

Hydrogen Treatment-Induced Surface Reconstruction: Formation of Superoxide Species on Activated Carbon over Ag/Activated Carbon Catalysts for Selective Oxidation of CO in H₂-Rich Gases

Limin Chen, Ding Ma, 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, People's Republic of China

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Superoxide species were detected on activated carbon (AC) after H₂ treatment at high temperatures (> 300 °C) and subsequent oxygen adsorption at 80 °C. The introduction of Ag onto the carbon surface promoted the formation of superoxide species. For Ag/AC catalysts, the superoxide species may be able to spill over from the carbon surface to the silver particles and react with CO under reaction conditions; while over AC itself, superoxide species have no activity toward CO oxidation. This is another active oxygen species for CO oxidation over carbon-supported silver catalysts.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs), operating at relatively low temperatures (e.g., 60–80 °C) with pure hydrogen or reformed gas as fuels, have attracted much attention as a potential power source for electric vehicles.^{1–5} However, the Pt anode catalysts can be seriously poisoned by traces of CO in the reformed gas. This has motivated the search for highly efficient catalysts for CO preferential oxidation in excess H₂ at low temperatures. The outstanding catalytic performances of noble metals, such as Pt, Rh, and Au, are widely recognized.^{6–11} However, there are only a few reports about the use of relatively cheap silver catalysts for CO-selective oxidation in excess H₂, even though silver catalysts have been acknowledged to be very effective catalysts in partial oxidation reactions such as ethylene epoxidation, formaldehyde synthesis, etc.^{12–14} Recently, we have observed that silver catalysts supported over silica are also active in CO oxidation and CO-selective oxidation reactions. However, carbon materials as the support for metal catalysts are more attractive because most of carbon materials are electron-conductive, which enables carbon-supported catalysts be integrated directly into fuel cells.¹⁵

The active oxygen species determine the oxidation activity in CO oxidation or selective oxidation reactions. For Ag/SiO₂ catalysts, under the reaction conditions, two kinds of atomic oxygen species have been reported on the Ag surface, i.e., surface oxygen species formed via gas-phase oxygen adsorption, and subsurface oxygen formed during oxygen pretreatment at high temperatures.^{16–19} CO reacts with both surface and subsurface oxygen species under reaction conditions. On the other hand, for Ag/carbon catalysts, Ag₂O was considered as the active component for CO oxidation, but only relatively low activity of CO oxidation was detected over the catalyst.²⁰

At the same time, molecular oxygen was reported to be the active species for CO oxidation over model Ag catalysts.^{21–24} For example, CO oxidation by molecular oxygen on Ag (110) surface has been intensively investigated by Conrad and co-worker.^{21–23} Barth and Zambelli also observed that CO was

oxidized by molecular oxygen through scanning tunneling microscopy (STM).²⁴ Recently, Mou et al. has reported that molecular oxygen species (O₂⁻) are responsible for the CO oxidation over Au–Ag alloy catalysts supported on Al-containing mesoporous silica (denoted as MAS).^{25,26} The active O₂⁻ species originated from both the defects on the MAS and the Au–Ag nanoparticles. That is to say the existence of defect sites on the silica surface favors the formation of reactive O₂⁻ species, leading to an enhanced activity for CO oxidation.

In the present work, we used activated carbon (AC) as the support of silver catalysts. It has been observed that a hydrogen treatment at temperatures higher than 300 °C before the oxygen adsorption will lead to the formation of superoxide species on inert AC support. The higher hydrogen treatment temperature is, the easier the formation of superoxide species. The superoxide species over AC cannot react with CO directly. Instead, the presence of Ag on AC surface can promote the formation of superoxide species over AC, and more importantly, catalyze the reaction of CO and superoxide species.

2. Experimental Section

2.1. Catalyst Preparation. The coconut shell based AC was purchased from Beijing Guanghai Woods Ltd. (Beijing, China). The AC was first crushed, washed, and sieved, and the fraction of 40–60 mesh was used as the support.²⁷ The textural structure is listed in Table 1. Ag/AC catalysts (12 wt %) were prepared by the conventional wetness impregnation method using aqueous silver nitrate (AgNO₃, Shanghai Chemical Reagent Company, 99.9%), followed by drying at 120 °C for 12 h. The Ag/AC catalysts were pretreated in H₂ at various temperatures for 2 h before catalytic tests. For some catalysts, AC was pretreated with hydrogen or helium at high temperature (550 °C) before loading silver. Details are specified in the manuscript.

2.2. Catalyst Characterization. The temperature-programmed desorption (TPD) experiments were performed in a quartz U-type microreactor, connected with an on-line quadrupole mass spectrometer (Balzers, OmniStar GSD300 O). Samples (about 0.1 g) were first activated under H₂ (30 mL/min) at various temperatures for 2 h and then cooled down to room

* Corresponding author. Tel.: +86-411-84686637. Fax: +86-411-84694447. E-mail: xhbao@dicp.ac.cn.

TABLE 1: The Textural Structure of AC Support

sample	BET surface area (m ² /g)	S _{meso} (m ² /g)	V _{total} (mL/g)	V _{meso} (mL/g)	mean pore size (nm)
AC	1058	227	0.54	0.28	2.16

temperature in He (30 mL/min) before an oxygen adsorption (10 vol % O₂ in He; 30 mL/min) at 80 °C for 1 h. In some cases, the samples were further treated with CO (1 vol % CO, 0.5 vol % Ar in H₂ or 30 vol % CO in He; 30 mL/min) at 80 °C for 1 h before reexposure to oxygen. Finally, the temperature was increased to 990 °C at a rate of 5 °C/min in He (30 mL/min). MS intensities for $m/z = 2, 4, 15, 28, 30, 32, 44,$ and 46 were recorded as a function of temperature.

2.3. Catalyst Test. The catalytic reactions were evaluated in a fixed-bed flow reactor. Gas mixture containing 1% CO, 0.5% O₂ (volume ratio) and balanced with H₂ was fed at a flow rate of 50 mL/min. The composition of the effluent gas was monitored by an on-line gas chromatograph (Agilent Technologies GC-6890N) equipped with PN and TDX-01 columns. Besides the feed, only two products, CO₂ and H₂O, were detected. CO and O₂ conversions were calculated from the differences between their inlet and outlet concentrations, respectively, while the selectivity toward CO oxidation (*S*) is defined as the fraction of oxygen consumed to oxidize CO to CO₂:

$$S = \{0.5 \times ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}) / ([\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}})\} \times 100\%$$

where [O₂]_{in} and [CO]_{in} are inlet and [O₂]_{out} and [CO]_{out} are outlet concentrations of O₂ and CO, respectively.

3. Results and Discussion

3.1. Existence of Superoxide Species. Figure 1 shows O₂ (A) and CO (B) conversions over the Ag/AC catalysts treated in H₂ at different temperatures versus the reaction temperature. As presented in Figure 1A, except Ag/AC treated in hydrogen at 200 °C, O₂ conversion increased with the reaction temperature and finally reached 100%. At the same time, as shown in Figure 1B, CO conversion increased with the reaction temperature and passed a local maximum around 75–100 °C. The decrease of CO conversion at even higher reaction temperatures has been caused by the competitive hydrogen oxidation reaction in the same system. It is interesting to note that, at the same reaction temperature, O₂ conversion and CO conversion increase with the catalyst pretreatment temperatures, and decrease when the pretreatment temperature is higher than 500 °C.

To better understand the roles of the hydrogen pretreatment in the catalytic performances, the H-TPR of the AgNO₃/AC and AC samples were carried out, and the results were shown in Figure 1C. The H-TPR profile of the AgNO₃/AC exhibits three H₂ consumption peaks, centered at 150 °C, 350 °C, and 600 °C, respectively. The peak at 150 °C (peak I) is assigned to decomposition/reduction of silver nitrate, which is accompanied by the MS signals of nitrogen oxides ($m/z = 30, 46,$ not shown here). The peak at 600 °C (peak III) is contributed to the gasification of carbon support with generation of light hydrocarbons, mainly methane, as indicated by the detection of MS signal of it ($m/z = 15$).²⁸ The H-TPR profile of raw AC (as shown in Figure 1C) shows a single peak, starting from 500 °C or so and centered at 670 °C. This peak can be attributed to the reduction of oxygen-containing functional groups of the carbon and the gasification arising from the carbon.²⁸ The higher carbon gasification temperature, compared with AgNO₃/AC, is due to the absence of Ag catalyst. Then, the H₂ consumption of AgNO₃/

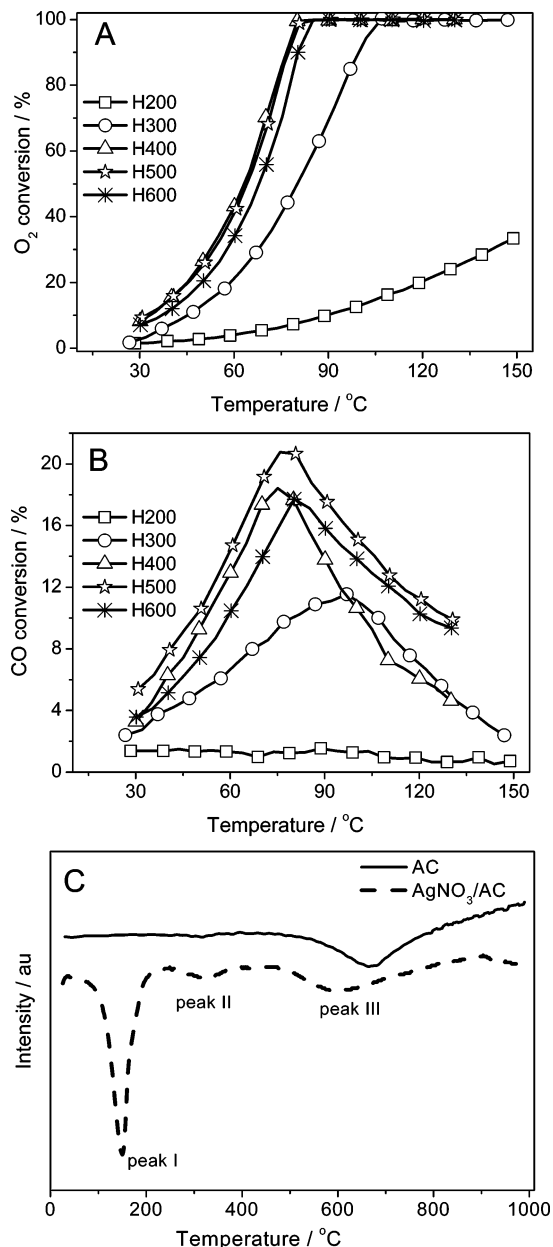


Figure 1. O₂ conversion (A), CO conversion (B) over Ag/AC catalyst treated in H₂ at different temperatures versus reaction temperatures (for example: H200 means treated with hydrogen at 200 °C for 2 h), and H-TPR (C) profiles of AC and AgNO₃/AC in 10 vol % H₂ in Ar.

AC catalyst at peak II is ascribed to the reduction of oxygen-containing functional groups of carbon support, catalyzed by silver. When the TPR profiles are coupled with the reaction results, it is obvious that the AC reduction at 250–350 °C (peak II) is critical to the improvement of catalytic activity.

In order to elucidate what kind of structure change has happened after hydrogen treatment around 350 °C, O₂-TPD experiments of AC support (Figure 2A) and Ag/AC catalyst (Figure 2B), after hydrogen treatment at different temperatures, were conducted.

As shown in Figure 2, after the pretreatment at 200 °C (temperature lower than peak II), no obvious oxygen desorption was observed over the AC support (Figure 2A, a). For the corresponding catalyst (Figure 2B, e), oxygen desorption at 125 °C was detected, accompanied with a broad peak centered at 430 °C. The intensity of the peak at 430 °C decreased and finally disappeared when the pretreatment temperature was higher than

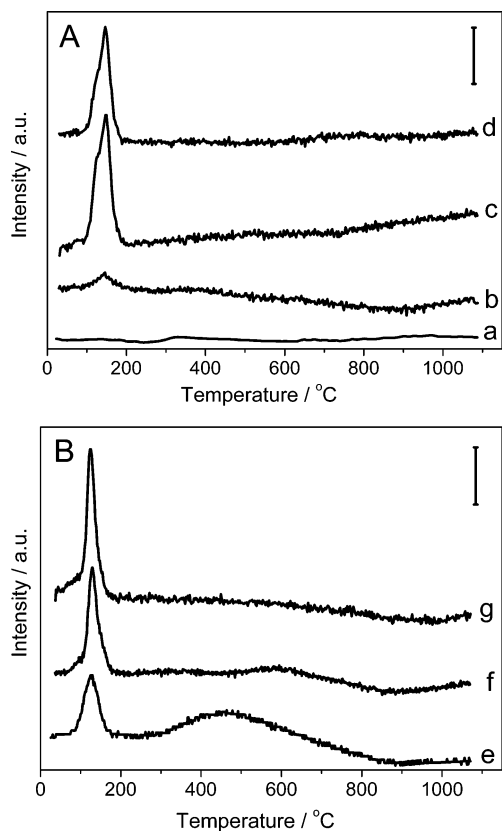


Figure 2. O₂-TPD profiles of the AC (A) and Ag/AC catalyst (B) after different pretreatments. From a to c, AC after pretreatment with H₂ at 200 °C, 300 °C, and 500 °C, respectively, followed by O₂ adsorption at 80 °C; (d) (c) further treated with CO (1 vol % CO, 0.5 vol % Ar, in H₂, 30 mL/min) at 80 °C for 1 h; from e to g, Ag/AC catalyst after pretreatment with H₂ at 200 °C, 300 °C, and 500 °C, respectively, followed by O₂ adsorption at 80 °C for 1 h. (The bar graphs display the intensities on the same scale.)

300 °C. This peak is attributed to the desorption of the bulk oxygen species from Ag which has been reported to be devoid of catalytic activity.¹⁶ When the pretreatment temperature was raised up to 300 °C (temperature range of peak II), there was a little oxygen desorption from the AC support at 140 °C (Figure 2A, b); furthermore, the intensity of oxygen desorption from the corresponding catalyst increased dramatically (Figure 2B, f). When the pretreatment temperature was further increased to 500 °C (temperature higher than that of peak II), both AC support (Figure 2A, c) and the catalyst (Figure 2B, g) presented a sharp oxygen desorption at 120–140 °C.

According to the literature, the O₂ desorption peak at 120–140 °C is the desorption of superoxide species from the carbon surface.^{29,30} In 1973, Mash and Foord observed the oxygen desorption from microporous carbon in the temperature range 150–200 °C.³¹ Later, Boehm and Schlögl et al. reported the strong broad desorption peaks of O₂ at ca. 130 °C over NH₃-pretreated carbons after adsorption of O₂ at 100 Pa for 1 min.²⁹ The oxygen desorption was assigned to superoxide species, O₂⁻, by the same group.²⁹ Here, for the AC support and Ag/AC catalyst, the shape of this oxygen desorption is similar and the desorption temperature is in the similar range. More importantly, molecular oxygen will dissociatively adsorb on Ag at temperatures higher than 140 K,^{21–23} and the dissociative atomic oxygen species desorbs at much higher temperatures (>300 °C).^{16,32} Thus, it is safe to be concluded that the desorption of superoxide species is from the AC surface. It should be noted that after the same temperature (200 °C and/or 300 °C) H₂

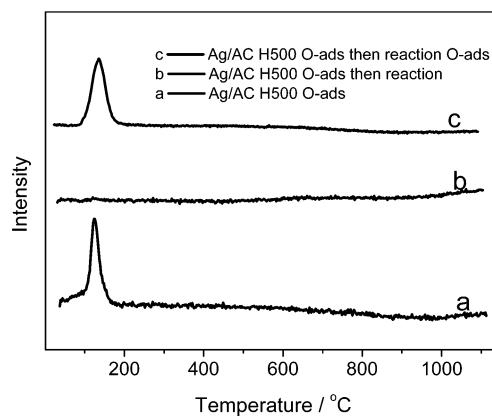


Figure 3. The O₂-TPD profiles of the Ag/AC catalyst treated in H₂ at 500 °C followed by O₂ adsorption at 80 °C for 1 h (a), after O₂ adsorption further by CO treatment (30 vol % CO in He, 30 mL/min) at 80 °C for 1 h (b), and after CO treatment followed by reexposure to O₂ at 80 °C for 1 h (c).

treatment, with the introduction of Ag, the amount of superoxide species increases and desorption temperature decreases (125 °C vs 140 °C, as shown in Figure 2) compared with those of AC support. This fact indicates that the existence of Ag promotes the formation of superoxide on AC and favors its desorption.

To check whether those superoxide species are active or not in CO oxidation reaction, AC support loaded with superoxide species was exposed to CO mixture (1 vol % CO, 0.5 vol % Ar in H₂) at 80 °C for 1 h and followed by the TPD experiment. The TPD profile is shown in Figure 2A, d. Obviously, no intensity loss of superoxide desorption was observed as compared with the same sample without exposure to the reaction mixture (Figure 2A, d vs Figure 2A, c). This result demonstrates that superoxide species on pure AC support cannot react with CO and/or H₂. Naturally, no CO oxidation activity has been observed in the CO selective oxidation reaction for pure AC support treated in H₂ at 500 °C for 2 h.

On the basis of the above results, the following conclusions can be drawn: superoxide species can be generated on pure AC support or on Ag/AC catalyst after hydrogen treatment. The existence of Ag promotes the formation of superoxide on AC, while the reduction of the catalyst at temperatures higher than 350 °C (higher than that of Peak II) is crucial for the formation of superoxide species. Without silver, superoxide cannot react with CO and/or H₂.

3.2. Reactivity of Superoxide with CO over Ag/AC Catalyst. Figure 3, the O₂-TPD (*m/z* = 32) spectra of the Ag/AC catalyst after different treatments/reactions, is shown to offer more insight into the reactivity of superoxide species with CO. A sharp superoxide desorption peak (Figure 3a) was observed at 125 °C from Ag/AC catalyst after pretreatment with H₂ at 500 °C followed by O₂ adsorption at 80 °C. When the catalyst was further exposed to CO (30 vol % CO in He) at 80 °C for 1 h, the superoxide desorption peak at 125 °C disappeared (Figure 3b). This means the superoxide species on Ag/AC catalyst can react with CO. The superoxide peak can be regenerated with an additional O₂ adsorption at 80 °C (Figure 3c), indicating that the consumed oxygen can be restored by oxygen adsorption at 80 °C.

Over Ag/AC catalyst, the superoxide species can react with CO. Thus, the superoxide species formation capacity of AC support after pretreatment with H₂ represents the corresponding catalytic activity for CO oxidation, which agrees well with the reaction results in Figure 1A and 1B. However, a pretreatment

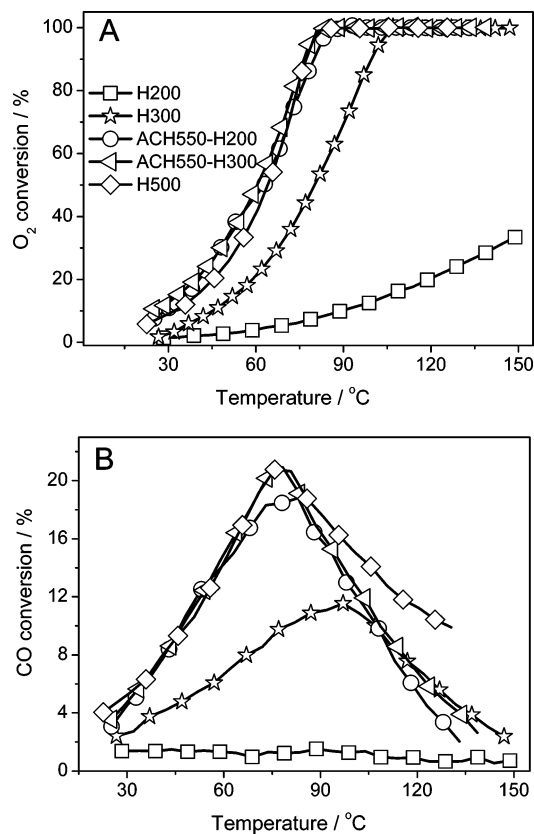


Figure 4. O₂ conversion (A) and CO conversion (B) of the Ag/AC and Ag/AC-H550 catalysts after activation in H₂ at different temperatures (H200 indicates Ag/AC catalyst activated in H₂ at 200 °C; AC H550-H200 means Ag/AC-H550 catalyst activated in H₂ at 200 °C).

temperature higher than 500 °C is detrimental to the reaction, which might cause aggregation of silver particles.

With the aim of clarifying the importance of superoxide species for CO oxidation, the AC support after pretreatment with H₂ at 550 °C was used to support Ag to obtain 12 wt % Ag/AC-H550 catalyst. The catalyst was then tested in the CO selective oxidation in excess H₂ reaction after pretreatment with H₂ at 200 °C or 300 °C, and the results were shown in Figure 4. The Ag/AC-H550 catalyst after pretreatment with H₂ at 200 °C or 300 °C showed much higher O₂ and CO conversions compared with those of the Ag/AC catalyst after the same temperature hydrogen pretreatment. Moreover, the Ag/AC-H550 catalyst after pretreatment with H₂ at temperature higher than 200 °C exhibits the similar catalytic performances with those of the Ag/AC catalyst after pretreatment with H₂ at 500 °C. These results indicate that, if the AC surface has been reconstructed by high-temperature hydrogen treatment before loading silver, the corresponding catalyst is suitable for the formation of superoxide species, and its formation promotes CO oxidation and leads to the improved catalytic activity of Ag/AC-H550 catalyst.

3.3. Other Active Oxygen Species. Although superoxide species can react with CO over Ag/AC catalyst, one cannot rule out the existence of other active oxygen species and their active roles in CO oxidation reaction. Indeed, atomic oxygen species that desorb at relatively high temperatures (>300 °C) have been reported to be the active species for CO oxidation.^{16,32} In the present work, if the atomic oxygen species exist, it can oxidize carbon support in the TPD experiments, leading to the formation of CO and CO₂ due to their relatively high desorption temper-

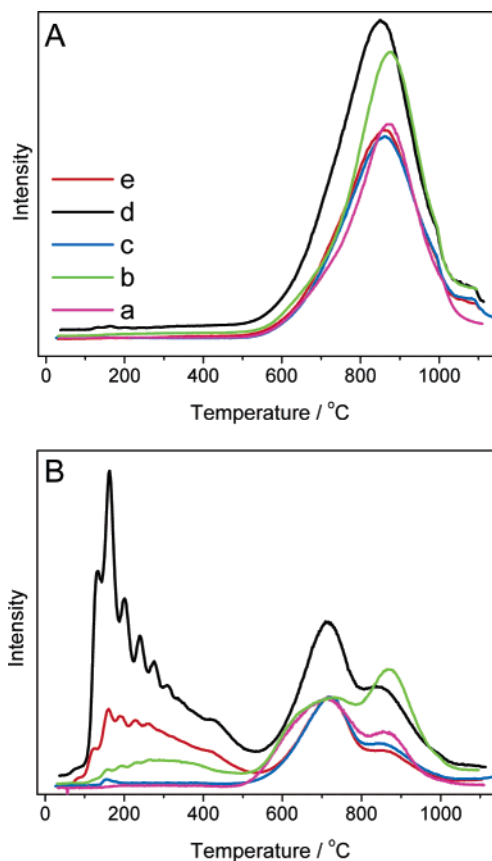


Figure 5. The CO- (A) and CO₂-TPD (B) spectra of the AC and Ag/AC catalyst after different pretreatments. (a) AC after pretreatment with H₂ at 500 °C, (b) AC after H₂ pretreatment followed by O₂ adsorption at 80 °C for 1 h, (c) Ag/AC catalyst after pretreatment with H₂ at 500 °C, (d) Ag/AC catalyst after H₂ pretreatment followed by O₂ adsorption at 80 °C for 1 h, and (e) Ag/AC catalyst after O₂ adsorption followed by CO treatment (30 vol % CO in He, 30 mL/min) at 80 °C for 1 h.

atures. Therefore, CO ($m/z = 28$) and CO₂ ($m/z = 44$) signals of the AC support and Ag/AC catalyst during O₂-TPD measurements were also recorded as shown in Figure 5. The support and catalyst treated in H₂ at 500 °C had a small amount of CO and CO₂ emission. Upon further exposure to O₂, the intensities of CO and CO₂ signals increased. It means that the adsorbed oxygen species can oxidize the carbon to release CO and CO₂ during the TPD experiments. The sample after oxygen adsorption was followed by treatment with 30 vol % CO in He at 80 °C for 1 h. It is interesting to find that the intensities of CO and CO₂ signals decrease but the profiles are similar to those of the catalyst after activation in H₂ with O₂ adsorption. These results indicate that the oxygen species have been consumed during the CO treatment. In summary, besides superoxide species, other oxygen species also exist and take part in the reaction with CO.

3.4. Formation of Superoxide Species on AC. As reported, AC can be reconstructed under H₂ treatment at temperatures higher than 400 °C, which is in agreement with our H-TPR results (Figure 1C, the H-TPR profile of AC).^{33,34} Treatment with H₂ or He on one hand removes the less stable oxygen functional groups but on the other hand generates reduction species on the carbon surface. The formation of reduction species might be related to the basic sites.³⁰ Oliveira has used iodometric titrations to quantify the amount of the reducing sites of carbons after H₂ treatment.³⁰ It was reported that the concentration of reducing sites increased with increase of the

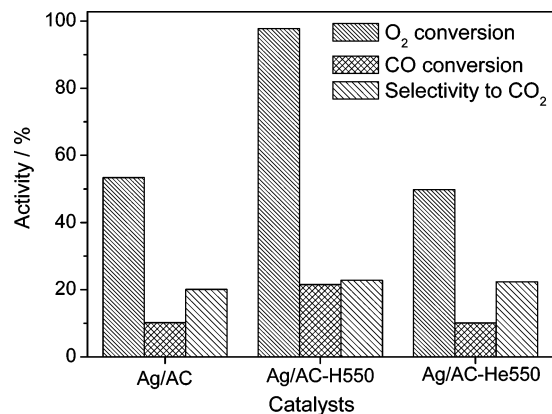
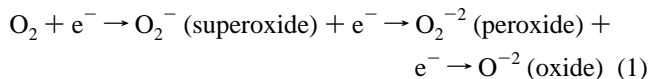


Figure 6. The catalytic performances at 80 °C over Ag/AC, Ag/AC-H550, and Ag/AC-He550 catalysts after activation in H₂ at 300 °C for 2 h.

treatment temperature. Furthermore, the reducing sites can react with oxygen. Similar results were also reported by Radovic et al., i.e. carbon, after treatment with H₂ at high temperatures, presented a strong oxygen adsorption even at room temperature.^{33,34} These reports demonstrated that, upon thermal treatment in H₂, oxygen-containing groups on carbon surface will decompose, leaving unsaturated carbon atoms at crystallite edges. Part of these unsaturated carbons may react with H₂, producing stable basic sites, whereas other sites will be available for the adsorption of O₂. The activation and incorporation of O₂ gaseous molecules have been suggested to take place via a stepwise reduction to form superoxide, peroxide, and finally the oxide (eq 1).³⁵



Therefore, the pure AC can form superoxide species after pretreatment with H₂ at temperatures higher than 350 °C. However, the Ag/AC catalyst can even generate superoxide species after pretreatment with H₂ at 200 °C, due to the existence of Ag catalyst.

3.5. Reactivity of Superoxide Species Formed on AC. As presented, AC has no catalytic activity for CO-selective oxidation in excess H₂ after pretreatment with H₂ at temperatures above 300 °C, although it can create superoxide species after the pretreatment. However, Ag/AC catalyst, after pretreatment with H₂, exhibits high activity, and superoxide species take part in the reaction. It is proposed that superoxide species formed on AC may spill over to Ag particles to react with CO.

As mentioned in sections 3.1. and 3.4., AC, after pretreatment with H₂ at 550 °C, can produce superoxide species, as well as remove some unstable oxygen functional groups and form basic sites related to the reducing sites. These factors may influence the catalytic properties of Ag/AC-H550 catalyst. However, AC treated in He at 550 °C (AC-He550) only removes some unstable oxygen functional groups and forms basic sites related to the reducing sites. In order to determine which factor is essential for the better CO oxidation activity, Ag/AC-H550 and Ag/AC-He550 (the catalyst prepared from AC-He550) after activation in H₂ at 300 °C were evaluated for CO selective oxidation in excess H₂. The reaction results at 80 °C are presented in Figure 6. As seen, after the same activation treatment, the catalytic activity in excess hydrogen follows the order: Ag/AC-H550 > Ag/AC ≈ Ag/AC-He550. These results indicate that the reduction of AC enhances the catalytic activity,

and the remove of oxygen functional groups and basic site generation do not apparently change the catalytic performances after the activation in H₂ at 300 °C. Hence, it is confirmed that the good activity of Ag/AC-H550 catalyst, after activation in H₂ at 200 or 300 °C, is attributed to the increase of superoxide species formation ability on AC-H550.

4. Conclusions

AC-supported Ag catalysts were prepared by the wetness impregnation method and tested for CO selective oxidation in excess H₂. AC, after pretreatment with H₂, can form superoxide species, O₂⁻; and the existence of Ag promotes the formation of superoxide species. Without silver species, superoxide cannot react with CO; instead, for Ag/AC catalyst, superoxide species formed on AC may spill over to silver particles to react with CO under the reaction conditions. The higher pretreatment temperatures enhance the formation ability of superoxide species over AC support, leading to better catalytic performance. In addition, other atomic oxygen species also generate on Ag/AC catalyst after pretreatment in H₂, which are also active for CO oxidation.

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