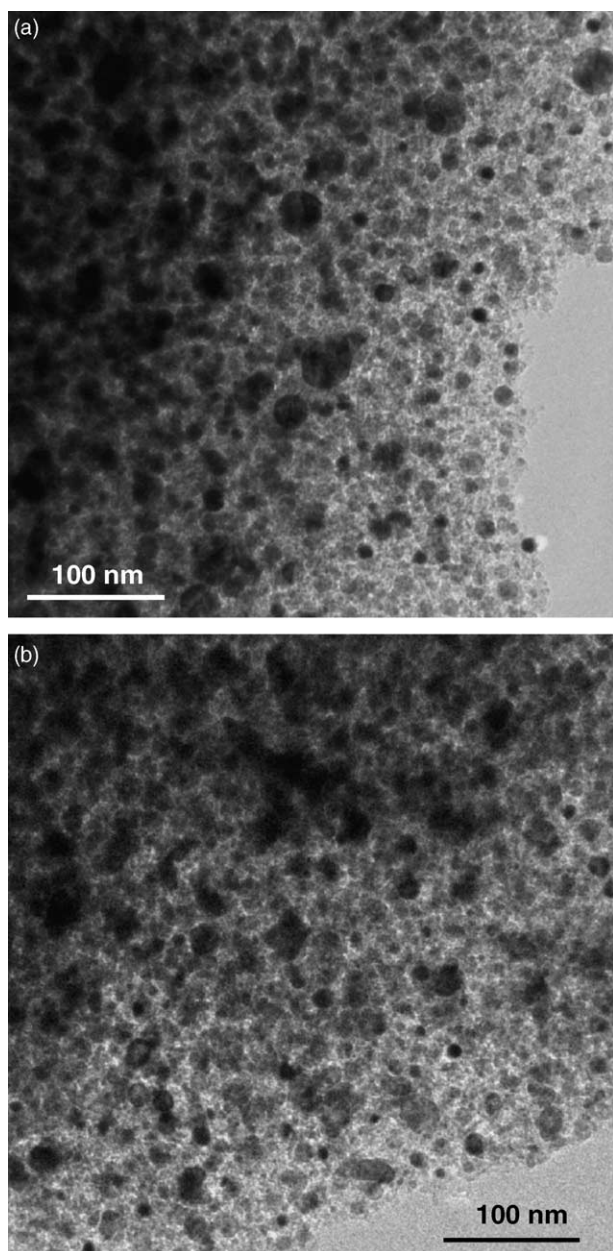


Fig. 4. TEM micrographs of Ag/SiO<sub>2</sub> catalysts treated with oxygen (a), and hydrogen (b) at 500 °C for 2 h.

### 3.2. Catalytic properties

#### 3.2.1. Effects of supports on the activity and selectivity

Table 3 shows the catalytic activity of silver catalyst supported on the different supports. The maximum CO

Table 3  
Catalytic activities of silver catalysts supported on different supports

Catalysts	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	CeO <sub>2</sub>	H-ZSM-5 (SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> )=24)	C	MgO	SiO <sub>2</sub>	TiO <sub>2</sub>
He 500 °C/2 h							
C <sub>CO</sub> (%)	13	7.94	–	–	4.48	23.35	5.11
S (%)	15.85	9.07	–	–	4.48	29.75	39.36
T <sub>CO</sub> (°C)	65	95	–	–	150	60	130

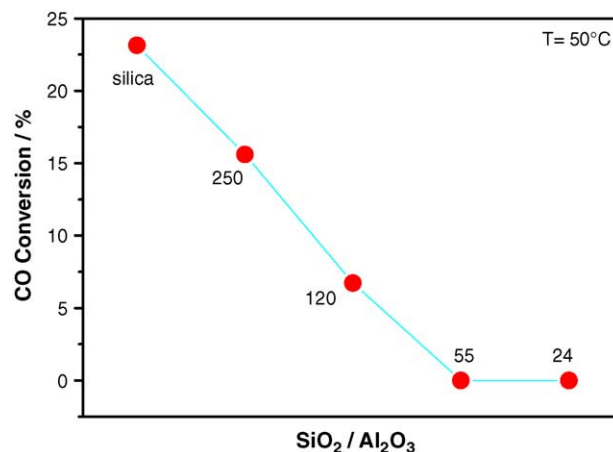


Fig. 5. Variations of CO conversion as a function of different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of zeolite H-ZSM-5 at 50 °C.

conversion, the corresponding O<sub>2</sub> selectivity and the reaction temperature are presented. No CO conversion is observed on the silver catalyst supported on the zeolite H-ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 24) and activated carbon during the detection temperatures, moreover the oxygen is completely converted only at the temperature higher than 140 and 220 °C. The catalytic activity of silver catalyst supported on different supports follows: SiO<sub>2</sub> > Al<sub>2</sub>O<sub>3</sub> > CeO<sub>2</sub> > TiO<sub>2</sub> > MgO ≫ H-ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 24) and activated carbon. It has been known from XRD patterns that a fine dispersion of silver particles on the Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and H-ZSM-5 is obtained and larger silver particle is observed on the MgO and C supports. So it is thought that the main reason for the higher catalytic activity for CO selective oxidation over silver catalyst is not due to the smaller or larger size of silver particles, and should be related with the properties of support and the interaction between support and silver particles.

The catalytic activities of silver catalyst supported on the H-ZSM-5 with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio are also tested, as shown in Fig. 5. The best catalytic activity is obtained on the silver catalyst supported on the pure-silica-zeolite H-ZSM-5, and the activity decreases with the decreasing of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio. The Al<sub>2</sub>O<sub>3</sub> in the zeolite easily interacts with the silver species supported, and changes the properties of silver particles dispersed on the support. From the above results, we can also get that the reaction for CO selective oxidation over silver catalyst does not need the acidity of the support. Then the MCM-41 and SBA-15 zeolites are also chosen to support silver particles to examine the activity of silver catalyst and the effect of support. The CO conversion of about 30% at

45–50 °C can be obtained, which is very similar with that of silver catalyst supported on SiO<sub>2</sub>. Anyway, the silica and the pure silica zeolites are better supports for silver catalyst. The effects of support on the properties of silver species and the catalytic activity need to be further investigated in the future. In the following research, SiO<sub>2</sub> is chosen as the support of silver catalyst.

### 3.2.2. Effects of silver loading

The catalytic behaviors of the Ag/SiO<sub>2</sub> catalysts with various Ag loadings for the selective oxidation of CO in H<sub>2</sub> atmosphere are shown in Fig. 6. The same pretreatment is

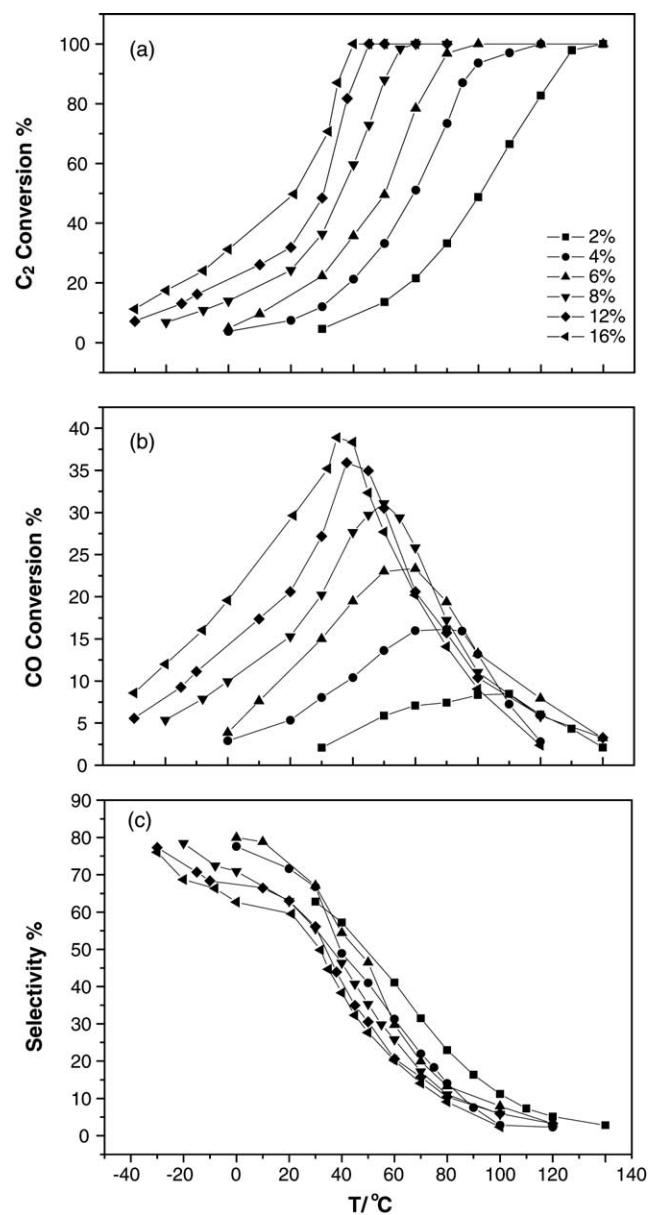


Fig. 6. Variations of O<sub>2</sub> conversion (a), CO conversion (b), and selectivity *S* (c) over Ag/SiO<sub>2</sub> catalysts with different loadings as a function of the reaction temperature. CO 1.0%, O<sub>2</sub> 0.5%, H<sub>2</sub> balance. Flow rate: 50 ml/min, pretreatment with He at 500 °C for 2 h.

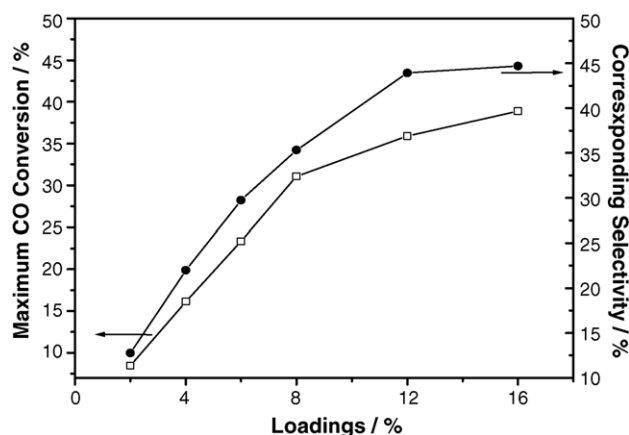


Fig. 7. Maximum CO conversion and the corresponding selectivity over Ag/SiO<sub>2</sub> catalysts as a function of silver loading.

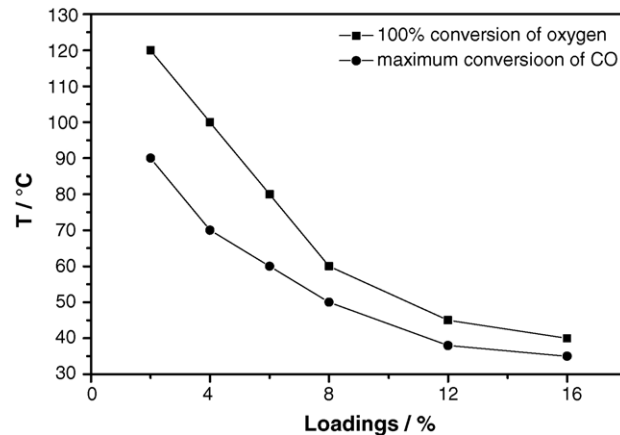


Fig. 8. The temperatures for 100% conversion of oxygen and the maximum conversion of CO as a function of silver loading.

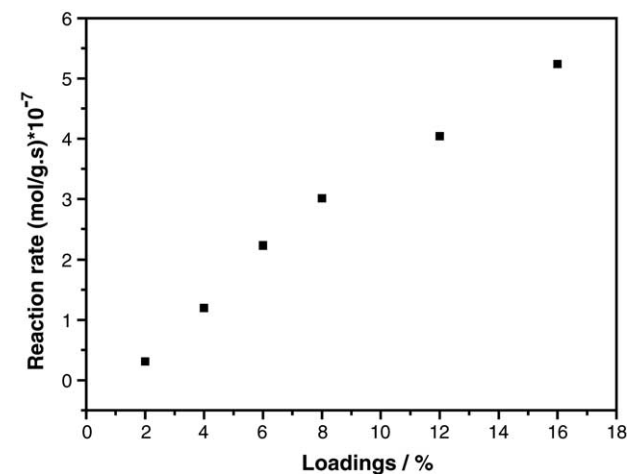


Fig. 9. The reaction rate of silver catalysts with different loadings for CO selective oxidation at 30 °C.

done before the activity tests. No activity was found on the SiO<sub>2</sub> support for the selective oxidation of CO. Over all catalysts, the O<sub>2</sub> conversion increases monotonously with the reaction temperature, and oxygen can be totally consumed above a certain temperature. The oxygen conversion at the same temperature also increases with the silver loading. It is interesting to note that the CO conversion curves are

“volcano-shaped” on all of the catalysts. The temperature corresponding to maximum CO conversion decreases with the increase of the silver loading. Furthermore, the maximum CO conversion again increases with the silver loading, which is consistent with the result of Table 1, namely the adsorption amounts of CO and O<sub>2</sub> increase with the silver loading. It is found that there is little change for the oxygen and CO con-

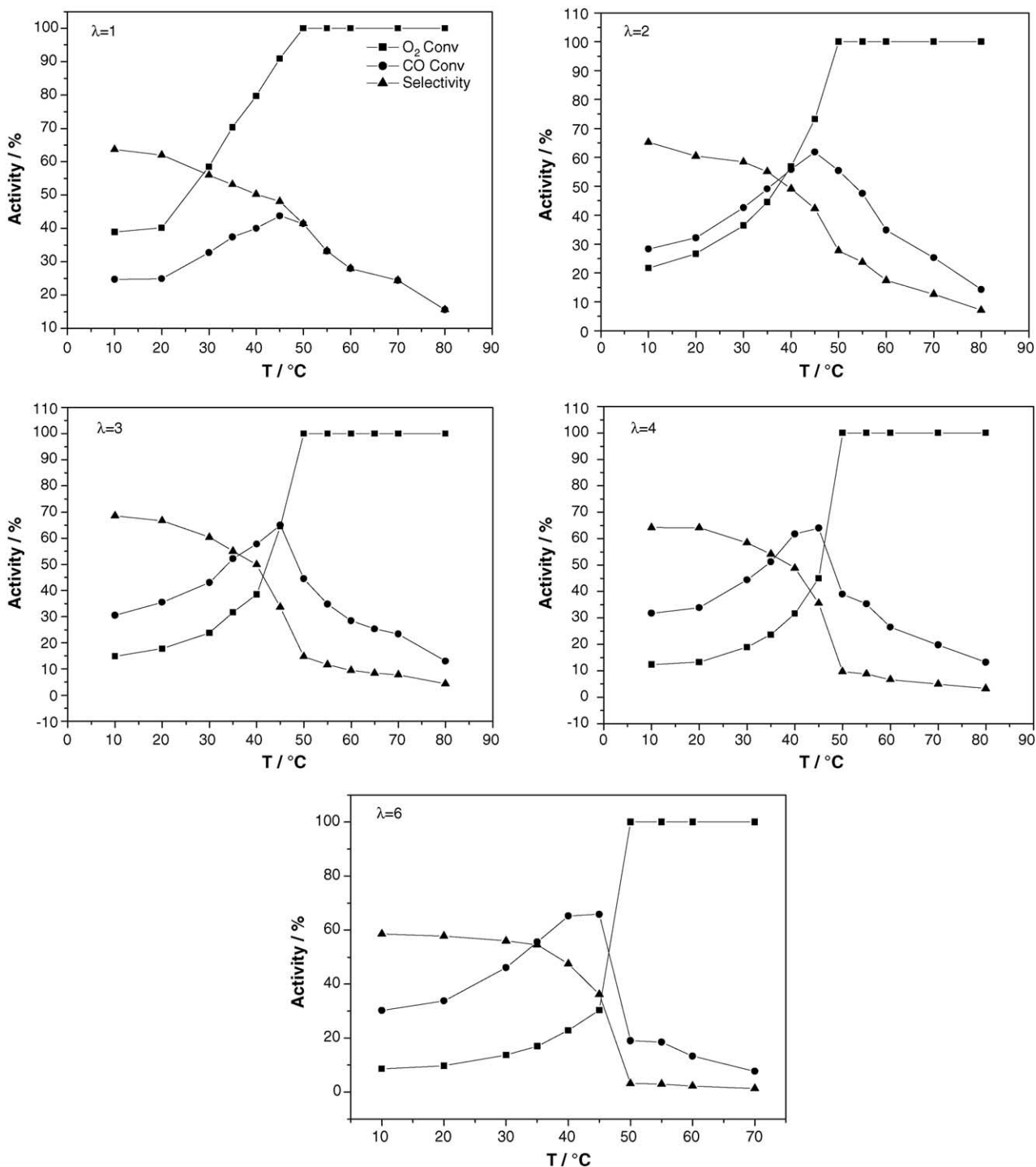


Fig. 10. Conversion of CO and O<sub>2</sub>, and the selectivity towards CO<sub>2</sub> vs. reaction temperature on 16% Ag/SiO<sub>2</sub> catalysts pretreated with He at 500 °C for different λ.

versions over the catalysts with silver loadings higher than 16% (not shown here). On the other hand, the selectivity for CO oxidation of the catalysts decreases with the reaction temperature, which indicates that the consumption of oxygen at high temperatures is mostly contributed by the oxidation of hydrogen. Therefore, for CO selective oxidation over the Ag/SiO<sub>2</sub> catalysts, oxygen preferentially reacts with carbon monoxide at low temperatures, but with hydrogen at high temperatures. In other words, Ag/SiO<sub>2</sub> catalysts seem to be a kind of promising catalysts for the selective oxidation of carbon monoxide at low temperatures.

The effects of silver loading on the activity of Ag/SiO<sub>2</sub> catalysts for selective CO oxidation can be seen more clearly in the Figs. 7 and 8. Fig. 7 shows the maximum CO conversion and corresponding selectivity over Ag/SiO<sub>2</sub> catalysts with different silver loadings. Both the maximum CO conversion and the corresponding selectivity increase with the Ag loading. The temperatures corresponding to the oxygen complete conversion and the maximum CO conversion decrease with the increase of the Ag loading, as shown in Fig. 8. The reaction rates of Ag/SiO<sub>2</sub> with different silver loading at 30 °C are shown in Fig. 9. The reaction rate of the catalyst for CO selective oxidation increases with silver loading at low temperatures, however, the increase is not linearity. That is to say that the silver species loaded on supports does not completely exert the role of catalytic sites for CO selective oxidation. It has been found that more bulk oxygen species form, and the initial temperature of reaction for CO with surface oxygen species decreases obviously for silver catalysts with higher loading after treated with He at 500 °C [27]. When the silver loading is increased, the ability of supplying active oxygen species of silver catalysts increases obviously. We believe that the activity increase of the silver catalyst should be related with the structure (oxygen species) of silver particles.

### 3.2.3. O<sub>2</sub> effect

To avoid an accidental explosion, the feed gas consisted of 1% CO, 77.08% H<sub>2</sub>, oxygen and He balance. Fig. 10 shows the CO conversion, oxygen conversion and selectivity for different  $\lambda$  as a function of temperature. In all cases, there exists a maximum value for CO conversion, and oxygen can be totally consumed above a certain temperature (50 °C). The selectivity towards CO<sub>2</sub> is not changed obviously at low temperatures. However, the slopes of the curves for oxygen conversion, CO conversion and the selectivity become larger above 45 °C with increasing  $\lambda$ . That is to say that above certain temperature hydrogen can react with oxygen quickly, at the same time the CO conversion and selectivity decrease sharply with increasing oxygen concentration. Oxygen preferentially reacts with hydrogen at high temperatures; moreover it becomes stronger and more obvious with high oxygen concentration. This means that most of the oxygen added is used for the oxidation of hydrogen under such a condition.

Changes in the activities for the oxidation of CO on the oxygen content in the feed gas at 45 °C are shown in Fig. 11. When increasing the oxygen content to 1%, the CO conver-

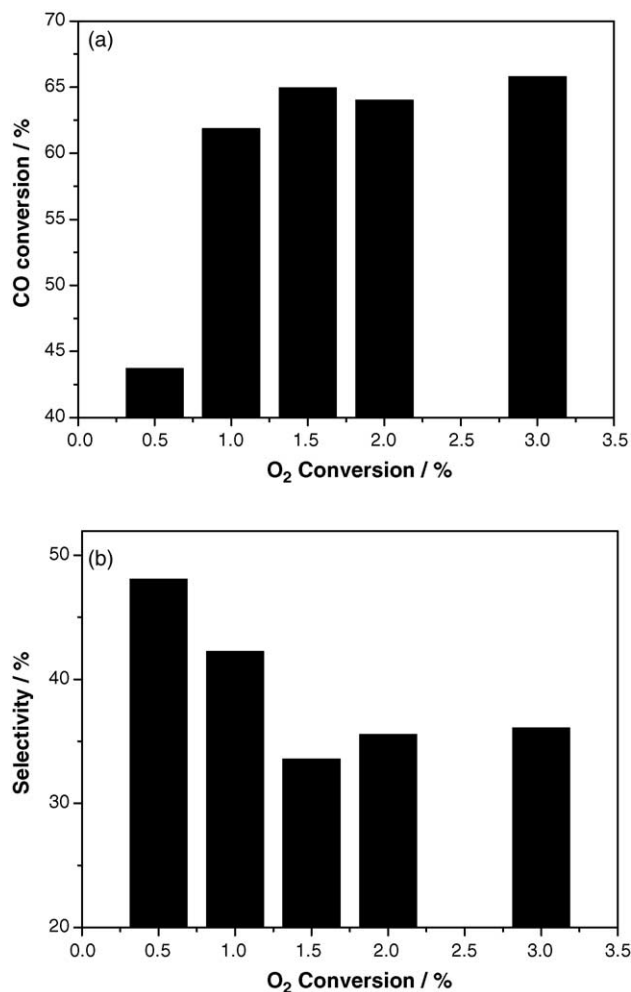


Fig. 11. Dependencies of the CO conversion (a), and the selectivity (b) as a function of O<sub>2</sub> concentration at 45 °C. CO 1%, H<sub>2</sub> 77.08% and He balance.

sion increases from 43.72 to 61.88%. At high O<sub>2</sub>:CO ratio ( $\lambda = 3$ ) the CO conversion is 64.96%. However, no obvious increase of CO conversion is observed for increasing oxygen concentration further. Only 0.5% oxygen is necessary for stoichiometric oxidation of 1% CO, but CO still remains in the outlet gas even in case of the 3% oxygen on silver catalysts. The CO is not converted completely even in excess of oxygen. The selectivity is plotted against the oxygen concentration in Fig. 11b. The selectivity is increased by reducing the oxygen concentration at 45 °C, and it decreases sharply when the oxygen concentration is increased to 1.5%. The oxygen concentration of 1% in the feed gas is suitable to oxidize CO in a large excess of hydrogen on Ag/SiO<sub>2</sub> catalysts, taking into consideration both the high CO conversion, the high selectivity and the high safety for the oxidation of CO.

### 3.2.4. Activity after pretreatment with H<sub>2</sub>, O<sub>2</sub> and He at 500 °C

Fig. 12 shows the catalytic behaviors of the 16% Ag/SiO<sub>2</sub> pretreated in different atmospheres (O<sub>2</sub>, H<sub>2</sub>, He) at 500 °C. It can be clearly seen that the pretreatment conditions strongly



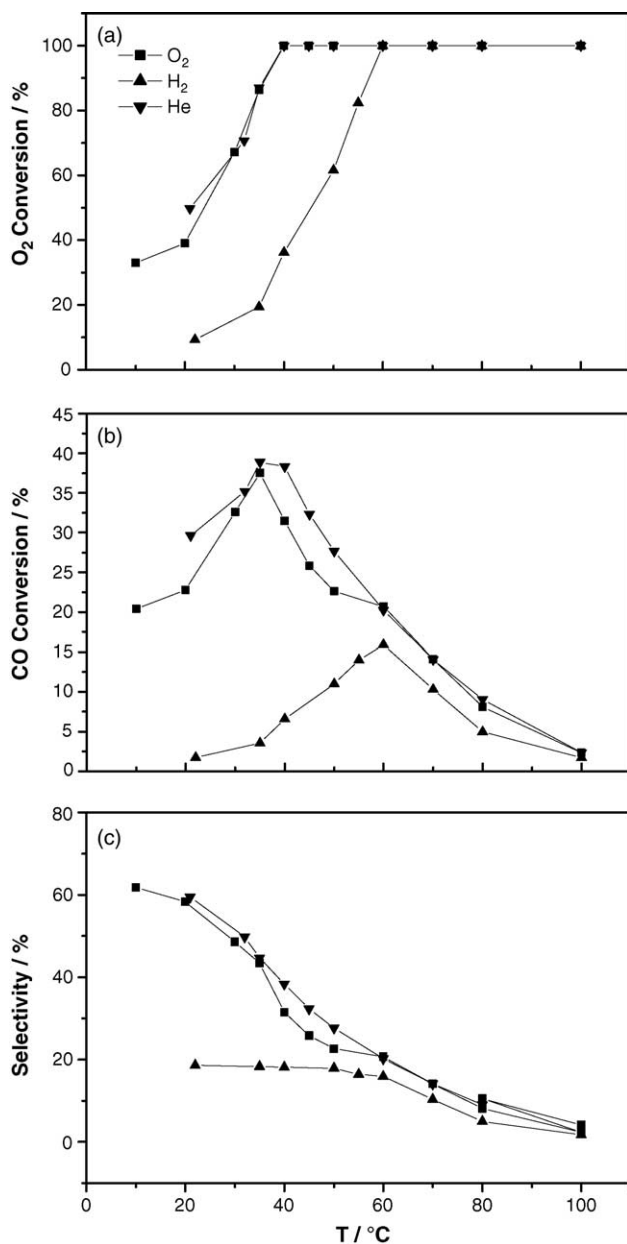


Fig. 12.  $\text{O}_2$  conversion (a), CO conversion (b), and selectivity  $S$  (c) over 16%  $\text{Ag}/\text{SiO}_2$  catalysts treated with different gases as a function of the reaction temperature.

influenced the activity and selectivity of the catalysts towards the selective oxidation of CO. The  $\text{O}_2$  conversion can reach 100% for all catalysts treated under the three different gases. However, the  $\text{O}_2$  pretreated and the He pretreated catalysts exhibit higher activity and selectivity at low temperatures than those of the  $\text{H}_2$  pretreated catalyst. Meima et al. have reported that a severe deactivation of an alumina supported silver catalyst for CO oxidation occurred after reduction at 400  $^\circ\text{C}$  and subsequent cooling in nitrogen [28]. Accordingly, similar deactivation phenomenon of the  $\text{Ag}/\text{SiO}_2$  catalyst treated with hydrogen at high temperatures can also be observed.

It has been reported that larger silver particles were present on  $\text{Ag}/\text{ZrO}_2$  with high loadings, but were not present at lower silver contents, and the catalysts with high loadings were more active for the complete oxidation of methane [29]. Therefore, the small number of surface defects and the low reactivity of the predominant (1 1 1) face could explain the low activities of the catalysts, and larger silver particles appear to be polycrystalline with a large number of defects and grain boundaries, which increased the reaction activity [29]. In this paper, the size of silver particles and activity of catalysts also increase with the silver loading, moreover XRD results indicate that the metal silver particle sizes for the  $\text{O}_2$  pretreated and He pretreated catalysts are similar and are much larger than that of the  $\text{H}_2$  pretreated catalyst (Fig. 3). From the results above, it is believed that the polycrystalline formation due to the aggregation of silver particles is in favor of the reaction for CO selective oxidation and the increase of the adsorption ability of the catalyst. On the other hand, it has been reported that the formation of subsurface oxygen species on the silver surface would result in an activity increase of some reactions [30,31]. Moreover, in our research we found the formation of the subsurface oxygen species after pretreatment with oxygen or He at certain temperatures and its higher activity [20], and also observed the increasing of the amount of subsurface oxygen species with silver loading [27]. Reports of strongly adsorbed subsurface oxygen species associated with silver catalysts are prevalent in the literature, and evidence that large silver particles favors the formation of subsurface oxygen and oxygen can remain occluded in large silver particles after prolonged evacuation at 500  $^\circ\text{C}$  [32]. Therefore, small silver particles have to aggregate into large one prior to the formation of the special silver-oxygen compound. Higher oxygen pretreatment temperature is required on the silver catalyst with low loading, which possesses smaller silver particle size, in order to obtain a higher reaction activity [20]. Interestingly, the deactivated catalyst can be re-activated after re-pretreatment with oxygen. The deactivation of silver catalyst after pretreatment with  $\text{H}_2$  at high temperatures is mainly due to the structure

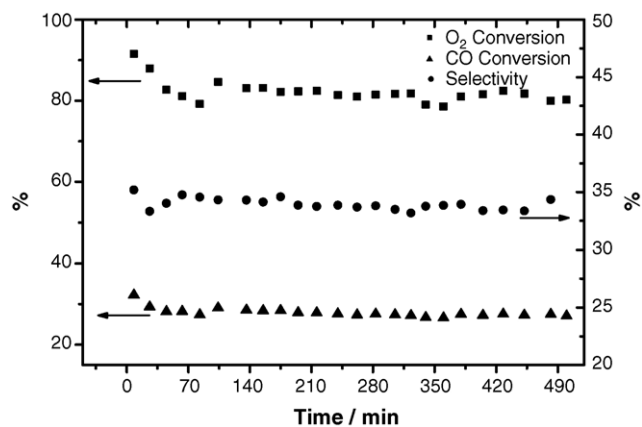


Fig. 13. Stability of the 8%  $\text{Ag}/\text{SiO}_2$  catalyst for CO selective oxidation at 50  $^\circ\text{C}$ .

change of silver particles compared with that after oxygen pretreatment, and the absence of subsurface oxygen species.

The stability of the 8% Ag/SiO<sub>2</sub> catalyst for the selective oxidation of CO at a 50 °C is shown in Fig. 13. During this study, all of the catalysts show good stabilities. Only an initial activity decreasing within the first hour of the stream time was observed. Then a steady state is acquired. These observations of ours are consistent with some previous observations, in which the deactivation processes were investigated during the kinetic studies on CO selective oxidation on Au/α-Fe<sub>2</sub>O<sub>3</sub> and CO oxidation on Au/TiO<sub>2</sub>, and the authors concluded that the steady states could only be attained after a period of time [33,34].

#### 4. Conclusions

The effects of the supports, silver loading, oxygen concentration and pretreatment conditions on the activity and selectivity for CO selective oxidation are investigated in this paper. SiO<sub>2</sub> and the pure silica zeolites are found to be better supports for silver catalyst. The activity and selectivity for CO oxidation as well as the CO maximum conversion increase with the silver loading. XRD patterns show that the intensity of the metallic silver peak and the size of the silver particles increase with the silver loading. The CO conversion increases with increasing oxygen concentration properly. However, the CO is not consumed completely even in case of 3% oxygen in the feed gas. The selectivity at low temperatures is not changed obviously, but the selectivity above 45 °C decreases with oxygen concentration sharply. Above a certain temperature hydrogen reacts with oxygen easily and sharply. A pretreatment process exerts a strong influence on the activities of these catalysts towards CO selective oxidation. Under different pretreatment conditions, a change in the particle size and structure of silver occurs, which could influence the activity for CO oxidation. We also find that oxidation induces the aggregation of silver particles at high temperatures, whereas metallic silver can be caused to be finely dispersed by the reduction process. High activity and selectivity for CO oxidation are obtained over an Ag/SiO<sub>2</sub> catalyst pretreated under oxygen atmosphere. The reversibility of changes in activity and selectivity for CO oxidation indicates that the activity and selectivity of silver catalysts might be related with the structure of silver particles.

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#### References

- [1] R.A. Lemons, *J. Power Sources* 29 (1990) 251.
- [2] A.J. Appleby, F.R. Foulkes, *Fuel Cell Handbook*, van Nostrand Reinhold, New York, 1989.
- [3] S. Gottesfeld, J. Pafford, *J. Electrochem. Soc.* 135 (1988) 2651.
- [4] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, *J. Catal.* 171 (1997) 93.
- [5] M.M. Schubert, H.A. Gasteiger, R.J. Behm, *J. Catal.* 172 (1997) 256.
- [6] S.H. Oh, R.M. Sinkevitch, *J. Catal.* 142 (1993) 254.
- [7] H. Igarashi, H. Uchida, M. Watanabe, *Chem. Lett.* 29 (2000) 1262.
- [8] G.K. Bethke, H.H. Kung, *Appl. Catal. A* 194 (2000) 43.
- [9] H. Igarashi, H. Uchida, M. Suzuki, Y. Sasaki, M. Watanabe, *Appl. Catal. A* 159 (1997) 159.
- [10] M. Watanabe, H. Uchida, H. Igarashi, M. Suzuki, *Chem. Lett.* 24 (1995) 21.
- [11] M.M. Schubert, V. Plzak, J. Garche, R.J. Behm, *Catal. Lett.* 76 (2001) 143.
- [12] A. Manasilp, E.E. Gulari, *Appl. Catal. B* 37 (2002) 17.
- [13] K. Tamaru, *Appl. Catal. A* 151 (1997) 167.
- [14] J.G. Serafin, A.C. Liu, S.R. Seyedmonir, *J. Mol. Catal. A* 131 (1998) 157.
- [15] G.G. Xia, Y.G. Yin, W.S. Willis, J.Y. Wang, S.L. Suib, *J. Catal.* 185 (1999) 91.
- [16] S. Imamura, H. Yamada, K. Utani, *Appl. Catal. A* 192 (2000) 226.
- [17] K. Song, S. Kang, S.D. Kim, *Catal. Lett.* 49 (1997) 65.
- [18] C. Güldür, F. Balıkcı, *Int. J. Hydrogen Energy* 27 (2002) 219.
- [19] Z.P. Qu, M.J. Cheng, X.L. Dong, X.H. Bao, *Catal. Today* 93 (2004) 247.
- [20] Z.P. Qu, M.J. Cheng, W.X. Huang, X.H. Bao, *J. Catal.* 229 (2005) 446.
- [21] Z.P. Qu, S.T. Zhou, W.C. Wu, C. Li, X.H. Bao, *Catal. Lett.* 101 (2005) 21.
- [22] P. Scherrer, *Goettingen Nachr.* 2 (1918) 98.
- [23] S. Imamura, H. Yamada, K. Utani, *Appl. Catal. A* 192 (2000) 221.
- [24] M.C. Kung, K.A. Bethke, J. Yan, J.H. Lee, H.H. Kung, *Appl. Surf. Sci.* 121 (1997) 261.
- [25] M.X. Yang, P.W. Jacobs, C. Yoon, L. Muray, E. Anderson, D. Attwood, G.A. Somorfai, *Catal. Lett.* 45 (1997) 5.
- [26] N. Aoyama, K. Yoshida, A. Abe, T. Miyadera, *Catal. Lett.* 43 (1997) 249.
- [27] Z.P. Qu, M.J. Cheng, C. Shi, X.H. Bao, *Chin. J. Catal.* 23 (2002) 460–464.
- [28] G.R. Meima, L.K. Knijff, A.J. Van Dillen, J.W. Geus, *J. Chem. Soc., Faraday Trans. I* 85 (1989) 293.
- [29] Lj. Kundakovic, M. Flytzani-Stephanopoulos, *Appl. Catal. A* 183 (1999) 35.
- [30] C. Backx, J. Moolhuysen, P. Geenen, R.A. Van Santen, *J. Catal.* 72 (1981) 364.
- [31] X. Bao, J. Barth, G. Lempfuhr, R. Schuster, Y. Uchida, R. Schlögl, G. Ertl, *Surf. Sci.* 284 (1993) 14.
- [32] Y.L. Sandler, W.M. Hickam, in: W.M.H. Sachtler, G.C.A. Schuit, P. Zwietering (Eds.), *Proceeding of Third International Congress on Catalysis*, Amsterdam, vol. 1, 1964, p. 227.
- [33] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, *J. Catal.* 182 (1999) 430.
- [34] M.A. Bollinger, M.A. Vannice, *Appl. Catal. B* 8 (1996) 417.