Highly active mesostructured silica hosted silver catalysts for CO oxidation using the one-pot synthesis approach†

Hongyang Liu,[a] Ding Ma,*[a] Ross A. Blackley,[b] Wuzong Zhou[b] and Xinhe Bao*[a]

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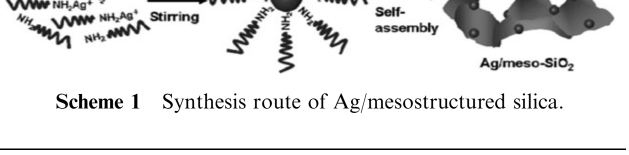
A facile one-pot approach gave isolated silver nanoparticles anchored on a mesostructured silica matrix in a self-assembled way; these gave 100% CO conversion in CO oxidation at room temperature, which is higher than or comparable to the conversion obtained using noble metal catalysts.

Silver is an excellent catalyst for catalytic oxidation. For example, it is very active in ethylene epoxidation,[1] formaldehyde synthesis,[2] partial oxidation of benzyl alcohols,[3] and the oxidative coupling of methane.[4] Recently, the application of silver catalysts has been extended to the catalytic oxidation of carbon monoxide,[5] which is important in cleaning the air in buildings and the exhaust from cars, and they are used in gas masks for mining applications and CO detectors.[6–8] Although catalysts comprising noble metals such as Au, Pd, Pt supported over silica are effective in CO oxidation, a temperature higher than 373 K is normally required to attain 100% CO conversion.[9–11] Indeed, it was reported recently that Au–Ag alloy catalysts or Au/silica catalysts prepared by a unique deposition–precipitation method were very active in CO oxidation even at room temperature;[12,13] however, there is no report on the highly active Ag catalyst, a less expensive and more accessible alternative, for CO oxidation at ambient temperature.

Supported silver catalysts such as Ag/Mn/perovskite have shown stable activity for CO oxidation at relatively low temperatures (373 K).[14] Xu *et al.* reported that Ag supported on α-MnO_2 has good activity for CO oxidation, and the conversion of CO was 90% at 399 K.[15] In our previous work,[16,17] it was concluded that commercial SiO_2 is a good support for a silver catalyst for CO oxidation, but quite a high silver loading (16%) was required to achieve good catalytic activity. The CO conversion over this Ag/SiO_2 was 75% at 323 K, and therefore it still has room for improvement. At the same time, fabrication of highly active metal catalysts using a simple method is attractive for various research groups. For example, non-ionic surfactant-templated assemblage of metal (Pd, Ir, Fe, PtCo, *etc.*) nanoparticle-containing mesoporous silicas was reported by King *et al.*[18,19] Although the authors did not demonstrate whether the metal catalysts obtained were catalytically active or not, it shows that it is possible to obtain mesoporous silica encapsulated metal nanoparticles through a simple and easy-handling method. With the above considerations, the aim of this study is to develop a catalyst with excellent CO oxidation activity but with less silver. Here, we report a facile one-pot method to fabricate highly dispersed silver nanoparticles supported on mesoporous silica (Ag/meso-SiO_2). The novel Ag/meso-SiO_2 catalyst gave 100% CO conversion at ambient temperature, as compared to 30% CO conversion with a conventional impregnated Ag/SiO_2 catalyst with a similar silver loading.

Scheme 1 shows the schematic procedure for the one-pot fabrication of Ag/meso-SiO_2. 1.25 g dodecylamine was dissolved in 10 ml ethanol, followed by mixing with silver nitrite solution (10 ml, 0.05 M) under vigorous stirring to form dodecylamine capped Ag^+ ions. An appropriate amount of formaldehyde was quickly added to the above solution while stirring, and a red solution was formed, which indicated the reduction of the silver species. After further stirring, 5.0 ml of tetraethoxyl silicate (TEOS) were added to the red solution with vigorous stirring. The stirring was continued at room temperature for about 12 h. The molar ratio of dodecylamine : TEOS : silver nitrite : formaldehyde : water : ethanol was 13 : 45 : 1 : 5 : 950 : 350. The products were collected by filtration, dried in air, and calcined at 723 K for 4 h to remove residual surfactants. Conventional Ag/SiO_2 catalysts were prepared by the impregnation method.[20] The silver loading of all the catalysts was about 4 wt%.

Fig. 1 shows the wide angle X-ray diffraction (XRD) patterns of the catalysts prepared by the one-pot synthesis (Ag/meso-SiO_2) and conventional impregnation (Ag/SiO_2) methods. The XRD pattern of a commercial SiO_2 support is also displayed. The diffraction peaks correspond to the cubic crystal structure of silver with $a = 0.4086$ nm. The peaks of Ag/meso-SiO_2 were lower and broader than those of Ag/SiO_2, which indicated the formation of smaller silver nanoparticles on the meso-SiO_2 matrix. From the half-peak width of the Ag(111) diffraction peak, the average sizes of the silver



Scheme 1 Synthesis route of Ag/mesostructured silica.

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[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, Dalian 116023, P. R. China. E-mail: xhbao@dicp.ac.cn. E-mail: dma@dicp.ac.cn; Fax: +86-0411-8469444; Tel: +86-0411-84379256*
[b] *School of Chemistry, University of St. Andrews, St. Andrews, UK KY16 9ST*

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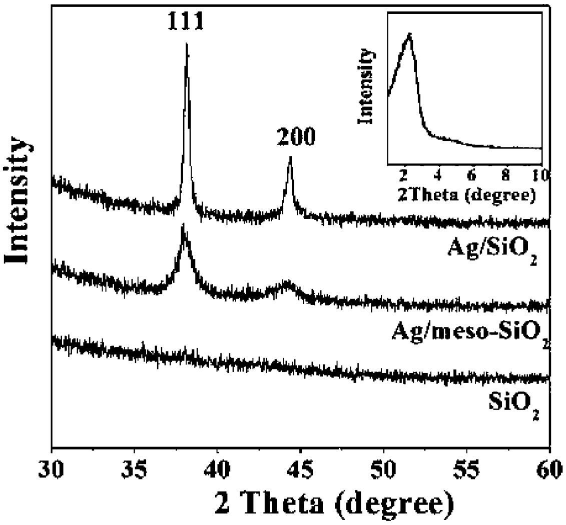

Fig. 1 XRD profiles of Ag/meso-SiO$_2$, conventional Ag/SiO$_2$ and SiO$_2$; inset is the small angle XRD pattern of Ag/meso-SiO$_2$.

crystallites were calculated as 4 and 17 nm for Ag/meso-SiO$_2$ and Ag/SiO$_2$, respectively. Only one peak centered at 2.5° (2θ) was observed in the low angle XRD profile of Ag/meso-SiO$_2$ (inset of Fig. 1), indicating that the mesopores were disordered, which was confirmed by TEM images.[21] Fig. 2(a) reveals that the interparticle voids are responsible for the textural mesoporosity on the length scale of the silica particles, with the formation of worm-like mesostructures. The surfactant-capped silver nanoparticles formed in the first step shown in Scheme 1 probably influenced the assembly of dodecylamine/silicate in the ethanol/water system, and resulted in a disordered structure. The N$_2$ adsorption–desorption[21] curve of the Ag/meso-SiO$_2$ was a typical type IV isotherm with a hysteresis loop (as shown in the ESI†). The area of the sample was 800 m^2 g^{-1}. The relatively large surface area ensured the nearly isolated dispersion of silver nanoparticles over the silica matrix.

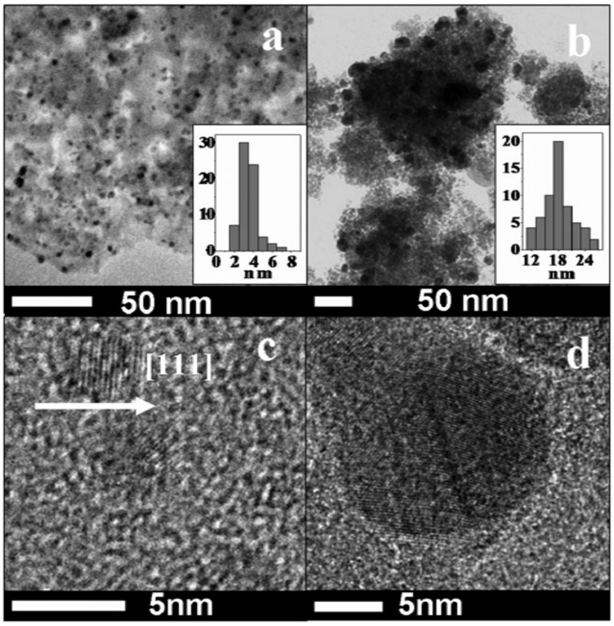

Fig. 2 TEM and HRTEM images of (a, c) Ag/meso-SiO$_2$; (b, d) conventional Ag/SiO$_2$; insets are the size distributions of silver nanoparticles.

TEM gives direct images of the products and provides the sizes and structural information. Fig. 2(a) shows an overview of the Ag/meso-SiO$_2$ sample. The silver nanoparticles had a uniform size of around 3–5 nm and were well dispersed and embedded in the mesostructured silica matrix. The *in situ* fabrication method enabled the anchoring of a large number of silver nanoparticles and prevented their aggregation even under a high temperature treatment (723 K for 4 h) for removing the surfactant. The fringes in Fig. 2(c) gave a *d*-spacing of 0.23 nm, corresponding to the (111) atomic planes of the cubic silver lattice. Fig. 2(b) and 2(d) show TEM and HRTEM images from Ag/SiO$_2$ prepared by incipient wetness impregnation. Silver nanoparticles with larger sizes and a wider size distribution were observed, in good agreement with the XRD results. It was also noted that the dispersion of the particles over the silica support was relatively poor compared with Ag/meso-SiO$_2$. This confirms the advantage of the one-pot method over the conventional impregnation method in the preparation of Ag/silica catalysts. This method can be extended to other metals and catalyst supports, and more experiments are in progress.

Ag/meso-SiO$_2$ and Ag/SiO$_2$ were tested as the catalysts in CO oxidation (the detailed catalytic reaction conditions can be found in note 21). As shown in Fig. 3(a), the CO oxidation activity of the conventional Ag/SiO$_2$ catalyst increased gradually with increasing temperature, and reached 100% CO conversion at around 373 K, which could match the results of previous reports where a much higher (16 wt%) silver loading was used.[16,17] With the Ag/meso-SiO$_2$ catalyst, 90% CO conversion was achieved at 295 K, while CO was completely converted at 303 K, 70 K lower than for the conventional Ag/SiO$_2$ catalyst. The full conversion remained unchanged for the temperature range investigated (303 K to 393 K). For the one-pot synthesis method, the surfactant-capped silver species may play an important role in the assembling process of mesostructured silica which leads to a strong interaction of silver nanoparticle and the silica host, and thus higher density of silver–silica interfaces. It was believed that the reaction centers were located at the perimeter interfaces between metal and silica.[22] Therefore, the observed high activity of the new mesostructured silica hosted silver catalyst can possibly be attributed to the isolated dispersion mode of the silver nanoparticles with a narrow size distribution (3–5 nm) on the silica matrix, and the resulting larger amount of silver–silica interfaces. Significantly, the catalytic activity of the newly developed catalyst was very stable during the reaction time (303 K; 1 atm; flow rate = 50 ml min^{-1}), showing no obvious deactivation over the 20 h catalytic life test (Fig. 3b). These results imply that the synthesized Ag/meso-SiO$_2$ catalyst has a high potential in future applications involving CO oxidation where an ambient temperature working environment is required.

In summary, a facile one-pot method to prepare a mesostructured silica hosted highly dispersed silver catalyst was developed that produced a very efficient catalyst for CO

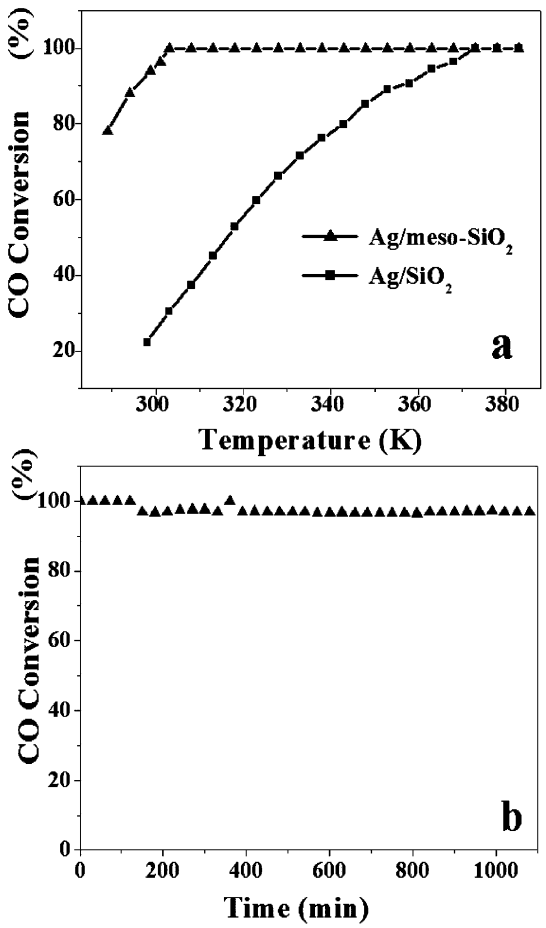

Fig. 3 (a) Conversion of CO *vs.* temperature over Ag/meso-SiO_2 and conventional Ag/SiO_2 catalysts. (b) Reaction performance of Ag/meso-SiO_2 catalyst with time on stream (303 K; 1 atm; flow rate = 50 ml min^{-1}).

oxidation. It was demonstrated for the first time that a 100% CO conversion could be attained over a silver catalyst at ambient temperature. Its catalytic activity is comparable to those of the most active noble metal catalysts. Further investigations on the replacement of precious metal catalysts by silver catalysts in oxidation reactions are currently in progress.

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20 The synthesis of the conventional Ag/SiO_2 catalyst was achieved by impregnating commercial SiO_2 (Qingdao Chemicals Co.) with an aqueous solution of silver nitrate, followed by drying at 393 K overnight and then calcination at 723 K for 4 h. The silver loading of conventional Ag/SiO_2 is the same as that of the Ag/meso-SiO_2 catalyst, *i.e.* 4 wt%.

21 Other experimental details. The N_2 adsorption–desorption isotherms were recorded on an ASAP 2000 instrument. TEM images were obtained with a Philips CM 200 transmission electron microscope equipped with a CCD camera. XRD patterns were collected on a Rigaku D/MAX 2400 diffractometer equipped with a CuKα X-ray source. The catalytic activities for CO oxidation were evaluated in a fixed-bed quartz tubular reactor. The catalyst (250 mg) was activated under flowing H_2 (573 K, 2 h), and then cooled down in a He atmosphere to room temperature. A gas mixture of He/O_2/CO (volume ratio: 79/20/1) was then fed at a flow rate of 50 ml min^{-1}. The composition of the effluent gas was monitored with an on-line gas chromatograph (Agilent Technologies GC-6890N) equipped with PN and TDX-01 columns.

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