Morphology Impact of $Mn_{0.3}Ce_{0.7}O_x$ in Ethanol Oxidation

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Introduction

Catalytic abatement of toxic oxygenates like ethanol, acetaldehyde, and formaldehyde emitted from ethanol blended gasoline-fueled engines raises a new challenge in the emission control of automobile exhausts. MnOx-CeO_2 oxides have long been known to be highly active for the oxidation of light oxygenates [1, 2], but most of the reports are focused on the size effect of the traditional spherical nanoparticles. Here, we report the morphology impact of MnOx-CeO_2 nanostructures in the shapes of cubes and rods for ethanol oxidation.

Experimental

The $Mn_{0.3}Ce_{0.7}$ O_x nanocubes and nanorods were synthesized with a hydrothermal process by varying the temperature and the pH value of the solution. Transmission electron microscopy (TEM) images were recorded on a FEI Tecnai G2 F30S-Twin microscope operated at 300 kV. Oxygen storage capacity (OSC) was measured at 473 K using an Autochem II 2920 instrument. Ethanol oxidation was conducted in a fixed-bed quartz tubular reactor under atmospheric pressure with a typical feed gas of 0.16 vol. % ethanol and 20 vol. % O_2 balanced with N_2. The effluent from the reactor was analyzed by an on-line gas chromatograph.

Results/Discussion

The nanocubes have an average diameter of about 20 nm, and exclusively expose the {100} planes. The nanorods have a diameter of about 7 nm and a length of 50-100 nm, and the real shape is determined to be a hexangular block surrounded by four {111} (74 %) and two {100} (26 %) planes. The shape of the mixed oxides is predominately determined by ceria crystalline structure where manganese oxide has incorporated into ceria lattice as confirmed by the XRD patterns. The BET surface areas are 99 m^2 g^{-1} for the nanorods and 41 m^2 g^{-1} for the nanocubes. When the reaction rate is correlated with the surface area, the nanocubes have obviously higher specific reaction rates of ethanol conversion and acetaldehyde/carbon dioxide formation, and the difference becomes significantly large above 453 K as shown in Figure 1. Detailed kinetic studies on the basis of the surface portion of the {111} and {100} panes in the nanostructures reveal that the conversion rate of ethanol on the {100} plane is almost two times greater than that on the {111} surface, in good correlation with the specific OSC measured at 473 K. A similar pattern is observed for the production of acetaldehyde, but the formation rate of CO_2 is only slightly higher on the {100} plane than that on the {111} facet. This result indicates that the oxidation of ethanol to acetaldehyde occurs very fast on the {100} surface, whereas the subsequent oxidation of acetaldehyde to CO_2 is relatively slow on both surfaces and proceeds only slightly faster on the {100} plane. Mechanistic investigations further indicate that the manganese ions serve as the active species in both nanostructures while the morphology of CeO_2 indirectly but essentially mediates the reaction rates. CeO_2 acts as an oxygen reservoir and the mobility of surface oxygen species on the exposed planes plays a vital role. In other words, the morphology of the binary oxides significantly affects the catalytic property in ethanol oxidation, showing a salient morphology-dependent effect.

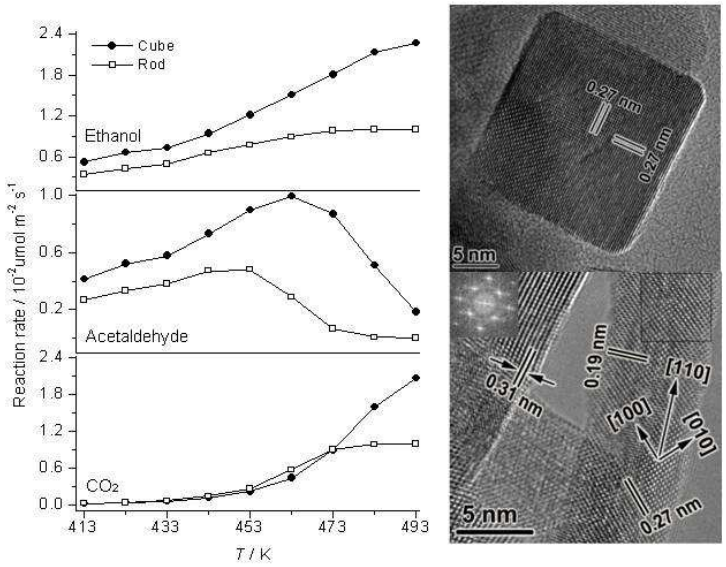

Figure 1. Specific rates of ethanol conversion, acetaldehyde and CO_2 productions.

References

1. X. Tang, Y. Li, X. Huang, Y. Xu, H. Zhu, J. Wang, W. Shen, *Appl. Catal. B*, **62,** 265 (2006).
2. D. Delimaris and T. Ioannides, *Appl. Catal. B*, **84,** 303 (2008).