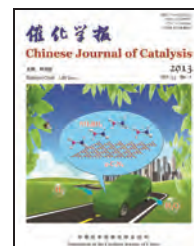


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Review

Progress in carbon monoxide oxidation over nanosized Ag catalysts

ZHANG Xiaodong, QU Zhenping*, YU Fangli, WANG Yi

Key Laboratory of Industrial Ecology and Environmental Engineering, Ministry of Education, School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, Liaoning, China

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ABSTRACT

Nanosized Ag catalysts have attracted much attention because of their unique catalytic properties for various reactions, in particular for CO oxidation at low temperatures. Recently, Ag catalysts displaying high catalytic activities and reaction stabilities, and good application prospects in the elimination of CO, even at ambient temperature, have been developed. In this review, combined with our group's research, the different influencing factors such as the preparation method, support, pretreatment conditions, second component, other atmosphere, and reaction mechanisms are discussed in detail and summarized.

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1. Introduction

CO is one of the key pollutants in many industrial and indoor environments. CO combines easily with hemoglobin in the human body, and this damages the central nervous system. At present, the catalytic oxidation of CO is a common way of removing CO. The catalytic oxidation of CO to CO₂ at low temperatures is an important process for environmental protection and has widespread applications in air purification for buildings or vehicles, closed-cycle CO₂ lasers, CO detectors [1,2], and CO selective oxidation in reformer gas for fuel-cell applications [3–5]. In addition, the CO molecule is used as a probe molecule to study the relationship between the catalyst structure and performance. Catalytic CO removal is therefore important in basic research and practical applications.

Since the 1980s, the hopcalite catalyst and noble-metal catalysts containing Au, Pd, or Pt have been used in the catalytic oxidation of CO to CO₂. However, the hopcalite catalyst has poor

water resistance, and noble-metal catalysts are expensive [6]. In recent years, many reviews of Au catalysts [2,7–14] and some non-noble-metal catalysts [15–20] for CO oxidation have been published. Ag catalysts, which are relatively cheap, show excellent low-temperature activities for many catalytic oxidation reactions such as NO_x abatement, ethylene epoxidation, and methane oxidation [21–23]. As the *d*-orbital of the Ag atom is completely filled (first ionization energy = 731 kJ/mol (7.58 eV), electronegativity = 1.9), it is difficult for Ag to lose electrons. The interactions between Ag and reactant molecules are therefore very weak. Studies have indicated that new oxygen species are formed on restructured Ag(111) [24]; the activities of these species are much higher in some reactions (e.g., CO oxidation) than those of surface-adsorbed oxygen species. However, few reviews of Ag catalysts for CO oxidation have been published.

In this review, based on our studies of Ag catalysts for low-temperature CO oxidation, different factors such as the

* Corresponding author. Tel: +86-15542663636; Fax: +86-411-84708083; E-mail: quzhenping@dlut.edu.cn

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preparation method, support, pretreatment conditions, second component, other atmosphere, and reaction mechanisms are discussed in detail and summarized. This review will further promote research and development of Ag catalysts for low-temperature CO oxidation.

2. Effect of preparation method

The melting point of Ag (960 °C) is lower than those of Au (1063 °C), Pd (1550 °C), and Pt (1769 °C), and Ag nanoparticles tend to sinter at high temperatures. The design of the preparation method is therefore very important. It is known that the dispersion and particle size of Ag affect the interactions between Ag and the carrier, resulting in different catalytic activities for CO oxidation [25]. At present, supported Ag catalysts are usually prepared by methods such as impregnation [26–28], cation-exchange [29], mixing [30,31], combustion [32], simple solid-state reactions [33], supercritical fluid deposition [34,35], post-synthesis grafting [36–38], direct synthesis [25,39–43], coprecipitation [44–49], and deposition-precipitation [50,51].

AgAu/SiO₂-Al₂O₃ catalysts have been prepared using a modified incipient wetness impregnation method (using sinensis as a reducing agent) [28]. The one-step bioreduction procedure has two advantages compared with conventional deposition-precipitation methods: (1) the method is simple and the metallic particles can be obtained in one step, and (2) the synthesized nanoparticles are small and homogeneously distributed. Xia et al. [29] reported that Ag/OMS-2 catalysts prepared using a cation-exchange method exhibited very stable performance over long times on stream (1800 min). In our previous study [30], Ag nanoparticles and SiO₂ powder were mechanically mixed and ground to form a uniform mixture. The supported Ag catalysts prepared with O₂ at 500–700 °C displayed high thermal stability, and the Ag particles were much smaller than unsupported Ag nanoparticles. Bera et al. [32] reported a combustion mixture for the preparation of Ag/CeO₂. The combustion technique produces ionically dispersed Ag on a nanocrystalline CeO₂ surface. The higher catalytic activity of combustion-synthesized Ag/CeO₂ has been attributed to the ionically dispersed Ag⁺ on the CeO₂ surface. Chen et al. [33] reported the synthesis of Ag-OMS-2 catalyst, and it was found that extensive substitution of K⁺ by Ag⁺ induced the formation of a large number of active sites. The tunnel structure and nanorod morphology favored effective CO adsorption and the activation of oxygen molecules, giving high activity for CO oxidation at low temperatures ($T_{100} = 90$ °C).

The Ag catalysts prepared by the methods mentioned above have good catalytic activities, but the subsequent activation and reaction processes easily induce aggregation of Ag particles, resulting in decreased catalytic activity. Recently, many researchers have found that confinement by ordered mesopores of mesoporous silica materials plays a crucial role in improving the thermal stabilities of Ag nanoparticles. Yin et al. [34] reported the preparation of Ag/SBA-15 nanocomposites using the supercritical fluid deposition method. This method mainly takes advantage of the fact that the surface tension of a super-

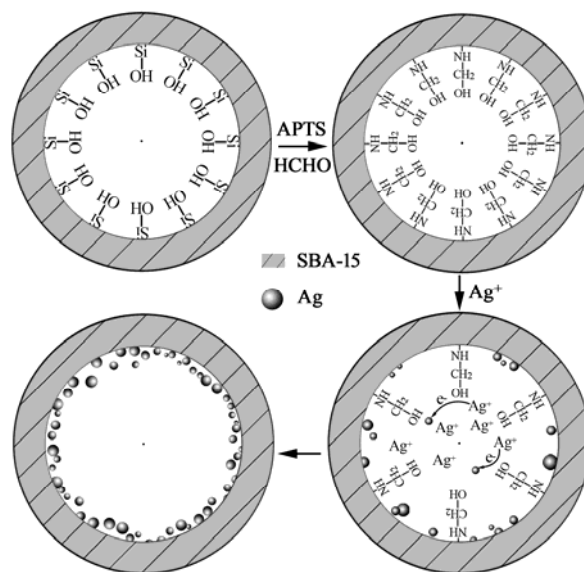


Fig. 1. Formation mechanism of Ag/SBA-15 catalyst using post-grafting method.

critical fluid is zero, and larger numbers of Ag precursor species are likely to spread to the slit and form small metal Ag particles. The addition of a cosolvent significantly improved the solubility of AgNO₃ in supercritical CO₂ and resulted in the formation of Ag nanowires. These nanowires did not improve the catalytic activity and only gave 100% conversion of CO at 300 °C. Tu et al. [36] reported the confinement of Ag nanoparticles in SBA-15 channels using the post-grafting method (Fig. 1). Importantly, the Ag/SBA-15 catalyst was found to exhibit high activity for CO oxidation. Yen et al. [37] reported the preparation of Au-Ag bimetallic nanoparticles supported on mesoporous silica by the above method; the nanoparticles were very active for low-temperature CO oxidation ($T_{100} = 30$ °C). Recently, a post-grafting method has been developed for the synthesis of very small and sintering-resistant bimetallic Au-Ag particles on commercial silica [38]; the particles were highly catalytically active for CO oxidation ($T_{100} = 0$ °C). However, the post-grafting method is relatively complicated, and in some cases the process has to be carried out under conditions that exclude water and oxygen.

Direct synthesis procedures are relatively simple and have attracted much attention recently. It is difficult to graft Ag particles onto SBA-15 in strongly acidic media. To solve this problem we prepared Ag/SBA-15 using a method, in which the pH was adjusted [39,40]. Compared with the catalysts obtained in previous studies [41–43], highly ordered Ag/SBA-15 with a high Ag content (7.9 wt%) and highly dispersed Ag nanoparticles was successfully synthesized and showed good catalytic activity (Fig. 2). In addition, Liu et al. [25] recently reported a modified one-pot approach to the preparation of Ag nanoparticles on silica; the prepared Ag catalysts displayed good catalytic activity, and 100% conversion of CO was achieved at 30 °C (Fig. 3).

3. Effect of pretreatment

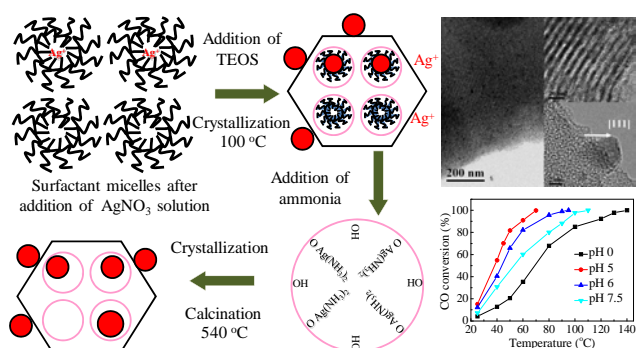


Fig. 2. Formation mechanism of Ag/SBA-15 nanocomposites using the pH-adjusting method (left); transmission electron microscopy images (upper right) and CO conversions (lower right) of Ag/SBA-15 nanocomposites [39,40].

Calcination is a necessary process for the preparation of supported Ag catalysts, and the process can induce interactions between the metal and the support. Our previous studies indicated that if the Ag nanoparticles and SiO₂ were only mechanically mixed and ground to form a uniform mixture, the catalyst showed low activity for CO oxidation. However, it became catalytically active after treatment with oxygen at a certain temperature [30]. Recently, it was reported [31] that the Ag/Al₂O₃ catalyst prepared from a physical mixture of Ag and Al₂O₃ powders showed high catalytic activity and durability for CO oxidation after calcination at high temperature (1000 °C). Aging- and catalysis-induced restructuring are therefore important concepts in designing active and durable catalysts.

Recently, we reported that a Ag/SBA-15 catalyst with low loading (1.42 wt%) showed excellent activity in CO oxidation at 20 °C after oxygen pretreatment at 900 °C (*T*₉₈ = 20 °C) [52]. An evaporation-deposition-diffusion mechanism for the Ag/SBA-15 catalyst was proposed (Fig. 4). The oxygen adsorbate caused a decrease in the surface free-energy at 900 °C and induced redeposition of the evaporated Ag atoms on the support, and Ag diffused into the channels of SBA-15, forming more highly dispersed small Ag particles inside the channels. We have also found that different pretreatment atmospheres

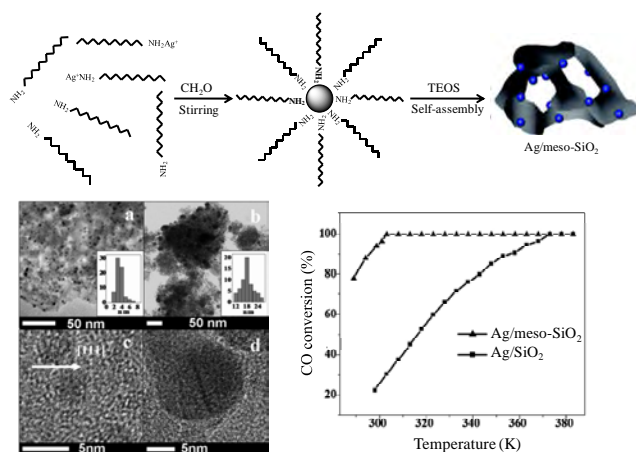


Fig. 3. Formation mechanism of Ag/mesostructured silica catalyst (top); transmission electron microscopy images (bottom left) and CO conversions (bottom right) of supported Ag catalysts [25].

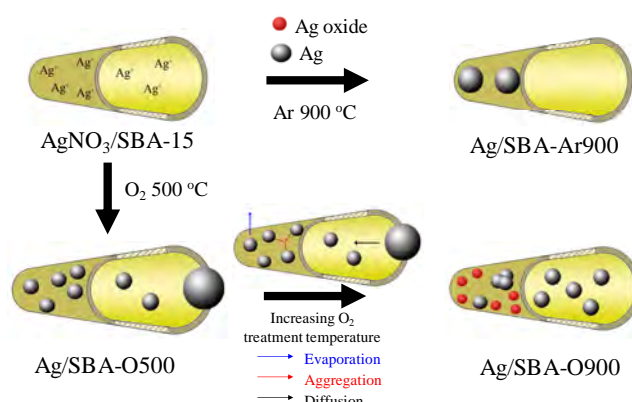


Fig. 4. Schematic diagram of structural changes in Ag/SBA-15 pretreated with different atmospheres (O₂ and Ar) at 500 and 900 °C [52].

(Ar, O₂) and Ag loadings resulted in large differences in the structures of Ag catalysts and their catalytic activities [53] (Fig. 5). Ar pretreatment was favorable for the formation of small Ag particles in a Ag/SBA-15 catalyst with a low Ag loading (2 wt%). O₂ pretreatment was conducive to the formation of subsurface oxygen species on larger Ag particles in a Ag/SBA-15 catalyst with high Ag loading (8 wt%). The small metal Ag particles were the key factor in the higher catalytic activity of the Ag/SBA-15 catalyst with a low Ag loading, whereas the large number of subsurface oxygen species played an important role in the higher catalytic activity of Ag/SBA-15 catalyst with a high Ag loading.

Irradiation with γ-rays was successfully used to reduce Ag⁺ anchored on SiO₂ to Ag nanoparticles at room temperature [54]; poor low-temperature activity and high activity at high temperature for CO oxidation were found. However, the Ag/SiO₂ catalyst prepared by calcination showed the opposite activity trend. Different pretreatments induce the formation of different Ag species, resulting in different activities for CO oxidation. In addition, it has been found that Ag catalysts supported on different supports need different pretreatment conditions for high activity. Our previous studies [25–27,42,55,56] showed that H₂ treatment was favorable for improving the catalytic activity of SiO₂-supported Ag catalysts. It was proposed that the high-temperature oxygen treatment induced faceting of the Ag surface and facilitated the formation of sub-

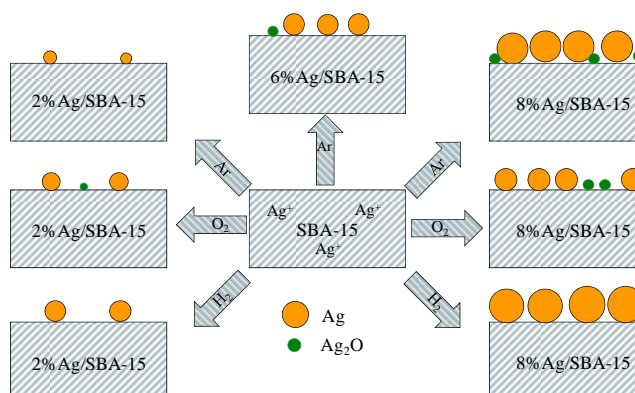


Fig. 5. Schematic diagram of Ag/SBA-15 catalysts with various Ag loadings pretreated under different atmospheres [53].

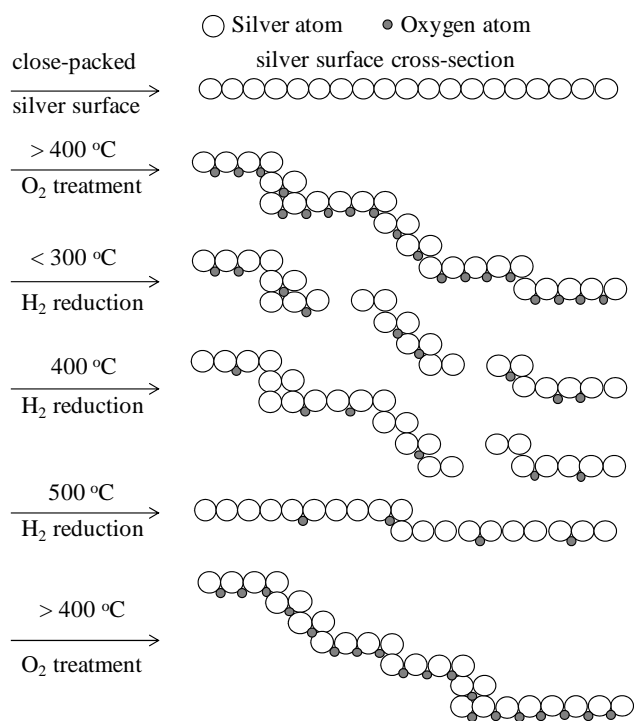


Fig. 6. Surface restructuring, subsurface oxygen formation, and redispersion model of Ag crystallites under oxidation/reduction cyclic treatment [57].

surface oxygen species and migration between the surface and the bulk of oxygen species on the Ag catalysts. When the Ag catalyst was further treated with H₂ at low temperature, the redispersion of Ag particles resulted in larger numbers of small Ag particles, resulting in increased catalytic activity [57] (Fig. 6).

For some supports such as Ce oxide [32] and Mn oxide [58], many researchers have found that calcination improved the catalytic activity. Reduction with H₂ following calcination reduced Ag₂O species and also affected the structure of the carrier, which decreased the activity. Gac [58] investigated the influence of the pretreatment on the CO catalytic activity of Ag/MnO_x catalysts and found that a large amount of active oxygen species (Mn–O) were formed on the surface of the Ag/MnO_x catalyst after calcination. However, reduction with H₂ after calcination slightly decreased the activities at low temperatures of the catalysts because the MnO_x structure was destroyed. Interestingly, the formation of new active sites for CO oxidation on Ag/MnO_x catalysts after H₂ reduction increased the activity at high temperatures. For all two-component catalysts containing Ag, reduction with H₂ was found to be necessary to obtain high activities for CO oxidation [37,38] (Fig. 7). Such reduction treatments reduce Ag₂O and restructure the particles, which resulted in enhancement of the CO catalytic activity.

4. Effect of support

It is known that the catalytic activities of supported Ag catalysts are higher than those of unsupported Ag catalysts. The

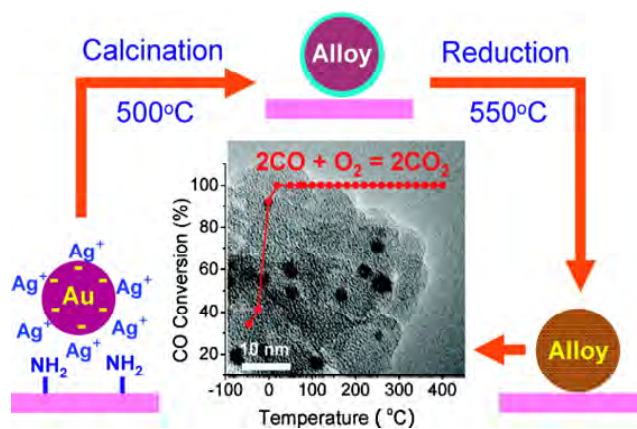


Fig. 7. Schematic diagram of structural changes and CO oxidation activity of Au-Ag/SiO₂ under calcination and reduction conditions, and transmission electron microscopy image [38].

support can disperse the metal particles and induce interactions between Ag and the support [25]. At present, supports for Ag catalysts are divided into two main categories: (1) inert supports such as silica materials [25–27,42,52,53,55,56,59] and Al₂O₃ [60]; and (2) active supports such as CeO₂ [32], FeO_x [45–47], CoO_x [48], TiO₂ [61–64], and MnO_x [29,58,65–69]. The CO oxidation activities of Ag catalysts supported on different supports are listed in Table 1.

Silica-based Ag catalysts have been widely introduced in the pretreatment and preparation of catalysts, and it was found that silica-based Ag catalysts showed excellent activities for CO oxidation at room temperature [25,55], unlike silica-based Au catalysts. In the following part, we will discuss Ag catalysts on supports other than silica and the different active Ag species on different supports for CO oxidation.

The oxygen species and catalytic activities for CO oxidation over Ag/Al₂O₃, Ag/CeO₂, and Ag/TiO₂ catalysts have been investigated using X-ray diffraction (XRD), temperature-programmed desorption, and temperature-programmed reduction [70,71]. The highest catalytic activity for CO oxidation was found on the Ag/Al₂O₃ catalyst, and the catalytic activity for CO oxidation was strongly related to the reduction activity of the catalyst. Comsup et al. [62] found that stronger Ag–TiO₂ interactions improved the catalytic activity for CO oxidation. Doping of P and Si into TiO₂ resulted in different activities [63,64]. The incorporation of P into the TiO₂ lattice in the form of Ti–O–P resulted in an increase in both surface area and metal dispersion, and the adsorption ability for oxygen depended on the P precursor. The formation of Ti–O–Si inhibited the agglomeration of TiO₂ crystallites, promoted the formation of active oxygen species, and increased the mobility of lattice oxygens and the catalytic activity. Hu et al. [72–74] found that CO was reversibly adsorbed on the surface of the catalyst and reacted with lattice oxygens to form CO₂. The XRD results showed that the catalysts had the typical cryptomelane structure with a one-dimensional channel. Doping with Ag resulted in a higher specific surface area and narrower pore size distribution in OMS-2. The synergistic effect of ion-exchanged Ag ions and substituted Co atoms of a mordenite zeolite enhanced the CO oxidation activity [75].

Table 1

CO oxidation activities of Ag catalysts on different supports.

Catalyst	Ag (wt%)	Preparation method	Treatment condition	$T_{100}(\text{CO})^a$ (°C)	Ref.
Ag/Silica	4	One-pot synthesis method	O ₂ -H ₂	30	[25]
Ag/SiO ₂	8	Impregnation method	O ₂ -H ₂	50	[27]
Ag/SBA-15	6.86	In-situ reduction method	O ₂	120	[42]
Ag/SBA-15	1.42	Impregnation method	O ₂ -H ₂	22	[52]
Ag/fumed silica	4	Impregnation method	O ₂ -H ₂	30	[55]
Ag/Silica	0.99	One-pot synthesis method	O ₂	170	[59]
Ag/Al ₂ O ₃	29	Impregnation method	O ₂	80	[60]
Ag/CeO ₂	1	Combustion method	O ₂	260	[32]
AgFeO ₂	Ag:Fe = 1:1 (mol/mol)	Coprecipitation method	O ₂	130	[45]
Silver cobalt composite oxide	Ag:Co = 1:1 (mol/mol)	Cocipitation method	O ₂	50	[48]
Ag/TiO ₂	10	Solvothermal method	O ₂	150	[63]
Ag-OMS	8.7	Cation exchange method	O ₂	>100	[29]
Ag/MnO ₂	15	Hydrothermal method	O ₂	>130	[68]

^aTemperature for 100% conversion of CO.

The nature of the support also affects the reaction mechanism of CO oxidation on Ag catalysts. For inert supports, the adsorption and dissociation processes of CO and O₂ molecules occur on the Ag surface or at the interface between Ag and the inert support. The catalytic activities of Ag catalysts are therefore largely dependent on the particle size [57,76]. However, because of the low Tamman temperature of Ag (344 °C), Ag catalysts have not been found to have size dependence, unlike Au catalysts. Our previous study indicated that Ag particles of size ca. 3–5 nm showed relatively high activity for CO oxidation, and Ag⁰ species were proposed as the active species [27]. It is known that interactions between Ag and hydroxyl groups on a silica surface are conducive to the formation of highly dispersed Ag particles. We therefore tried to prepare Ag catalysts with particles of different sizes by calcining silica at different temperatures and tested their CO oxidation; it was found that highly dispersed metal Ag particles showed high activity for CO oxidation at low temperatures [77]. For active supports, the lattice oxygens of the support and electron transfer between Ag-oxygen and transition metals play an important role in the catalytic activity [29]. However, the active Ag species for CO oxidation are still not clear. Luo et al. [78] thought that Ag₂O was the active species for low-temperature CO oxidation.

As alternatives to oxide supports, some researchers have recently tried to use graphite [79] and carbon [51,80] as the support. Lim et al. [79] found that CO oxidation activity on Ag/graphite was very sensitive to the particle size. For Ag nanoparticles larger than 3 nm, two different oxygen species were identified, one of which readily reacted with CO to form CO₂ at room temperature; the activity increased with decreasing particle size. For smaller Ag nanoparticles (< 3 nm), the formed oxygen species only reacted with oxygen atoms in the gas phase and were inert towards CO oxidation. Dai et al. [51] found that highly dispersed Ag nanoparticles were easily attached to modified carbon nanotube supports by anchoring them to oxygen-containing functional groups, and these nanoparticles exhibited higher activities for CO oxidation at low reaction temperatures. From the above results, we can deduce that the support plays an important role in the formation of active oxygen species and the particle size, and thus the catalytic activity.

5. Effect of second component

Because of their good O₂ adsorption capabilities, Ag catalysts have been widely used in CO oxidation reactions. At present, research on Ag catalysts is mainly focused on investigation of structures and activities. However, one-component Ag catalysts have inevitable shortcomings such as high loadings and poor catalytic activities at low temperatures. Based on the current research status, some researchers have expanded the investigation of single active Ag species and have modified Ag catalysts with other components: (1) additives and (2) bimetallic catalysts (Au-Ag, Ag-Pd, etc.).

5.1. Additives

In an Ag catalyst, interactions between additives and Ag species can change the electronic structure and surface properties of the catalyst, increase the stability of Ag nanoparticles, and promote Ag dispersion, thus increasing the catalytic activity for CO oxidation.

Luo et al. [60,81–83] reported the catalytic activities for CO oxidation on Ag-Mn/γ-Al₂O₃, Ag-Co/γ-Al₂O₃, and Ag-Ce/γ-Al₂O₃ catalysts, and the addition of MnO_x, CoO_x, and CeO₂ increased the amount of adsorbed oxygen and the capacity for surface oxygen renewal of the catalysts, consequently improving the activity. In addition, it was found that CeO₂ favored the dispersion of Ag particles on the surface of Al₂O₃ [81]. With increasing amounts of CeO₂, the Ag₂O amount increased. However, the relationship between structure and activity was not discussed in this paper. Recently, we found that a small amount of CeO₂ promoted dispersion of metal Ag particles and increased the stability of Ag nanoparticles during high-temperature H₂ pretreatment, consequently improving the activity [26].

5.2. Ag-based bimetallic catalysts

Oxygen molecules are more easily adsorbed and activated by Ag than they are by Au and Pd. Many researchers have therefore tried to prepare Ag bimetallic catalysts to improve the activation of molecular oxygen and accelerate the catalytic

oxidation of CO.

Although supported Au catalysts have good catalytic activity for CO oxidation and 100% conversion of CO has been achieved at 0 °C [2], these Au catalysts have poor thermal stability and are easily deactivated in the reaction process. In order to solve these problems, Ag was used to change the electronic structure of the active metal and to activate oxygen molecules, consequently improving the reaction activity and stability of the catalyst [37,38,84–94]. Mou's group [37,38,84–87] reported that oxygen molecules activated by Ag can easily react with CO molecules activated by Au to form CO₂, improving the catalytic activity and reaction stability. Wang et al. [88] found that oxygen species activated by Ag can be easily stored on nanoporous Au catalysts at room temperature. CO oxidation on an Au-enriched Ag(110) surface led to an exponential depletion of oxygen with time, shown by an in-situ time-lapsed scanning tunneling microscopy (STM) image series and density functional theory (DFT) [90]. Investigation of the kinetic mechanism of CO oxidation with O₂ on Au-Ag alloy indicated that (CO₃)^{*}, which was formed on the Au-Ag interface as a result of co-adsorption of CO and O₂, was decomposed to CO₂, and the process was enhanced by the interactions [91]. Pd-Ag bimetallic catalysts were also investigated by changing the pretreatment conditions, and it was found that Ag reappeared at the surface, further increasing the catalytic activity. The results were explained in terms of rearrangement of the most active metallic particles, namely clean particles of pure Pd next to dispersed Ag particles [92].

6. Effects of different atmospheres

Different applications require different CO oxidation catalysts to be designed and developed. Investigation of the effects of different environmental atmospheres on the catalytic activity for CO oxidation at low temperatures not only gives insights into the catalytic reaction mechanism, but is also of great importance for catalyst development. The presence of other components in the CO feed, such as H₂, water, and CO₂, affect the activity for CO oxidation.

6.1. Effect of H₂

It is known that a small amount of CO in H₂ strongly affects the performance of Pt anodes and fuel-cells, and it is essential to remove traces of CO from the H₂ feed gas. A large number of studies of Ag catalysts for CO selective oxidation in H₂ have been performed, but the selectivities were too low. We prepared different Ag/SiO₂ catalysts [30,95–99], but the maximum CO conversion was 60%, and the selectivity was not more than 40%. Derekayal et al. [49] reported that 100% CO conversion over a Ag/Co/Ce catalyst was achieved at 150 °C. The selectivity was very low (< 20%) and the low-temperature (< 80 °C) activity was also poor. Chen et al. [100,101] reported that Ag supported on active carbon can achieve 100% CO conversion at 100 °C, but the selectivity was again very low (< 20%). In contrast, Ag-Co and Ag-Mn catalysts showed higher selectivities, but the temperature for complete CO conversion was high

[102,103]. Hu et al. [103] reported that 100% CO conversion can be maintained for 250 h at 120 °C, with about 90% selectivity.

6.2. Effect of water

Water is inevitably present in various environments, but, so far, the effects of water on the performance of Ag catalysts have rarely been studied. Studies showed that water vapor at the parts per million (10⁻⁶) level in the feed had a positive effect on the catalytic activity [55,104,105]. A small amount of water could prevent carbonate formation on the surfaces of Ag catalysts, resulting in increased catalytic activity for CO oxidation [55,104]. Moreover, Su et al. [105] reported that adsorbed water affects not only the adsorption of reactants but also the transition states and intermediates. The formation of hydrogen bonds as a result of adsorption of water facilitates the dissociation of O₂. The formed atomic oxygen can further react with the adsorbed water to form hydroxyls, which promotes CO oxidation. However, there is still a lack of systematic data regarding the effect of water on catalytic performance for CO oxidation at low temperatures; this needs to be further investigated in the near future.

7. CO and O₂ adsorption processes and reaction mechanisms

7.1. CO and O₂ adsorption processes

The adsorption of CO and O₂ on the surface of Ag catalysts is of interest in many research areas, such as physical chemistry and surface science. Research on the adsorption of CO and O₂ is very helpful in understanding the activation processes of CO and O₂, the role of Ag, and the intrinsic character of the surface reactions and catalytic process. So far, most studies have focused on theoretical calculations and catalyst models [106–127].

Zhou and Hagen et al. [107–112] reported that the adsorption of CO on top sites, among various possible sites, was energetically preferred, based on DFT calculations and temperature-dependent gas-phase kinetic data. CO easily reacted with Ag clusters with adsorbed oxygen species. In addition, B3LYP DFT has been used to study the electronic and geometric structures of Ag anion dimers bonded with CO and oxygen. It appears that CO oxidation can be achieved, cost effectively, at room temperature using Ag without any external supply of energy [113]. Moreover, ultraviolet photoelectron spectroscopy showed that O₂ partially dissociated on Ag₂⁻, and these dissociative chemisorptions were a kinetically hindered step [114]. Recently, it was found that there were four possible reaction pathways for CO oxidation catalyzed by Ag₂⁻ [115]. The most feasible pathway was CO insertion into the Ag–O bond of Ag₂O₂⁻ to produce an intermediate, [Ag–AgC(O–O)]⁻, and then the intermediate decomposed to the products CO₂ and Ag₂O⁻, or another CO molecule attacked [Ag–AgC(O–O)]⁻ to form two CO₂ molecules and an Ag₂⁻ anion.

The adsorption behavior of CO and O₂ on different Ag crystal

faces has also been investigated using X-ray photoelectron spectroscopy, scanning tunneling microscopy, and theoretical calculation methods. The results showed that CO on an Ag(001) surface tended to react with surface O atoms [116]. The most feasible pathway is $\text{CO} + \text{O}_2 \rightarrow \text{O}_2\cdots\text{CO} \rightarrow \text{CO}_2 + \text{O}$ [117]. Burghaus et al. [118,119] reported that CO tended to react with molecularly adsorbed oxygen on the Ag(110) surface below the dissociation temperature of molecularly bonded oxygen. However, only weakly adsorbed CO species were observed on the surface of Ag(111) under high pressure and at low temperatures [120]; this is consistent with the results of Schmeisser et al. [121] and Jänsch et al. [122]. Hammer et al. [123] and Jiang et al. [124] found that CO molecules were dissociatively adsorbed on the surface of Ag single-crystals.

7.2. CO oxidation reaction mechanisms

It has been reported that the mechanism for CO oxidation on Ag catalysts differs, depending on the supports. There are different rate-limiting steps for CO oxidation on Ag/SiO₂ catalysts in different reaction temperature regions [54]. At low reaction temperatures, oxygen dissociation is the rate-limiting step and occurs easily on fine Ag nanoparticles; however, at high reaction temperatures, oxygen is easily thermally activated and reversible CO adsorption on the Ag surface becomes the rate-limiting step. It was found that reduction of Ag⁺ on a Ag/NaY catalyst was very important for the enhancement of CO oxidation activity, and the CO oxidation reaction followed first-order reaction kinetics [128].

The CO oxidation mechanism on Ag on active supports is relatively complicated. The active oxygen on Ag is mainly consumed in the oxidation of CO, and M (Mn, Co, Ce) serves as an oxygen carrier to supply oxygen species to Ag (Fig. 8). Ag reoxidation occurs, releasing oxygen from M (Mn, Co, Ce) [60,66,81]. CO oxidation follows a redox reaction mechanism on Ag/transition-metal oxide catalysts [72]. At low temperatures, the CO oxidation reaction on the surface of the catalyst is the rate-determining step, and at higher temperatures, i.e., above 473 K, the CO adsorption rate on the surface of the catalyst becomes the key step.

8. Conclusions and prospects

Supported Ag catalysts have a wide range of applications in low-temperature CO oxidation. Many factors such as preparation method, pretreatment conditions, carriers, and particle

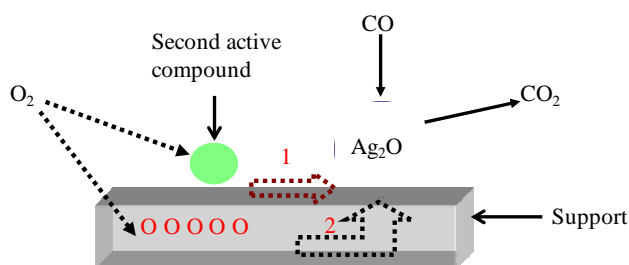


Fig. 8. Possible reaction scheme for CO oxidation over supported Ag catalysts (Ag/Co, Mn oxides) [97].

size have important effects on the catalytic activities of supported Ag catalysts. Among the various preparation methods, direct synthetic methods and impregnation methods are the main techniques used to synthesize Ag catalysts that can catalyze CO oxidation at room temperature. Silica materials (such as SBA-15, HMS, or fumed silica) are the best supports for preparing Ag catalysts with high activities by these methods. The preparation of highly active Ag catalysts depends significantly on the pretreatment conditions, including the atmosphere and temperature. There is therefore a synergistic effect between these influencing factors in the preparation of supported Ag catalysts with high activities for CO oxidation.

Three main conclusions can be drawn from investigation of Ag catalysts for CO oxidation. (1) An obvious dependence of catalytic activity on the Ag nanoparticle size can be seen in reactions on inert supports. (2) Different pretreatment atmospheres are required for different supports. For inert supports such as silica, low-temperature H₂ treatment after calcination is conducive to Ag dispersion and improvement of the activity. However, for active supports such as CeO₂ and MnO₂, calcination is more beneficial in improving the activity. (3) The reaction mechanism is different for Ag on different supports. For inert supports, the adsorption and dissociation of CO and O₂ molecules occur on the Ag surface or at the interface between Ag and the inert support. The catalytic activities of Ag catalysts are therefore largely dependent on the particle size. For active supports, the lattice oxygens in the support and electron transfer between Ag-oxygen and transition metals play an important role in the catalytic activity. Although researchers have paid much attention to supported Ag catalysts for CO oxidation in recent years, little attention has been given to catalysis in practical industrial atmospheres, and there have been few investigations of the influence of water and CO₂ on the structures and catalytic activities of supported Ag catalysts. Furthermore, the reaction mechanism of CO oxidation over supported Ag catalysts is unclear, and the migration and transformation processes of CO and O₂ on the catalyst surface need to be studied in detail using in-situ techniques. With further investigation, we believe that supported Ag catalysts will be widely used in industry and environmental protection (including air purification in tunnels and indoors) in the near future.

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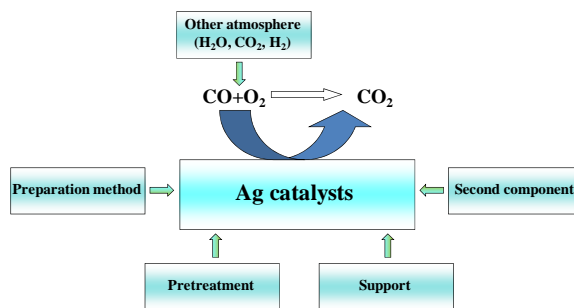
Graphical Abstract

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Progress in carbon monoxide oxidation over nanosized Ag catalysts

ZHANG Xiaodong, QU Zhenping*, YU Fangli, WANG Yi
Dalian University of Technology

Recent developments of Ag catalysts for CO oxidation mainly focus on the structures of Ag catalysts (particle size, species states, etc.) and their catalytic activities.



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纳米银催化剂上CO氧化反应研究进展

张晓东, 曲振平*, 于芳丽, 王 奕

大连理工大学环境学院, 工业生态与环境工程教育部重点实验室, 辽宁大连116024

摘要: 纳米Ag催化剂由于具有独特的物理和化学性质, 在很多反应中受到了越来越多的关注, 尤其对低温催化一氧化碳氧化反应. 近年来, 银催化剂表现出较高的催化活性、稳定性以及良好的应用前景, 能够在常温下将CO氧化为CO₂. 本文结合本课题组的研究进展, 从制备方法、载体、预处理、第二组分、其它气氛和催化反应机理等方面对Ag基催化剂上CO氧化反应进行了系统的讨论和总结.

关键词: 负载型银催化剂; 一氧化碳氧化; 制备方法; 预处理条件

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*通讯联系人. 电话: 15542663636; 传真: (0411)84708083; 电子信箱: quzhenping@dlut.edu.cn

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1. 前言

CO是许多工业环境和室内环境的主要气体污染物之一, 易与人体内的血红蛋白结合, 损害人的中枢神经系统. 目前, 最常用且有效的消除CO的方法是低温催化氧化法. 而且, 在空气及汽车尾气净化, CO₂激光器气体纯化^[1], CO气体传感器^[2], 燃料电池^[3-5]等领域也涉及到CO的净化. 另外, 由于CO分子量较小, 氧化反应过程简单, 常被用作探针分子来研究催化剂的表面结构. 因此, 研究CO的消除在基础研究和实际应用方面都具有重要的意义.

自20世纪八十年代以来, Hopcalite催化剂和以Au, Pd或Pt为活性组分的贵金属催化剂广泛应用于CO氧化中. 由于Hopcalite催化剂抗水性差, 贵金属价格昂贵, 限制了其在工业中的应用^[6]. 近年来, 有关金催化CO氧化的综述很多^[2,7-14], 而其它用于CO氧化的非贵金属催化剂的综述也见诸报道^[15-20]. 相对廉价的银催化剂在NO_x消除, 乙烯环氧化及甲烷氧化等^[21-23]反应中都表现出较好的低温氧化活性. 由于银的d轨道电子是完全充满的(第一电离能731 kJ/mol (7.58 eV), 电负性1.9), 很难失去电子, 所以Ag的表面与表面反应物分子之间的相互作用力很弱. 研究表明, 对银结构进行再构使得Ag(111)面上形成一个全新的氧化物, 其反应性(如CO氧化)远远高于表面氧化物^[24]. 然而, 有关CO氧化用银催化剂的综述相对较少. 鉴于近期Ag催化剂研究进展较快, 本文结合本课题组研究成果, 从制备方法、预处理气氛和温度、载体、助剂及反应机理等方面, 对Ag催化剂上CO低温氧化反应进行系统的总结和讨论, 以期得到一些有意义和价值的结果, 进一步促进CO低温氧化用银催化剂的研究与开发.

2. 制备方法的影响

由于Ag的熔点(960 °C)比Au (1063 °C), Pd (1550 °C)

和Pt (1769 °C)的低, 粒子易发生聚集, 因此制备方法的选择和设计至关重要. 研究表明, Ag颗粒的尺寸及分散度影响它与载体间相互作用力^[25], 从而表现出不同的催化活性. 因此, 采用不同的制备方法, 可制备出具有不同活性的负载型银催化剂. 目前应用于CO氧化反应的银催化剂制备方法主要有浸渍法^[26-28]、阳离子交换法^[29]、混合法^[30,31]、燃烧法^[32]、简单固态混合法^[33]、超临界流体沉积法^[34,35]、后嫁接法^[36-38]、直接合成法^[25,39-43]、共沉淀法^[44-49]和沉积-沉淀法^[50,51]等.

通过改进的浸渍法制备的AgAu/SiO₂-Al₂O₃催化剂(以虫草菌丝萃取物为还原剂)^[28], 与传统的沉积-沉淀法相比, 该法合成过程简单且制备的粒子小且均一. Xia等^[29]以八面体分子筛为载体, 利用阳离子交换法制备了高分散的纳米银催化剂, 在催化氧化CO反应较长时间(1800 min)而不失活. 我们之前^[30]利用混合法将银粒子与载体以机械混合的方式进行研磨, 经过一定的处理制得催化剂, 其中银粒子用氧气于500~700 °C处理后表现出较高的热稳定性, 粒子尺寸远远小于未负载的银粒子. Bera等^[32]采用燃烧法制备银催化剂, 其中Ag⁺高度分散于CeO₂载体上, 从而表现出更高催化活性. Chen等^[33]采用简单固态混合法制备了Ag-OMS-2催化剂, 发现Ag⁺大量取代K⁺, 形成更多的活性位, 明显提高了吸附CO和活化氧分子的能力, 催化剂在90 °C可以完全转化CO.

上述制备方法制得的Ag催化剂虽能获得较好的催化活性, 但银粒子在随后的活化及反应过程中仍然很容易发生聚集, 从而导致活性降低. 最近, 人们发现有序介孔硅材料的孔道限域作用可大大提高Ag纳米粒子的热稳定性. 银建中等^[34]采用超临界流体沉积法制备了Ag/SBA-15催化剂. 该方法利用超临界流体表面张力为零的特点, 使得银前驱体更易扩散到多孔狭缝之中形成小的Ag粒子. 但由于共溶剂的加入显著提高了硝酸银在超临界CO₂中的溶解度, 在孔道内很容易形成纳米线, 而这些纳米线并不利于提高反应活性, 该反应300 °C时

CO才能完全转化。涂彩华等^[36]通过后嫁接法(图1),利用SBA-15的规则孔道限域组装,在孔道内形成了高分散的银粒子,表现出较高的催化CO活性。Yen等^[37]也采用相同的方法对Au-Ag合金粒子进行可控组装,所得催化剂CO在30 °C可完全转化。最近,Liu等^[38]以商业SiO₂为载体,采用后嫁接法合成了高度分散且热稳定性高的Au-Ag合金粒子,催化CO完全转化温度降至0 °C,但该方法存在的最大问题是制备过程复杂,需要无水无氧,条件苛刻。

直接合成法因其合成过程简单而备受关注。针对银在合成SBA-15的强酸溶液中很难负载的问题,本课题组采用调节pH的方法在中性溶液中制备出高负载量(7.9 wt%)的Ag/SBA-15催化剂^[39,40]。所得催化剂负载量和催化CO氧化性能较之前^[41–43]都有大幅度的提高(图2)。此外,Liu等^[25]利用模板剂十二胺来保护还原过程的银,制备了高分散的银纳米粒子,使其催化CO氧化性能大幅度提高,其完全转化温度降至30 °C(见图3)。

3. 预处理的影响

焙烧是制备负载型银催化剂的必要过程。样品经过焙烧和活化处理后,纳米银与载体之间可产生一定的相互作用。将银纳米粒子与SiO₂物理性的机械混合,活性很低,但如果O₂一定温度的焙烧,活性会显著增加^[30]。最近,Shimizu等^[31]将银粒子与载体Al₂O₃机械混合制备了Ag/Al₂O₃催化剂,发现催化剂在经高温空气(1000 °C)处理后,银与载体相互作用形成的更多银簇有利于CO氧化,进一步证实了温度诱导或反应诱导引起的银催化剂结构再构是设计具有高活性和高稳定性催化剂的关键步骤。

最近,本课题组^[52]首次利用氧气高温(900 °C)处理及SBA-15的孔道,采用等体积浸渍法制备出低担载量(1.4 wt%)高活性的CO催化氧化催化剂($T_{98} = 20$ °C),并提出了高温氧气处理导致蒸发-沉积-诱导的模型(图4)。在此过程中,氧吸附质在900 °C下能够降低催化剂的表面自由能,从而使得蒸发的银原子重新沉积在催化剂表面;同时,银在孔道及气氛的作用下被诱导进入SBA-15孔道内,形成高分散的小尺寸银粒子。此外,我们^[53]还发现,预处理气氛和银负载量均对Ag/SBA-15催化剂的结构和活性影响非常大(图5)。当银负载量为2 wt%时,Ar处理有利于得到高分散的小的银粒子;至8 wt%时,O₂处理有利于形成高分散的小的银粒子。我们认为,当银负载量较低时,小尺寸的银粒子有利于催化反应活性

的提高;而当银负载量较高时,催化剂再构所形成的次表层氧是催化剂获得高活性的关键因素。

Jin等^[54]研究发现,在 γ 射线照射过程中,银离子被还原成金属银,与焙烧处理的Ag/SiO₂催化剂相比,经 γ 射线照射处理的银物种以金属态存在,而且生成的粒子较小。在CO氧化反应中表现出较低的低温活性和较高的高温活性。不同的预处理过程导致了不同的银物种,相应表现出不同的催化CO氧化活性。其次,研究者还发现,负载银的载体不同,所得催化剂所需预处理条件也不同。在氧化硅载体上,焙烧处理后低温氢气还原一般有利于活性的提高^[25–27,42,55,56]。我们^[57]也发现,高温氧气处理使银催化剂表面发生再构,同时也在银的体相中形成了大量的次表层氧物种。随后的H₂低温还原有利于银粒子的再分散,形成了更多小的银粒子,从而提高了其催化活性(图6)。

而对于氧化铈^[32]和氧化锰^[58]等载体,焙烧处理有利于其负载Ag催化活性的提高,随后的H₂处理可生成更多的银,但同时也影响了载体结构,因而催化剂活性降低。这主要是由于载体本身也具有一定的催化CO氧化活性。Gac^[58]考察了预处理气氛对Ag/MnO_x催化剂结构和活性的影响,发现焙烧后催化剂表面形成了大量的活性氧物种(Mn–O),经H₂还原后,催化剂上Ag₂O消失的同时也破坏了Mn结构,从而导致催化剂的低温活性降低;但由于还原使得锰氧化物形成了新的活性位点,又提高了催化剂的高温活性。对于含有银的双组分催化剂,均需用H₂高温还原处理^[37,38](图7)。使得Ag₂O还原以及再构形成合金粒子,从而提高了催化剂对CO氧化的催化活性。

4. 载体的影响

研究表明,负载型银催化剂活性远远高于未负载的。这主要是由于载体能够分散银粒子,同时两者间能产生一定的相互作用^[25]。用于负载银催化剂的氧化物载体主要分为两类:(1)惰性载体,例如SiO₂^[25–27,42,52,53,55,56,59]和Al₂O₃^[60]等;(2)活性载体,即载体自身能够活化反应分子而使之发生反应,例如CeO₂^[32],FeO_x^[45–47],CoO_x^[48],TiO₂^[61–64]和MnO_x^[29,58,65–69]等。不同载体负载的银催化剂上CO氧化反应活性如表1所示。

前面有关预处理气氛以及制备方法中,我们已经介绍了很多硅基材料负载的Ag催化剂对CO的催化氧化活性。与Au催化剂不同,氧化硅负载的Ag催化剂表现出很高的催化CO氧化活性,CO在常温即可完全转化^[25,55]。下文着重介绍各载体负载的银催化剂以及不同载体导

致的不同的CO催化氧化活性物种。

钟依均等^[70,71]运用X射线衍射(XRD), 程序升温脱附(TPD)和程序升温还原(TPR)技术研究了Ag/Al₂O₃, Ag/CeO₂和Ag/TiO₂催化剂的氧性质及CO氧化活性, 发现Ag/Al₂O₃催化剂上CO氧化活性最高, 催化剂上CO氧化活性顺序与其还原难易顺序一致。Comsup等^[62]发现, Ag与TiO₂间很强的相互作用有利于催化活性的提高。P和Si对TiO₂进行掺杂可导致不同的活性^[63,64]。研究发现, P进入TiO₂晶格形成Ti-O-P键使得载体比表面积和银分散度提高, 而催化剂对氧的吸附能力取决于P源; 而Ti-O-Si键的形成抑制了TiO₂晶粒的聚集, 同时促进了活性氧物种的形成, 加快了晶格氧的移动, 从而导致活性提高。CO在Ag掺杂的氧化锰八面体分子筛(OMS-2)表面发生化学吸附, 并与晶格氧反应生成CO₂; XRD结果表明, 合成的OMS-2材料属于锰钾矿一维隧道结构, 适量Ag的掺杂改善了分子筛的有序性, 比表面积更高, 孔径更均一^[72-74]。丝光沸石中Co与银离子之间存在的协同作用有利于催化活性的提高^[75]。

此外, 不同载体负载的银催化剂上CO氧化反应机理也不同。对于惰性载体, CO和O₂分子的吸附和解离过程发生在Ag表面或Ag-载体界面上, 因此其反应活性与银粒子的尺寸有很大关系^[57,76]。由于Ag的塔曼温度(344 °C)很低, 与Au的性质有所不同, 目前研究还未发现类似于金催化活性与粒径之间的关系。本课题组研究表明, 3~5 nm的银粒子表现出较高的催化活性^[27], 通常认为Ag⁰是活性物种^[27]。由于Ag很容易与SiO₂表面羟基发生相互作用形成高分散的银粒子, 因此, 我们通过在不同温度焙烧处理载体表面羟基, 制备出不同粒径的银催化剂^[77]。对于活性载体, 载体的晶格氧以及银-氧-过渡金属之间的电子传递对于催化活性起着至关重要的作用^[29], 具体的活性物种还存在争议。Luo等^[78]研究认为, Ag₂O是活性物种。

近年来人们还尝试使用非氧化还原载体如石墨^[79]、活性炭^[51,80]等。Lim等^[79]发现, 负载在石墨上的Ag催化剂活性与银粒子上形成的氧物种有关。当银粒子大于3 nm时, 在银上形成两种氧物种, 其中一种能够很容易在常温下与CO反应生成CO₂, 此时催化活性随粒子尺寸的减少而增加; 但当银粒子小于3 nm时, 仅在银表面形成一种氧物种, 而这种氧物种只和气相氧结合, 不与CO反应。Dai等^[51]发现, 碳纳米管含氧基团可更好地锚合和分散银纳米粒子, 并表现出较好的低温催化活性。因此, 载体对银粒子尺寸及其氧物种形成的影响很大, 从而强烈

地影响着催化活性。

5. 第二组分的影响

银催化剂因其良好的吸附O₂能力而广泛应用于CO氧化反应中。目前国内外对银催化剂的研究主要集中在银的结构及活性。然而, 单组分银催化剂仍然存在一些无法避免的弊端, 如负载量高, 低温活性差等。基于此, 人们对银催化剂进行改性, 如加入助剂或采用双金属催化体系(如Au-Ag和Pd-Ag等)。

5.1. 助剂的加入

添加助剂能够改变银催化剂的电子结构, 改变催化剂的表面性质或对反应物分子的吸附能力; 此外, 还能够稳定银纳米颗粒, 提高其分散度。

罗孟飞等^[60,81-83]考察了添加MnO_x, CoO_x或CeO₂后Ag/ γ -Al₂O₃催化剂的活性, 发现这些助剂的加入有助于催化剂表面氧的吸附和恢复, 从而提高活性。此外, 他们还发现^[81], Ce的加入有利于银粒子的分散, 随着CeO₂的加入, Ag₂O增多, 但是文中没有建立构性关系。我们也发现^[26], 适量的CeO₂有利于金属银粒子的分散, 并且在一定程度上减缓了氢气处理后银粒子的大量聚集, 从而提高了催化活性。

5.2. 银基双金属催化剂

相对于其它贵金属Au和Pd等, Ag更容易吸附和活化氧分子, 因此近年来很多人合成出银基双金属催化剂以提高催化剂对分子氧的活化能力, 加速CO的催化氧化。

Au等负载型贵金属催化剂虽然表现出较高的催化CO氧化活性, 甚至在0 °C以下完全转化^[2], 但是存在热稳定性差和易失活等缺点。最近很多人用Ag来改变主活性金属的电子结构, 活化氧分子, 从而提高催化剂活性和稳定性^[37,38,84-94]。Mou课题组^[37,38,84-87]通过制备Au-Ag合金粒子, 使得Ag活化的氧分子很容易与Au活化的CO分子反应生成CO₂。Wang等^[88]通过产物瞬时分析反应器(TAP)发现, Ag活化的氧可以在常温下被Au粒子所储存。Chou等^[90]通过原位定时扫描隧道电子显微镜和密度泛函理论(DFT)计算证实, Au的存在使得Ag(110)上的氧在CO氧化过程中被迅速消耗。Au-Ag合金粒子催化氧化CO过程的动力学研究显示, 当Au表面含有少量Ag时, 在Au-Ag界面处共吸附CO和O₂形成的(CO₃)*被CO和O₂之间的作用力成功分解为CO₂^[91]。此外, 通过改变处理条件调变Pd-Ag粒子结构, 结果表明, 合金粒子以Pd粒子挨着分散的Ag粒子方式重排表现出最高的催

化活性^[92].

6. 反应过程中其它气氛的影响

不同的应用领域对其所需CO低温氧化催化剂的要求也不尽相同. 研究不同环境气氛对低温催化CO氧化性能的影响, 不仅可以深入了解催化反应机理, 而且对于相关催化体系的开发及应用具有重要意义. CO中H₂, H₂O和CO₂的存在必然会对催化剂低温活性和稳定性产生一定的影响.

6.1. H₂的影响

由于燃料电池的电极对燃料氢气中存在少量的CO具有极高的敏感性, 因此寻找在富氢气氛下选择性氧化脱除CO的催化剂成为研究热点之一. 目前, 相关银催化剂的研究很多, 但是最大的问题就是选择性低. 我们^[30,95–99]通过调节处理条件等因素制备了不同结构的Ag/SiO₂催化剂, CO的最大转化率不超过60%, CO₂选择性低于40%. Derekayal等^[49]研究发现, Ag/Co/Ce催化剂能在150 °C左右实现CO完全转化, 但选择性极低(<20%), 且其低温(<80 °C)下基本没有活性. Chen等^[100,101]把Ag负载在活性炭上, 在100 °C左右能够实现CO完全转化, 但选择性仍不到20%. 研究表明, Ag-Co和Ag-Mn催化剂在CO选择氧化中表现出较高的选择性, 但是其完全转化温度较高^[102,103]. Hu等^[103]发现, Ag/OMS-2催化剂在富氢气氛下于120 °C可实现CO的完全转化, 而且具有较高的选择性(90%)和稳定性(250 h).

6.2. 水的影响

各种环境中都不可避免地存在水, 但有关水对银催化剂催化CO低温氧化性能影响的报道并不多. 研究表明^[55,104,105], 微量水的存在提高了催化剂性能. Afanasev等^[55]和Wu等^[104]研究显示, 微量水能阻止银表面碳酸盐的形成, 从而增加其活性. Su等^[105]通过DFT计算发现, 吸附的水不仅影响CO和O₂的吸附, 还影响反应过程的过渡态和中间产物. 吸附的水能够在Ag(111)面上形成氢键, 促进O₂的解离, 形成的原子O进一步与水形成羟基, 可促进CO氧化. 然而, 目前仍缺乏水含量对CO低温氧化催化剂性能影响的系统研究, 有待于进一步进行.

7. CO和O₂的吸附过程及反应机理

7.1. CO和O₂的吸附过程

CO和O₂在Ag表面的吸附过程涉及到物理化学、表面科学等众多研究领域, 对其进行深入研究. 有助于理解CO和O₂的活化过程及与Ag的作用, 以及表面反应和

催化过程的本质. 目前这方面的研究主要集中在理论计算及模型催化剂上^[106–127].

DFT和质谱和动力学研究发现^[107–112], CO在银簇上的最优吸附位是顶位吸附, 易与吸附氧之后的银簇发生反应. 此外, 采用DFT B3LYP方法研究Ag₂⁻催化CO氧化反应机理发现, CO能在室温下被完全转化^[113]; 并且O₂分子很容易在Ag₂⁻上发生部分解离, 这种游离的化学吸附影响了O₂分子在Ag₂⁻上的吸附^[114]. 在Ag₂⁻银簇上, CO催化氧化反应共有四条可能的反应途径: 其中最可能的是CO插入Ag₂O₂⁻中的Ag–O键形成中间体[Ag–AgC(O–O)O], 然后直接分解形成产物CO₂和Ag₂O⁻, 或另一分子CO进攻中间体[Ag–AgC(O–O)O]形成两分子产物CO₂和Ag₂⁻^[115].

此外, 人们还采用X射线光电子能谱(XPS), 扫描隧道电子显微镜(STM)和理论计算等方法研究了CO和O₂在Ag不同晶面上的吸附行为. CO和O在Ag(001)表面共吸附的XPS谱显示, CO倾向于与表面上可扩散的O原子相互作用, 并且通过这种方式将氧固定在表面^[116]. 此过程的反应途径是CO + O₂ → O₂…CO → CO₂ + O^[117]. 在Ag(110)表面上, 低于O₂的分解温度时, CO以分子束形式进入O₂阶层^[118,119]; 而CO只能在高压和低温条件下在Ag(111)表面发生很弱的化学吸附^[120]. 与Schmeisse等^[121]和Jansch等^[122]的实验一致. 而Hammer等^[123]和江凌等^[124]研究发现, CO分子在Ag单晶表面上发生的是解离性吸附.

7.2. CO氧化机理

研究发现, 载体不同, 其负载的银催化剂上CO氧化反应不同. 在Ag/SiO₂催化剂上, 不同的反应温度区间存在着不同的速控步骤^[54]. 在低温区, 氧解离是速控步骤, 能相对容易地发生在小尺寸银粒子上; 高温区氧更容易活化而不依赖于银粒子尺寸, CO在银表面的可逆吸附成为速控步骤. 而在Ag/NaY催化剂上, Ag⁺的还原是增强CO氧化活性的必要步骤, CO氧化过程遵循一级反应动力学^[128].

活性载体负载的纳米银催化剂上CO氧化反应机理比较复杂. 通常认为, 在Ag和M (Mn, Co, Ce)催化剂体系中, CO能在Ag⁺–O位上快速氧化, 而M上的O会重新氧化Ag⁰ (见图8), 银的再氧化所需的O来自于M (Mn, Co和Ce)氧化物的氧脱附^[60,66,81]. 在Ag/过渡金属氧化物催化剂上, CO的氧化遵循着氧化还原反应机理^[72]. 在温度较低时, 催化剂表面CO的氧化是整个反应的速控步骤; 当温度升至473 K后, CO的吸附开始成为影响反应过程的

控制因素.

8. 结论与展望

综上所述, 负载型银催化剂低温催化CO具有广泛的应用前景. 其性能主要受制备方法, 预处理条件, 载体和粒子尺寸等因素影响. 目前有效的常温CO催化氧化催化剂的制备方法主要为直接合成法和浸渍法等, 载体通常为介孔硅基材料, 所制催化剂的高活性离不开有效的预处理(包括气氛和温度). 在制备CO氧化的银催化剂过程中, 各种影响因素是相互影响、相互制约的.

有关Ag基催化剂上CO氧化反应的研究, 人们已经形成了三点共识: (1)在惰性载体上, 银粒子在反应过程中表现出明显的粒子尺寸效应; (2)载体不同, 银催化剂的活化气氛有所不同, 对于惰性载体, 如二氧化硅, 焙烧

之后的低温氢气处理更有利于银的分散和反应活性的提高, 而对于活性载体, 如CeO₂和MnO₂, 焙烧更有利于催化活性的提高; (3)不同载体催化剂上的反应机理也有所不同, 对于惰性载体, CO和O₂分子的吸附和解离过程发生在银表面或界面上, 因此其反应活性与银粒子的尺寸有很大关系; 而对于活性载体, 载体的晶格氧及银-氧-过渡金属之间的电子传递对于催化活性起着至关重要的作用. 然而, 在真实气氛下的相关研究还不多, 如考察水及CO₂对银催化剂结构及活性的影响等; 银催化剂上CO氧化反应机理也还不明确, CO和O₂分子是如何在催化剂表面迁移和转化的, 还需要进一步采用原位等谱学手段进行研究与探讨. 深入系统地研究银催化剂上真实气氛中的CO氧化过程, 必将使其在实际工业和环境(包括隧道以及室内净化)中得到更广泛的应用.