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CO selective oxidation in H_2-rich gas over Ag nanoparticles—effect of oxygen treatment temperature on the activity of silver particles mechanically mixed with SiO_2

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Abstract

In order to elucidate the roles of pretreatment with oxygen at high temperatures and the interaction between Ag nanoparticles and SiO_2 in low-temperature CO selective oxidation, a mechanical mixture of Ag nanoparticles and SiO_2 powder was prepared and pretreated with oxygen at different temperatures. The samples calcined at 300 and 400 °C have poor activities for CO oxidation, while oxygen reacts totally with H_2 at temperatures of 160 and 120 °C, respectively. It becomes catalytically active after treatment with oxygen at 500 °C, and the activity increases with the treatment temperature up to 700 °C, reaching nearly the same level of CO conversion as that of the 8%Ag/SiO_2 prepared by the incipient wetness impregnation method and treated with He at 500 °C. XRD and TEM results show that calcinations under oxygen atmosphere between 500 and 700 °C help dispersing the silver nanoparticles on the surface of SiO_2, as well as induce an interaction between the silver nanoparticles and SiO_2. Moreover, the ability of CO adsorption at low temperatures is obviously enhanced. However, further increasing the pretreatment temperature decreases the catalytic activity due to the heat-induced aggregation of silver nanoparticles on the surface of SiO_2 and the corresponding decrease of the CO adsorption ability, but higher than that of the initial Ag–SiO_2 mixture. CO adsorbed on the Ag nanoparticles dispersed on the surface of silica shows a high activity toward CO selective oxidation, and it is proved that the sub-surface oxygen species plays a very important role in this reaction.

Keywords: CO selective oxidation; Silver powder; SiO_2; Mechanical mixing; Oxygen treatment

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) that have the better energy efficiency than the conventional combustion engines and a zero-emission of air pollutants, have received much attention as a potential power source of electric vehicles. However, the Pt anode catalysts can be seriously poisoned by traces of CO in reformed gases [1]. Most catalysts employed previously for CO removal are based on expensive noble metals, e.g. Pt, Rh, Ru and Au [2–5]. However, one important present issue is to improve the catalysts performance under dynamic conditions of PEMFC low operating temperatures. Lower operating temperatures facilitate the system integration of mobile electric powers, such as improving the cold start properties, implementing the catalyst directly into the fuel cell and preventing the occurrence of the reverse water gas shift reaction. Decreasing the reaction temperatures and seeking for more economic catalysts for CO selective oxidation are the main research focus of near future.

Recently we found that silver catalyst shows a relatively high activity and selectivity at low temperatures in feedgas which contains 1% CO–0.5% O_2–98.5% H_2, and SiO_2 is a relatively good support for silver catalysts compared with other supports such as Al_2O_3, MgO, HZSM-5, MCM-22, carbon, etc. [6,7]. Moreover, the catalytic behavior of Ag/SiO_2 catalysts for CO selective oxidation exhibited remarkable changes when the catalysts were treated

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with different pretreatment methods. Hydrogen treatment at high temperatures (>400 °C) deactivated the catalysts, while oxygen pretreatment at high temperatures (>350 °C) could reactivate the deactivated catalysts. The formation of sub-surface oxygen species is essential to obtain a high catalytic activity and selectivity. Tsubota et al. [8] reported that, in case of Au/TiO_2 system, a strong interaction between Au nanoparticles and the TiO_2 support was observed after oxygen treatment of a mechanical mixture of them at high temperatures, and actually it is just the interface of Au and TiO_2 which is responsible for CO oxidation. Moreover, oxygen treatments of the catalyst at high temperatures can redisperse some metals, such as Pt, on a support [9].

In case of metal/silica system, albeit SiO_2 is relatively inert compared with TiO_2, it can still be assumed that there is an interaction between the metal nanoparticles and the support after the oxygen pretreatment at high temperatures. Meanwhile, the high temperature oxygen treatment may alter the structure and size of the silver nanoparticles, which in turn modifies its adsorption ability towards different reactants, and changes the catalytic performances of these silver catalysts. However, all the Ag/SiO_2 catalysts mentioned above were prepared by chemical methods, it is difficult to know the detail about the interaction between Ag and silica and its effect on catalytic behavior on the CO selective oxidation reaction. In present work, the well-prepared silver nanoparticles with the mean particle diameter of 30–60 nm are mixed with silica powder mechanically. The catalytic behavior of the as-prepared catalyst and those after high temperature oxygen treatment in CO selective oxidation is tested, and the role of oxygen treatment in this reaction is disclosed by reaction evaluation and various kinds of characterization methods.

2. Experimental

2.1. Preparation of $Ag–SiO_2$ mixture catalysts

Ag nanoparticle was prepared by the arc discharge technique in methane (the same as that described in the previous work [10]), whose TEM image is shown in Fig. 1. The spherical silver nanoparticles with mean particle diameter of about 30–60 nm were observed. The SiO_2 with a specific surface area of 495 m^2/g and pore size of about 7 nm supplied by Qingdao Ocean Chemical Co., Ltd. was used to mix with silver nanoparticles. The Ag nanoparticles and SiO_2 powder were mechanically mixed and grounded to form a uniform mixture. The weight ratio of silver and SiO_2 was 19:100. The $Ag–SiO_2$ mixture was pretreated with a 30% O_2/He gas at different temperatures in the range of 300 and −800 °C for 1 h before reaction.

2.2. Characterization of catalysts

The mean diameter of the silver nanoparticles was determined by a Model H-600 transmission electron microscope (TEM) operated at 75 kV. XRD was used to identify the state and size of the silver nanoparticles, and the patterns were recorded on a Rigaku D/max-rb diffract meter equipped with a Cu Kα X-ray source operating at 40 kV and 100 mA. 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 [11].

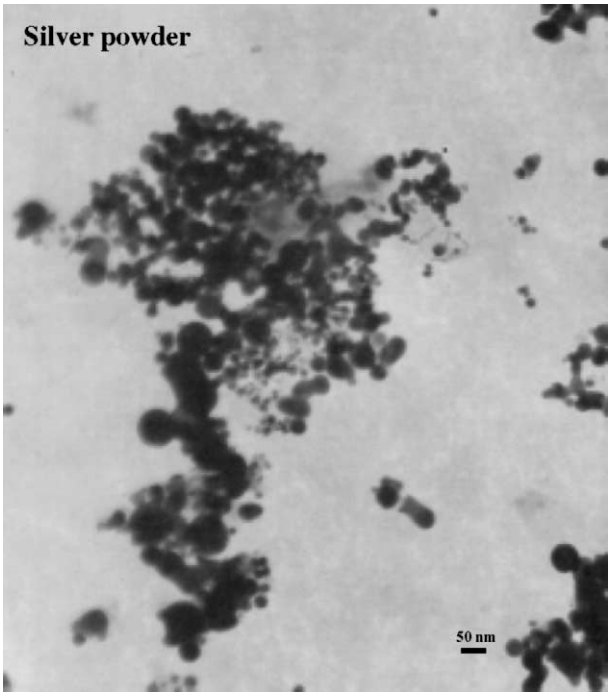

Fig. 1. TEM image of silver nanoparticles prepared by plasma electric arc method.

The O_2 (or CO)-TPD profiles were obtained in a setup coupled to a quadrupole mass spectrometer. The sample was pretreated with oxygen at different temperatures, and cooled down to room temperature under He atmosphere to remove the gas phase oxygen and physically adsorbed oxygen species on the catalysts. When the oxygen level was equal to the background level, the temperature was ramped with a heating rate of 15 °C/min from RT to 900 °C. For CO adsorption experiments, after silver catalyst was pretreated under certain conditions, it adsorbed CO at RT for 1 h, and was blown under He to reach the background level, then ramped with a heating rate of 10 °C/min to 900 °C. When testing the reaction of CO and sub-surface oxygen species, the catalyst pretreated with oxygen at 700 °C adsorbed CO at RT for 1 h, and then the thermal desorption of sub-surface oxygen species was detected.

The catalytic activity measurements were carried out in a fixed-bed reactor by passing a standard gas containing 1% CO and 0.5% O_2 in H_2 through the catalyst bed at a space velocity of GHSV = 5000 h^{-1}. Online gas chromatograph with a TCD detector was employed to measure the reactor inlet and outlet effluent gas streams. The CO conversion was calculated from the change of CO concentration, the O_2

conversion was based in oxygen consumption and selectivity toward CO oxidation was calculated from the oxygen mass balance.

$S = \{0.5 \times [CO_2]/[O_2]_{in} - [O_2]_{out}\} \times 100\%$, where $[O_2]_{in}$ is the inlet O_2 concentration, $[O_2]_{out}$ is the outlet O_2 concentration and $[CO_2]$ is the CO_2 production concentration.

3. Results and discussion

3.1. Catalytic activity for CO selective oxidation

Fig. 2 shows the O_2 conversion, CO conversion and the CO_2 selectivity of the Ag–SiO_2 mixture catalysts pretreated with oxygen at different temperatures as a function of reaction temperature. The trends of all the reaction curves with the reaction temperature were the same as that previous report, i.e. the O_2 conversion increases with the increase of temperature, and the CO conversion passes a maximum in the temperature range investigated [6]. The Ag–SiO_2 mixture with low temperature oxygen treatments exhibited poor catalytic activity for O_2 conversion and CO oxidation. When the temperatures of oxygen treatment were 300 and 400 °C, the temperature for the complete conversion of oxygen was higher than 120 °C. Moreover, no CO conversion was observed over the whole reaction temperatures. The temperature of complete oxygen conversion decreased to 100 °C when the treatment temperature was raised to 500 °C, and the catalyst exhibited obvious activity for CO oxidation above 40 °C. This trend keeps developed for that treated at 600 °C. By increasing the treatment temperature to 700 °C, the optimum reaction temperature decreased further, i.e. the 100% O_2 conversion was realized at a relatively low temperature of 60 °C while the maximum CO conversion (about 30%) was obtained consequently, reaching nearly the same level of CO conversion as that of the 8%Ag/SiO_2 catalysts prepared by the incipient wetness impregnation method. However, as the treatment temperature was increased to 800 °C, the activity for CO oxidation decreased and the temperatures corresponding to the complete oxygen consumption and maximum CO conversion increased to 80 and 75 °C, respectively, but much better than that of the initial Ag–SiO_2 mixture. The selectivity of CO oxidation at low temperatures was obviously increased after the catalyst was treated with oxygen at the temperatures higher than 500 °C.

To get more clear/direct picture of the reaction, the effect of treating temperature with oxygen on the activity of Ag–SiO_2 mixture (using that of 60 °C for comparison) was plotted in Fig. 3. The rate of CO oxidation shows a typical "volcano-shaped" curve, i.e. the catalytic activity initially increased with the calcination temperature, and a maximum activity was reached after treating at 700 °C. However, further increasing the treatment temperature led to an obvious decrease in activity.

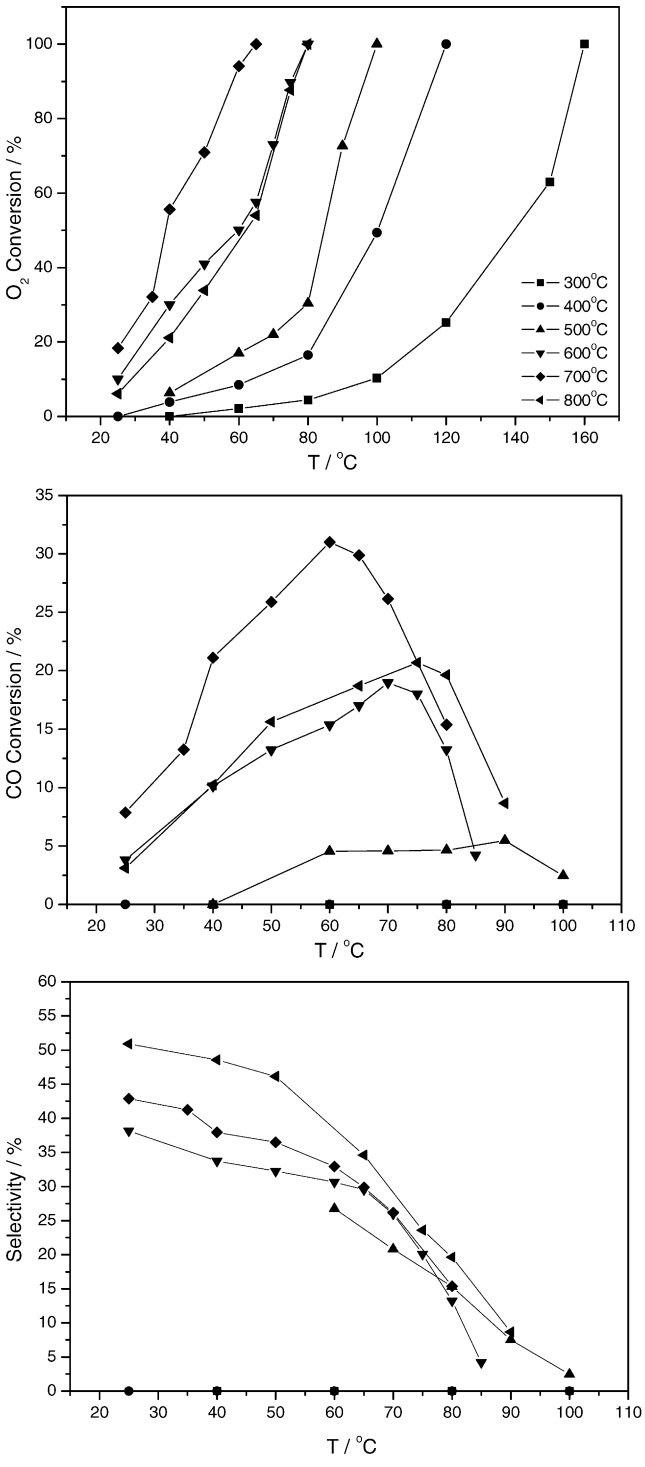

Fig. 2. O_2 conversion, CO conversion and the selectivity of Ag–SiO_2 mixture catalysts pretreated with oxygen at different temperatures as a function of reaction temperature.

3.2. XRD and TEM

XRD was employed to investigate the influence of oxygen treatment at different temperatures on the state and size of the silver nanoparticles. Fig. 4 shows the XRD patterns of

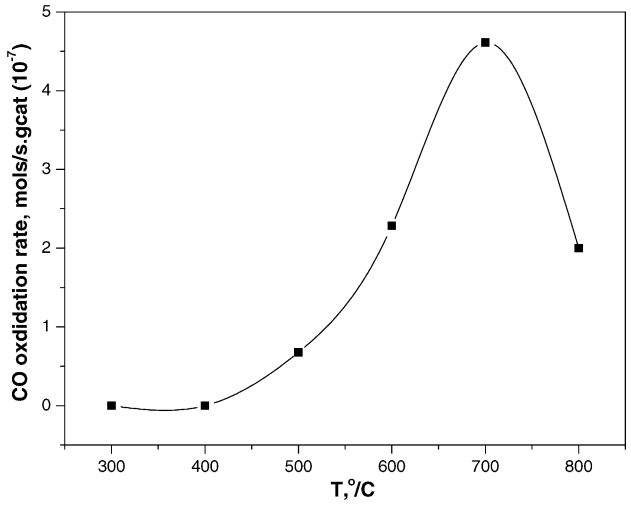

Fig. 3. Dependence of reaction rate for CO oxidation at 60 °C on the temperature of oxygen treatment.

the Ag–SiO_2 mixture treated with oxygen at different temperatures for 1 h. The original Ag–SiO_2 mixture was used as the standard. The size of the Ag particles can be simply calculated from the half-width of the main peak at $2\theta = 38^\circ$ according to the Scherrer's method. Thus, the mean size of the silver nanoparticles calculated from the XRD pattern was about 40 nm, which can also be seen clearly from the TEM picture. When the catalyst was treated with oxygen at 300 °C, the half-width of the silver diffraction peak at 38° did not show any changes, but the peak intensity obviously increased. The silver particles might contain some carbon species due to the use of CH_4 during the preparation of the silver nanoparticles, which is verified by the existence of CO_2 during the temperature-programming oxidation process of the as-prepared Ag–silica mixture. This will lead to the decrease of the silver peak intensity in the initial Ag–SiO_2 mixture, while it underwent a slight increase after removal of these carbon species by oxygen treatment at 300 °C. In order to prove the fact that the observed increase in activity of the silver catalysts after oxygen treatment at high temperatures was not related to the elimination of carbon, we mixed other kind of silver particles without carbon species with SiO_2, and evaluated their catalytic activities. No activity could be observed on the fresh sample and that treated with He at 700 °C, while relatively good activity and selectivity were obtained after treatment with oxygen at high temperatures. This strongly supports our conclusion that the lack of activity for CO oxidation over the initial Ag–SiO_2 catalyst was not due to the existing of the carbon species, and oxygen treatment at high temperatures was essential for increasing the activity of the catalysts. It should be related to the changes in the structure of the silver nanoparticles and the interaction between the silver nanoparticles and SiO_2. When increasing the temperature of oxygen treatment to 500 °C, the intensity of the silver peak at 38° decreased. It might be related to the interaction between the silver nanoparticles and SiO_2. The peak intensity keeps decreased until 700 °C. Gradually the peak intensity increased a little bit as further increasing the treatment temperature to 800 °C. Oxygen treatment at high temperatures may influence the mobility of the silver nanoparticles, which will be discussed in detail below.

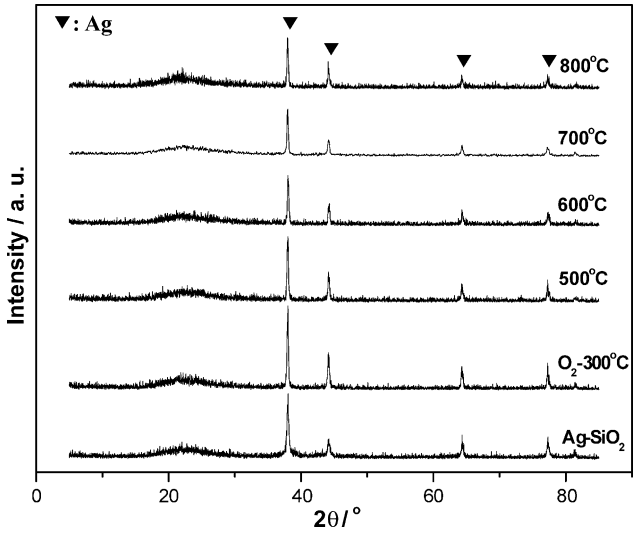

Fig. 4. XRD patterns of Ag–SiO_2 mixtures treated with oxygen at different temperatures.

Fig. 5 shows the TEM images of the Ag–SiO_2 mixture after oxygen treatment at different temperatures. It was found that very few silver particles were attached on the support, and the silver particles and SiO_2 powder were separated from each other on the initial Ag–SiO_2 mixture (see Fig. 5A). When the mixture was treated with oxygen at 300 °C, very few silver particles were dispersed on the SiO_2 support (Fig. 5B). After the treatment temperature was increased to 500 °C, some small silver particles were observed to attach on the surface of silica. Moreover, the number of silver particles attached on the SiO_2 support increased with the treatment temperature up to 700 °C (Fig. 5C). However, further increasing the treatment temperature to 800 °C resulted in the aggregation of silver nanoparticles on the surface of silica to form larger silver particles (Fig. 5D), which was consistent with the results of XRD, enhancing the intensity of silver diffraction peak.

XRD results show that the intensity of the silver diffraction peak at 38.2° decreases when the treatment temperature is increased to 500 °C, which is consistent with that of TEM observations, i.e. more small silver particles were well dispersed on the surface of SiO_2. It is known that the variation of the dispersion threshold value is related to the interaction between the active component and the supports, which is an important experimental parameter in the study of catalysts. Some groups have reported that salts and oxides tend to disperse on the support spontaneously with temperature. When the mixtures of a salt (or an oxide) and the support are calcined at an appropriate temperature below the melting point of the compound, a maximum dispersion

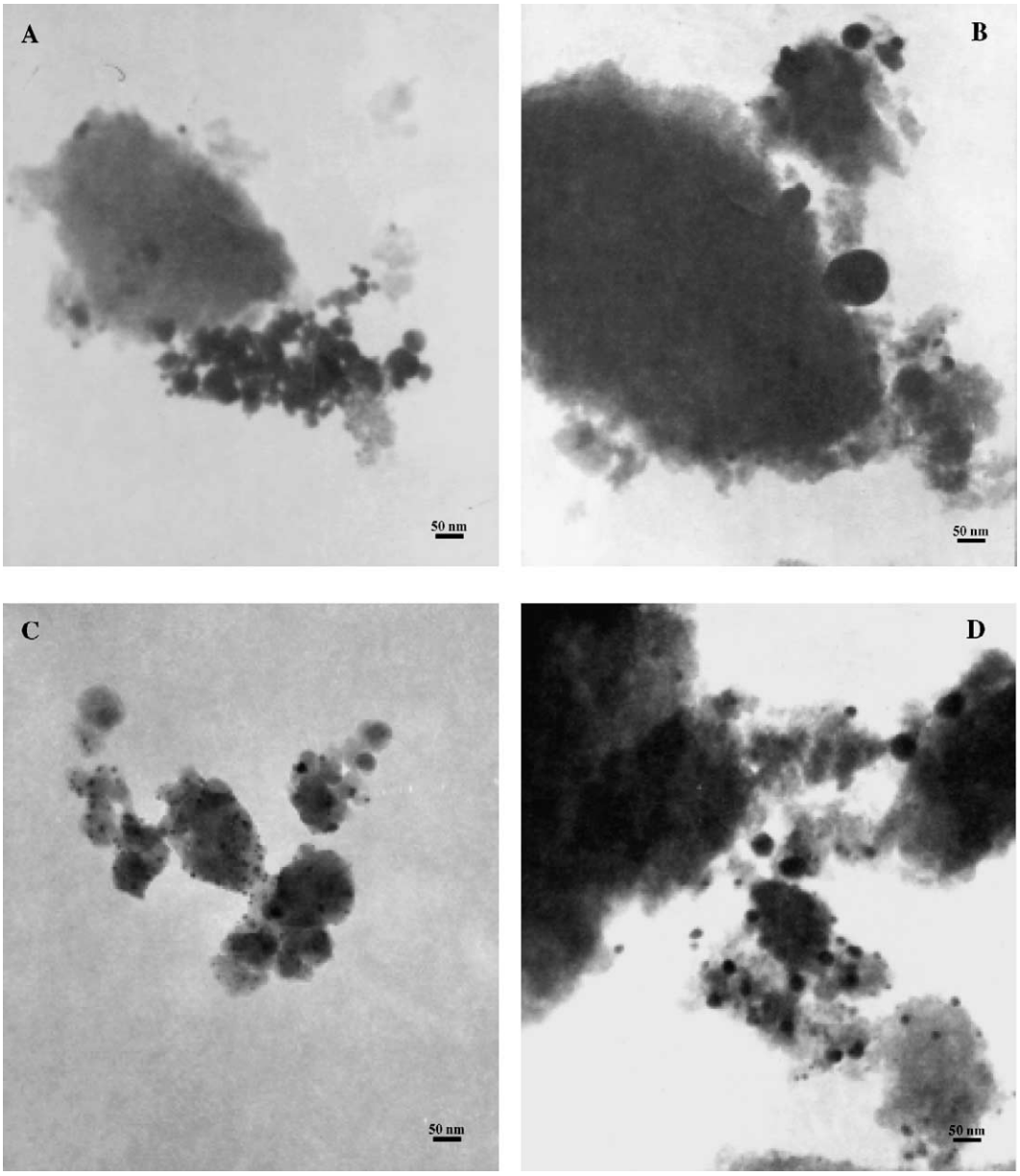

Fig. 5. TEM images of Ag–SiO_2 mixture (A) and those treated with oxygen at 300 °C (B), 700 °C (C) and 800 °C (D).

of the compound on the support can be obtained [12–14]. Liu et al. [12] observed that if the quantity of MoO_3 added was lower than the threshold value, then the X-ray diffraction (XRD) peaks of crystalline MoO_3 disappeared after calcination. If the quantity was higher than that value, however, the peaks did not disappear due to the residual MoO_3 crystalline, but just showing a decrease in the peak intensity. Generally the metal has a relatively strong metallic bond and a weak interaction with the ionic-type support, so it would be relatively difficult for the metal to disperse spontaneously on the support. The dispersion behavior of supported metal particles is affected by many factors, such as the support material, the reaction atmosphere, the metal–support interaction, etc. In general, when alumina or silica is used as the support, heating in H_2 would cause sintering of the metal particles, while heating in an oxidizing atmosphere, such as O_2 or steam, will lead to redispersion [15,16]. The behavior of supported silver has been reported by a number of authors. Presland et al. [17] investigated the effect of oxygen and hydrogen on a silver film supported on an amorphous silica substrate. They found that in an oxidizing atmosphere, hillocks were formed as the first stage, and then with further heating, silver islands were generated.

In the previous reports, the dispersion of metal on the support has been found to be difficult due to the strong metal bonding. In the present work, however, a decrease in the intensity of the silver peak was observed, and more small silver particles formed on the support after the silver catalysts were treated with oxygen at high temperatures. That is to say that the silver particles are well dispersed on the

support after treatment with oxygen at high temperatures (>500 °C), and the interaction between the silver particles and SiO_2 may exist. A similar behavior was observed on Pt metal [9]. At the same time, from TEM result it is clear that when treating the mixture at temperatures higher than 500 °C, oxygen induced the migration of the silver particles on the support, and parts of silver particles were dispersed on the surface and diffused into the pore of the support. Under the interaction with the support, the oxygen-treated catalyst becomes more stable state as compared with the silver aggregation. It was reported that exposure to oxygen could induce the migration of the silver atoms on the on Si (1 1 1)-7 × 7 surface by STM on a model catalyst [18], which is in good agreement with our current observation. These results indicated that oxygen treatment at high temperatures induced and enhanced the migration of silver particles, and more small silver particles were well dispersed on the surface of SiO_2, which may be responsible for the increase of the catalytic activity for CO selective oxidation.

When the treatment temperature with oxygen was up to 800 °C, the intensity of the silver peak increased and the silver particles on the support aggregated to form larger particles (see Figs. 4 and 5), which in turn, resulted in a decreased catalytic performance.

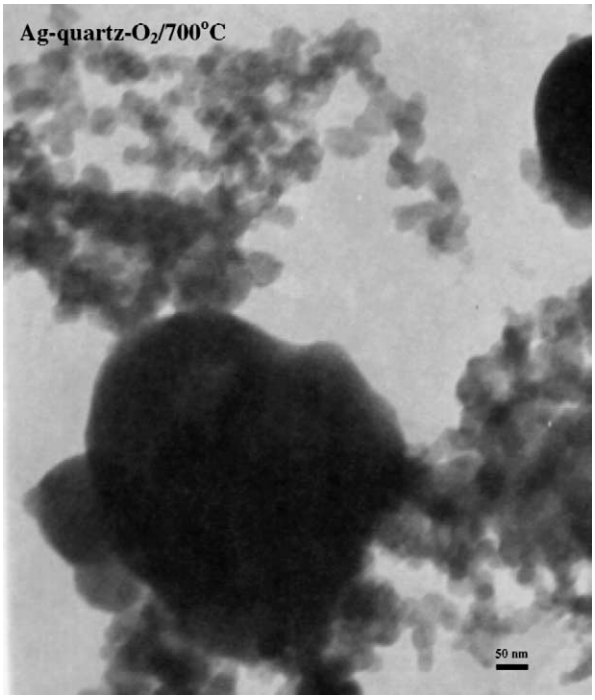

Fig. 6. TEM image of the mixture of silver particles and quartz sand treated with oxygen at 700 °C.

3.3. Effect of SiO_2

In this paper, in order to further explain the effects of SiO_2 on the properties and catalytic activity of the silver catalysts, different silver catalysts were prepared and evaluated in CO selective oxidation reaction. The first is a mixture of silver particles with SiO_2; the second is a mixture of silver particles with quartz sand and the last one is pure Ag nanoparticles. When evaluating the reaction activity of the last sample, SiO_2 was added into the reactor to obtain the same space velocity as those of former two. All catalysts were pre-treated with oxygen at 700 °C before reaction. No activity of CO selective oxidation was found over the mixture of silver and quartz sand, the pure silver particles and pure SiO_2 catalysts. This verified our previous conclusions that an appropriate content and distribution of silanol favor the dispersion of the silver particles on the silica [7]. The quartz sand has little BET area, pore size and hydroxyls, so the possibility of its interaction with the silver particles is negligible. Moreover, TEM results proved that no dispersion of silver particles on the quartz sand was observed after the sample was treated with oxygen at 700 °C (Fig. 6), again showing that the SiO_2 support as well as the interaction between the SiO_2 and the Ag nanoparticles are essential to obtain a high catalytic activity, i.e. only the silver particles dispersed on the high surface area SiO_2 are active for CO selective oxidation. The fact that the activity for selective CO oxidation over the Ag–SiO_2 catalysts pretreated with oxygen at 700 °C is similar to that of the 8%Ag/SiO_2 catalyst prepared by impregnation also supports it. Meanwhile, the results also suggested that the higher activity resulted from the true activation of silver catalyst but from the surface cleanliness of silver catalysts. If it was, all of the catalyst containing the silver component should have certain activity.

3.4. O_2-TPD and CO-TPD

It is recognized that to understand the interaction between the silver particles and oxygen is important for studying the catalytic activity of the silver catalysts, such as the mechanism of oxygen activation, the oxygen-induced silver reconstruction and the incorporation of oxygen into the silver bulk. Moreover, it has been found that more sub-surface oxygen species formed after the Ag/SiO_2 catalysts prepared by incipient wetness impregnation method were treated with oxygen at high temperatures, and the sub-surface oxygen species provided a path for CO oxidation, while the gaseous oxygen species could recruit parts of the sub-surface oxygen species which was lost at RT (see Fig. 7). The formation of sub-surface oxygen species was essential to obtain a high activity for silver catalyst. Fig. 8 shows the O_2-TPD results of the mixture of Ag nanoparticles and SiO_2 powder after treatment with oxygen at different temperatures. The temperature of oxygen desorption increased with the treatment temperature. Previous studies have shown that the peak of desorption at above 600 °C is attributed to sub-surface oxygen species, which diffuse via an interstitial diffusion mechanism and is termed as O_γ [19–22]. From the figure, it could be found that the quantity of O_γ increased with the temperature of oxygen treatment. The desorption peak

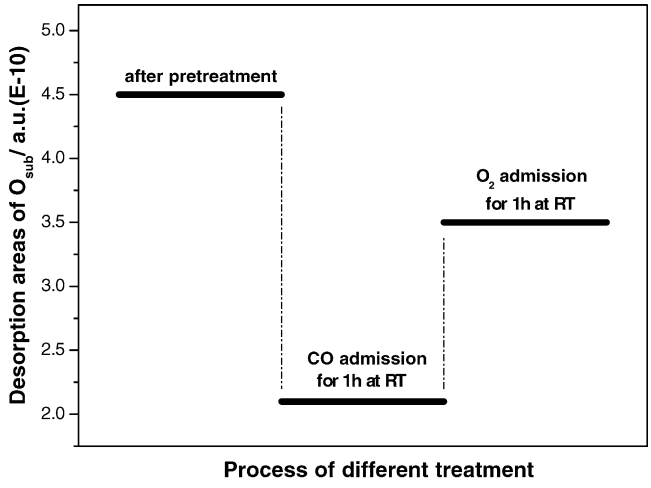

Fig. 7. Dependence of the amounts of sub-surface oxygen species over Ag/SiO_2 prepared by impregnation on the process of different treatments.

shifted remarkably to temperatures higher than 900 °C after oxygen treatment at 800 °C, and the oxygen desorption is not fully recorded in this case due to the heating limit of the furnace. Concluding from the above results, the formation of sub-surface oxygen species was observed after the Ag–SiO_2 mixture was treated with oxygen at high temperatures (>500 °C), and its quantity increased with the treatment temperature up to 700 °C.

Fig. 9 shows the O_2-TPD spectra of the Ag–SiO_2 mixture after treatment with oxygen at 700 °C and followed by CO adsorption at 40 °C. It is also found that the quantity of sub-surface oxygen species decreased after CO adsorption, as compared with that without CO adsorption. The initial desorption temperature of oxygen increased and a symmetric peak formed. Desorption of the sub-surface oxygen species needs a very high temperature, but CO can still react slowly with it at low temperatures. Current result suggested that the reaction of CO with sub-surface oxygen species decreased the quantity of the sub-surface oxygen species,

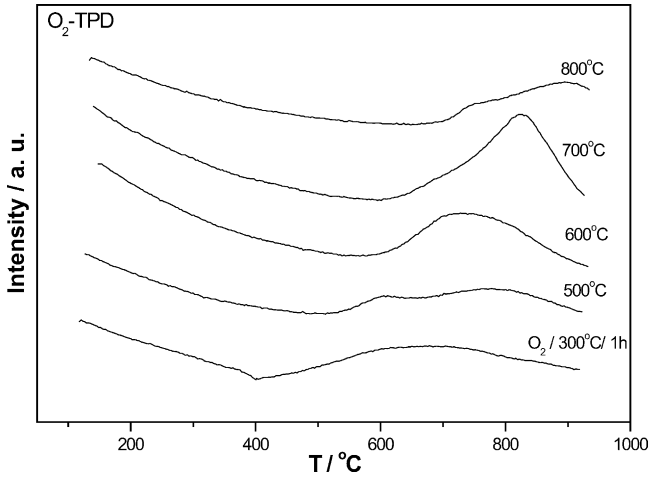

Fig. 8. Thermal desorption spectra of oxygen over Ag–SiO_2 mixtures after oxygen treatment at different temperatures.

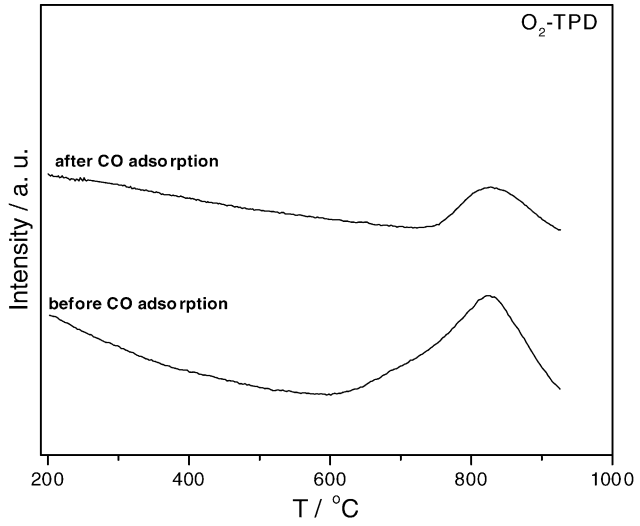

Fig. 9. O_2-TPD spectra of the mixture of silver particles with SiO_2 powder pretreated with oxygen at 700 °C for 1 h and followed by CO adsorption at 40 °C for 1 h.

and the formation of sub-surface oxygen species ignited the reaction of CO oxidation at low temperatures.

As is well known, the reaction of CO and O_2 follows the Langmuir–Hinshelwood mechanism [23]. It requires that both CO and O_2 should be adsorbed on the surface of the catalysts before they are able to react. Therefore, to understand the catalytic activity of silver catalysts for CO selective oxidation in H_2, it is essential to understand the adsorption of the reactants. Under this consideration, CO adsorption and desorption were conducted, and the results are shown in Fig. 10. The reason of the appearance of the multi-peak for CO desorption was not clear yet, which might be related to the heterogeneity of the Ag–SiO_2 mixture. When the Ag–SiO_2 mixture was pretreated with oxygen at

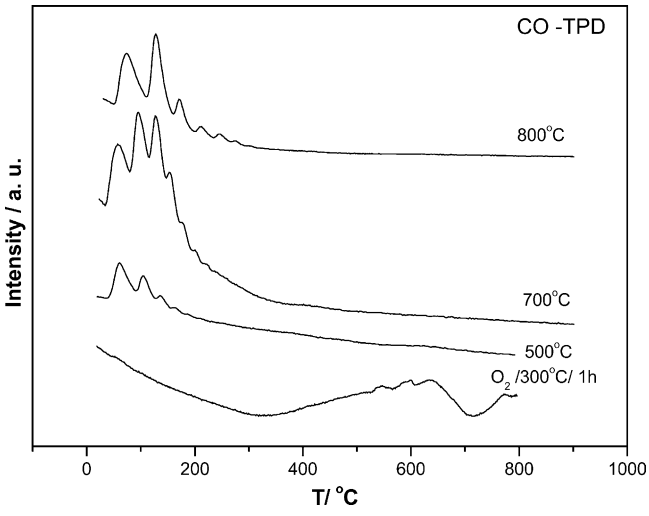

Fig. 10. CO-TPD spectra after Ag–SiO_2 mixtures were pretreated with oxygen at different temperatures. The temperature of CO adsorption was at 40 °C.

Table 1
The overall results of the peaks for CO desorption after Ag–SiO_2 mixtures were treated with oxygen at different temperatures

Oxygen treatment (1 h)	300 (°C)	500 (°C)	700 (°C)	800 (°C)
Area (E-11)	–	3.57	16.8	9.22
Peak T (°C)	>300	60.65	56.67	73.52

300 °C, the CO adsorbed on the silver surface can desorb only at the temperature higher than 300 °C. However, the desorption of CO began at 30 °C as the treatment temperature increased to 500 °C, and the area of the CO desorption peak increased with the treatment temperature up to 700 °C. By further increasing the treatment temperature to 800 °C, the area of the CO desorption peak decreased, meanwhile the temperature of CO desorption slightly increased. Table 1 shows the overall results of the peaks for CO desorption after the silver catalysts were treated with oxygen at different temperatures. The temperature of CO desorption was decided according to the first desorption peak, and the area was that of the overall CO desorption peak. Oxygen treatment at 700 °C increased the ability of CO adsorption over silver catalysts and decreased the temperature of CO desorption.

Krylov has found that it was impossible to oxidize CO on a vapor-deposited (pure silver) film even at elevated temperatures [24], and a defect-free Ag (1 1 1) surface did not adsorb oxygen [25]. Oxygen treatment can change the properties of silver particles and increase the ability of CO adsorption, which is consistent with the reaction results, namely, an increase in activity of the silver catalysts after treatment with oxygen at high temperatures (500–700 °C). However, no desorption of CO at low temperatures was observed after treatment with oxygen at 300 °C, moreover, silver particles were not well dispersed on the support. Consequently, no activity for CO selective oxidation was observed on this catalyst. Meanwhile, low catalytic activity for selective CO oxidation and poor dispersion of the silver particles on the support were also observed over the mixtures of silver particles and SiO_2 treated with He at 700 °C, which further indicated the essentiality of oxygen treatment at high temperatures. Oxygen treatment at high temperatures induced the migration and dispersion of silver nanoparticles on the surface of silica, meanwhile formed a more sub-surface oxygen species. Fig. 9 also shows that CO reacts easily with the sub-surface oxygen species formed after oxygen treatment at high temperatures. Thus, a fine dispersion of the silver particles on the support, the formation of sub-surface oxygen species and an increase of catalytic activity were obtained after the mixture of Ag nanoparticles and SiO_2 powder was treated with oxygen at high temperatures.

O_2-TPD experiments of Ag–quartz sand mixture and pure silver powder after treatment with oxygen at high temperatures were also conducted, and it was found that sub-surface oxygen species still existed for both samples after treatment with oxygen at 700 °C. The quartz sand has litter BET area and pore size, so silver particles are unable to be well dispersed on the surface of it (Fig. 6). However, the high BET area, pore size and more OH groups for SiO_2 support led to the fine dispersion of Ag nanoparticles on the support. More sub-surface oxygen species can form when the silver particles are well dispersed on the support (Fig. 11). The quantity of the sub-surface oxygen species increased with the extent of strong interaction between the silver particles and the support. The peak of oxygen desorption over Ag–quartz sand catalyst shifted to lower temperatures compared with that of the mixture of Ag nanoparticles and SiO_2. The temperatures for oxygen desorption and the reduction of catalysts increased when a strong interaction between the metal particles and the support or the smaller metallic particles was present [26]. As stated above, a relatively strong interaction between the silver nanoparticles and SiO_2 form, and more small silver particles were dispersed on the surface of the support after oxygen treatment at high temperatures. The non-symmetry properties of the oxygen desorption peak over the mixture of silver particles and silica also indicated that there existed different states of the silver species on the support. In the earlier research, it has been found that the ability of CO adsorption was enhanced after silver catalysts were treated with oxygen at high temperatures. However, no CO adsorption over the mixture of silver particles with quartz sand was observed, which suggested that CO was prone to adsorb on the surface of silver particles attached on the support. In other words, CO adsorbed on the silver nanoparticles shows a higher activity toward CO selective oxidation.

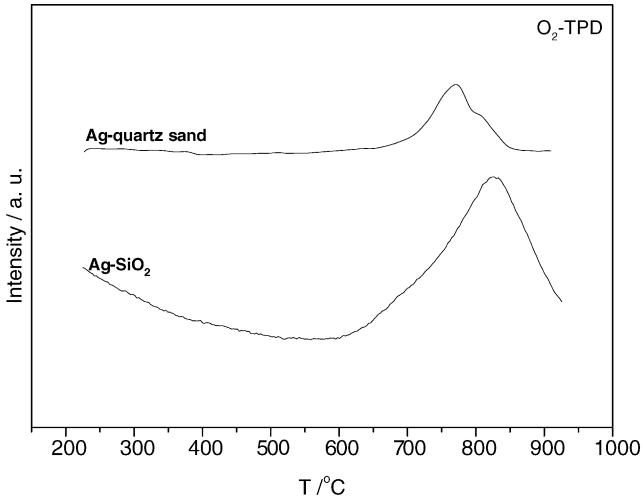

Fig. 11. O_2-TPD results of Ag–SiO_2 and Ag–quartz sand mixture pretreated with oxygen at 700 °C for 1 h.

When the Ag–SiO_2 mixture was treated with oxygen at 800 °C, the decrease of the ability for CO adsorption decreased the activity for selective CO oxidation and increased the reaction temperature. The increase of selectivity might be due to a decrease in the ability of H_2 oxidation, while the decrease of activity can be attributed to the aggregation of silver particles dispersed on the surface

of SiO_2, as shown in XRD and TEM experiments. However, from the reaction results, it can be found that the catalytic activity was higher than that of the initial Ag–SiO_2 even if Ag particles grew to larger ones (in case of 800 °C treatment), which can be attributed to the existence of many silver particles with sub-surface oxygen species attached on the support, keeping a relatively good activity and selectivity of the silver catalysts.

4. Conclusions

Based on the catalytic activity tests and the characterization of a mechanical mixture of silver particles and SiO_2 powder treated with oxygen at different temperatures, the following conclusions can be obtained:

(1) The catalyst with mechanical mixture of Ag nanoparticles and SiO_2 powder shows poor activity for CO selective oxidation. It becomes catalytically active after treatment with oxygen at 500 °C, and the activity increases with the treatment temperature up to 700 °C. However, further increasing the treatment temperature leads to an obvious decrease in activity.
(2) Treatments with oxygen at temperatures of 500–700 °C induce the dispersion of the silver particles on the support, and evidently increase the amounts of sub-surface oxygen species and the ability of CO adsorption. The silver particles attached to the support aggregate to form larger particles as the treatment temperatures further increase.
(3) The dispersion of Ag nanoparticles on the surface of SiO_2 and the formation of sub-surface oxygen resulted from the treatment with oxygen at high temperatures (500–700 °C) can be correlated with the higher catalytic activity. CO adsorbed on the Ag nanoparticles that are well dispersed on the surface of silica shows a higher activity toward CO selective oxidation, and it is proved that the sub-surface oxygen species plays a very important role in this reaction.

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