Structure-sensitivity of methanol steam reforming over ceria and gold-doped ceria nanocrystals

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Introduction

Clean and efficient hydrogen production is of interest because of the potential of hydrogen to be the energy carrier of the future. Methanol has been identified as a good source of hydrogen because of its high hydrogen/carbon ratio, safe handling and easy synthesis from renewable and fossil fuels. Steam reforming of methanol, which produces a satisfactory H_2 yield (75%) while maintaining high carbon dioxide selectivity, can be used to generate H_2 on demand for small-scale fuel cells [1]. Previous work in our group has investigated the activity of nanoscale ceria, suitably modified with minute amounts of gold for the low temperature water gas shift (WGS) reaction [2], and a strong correlation between the ceria structure and WGS activity was identified and reported recently [3]. Here, we explore gold -doped ceria as a new generation catalyst for the steam reforming of methanol. The dependence of the activity and selectivity of the methanol reactions on the crystal morphology (crystal shape and crystal face) of ceria is investigated with suitably synthesized nanoshapes (rods, cubes, polyhedra) of ceria.

Materials and Methods

Different shapes of ceria at the nanoscale were synthesized by adapting a hydrothermal method from the literature [4]. Doped ceria was prepared by deposition-precipitation, followed by air calcination at 400 ^oC[4]. Steam reforming of methanol was conducted in a quartz packed-bed flow reactor. The catalysts were reduced *in situ* at 300 ^oC with a gas mixture of 20%H_2/He for 1 h. The reactor was purged with high purity helium before introducing the methanol-water-helium gas mixtures for the activity tests. The product gas stream was analyzed by online mass spectrometry. CH_3OH-TPD/TPSR analysis was conducted in the same reactor. XPS and TEM were also used to investigate the interaction between the metal and different planes of ceria.

Results and Discussion

XPS data shows a distinct binding energy shifting of the Au 4f peaks between the rod and cube samples. With peak fitting it was found that highly dispersed, positively charged gold species are mainly present in the nanorods, while metallic gold is dominant in the ceria nanocubes. TEM images show that the ceria nanoparticles maintain their original crystal shapes after deposition of gold.

For pre-reduced samples, CH_3OH-TPD show that methanol interacts more strongly with the ceria nanorod (110) surfaces than with the nanocube (100) surfaces. Similar structure sensitivity for methanol decomposition over single crystals of ceria was previously documented in an UHV system [5]. Furthermore, in the doped samples we found that gold facilitates the formation of hydrogen at lower temperatures and greatly inhibits the formation of CO. CH_3OH-TPSR further demonstrated that on pure ceria, H_2 and CO began to increase at the same temperature, which points to a mechanistic pathway through decomposition of methanol or adsorption of methoxy groups on the surface. Different crystal planes affect the "light-off" temperature. For gold-doped ceria, formate was produced at low temperatures, indicative of a different reaction pathway.

Steam reforming of methanol was investigated in a gas mixture containing (mol) 2% CH_3OH, 2.6% H_2O balanced with He. In all reactions, the product gas contained H_2 and CO_2 as the major components, together with a small amount of CO. As shown in Figure 1, Au-ceria nanorods have considerably higher activity than the cubes. Furthermore, our data provide mechanistic insight on the importance of methanol decomposition followed by the WGS reaction sequence over the gold- doped ceria catalysts.

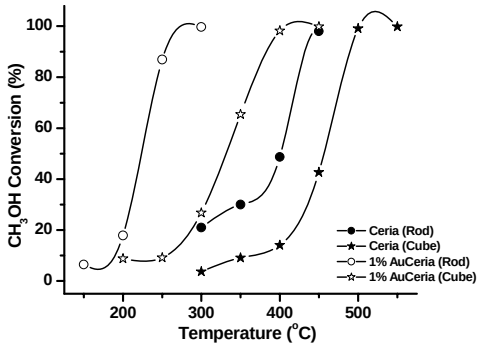

Fig. 1. CH_3OH conversion *vs.* temperature over ceria and Au-Ceria. WHSV= 42,000 $cm^3/g \bullet h$

Significance

We investigate nanoscale ceria suitably modified with minute amounts of gold as a new generation catalyst for the methanol steam reforming reaction. Also a strong shape/plane effect of ceria on the catalyst activity/selectivity for the methanol reactions has been identified.

References

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