Highly reducible CeO$_2$ nanorods for CO oxidation

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Abstract: CeO$_2$ nanorods were prepared through hydrothermal process. H$_2$-TPR results revealed that CeO$_2$ nanorods were highly reducible at low temperature. This indicated the presence of more active oxygen species. CeO$_2$ nanorods showed a higher activity than zero-dimensional CeO$_2$ particles for CO oxidation. The good activity could be attributed to the exposed crystal planes, which possess large number of oxygen vacancy sites.

Keywords: CO oxidation, ceria, nanorods

1. Introduction
CO oxidation is one of the most extensively investigated reactions in the field of heterogeneous catalysis because of its importance in both environmental protection and fundamental studies[1,2]. CeO$_2$ is an effective non-noble metal catalysts for low temperature CO oxidation. And the morphologies of CeO$_2$ particles have been proved to be important for its activity because of the conspicuous physiochemical and chemical properties which are significantly different from those of bulk CeO$_2$ materials [3]. In this paper, a kind of CeO$_2$ nanorods with highly reducible surface oxygen species was prepared through hydrothermal process. And its catalytic activity for CO oxidation was evaluated and compared to CeO$_2$ with other morphologies.

2. Experimental
Synthesis of CeO$_2$ nanorods was carried out via a hydrothermal process. Typically, 6 g of Ce(NO$_3$)$_3$·6H$_2$O, 84 g of NaOH and 150 mL of deionized water were mixed and stirred for 30 min. Then, the suspension was transferred to a teflon-lined stainless steel autoclave and underwent hydrothermal process at 110 °C for 24 h. After that, the solid was collected by filtration, repeatedly washed with deionized water and anhydrous ethanol till pH to 7 and then dried at 80 °C. Finally, the solid was calcined at 500 °C for 4 h in air. The sample was denoted as CeO$_2$-R. For comparison, zero-dimensional CeO$_2$ particles, denoted as CeO$_2$-P, was prepared using a water-in-oil microemulsion as a nanoreactor. The detailed process was previously reported [4].

Transmission electron microscope (TEM) images were obtained with a PHILIPS TECNOL 20 at an acceleration voltage of 200 kV. Temperature-programmed reduction by hydrogen (H$_2$-TPR) were carried out on a Micromeritics Auto Chem II-2920 apparatus. All samples (0.1 g) were pretreated in the flow of Ar (50 mL/min) at room temperature for 5 min. Then the flowing gas was switched to 10% H$_2$-Ar mixture (50 mL/min) and the sample was heated to 1000 °C at a ramping rate of 10 °C/min. The H$_2$ consumption was monitored by a thermal conductivity detector (TCD).

The catalytic performance of CeO$_2$ for CO oxidation was evaluated at 1.0 atm in a fixed bed reactor connected with a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). Typically, CO oxidation was performed with a catalyst (40-60 mesh) loading of 0.5 g under the flow of a mixed gas (200 mL/min) containing CO (1.0 vol. %) and O$_2$ (9.0 vol. %) in N$_2$ balance. Gas compositions of the catalytic reactions were monitored and recorded by the on-line GC.

3. Results and discussion
The CeO$_2$-R and CeO$_2$-P were characterized by TEM and results are shown in Figure 1. The CeO$_2$-R sample displayed a rod-like appearance with the diameter of 10-30 nm and lengths of more than 100 nm.
Figure 2 is the H$_2$-TPR results of CeO$_2$ samples. Two reduction peaks were observed at 477 and 811 °C over CeO$_2$-P. For CeO$_2$, the low temperature peak at 400-600 °C was due to the reduction of surface oxygen species attached to surface Ce$^{4+}$ ions in an octahedral coordination and the high temperature peak over 700 °C was due to the reduction of oxygen anion bonded to two Ce$^{4+}$ ions in the bulk phase. In the TPR curve of CeO$_2$-R, the peak corresponding to bulk lattice oxygen moved to 750 °C and the reduction temperature for the surface oxygen species decreased substantially to 217 °C. This indicates the presence of a large number of oxygen vacancy sites as well as more reactive surface oxygen species on CeO$_2$-R.

The two CeO$_2$ catalysts were evaluated for their activity in CO oxidation and the results are shown in Figure 3. The CeO$_2$-R ($T_{90}$=253 °C) catalyst was superior to CeO$_2$-P ($T_{90}$=393 °C) in catalytic activity. CeO$_2$ with different morphologies exposes different crystal planes, and the concentration of the oxygen vacancy sites is largely determined by the exposed crystal planes. Thus, the morphology will influence the catalytic activity of CeO$_2$. CeO$_2$-R exposed (110) and (100) crystal planes and CeO$_2$-P showed (111) planes. Among them, CeO$_2$(110) possesses a greater concentration of oxygen vacancies than CeO$_2$(100), thus the higher activity was observed over CeO$_2$(110), that is CeO$_2$-R.

4. Conclusions

CeO$_2$ catalyst with rod-like morphology was prepared through a simple hydrothermal process. It showed a higher activity than zero-dimensional CeO$_2$ particles for CO oxidation. The good activity could be attributed to the high concentration of highly reducible oxygen species that determined by the exposed crystal planes of CeO$_2$ nanorods.

References