In Situ Observations of Dynamic Formation of Highly Dense Isolated Metal Atom Catalytic Sites

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Abstract: We prepared an atomically dispersed silver catalysts with highly dense active sites on the surface of Hollandite-type manganese oxide (HMO) support by a thermal surface-mediated diffusion method starting from silver nanoparticles, which exhibited excellent activation ability to both lattice oxygen and molecule dioxygen at low temperature. A dynamic difussion of Ag atoms and the disintegration process of Ag nanoparticles on the support were observed directly by using advanced electron-microscopic tools (spherical aberration corrected electron microscopy and in situ transmission electron microscopy). The visual microscopic results matched well with the results of in situ synchrotron X-ray diffraction (SXRD). The atomic structure of this well-dispersed single-atom Ag-HMO catalyst was confirmed by high-resolution high angle angular dark field image (HAADF) and extended X-ray absorption fine structure (EXAFS) spectroscopy, which demonstrates a promising potential of well-designed oxide matrix in anchoring active single-atom sites with a considerable high content. This work provides a general strategy for designing atomically dispersed noble-metal catalysts with highly dense active sites. The results also highlight the importance of advanced TEM techniques in depicting the dynamic evolution of catalytically active sites at atomic levels.

Keywords: in-situ, TEM, catalytic oxidation

1. Introduction (11-point boldface)

Supported atomically dispersed noble-metal catalysts are promising materials with which to maximize metal efficiency and to display unique catalytic performance;[1] however, the fabrication of such single-atom catalyst with highly dense active sites is challenging because of the tendency of aggregation of single metal atoms, especially under reaction conditions.[2,3] Meanwhile, the characterization of formation of single-atom sites is another crucial factor that hinders the development of single-atom catalyst. Therefore, synthesis strategy of atomic-dispersed metal catalyst with highly dense catalytically active sites and advanced microscopic techniques providing direct local structural information of metal species on supports are urgent required in heterogeneous catalysis.

2. Experimental

The HMO NPs supported Ag precursor were prepared by a hydrothermal route.[4] All in-situ TEM works were done by using a special-designed TEM holder manufactured by DENSsolutions B.V., which enabled introduction of gaseous reactants into TEM sample holder and allowed directly recording gas-solid reaction at atomic scales.

3. Results and discussion

Silver nanoparticles supported on the surfaces of Hollandite-type manganese oxide (HMO) was synthesized as a prelude for single-atom Ag catalyst, where the oxygen atoms in HMO serving as electron donors to stabilize the single Ag atom.[4,5,6] Then an atomically dispersed Ag catalyst was synthesized by using a thermal surface-mediated diffusion method. Simultaneously, a dynamic formation process was observed directly by using in situ TEM techniques. As the in situ HRTEM results shown in Figure 1A, it was found that during the heating process, the atoms of Ag NPs gradually diffused along surface and migrated from Ag NPs to HMO surfaces. And in situ HAADF-STEM results in Figure 1B showed that with the increased temperature Ag NPs gradually shrank and ultimately disappeared at 270℃. Both cases indicated that during thermal process the Ag atoms became sufficiently active to detach from the Ag NPs, diffused on the HMO surfaces, and finally anchored on the HMO surfaces with a highly dispersed state as illustrated in the model of Figure 1C. From HRSTEM image of Figure 1D, one can clearly see that after heat treatment the Ag single atom (brighter dots), which can be easily distinguished from Mn and O atoms, was well-organized anchored on the HMO surfaces with a highly density.

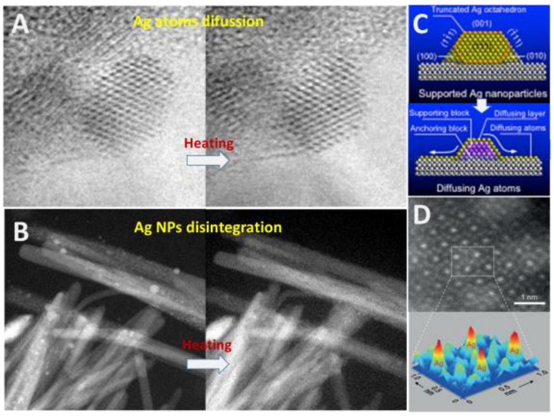

Figure 1. (A)-(B) In situ HRTEM and in situ HAADF-STEM images showing Ag atoms difusion and Ag nanoparticles disintegration process under heat treatment. (C) A schematic model illustrated the formation mechanism of atomic-dispersed Ag catalyst supported on HMO. (D) Aberration-corrected HAADF-STEM image and three-dimensional projected image of the atomically dispersed Ag/HMO (smoothed after Fourier transform).

The detailed surface-mediated disintegration process of the supported Ag NPs was further studied by using in situ SXRD (Figure 2A), which convincingly indicates that the Ag NPs gradually shrank and finally reached a highly dispersed state. The local structures of the Ag atoms at the initial and final states of the thermal surface-mediated diffusion process were determined by using extended X-ray absorption fine structure (EXAFS) spectroscopy. It proves that, after thermal treatment, the isolated Ag atoms were anchored on the five-fold oxygen-terminated cavities, as modelled in the inset of Figure 2B.

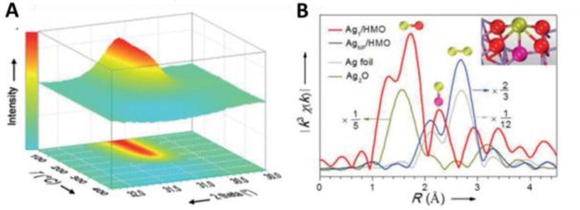

Figure 2. (A) Three-dimensional and contour maps of in situ differential SXRD patterns of Ag NP/HMO, showing the diffraction intensity of the Ag(111) reflection as a function of T. (B) Ag K-edge c(R) k3-weighted FT EXAFS spectra of the Ag atoms at the initial and final states during the thermal surface-mediated diffusion process of Ag NP/HMO, and two reference samples of Ag foil and Ag2O. Inset model: an isolated Ag atom anchored on the five-fold oxygen-terminated cavity of the HMO(110) surface. Yellow, red, pink and purple balls represent Ag, O with sp3 hybridization, O with sp2 hybridization, and Mn atoms, respectively

4. Conclusions

In summary, an atomically dispersed Ag catalyst with highly dense active sites was synthesized from Ag NPs by a specific surface-mediated diffusion process induced by heat treatment. A dynamic formation process of this single-atom catalyst was visualized by advanced TEM techniques (Cs-corrected TEM, in situ TEM, etc.), including the Ag atom diffusion process along the HMO surface and Ag NPs disintegration process. Combined with the results of high-resolution HAADF-STEM, and EXAFS, the geometric and electronic structures of single Ag atoms were determined. This work provides a general strategy for designing atomically dispersed metal catalysts with high metal content, and also highlights the importance of advanced TEM techniques in capturing the dynamic catalytic process of heterogeneous catalysts at atomic level

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