

Ag/SiO₂ catalysts prepared via γ -ray irradiation and their catalytic activities in CO oxidation

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Abstract

We explored the synthesis of Ag/SiO₂ catalysts via γ -ray irradiation at room temperature. AgNO₃/SiO₂ prepared by the conventional incipient wetness impregnation method was employed as the precursor. Ag/SiO₂ catalyst prepared by calcining AgNO₃/SiO₂ at 500 °C was also prepared for comparison. The Ag/SiO₂ catalysts were characterized with X-ray diffraction, X-ray photoelectron spectroscopy, and diffuse reflectance UV–vis spectrum, and their catalytic activities towards CO oxidation were also tested. γ -Ray irradiation successfully reduced Ag⁺ anchored on SiO₂ into silver nanoparticles at room temperature. Existence of excess water during the γ -ray irradiation led to the formation of larger silver nanoparticles. These catalysts behaved differently in CO catalytic oxidation. Compared with Ag/SiO₂ prepared by calcination that showed a certain low temperature catalytic activity but poor stability, Ag/SiO₂ prepared by room temperature γ -ray irradiation showed an inferior low temperature catalytic activity and a better stability. The different catalytic behavior is associated with the various crystalline sizes of silver nanoparticles in Ag/SiO₂ prepared by different methods.

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1. Introduction

Heterogeneous catalysis has wide and important applications in chemical industry, energy, and environmental protection. Numerous methods have been developed to prepare highly efficient and stable catalysts, which are the key issue in heterogeneous catalysis. The traditional methods for preparing supported metal catalysts are impregnation and precipitation, which are convenient and usually involve a step of high temperature calcination in order to convert the precursor into the active component [1]. In some cases, high temperature calcination will induce the agglomeration of metal nanoparticles on the support, particularly for those not interacting or interacting weakly with the support, which eventually affects the catalytic performance. An alternative method for converting the supported precursor to the supported metal nanoparticles, which is being frequently explored, is the in situ chemical reduction at low tem-

peratures [2]. This method has been successfully employed to synthesize free-standing metal nanoparticles protected by various stabilizing agents. However, when this method is cloned to prepare supported metal nanoparticles for their use as catalysts, an appropriate chemical reducing agent that will not result in any influence on the catalytic reaction should be chosen. In this sense, the reduction mediated by γ -ray irradiation is ideal, which is a “clean” process because no chemical reducing agent is involved.

γ -Ray irradiation has been successfully employed to synthesize metal nanoparticles and composites, among which silver is one of the mostly investigated systems. Zhu et al. combined γ -ray irradiation and hydrothermal treatment method to prepare pure polycrystalline silver powders with an average diameter of 8 nm from silver nitrate aqueous solutions [3]. They also successfully prepared the silver-silica glass and silver-titania nanocomposites by γ -ray irradiation [4,5]. Pan et al. investigated the optical absorption properties of the Ag/SiO₂ composite film prepared by γ -ray irradiation [6,7]. Choi et al. employed γ -ray irradiation to prepare various metal nanoparticles and composites, including polymer-stabilized Ag, Pd, Pt–Ru, and

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Pd–Ag nanoparticles and Ag/SiO₂, Ag/poly(ester), Ag/nylon, and Ag/polyaniline composites [8–13]. They also examined the catalytic properties of the prepared polymer-stabilized Pd–Ag bimetallic particles for hydrogenation of *cis,cis*-1,3-cyclooctadiene [11]. Henglein synthesized ultrafine colloidal Au particles, Ag nanoparticles, and Pt–Ag core-shell bimetallic nanoparticles by means of γ -ray irradiation [14,15].

We report here the preparation of Ag/SiO₂ catalysts by γ -ray irradiation. The AgNO₃/SiO₂ solid precursor prepared by the conventional incipient wetness impregnation method was employed as the precursor in our study. Precursors in solutions were usually employed in previously reported systems prepared by γ -ray irradiation. We also compared the catalytic activities of Ag/SiO₂ catalysts prepared by γ -ray irradiation in CO oxidation with those of Ag/SiO₂ catalyst prepared by calcination. This study aims to develop a method for synthesizing supported metal catalysts under mild conditions.

2. Experimentals and methods

Typically, 0.16 g AgNO₃ (Sinopharm Chemical Reagent Co., Ltd., $\geq 99.8\%$) was dissolved in 20 ml triply distilled water. The solution was then added to 2 g SiO₂ (40–120 mesh, Qingdao Haiyang Chemicals Company) under stirring. The mixture was stirred for 10 h, then aged for 2 days, and finally centrifuged. The acquired wet solid, AgNO₃/SiO₂, was used as the precursor to prepare three different kinds of Ag/SiO₂ catalysts: (1) the AgNO₃/SiO₂ precursor was bubbled using N₂ for 10 min and then irradiated in ⁶⁰Co γ -ray source for 6 h with a total irradiation dose of 30 kGy. The resulting powder was finally baked at 50 °C for 12 h to prepare the catalyst, which was denoted by Ag/SiO₂- γ -dry; (2) 5 ml triply distilled water was firstly added to the AgNO₃/SiO₂ precursor, followed by the same procedure as that in case (1). The resulting catalyst was denoted by Ag/SiO₂- γ -wet; (3) the AgNO₃/SiO₂ precursor was calcined at 500 °C for 4 h, and the resulting catalyst was denoted by Ag/SiO₂-heated. All these operations were performed in the absence of light.

The catalysts were characterized by X-ray diffraction (XRD), diffuse reflectance UV–vis spectroscopy, and X-ray photoemission spectroscopy (XPS). XRD measurements were performed on a Philips Xpert Pro Super X-ray diffractometer with a Ni-filtered Cu K α X-ray source operating at 40 kV and 50 mA. Diffuse reflectance UV–vis spectra were acquired on a DUV-3700 DUV-VIS-NIR Recording Spectrophotometer. XPS measurements were performed on an ESCALAB 250 high performance electron spectrometer using monochromatized Al K α excitation source ($h\nu = 1486.6$ eV). The binding energy of Si 2p in SiO₂, which was assumed to be 103.3 eV [16], was employed as the reference to correct the likely charging effect during the XPS measurements.

The catalytic activity of the Ag/SiO₂ catalysts in CO oxidation was evaluated with a fixed-bed flow reactor; 0.12 g catalyst was used and the reaction gas consisting of 1% CO and 99% dry air was fed at a rate of 20 ml/min. The composition of the effluent gas was detected with an online GC-14C gas chromatograph equipped with a TDX-01 column ($T = 80$ °C, H₂ as the carrier

gas at 30 ml/min). The conversion of CO was calculated from the change in CO concentrations in the inlet and outlet gases.

3. Results and discussion

Fig. 1 shows the XRD patterns of various catalysts. Ag/SiO₂- γ -dry and Ag/SiO₂- γ -wet do not show distinct diffraction peaks related with Ag. Ag/SiO₂-heated shows two diffraction peaks, a relatively strong one at 34.1° and a very weak one at 38.1°, which correspond to the diffraction peak arising from Ag₂O and Ag, respectively. This agrees with a previous report that calcining AgNO₃/SiO₂ at 500 °C in air leads to the formation of Ag₂O particles together with Ag particles [17].

The absence of diffraction peaks arising from Ag species in Ag/SiO₂- γ -dry and Ag/SiO₂- γ -wet might be due to two possibilities: firstly, the AgNO₃/SiO₂ precursor was not reduced during the γ -ray irradiation process; secondly, the AgNO₃/SiO₂ precursor was reduced during the γ -ray irradiation process, forming ultrafine Ag particles beyond the detection limit of XRD. Ag nanoparticles are well known to exhibit unique surface plasma resonance (SPR) peaks [18]; therefore, we examined the diffuse reflectance UV–vis spectra of the catalysts. The results are displayed in Fig. 2. Ag/SiO₂- γ -dry, Ag/SiO₂- γ -wet and Ag/SiO₂-heated show the characteristic SPR peak of Ag nanoparticles at 400, 423, and 388 nm, respectively. Besides the SPR peak of Ag nanoparticles, Ag/SiO₂- γ -dry and Ag/SiO₂- γ -wet also show an obvious minimum at 320 nm and also a very weak peak at 290 nm whereas Ag/SiO₂-heated does not. The minimum at 320 nm has been experimentally and theoretically demonstrated to be the inter-band transition in Ag nanoparticles [18], and the weak peak at 290 nm can be assigned to the Ag_n⁺ [19]. Ag/SiO₂-heated does not obviously show the minimum at 320 nm, in consistency with the XRD result that Ag₂O dominates in Ag/SiO₂-heated. Therefore, the results of the diffuse reflectance UV–vis spectra suggest that the AgNO₃/SiO₂ precursors were reduced during the γ -ray irradiation process,

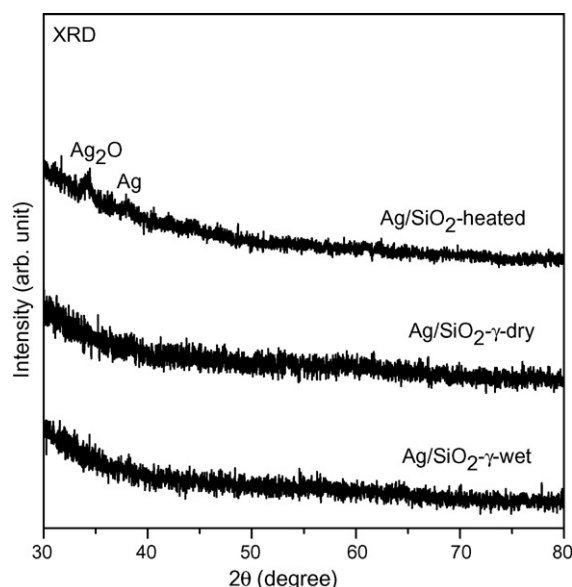


Fig. 1. XRD patterns of various as-prepared samples.

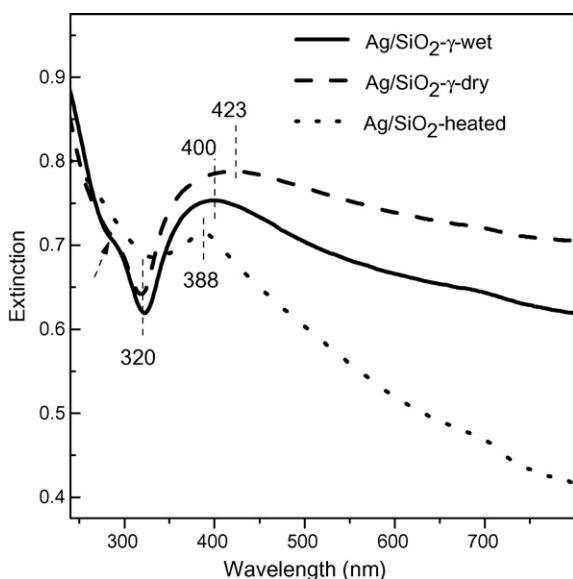


Fig. 2. Diffuse-reflectance UV-vis spectra of various as-prepared samples.

forming ultrafine Ag particles in Ag/SiO₂- γ -dry and Ag/SiO₂- γ -wet.

Further evidence comes from the XPS results (Fig. 3). Ag/SiO₂- γ -dry shows the Ag 3d_{5/2} binding energy at 368.3 eV whereas Ag/SiO₂- γ -wet at 368.0 eV. Both values are characteristic of metallic silver [16]. Ag/SiO₂-heated shows the Ag 3d_{5/2} binding energy at 367.7 eV, corresponding to the Ag 3d_{5/2} binding energy in Ag₂O [16]. Usually, the elements in the positive ionic state show a shift of core-level binding energy towards higher energies with respect to the neutral state due to the initial state effects [16]. Silver is one of the exceptions. A large contribution from the extra-atomic relaxation energy counteracts the effects caused by the initial state, and the binding energy of Ag 3d tends to shift towards lower energy in the oxidized states [20–22]. Quantitative analysis of the XPS results reveals that the

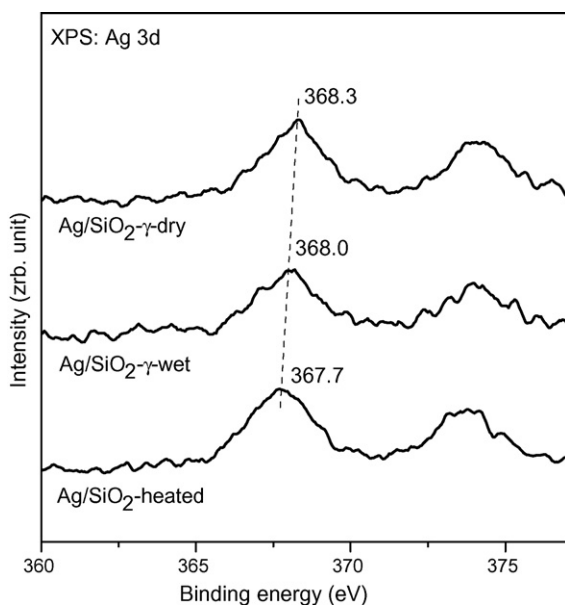


Fig. 3. Ag 3d XPS spectra of various as-prepared samples.

atomic ratios of Ag in the surface region are 0.35%, 0.21%, and 0.38% in Ag/SiO₂- γ -dry, Ag/SiO₂- γ -wet and Ag/SiO₂-heated, respectively.

Combining XRD, diffuse reflectance UV-vis spectra and XPS results leads to the conclusion that γ -ray irradiation successfully reduced the AgNO₃/SiO₂ precursor into ultrafine Ag particles supported on SiO₂ whereas calcining the same precursor at 500 °C forms larger particles. This demonstrates that room-temperature reduction can effectively avoid the agglomeration of metal nanoparticles induced by high temperature calcination. In the AgNO₃/SiO₂ precursor prepared by the impregnation method, Ag species (Ag⁺) highly disperses on SiO₂ by interacting with surface silanol groups [23], and subsequent room-temperature reduction forms highly dispersed ultrafine Ag particles on SiO₂.

An interesting result of our study is that the as-prepared AgNO₃/SiO₂ precursor could be reduced by γ -ray irradiation (Ag/SiO₂- γ -dry). Previous reported reduction of metal ions by γ -ray irradiation was mostly achieved in the aqueous/organic solution. In the as-prepared AgNO₃/SiO₂, Ag species more or less interacted with SiO₂. Meanwhile, water which, under γ -ray irradiation, generates electrons acting as the reducing agent was also trapped on/within SiO₂. Our results suggest that the reduction by γ -ray irradiation should not be profoundly affected by the bound states of Ag⁺ and water in AgNO₃/SiO₂. However, existence of excess water affects the structure of resulting Ag nanoparticles, as evidenced by the different XPS and diffuse reflection UV-vis spectra between Ag/SiO₂- γ -dry and Ag/SiO₂- γ -wet. The Ag 3d_{5/2} binding energy of Ag/SiO₂- γ -dry is at 368.3 eV, 0.3 eV higher than that of Ag/SiO₂- γ -wet (368.0 eV). For supported metal nanoparticles, the particle size exerts a great influence on the core level binding energy of metal nanoparticles in the absence of strong interactions (charge transfer) between metal nanoparticles and the support. Model catalyst studies have demonstrated that the core level binding energy of supported Au and Ag nanoparticles shifts to higher binding energy with the decreasing particle size, whose origin, either from initial state effects or final state effects, is still unclear [24–27]. Because of both the inertness of SiO₂ and the employed very mild preparation method of room temperature γ -ray irradiation, there should only be weak interactions between Ag nanoparticles and SiO₂ in Ag/SiO₂- γ -dry and Ag/SiO₂- γ -wet catalysts. Therefore, the higher Ag 3d_{5/2} binding energy in Ag/SiO₂- γ -dry than that in Ag/SiO₂- γ -wet indicates that Ag nanoparticles in Ag/SiO₂- γ -dry are averagely finer than those in Ag/SiO₂- γ -wet. This might be due to the weak anchoring of Ag⁺ on SiO₂. In the precursor of Ag/SiO₂- γ -wet, due to the existence of excess water, some Ag⁺ anchored on SiO₂ might re-enter into the solution and then was reduced by γ -ray irradiation; the formed species (Ag_n or Ag_n⁺) were mobile in solution and thus facile to aggregate, eventually forming large Ag nanoparticles in Ag/SiO₂- γ -wet. But in the precursor of Ag/SiO₂- γ -dry, Ag⁺ could only be reduced on SiO₂ where they were anchored, thus limiting the growth of the formed Ag clusters. Therefore, the Ag nanoparticles in Ag/SiO₂- γ -dry are averagely finer than those in Ag/SiO₂- γ -wet.

The diffuse reflectance UV-vis spectra of these samples mainly show the SPR peak of supported Ag particles. The silver

particles in Ag/SiO₂- γ -dry, Ag/SiO₂- γ -wet and Ag/SiO₂-heated exhibit the characteristic SPR peak of Ag nanoparticles at 423, 400, and 388 nm, respectively. With the decrease in the particle size of unsupported metallic spherical particles, the SPR peak will blueshift, and the surface plasma mode will be broadened and reduced in strength [18,28,29]. But for supported metal particles, a redshift of the SPR peak with the decreasing particle size induced by the strong matrix effect has been observed [18]. XRD results clearly show that the particles in Ag/SiO₂-heated are obviously larger than those in Ag/SiO₂- γ -dry and Ag/SiO₂- γ -wet, in consistency with the broader and weaker SPR peak of Ag particles in Ag/SiO₂- γ -dry and Ag/SiO₂- γ -wet than that in Ag/SiO₂-heated. But the SPR peak position in Ag/SiO₂-heated blueshifts compared with those in Ag/SiO₂- γ -dry and Ag/SiO₂- γ -wet. Therefore, there must be much stronger matrix effect in Ag/SiO₂-heated than in Ag/SiO₂- γ -dry and Ag/SiO₂- γ -wet, resulting in the observation that the Ag/SiO₂-heated shows the SPR peak position in a lower wavelength than Ag/SiO₂- γ -dry and Ag/SiO₂- γ -wet although the particles in Ag/SiO₂-heated are averagely larger than those in Ag/SiO₂- γ -dry and Ag/SiO₂- γ -wet. Pan et al. also reported similar results in which calcination of Ag nanoparticles in mesoporous SiO₂ at 700 °C leads to the aggregation of Ag nanoparticles accompanied by the great blueshift of the SPR peak [7]. We noticed that the particles in Ag/SiO₂-heated are actually mostly Ag₂O, which might also affect the SPR signal.

Compared with the SPR peak of Ag/SiO₂- γ -wet (400 nm), the SPR peak of Ag/SiO₂- γ -dry (423 nm) redshifts although XPS results demonstrate that Ag nanoparticles in Ag/SiO₂- γ -dry should be averagely finer than those in Ag/SiO₂- γ -wet. This again demonstrates the matrix effect for supported nanoparticles [18]. As discussed above, when reduced, Ag⁺ was anchored on SiO₂ in the precursor of Ag/SiO₂- γ -dry whereas Ag⁺ was in solution in the precursor of Ag/SiO₂- γ -wet. Reasonably the Ag–SiO₂ interactions in Ag/SiO₂- γ -dry should be stronger than that in Ag/SiO₂- γ -wet, although the interactions are generally quite weak. It is noteworthy that the Ag–SiO₂ interactions must be strong enough in which charge transfer occurs to exert an influence on the core level binding energy of Ag. Obviously, this kind of strong interactions is absent either in Ag/SiO₂- γ -dry or in Ag/SiO₂- γ -wet, as demonstrated by the XPS results. Therefore, only the SPR of Ag nanoparticles is influenced by the Ag–SiO₂ weak interactions in Ag/SiO₂- γ -dry and in Ag/SiO₂- γ -wet.

These Ag/SiO₂ catalysts exhibit different catalytic behavior in CO oxidation, as shown in Fig. 4. Ag/SiO₂-heated shows the best low temperature catalytic performance, becoming active at 363 K and reaching its highest activity at 473 K with a CO conversion of 96%. Ag/SiO₂- γ -dry becomes active at 473 K with a CO conversion of 43% and achieves a 100% CO conversion at 523 K. Ag/SiO₂- γ -wet also becomes active at 473 K with a CO conversion of 15% and then achieves a 100% CO conversion at 523 K. Qu et al. have previously reported that Ag₂O formed when Ag/SiO₂ is calcined in air at 500 °C (mainly subsurface oxygen species) can react with CO at low temperature [17]. Therefore, Ag/SiO₂-heated, consisting of Ag₂O, shows the best low temperature CO oxidation activity. The slight difference in the initial activity between Ag/SiO₂- γ -dry and Ag/SiO₂- γ -

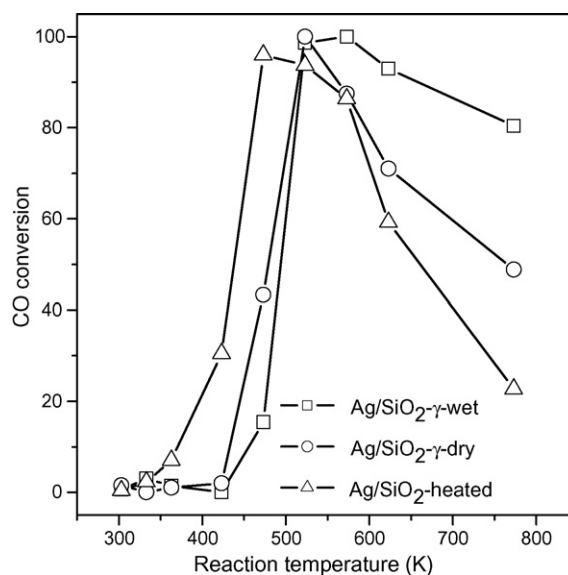


Fig. 4. The catalytic performances of various as-prepared samples in CO oxidation.

wet might be attributed to the different size distribution of Ag nanoparticles.

The activities of these catalysts interestingly depend on the reaction temperature. In the region of high reaction temperature, the activities of these catalysts follow the order: Ag/SiO₂- γ -wet > Ag/SiO₂- γ -dry > Ag/SiO₂-heated, whose trend is just opposite to the trend of the activities in the region of low reaction temperature. When the reaction temperature increases from 473 K to 773 K, the CO conversion over Ag/SiO₂-heated and Ag/SiO₂- γ -dry dramatically reduces from nearly 100% to 23% and 49%, respectively. But Ag/SiO₂- γ -wet still retains a CO conversion of 80%. In order to understand the observed results, we have measured the XRD patterns of the catalysts after the catalytic reaction (Fig. 5). After the catalytic reaction, Ag/SiO₂-heated shows a very weak Ag (1 1 1) diffraction

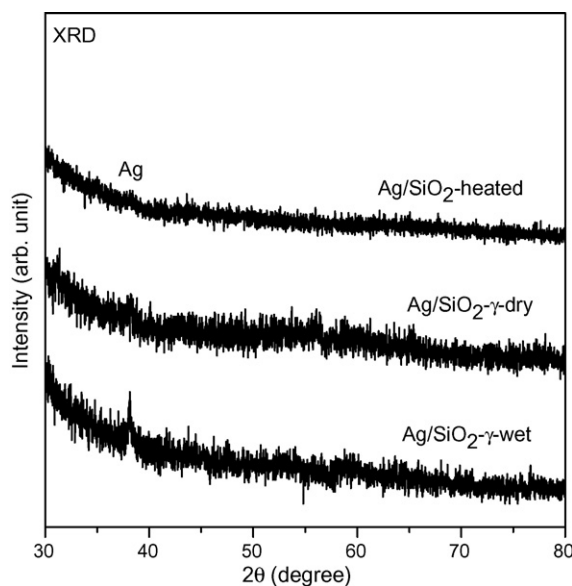


Fig. 5. XRD patterns of various samples after the catalytic reaction.

peak, Ag/SiO₂- γ -dry shows a weak Ag (1 1 1) diffraction and Ag/SiO₂- γ -wet shows an obvious Ag (1 1 1) diffraction peak. Compared with the corresponding XRD pattern before the catalytic reaction (Fig. 1), it can be inferred that, after the catalytic reaction, relatively large Ag₂O nanoparticles in Ag/SiO₂-heated are reduced into ultrafine Ag nanoparticles which interact with SiO₂ quite strongly so as not to grow; meanwhile, Ag nanoparticles in Ag/SiO₂- γ -dry underwent slight aggregation but Ag nanoparticles in Ag/SiO₂- γ -wet underwent obvious aggregation. This again proves that the Ag–SiO₂ interactions in Ag/SiO₂- γ -dry should be stronger than those in Ag/SiO₂- γ -wet. It has also been reported that low temperature reduction of Ag₂O on SiO₂ can lead to the formation of ultrafine Ag nanoparticles [30].

Therefore, as indicated by the XRD results, the average crystalline size of Ag nanoparticles before the catalytic reaction follows the order of Ag/SiO₂- γ -dry < Ag/SiO₂- γ -wet, but after the catalytic reaction follows the order of Ag/SiO₂-heated < Ag/SiO₂- γ -dry < Ag/SiO₂- γ -wet. Correlation of the size of Ag nanoparticles in various catalysts with their catalytic performance implies that finer Ag nanoparticles supported on SiO₂ exhibit a better catalytic performance at lower reaction temperatures whereas larger Ag nanoparticles supported on SiO₂ exhibit a better catalytic performance at higher reaction temperatures. Among these three catalysts, Ag/SiO₂-heated shows the best low temperature activity because of the presence of Ag₂O but the poorest high temperature activity because of the finest Ag nanoparticles formed by the reduction of Ag₂O during the catalytic reaction; because of the largest Ag nanoparticles both before reaction and after reaction, Ag/SiO₂- γ -wet shows the poorest low temperature activity but the best high temperature activity; Ag/SiO₂- γ -dry exhibits a catalytic performance between Ag/SiO₂-heated and Ag/SiO₂- γ -wet because their Ag nanoparticles have a size distribution between Ag nanoparticles in Ag/SiO₂-heated and in Ag/SiO₂- γ -wet. We proposed that the observed Ag particle size—reaction temperature relation in the CO oxidation catalyzed by Ag/SiO₂ catalysts might be attributed to the different rate-limiting steps in CO oxidation over Ag nanoparticles at different reaction temperature regions: at low reaction temperatures, oxygen dissociation is the rate-limiting step and can relatively more easily occur on fine Ag nanoparticles that are more chemically active; but at high reaction temperatures, oxygen is easily thermally activated no longer depending on the Ag particle size, and instead, CO adsorption which is usually reversible on the Ag surface and whose equilibrium adsorption amount usually decreases sharply with the increase in temperature becomes the rate-limiting step. There is evidence that CO adsorption prefers large and smooth Au surface [31]. Further investigations are required for the understanding of the observed Ag particle size—reaction temperature relation in the CO oxidation catalyzed by Ag/SiO₂ catalysts, which are undergoing in our laboratory.

4. Conclusions

We have successfully prepared Ag/SiO₂ catalysts via γ -ray irradiation at room temperature employing AgNO₃/SiO₂

prepared by the conventional incipient wetness impregnation method as the precursor. The γ -ray irradiation successfully reduces Ag⁺ supported on SiO₂ into metallic silver particles at room temperature. Existence of excess water during the course of γ -ray irradiation leads to the formation of larger silver particles. These catalysts behave differently in CO oxidation. Ag/SiO₂ prepared by calcining AgNO₃/SiO₂ at 500 °C shows a certain low temperature catalytic activity, which decreases sharply with increasing reaction temperature. Ag/SiO₂ prepared by room temperature γ -ray irradiation shows a poor low temperature catalytic activity but an improved high temperature catalytic activity. The different catalytic behavior is associated with the various sizes of silver nanoparticles in Ag/SiO₂ prepared by different methods.

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