Correlation between the crystal-plane effects and catalytic performances of CuO/CeO_2 catalysts for NO reduction by CO

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Introduction

Ceria, with high oxygen storage capacity and the excellent reduction behavior, has been widely adopted in Three-Way Catalysts (TWCs) for the elimination of toxic exhaust gases of automobiles. For example, copper oxide supported CeO_2 have been proven to be promising for the selective reduction of NO by CO. Generally, the performance of the catalyst was mainly influenced by the synergistic effect between CuO and CeO_2 support. Furthermore, the crystal plane effect might be another crucial part, which has not been paid so much attention on.

Previous studies have shown that the CeO_2 (111) facet is the most stable one in comparison with the (110), (100) and (211) facets [1,2]. In our previous work and some other works, CuO have been loaded onto ceria with different facets [3,4]. Results were not simply following the stability sequence of pure CeO_2. The interactions between CuO and different ceria facet were thought to be a significant factor to determine the property of CuO/CeO_2. Though obvious discrepancies of catalytic activities could be observed, the interaction between CuO and CeO_2 have not been well correlated with the surface structure through spectroscopic characterization. Understanding the properties of CuO/CeO_2 catalysts with different exposed crystal planes could provide insights into designing ideal catalysts.

In the present work, CuO/CeO_2 catalysts with different exposed CeO_2 facets were prepared, and characterized by TEM, XRD, H_2-TPR, and ^{17}O MAS NMR. The main aim is to clarify the synergetic effect between CuO and CeO_2 with different exposed planes.

Materials and Methods

Nano-CeO_2 supports with different morphology were prepared by hydrothermal method. CuO/CeO_2 (denoted as CuCe thereafter) catalysts were prepared by using the wet impregnation method. The copper loading amount was 6 Cu^{2+} atoms per nm^2 CeO_2 surface.

Results and Discussion

Structural characterizations (XRD, BET, TEM) showed that CeO_2 rods, cubes and octahedral (denoted as CeO_2-{110}, CeO_2-{100}, CeO_2-{111}, respectively) were in cubic fluorite phase with similar grain size and BET surface area. In agreement with Yan et al.[5], HRTEM image revealed the clear (111) edge for a nano octahedron, and also (100) edge for a nano cube. Nano rods predominantly exposed {110} and {100} planes. Noticeably, TEM and XRD data did not reveal any evidence of crystalline copper species in CuO/CeO_2 samples. The ceria nanocrystals in CuO/CeO_2 samples have kept the original morphology as well. It suggested CuO species were finely dispersed on the surface or subsurface of CeO_2.

Kinetic studies of NO reduction by CO showed that the activities of CuCe samples follow the order CuCe-{110} > CuCe-{111} > CuCe-{100}. It was generally accepted the formation energy of anion vacancies for different CeO_2 surfaces followed the order (110) < (100) < (111). Nano rods with {110} plane would be the most reactive. However, after the deposition of CuO, CuCe-{100} was the least reactive. One possibility was the polar (100) facet limited the interaction between CuO and CeO_2.

^{17}O Solid State NMR study was also performed. as shown in **Figure 1a**, ceria supports showed a resonance near 1000 ppm, which was attributed to the surface oxygen species. The position of this resonance was influenced by the coordination environment of surface oxygen. The NMR spectra for CuCe were similar to those for supports (**Figure 1b**). The surface oxygen resonance shifted obviously from 1007 ppm to 1045 ppm for CuCe-{110}, in comparison with the slight shift for CuCe-{111} and the hardly changed signal for CuCe-{100}. The change in surface O^{2-} environment could be due to the synergetic effect between CuO and ceria surface. The result suggested CuO species have stronger interaction with CeO_2 {110} plane, and it is weakly bonded with CeO_2 {100} plane, which is well correlated with the catalytic activity.

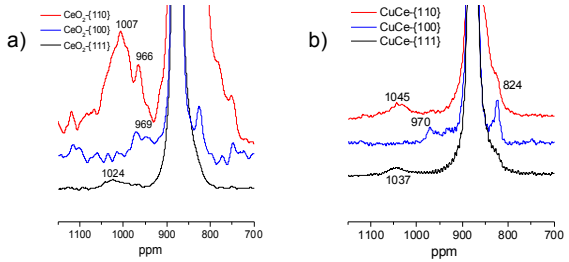

Figure 1 ^{17}O MAS NMR spectra of (a) CeO_2, (b) CuCe samples

Significance

The present work studied the crystal plane effects of ceria on the activity of CuO/CeO_2 by applying ^{17}O MAS NMR technique. The exposed ceria plane draws significant effect on the interaction of CuO and CeO_2, which determines the catalytic activity of CuO/CeO_2.

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