Short communication

Improved performance of supported single-atom catalysts via increased surface active sites

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ABSTRACT

Noble metals atomically dispersed and exclusively exposed on support's surfaces are desirable for improving catalytic performance, but fabrication of this kind of catalysts remains challenging. Herein we synthesize two atomically dispersed silver catalysts with hollandite manganese oxide (HMO) nanorods and HMO nanoparticles as supports. The HMO nanoparticles have abundant surface oxygen-terminated hollow sites, which allow all silver atoms to be anchored on surfaces, resulting in higher performance in catalytic oxidation than the other catalyst with the HMO nanorod support, which only exposes a fraction of silver atoms on the surfaces. Several characterization techniques are used to establish structure-activity correlations.

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1. Introduction

Precious metals atomically dispersed on suitable supports' surfaces, as a new class of catalysts, which have well-defined active centers and maximize atom efficiency, have attracted widespread attention [1–3]. The activity of supported precious metal catalysts is directly related to the number of catalytically active sites (CASs), which are available for the reactant molecules. However, for most supported metal catalysts, only a small fraction of the metal atoms are exposed on supports' surfaces [4,5], since only a minority of supports' surfaces have a fairly strong affinity for mobile single atoms, which causes a relatively low surface concentration of the CASs, thus low catalytic performance. Therefore, catalysts with abundant CASs are promising to improve catalytic efficiency.

We recently developed such a catalyst with a high silver (Ag) loading of 10 wt.% with respect to a rod-shaped support, hollandite manganese oxide (HMO) [6]. The HMO rods (HMO$_{rod}$) with a high aspect ratio have one-dimensional tunnels along the [001] growth direction, and it is energetically favorable for Ag atoms on the (001) surface to diffuse inside the tunnels if the tunnels are still fully unoccupied [7]. Ag atoms inside the tunnels cannot generally be accessible to reactants for catalytic reactions due to the small size of HMO tunnels [8], and thus it is beneficial to fully expose these Ag atoms on HMO surfaces.

To solve this problem, a straightforward strategy is to use inexpensive metal atoms, such as potassium, to pre-fill the HMO tunnels. An alternative is to downsize HMO to expose abundant oxygen-terminated cavities on surfaces. An ideal method is to combine the two strategies above to produce HMO nanoparticles (NPs) with fully occupied tunnels, and an approach based on multiple framework substitutions has been proven to be an efficient method for this purpose [9,10].

In this paper, we successfully prepared the HMO NPs (HMO$_{NP}$) with fully occupied tunnels. The HMO$_{NP}$ with abundant surface oxygen-terminated coordination cavities allow individual Ag atoms to be stably anchored at a highly dispersed state, and these surface-anchored Ag centers as catalytic sites show the high catalytic activity in oxidation reactions of CO and formaldehyde at low temperature. The structures and locations of surface-anchored atomic Ag centers and the Ag–O bonding were evidenced by electronic micrographs and X-ray absorption spectra. This could assist the design of supported noble-metal catalysts with the ultimate in atom efficiency.

2. Experimental

The HMO$_{NP}$ were prepared by a hydrothermal route [9,10]: KMnO$_4$ (11.600 g), Na$_2$MoO$_4$ (1.228 g), Na$_3$VO$_4$·12H$_2$O (3.840 g), and TiOSO$_4$·H$_2$SO$_4$·8H$_2$O (1.536 g) were dissolved in de-ionized water (170 mL) to get a solution, to which another aqueous solution (80 mL) containing MnSO$_4$·H$_2$O (17.600 g) and FeSO$_4$·7H$_2$O (2.432 g) was added drop-wise to get a brown slurry, and subsequently refluxed at 100 °C in a 1000 mL round-bottom flask for 24 h. The resulting solid was washed with de-ionized water, filtered, dried, and calcined at 400 °C for 4 h to give the HMO$_{NP}$.

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Ag$_1$/HMO$_{NP}$ was prepared by the same reported method except for the use of the different support of HMO$_{NP}$ [6]. The other two samples, HMO$_{rod}$ and Ag$_1$/HMO$_{rod}$, were synthesized as described elsewhere [6].

(High-resolution) transmission electron microscopy (TEM or HRTEM) images were carried out with a JEOL JEM-2100F field-emission gun transmission electron microscope operating at an accelerating voltage of 200 kV and equipped with an ultra-high resolution pole-piece that provides a point-resolution better than 0.19 nm. The X-ray absorption near-edge structure (XANES) spectra were measured at the Ag K-edge at BL14W of the SSRF with an electron beam energy of 3.5 GeV and a ring current of 200–300 mA. The dihydrogen (H$_2$) probe with a temperature-programmed procedure (H$_2$-TPR) was conducted by using a ChemiSorb 2720 adsorption instrument. The sample (~20 mg) was reduced in a stream of 10.0 vol.% H$_2$/Ar (50 mL min^{-1}) at a ramp of 10 °C min^{-1}.

Catalytic activity measurements for CO oxidation were performed using a continuous-flow fixed-bed reactor. The catalyst sample (40–60 mesh) was 26 mg and the feed gas (1.0 vol.% CO and 1.0 vol.% O$_2$ in He) was passed through the catalytic bed at a total flow rate of 35 mL min^{-1}. The reaction temperature began with room temperature at a ramp of 1 °C min^{-1}. The composition of the outgoing gas stream was determined by gas chromatography with TCD and FID detectors.

3. Results and discussion

The HMO$_{NP}$ were successfully synthesized by multiple framework substitutions [9,10]. A combination of the (HR)TEM images (Fig. 1) and the SXRD pattern (Fig. S1) of the HMO$_{NP}$ with the related discussion (Supplementary discussion 1) shows that the aspect ratio of the HMO$_{NP}$ significantly decreases with respect to the HMO$_{rod}$ [6] (Fig. 1). Furthermore, elementary analysis reveals that the tunnels of the HMO$_{NP}$ are almost completely occupied by potassium ions (Supplementary discussion 2). The HMO$_{NP}$ exposed the abundance of the surfaces due to small sizes of particles, increasing the number of oxygen-terminated hollow sites, which allow Ag atoms to be preferentially dispersed on the surfaces to achieve a single-atom Ag$_1$/HMO$_{NP}$ catalyst (Fig. 1f) from a corresponding supported Ag NPs. After the Ag loading, the intensity of the SXRD patterns of the Ag$_1$/HMO$_{NP}$ remains unchanged (Fig. S1), reflecting that the size of the HMO$_{NP}$ is preserved. After annealing, the diffractions of the Ag NPs vanish, and no new reflections arise due to Ag species such as Ag$_2$O in the SXRD pattern of the Ag$_1$/HMO$_{NP}$, while the SXRD diffraction of the hollandite crystal structure preserves except

for slight modifications [7,11]. It can be speculated that the Ag atoms have been highly dispersed on the HMO surfaces [6,12], consistent with the HRTEM images (Fig. 1f).

Catalytic evaluations of two atomically dispersed Ag catalysts together with two corresponding supports were conducted in CO oxidation, as shown in Fig. 2. The Ag$_1$/HMO$_{NP}$ shows evidently improving effects of the HMO$_{NP}$ for the CO oxidation. Typically, at low temperature (T) less than 100 °C, the Ag$_1$/HMO$_{NP}$ has the rather high CO conversions, but the HMO$_{NP}$ are not catalytically active, indicating that Ag atoms are the CASs. The intrinsic reaction rates were calculated (Supplementary discussion 3) and shown in the inset of Fig. 2, and the catalytic activity of the Ag$_1$/HMO$_{NP}$ is 4–5 times as that of the Ag$_1$/HMO$_{rod}$ under the identical conditions. Similarly, in the complete oxidation of formaldehyde at low temperature, the Ag$_1$/HMO$_{NP}$ has also much higher catalytic activity than that of the Ag$_1$/HMO$_{rod}$ under the same reaction conditions (Fig. S2).

The apparent activation energy (E_a) over the Ag$_1$/HMO$_{NP}$ is ~42 kJ mol^{-1} in the CO oxidation, which is almost the same as that (~45 kJ mol^{-1}) of the Ag$_1$/HMO$_{rod}$, as shown in the inset of Fig. 2. These results demonstrate that the CASs of both single-atom catalysts are essentially identical to each other, which possess the similar oxygen-terminate hollow sites for both cases. Especially for Ag-based catalysts, the oxidation reactions predominantly follow a Mars–van Krevelen mechanism [13], in which the intrinsic nature of metal active sites plays a critical role in determining catalytic activity [12,14]. Owing to almost the same E_a for both cases, the catalytic activity of the Ag$_1$/HMO$_{NP}$ higher than that of the Ag$_1$/HMO$_{rod}$ may result from the more CASs of the Ag$_1$/HMO$_{NP}$.

In order to demonstrate the cause of the enhanced catalytic performance, XANES spectroscopy is used to detect the electronic properties of the samples. The Ag K-edge XANES spectra of the samples as a function of absorption energy (E) are shown in Fig. 3. Both of the edge positions for the Ag$_1$/HMO$_{NP}$ and the Ag$_1$/HMO$_{rod}$ appear between those of the Ag foil and Ag$_2$O, indicating that the oxidation states of Ag atoms of the two samples are at the intermediate valence states. The same results are obtained from X-ray photoelectron spectra (Fig. S3). The Ag $3d_{5/2}$ binding energy values of both the two samples are lower than that of the metal Ag and slightly higher than that of Ag$_2$SO$_4$, and the corresponding Ag M$_4$VV Auger spectra also give the similar results (Fig. S3), indicating that the Ag oxidation states of both the two samples are between Ag^0 and Ag$^+$ (Fig. S3) [6]. A differential XANES (ΔXANES) spectrum at the Ag K-edge with respect to the Ag$_2$O spectrum is highly sensitive and highly accurate for exploring electronic structures of the
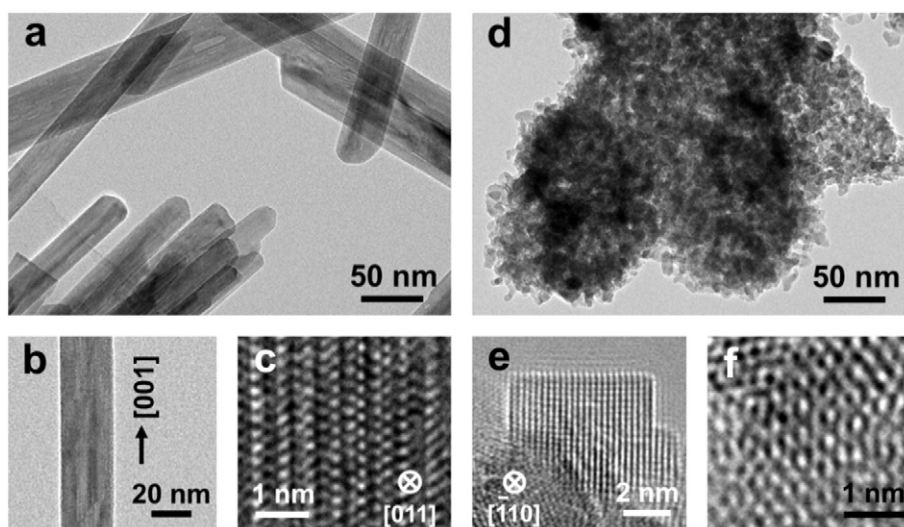
Fig. 1. TEM (a,b) and HRTEM (c) images of Ag$_1$/HMO$_{rod}$. (b) A typical Ag$_1$/HMO$_{rod}$ rod closed by four {110} side-facets and two {001} top facets. TEM (d) and HRTEM (e,f) images of Ag$_1$/HMO$_{NP}$. (e) A HRTEM image showing a square (001) facet of a typical HMO$_{NP}$.