Highly reducible CeO_2 nanorods for CO oxidation

Wei Xue, **Gang Feng, Zhaoyang Tan, Fang Li*, Yanji Wang**

Hebei Provincial Key Laboratory of Green Chemical Technology & High Efficient Energy Saving, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin, 300130, China

**Corresponding author: 86-22-60202419, lifang@hebut.edu.cn*

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 physicochemical 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 $Ce(NO_3)_3\cdot 6H_2O$, 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.

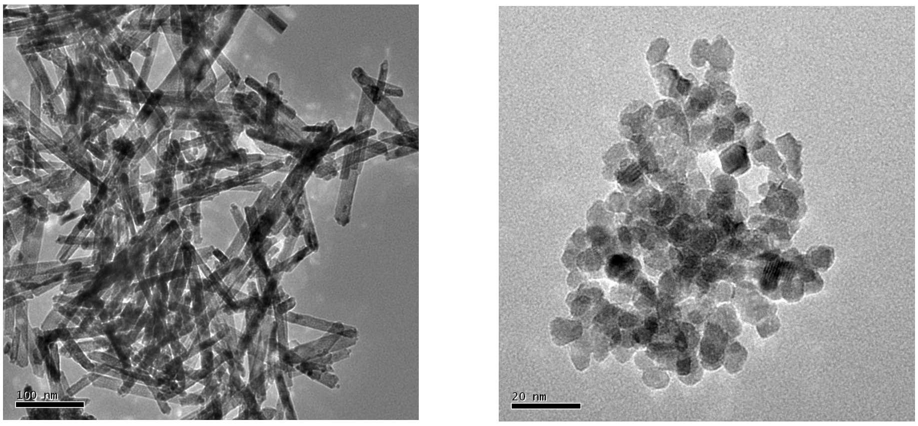

Figure 1. TEM images of CeO_2-R (a) and CeO_2-P (b).

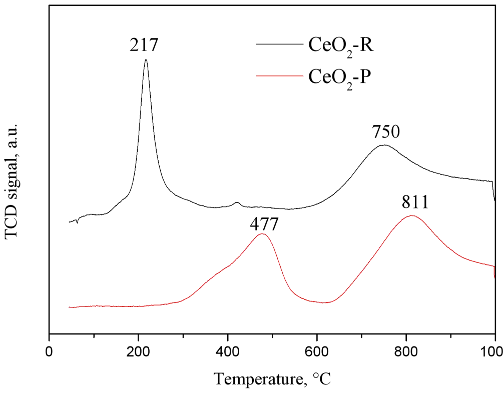

Figure 2. H_2-TPR curves of CeO_2-R and CeO_2-P.

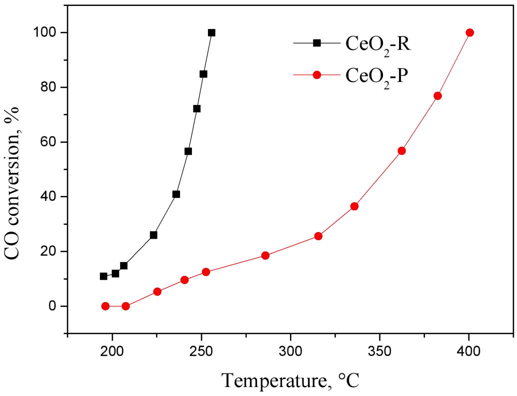

Figure 3. CO oxidation over CeO_2-R and CeO_2-P.

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

1. M. A. van Spronsen, J. W. M. Frenken, I. M. N. Groot, Chem. Soc. Rev. 46 (2017) 4347.
2. Y. Zhou, Z. Wang, C. Liu, Catal. Sci. Technol. 5 (2015) 69.
3. X. Zhang, F. Hou, Y. Yang, Y. Wang, N. Liu, D. Chen, Y. Yang, Appl. Surf. Sci. 423 (2017) 771.
4. Y. Yuan, Z. Wang, H. An, W. Xue, Y. Wang, Chin. J. Catal. 36 (2015) 1142.