A highly selective and stable ZnO-ZrO_2 solid solution catalyst for CO_2 hydrogenation to methanol

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Abstract: A binary metal oxide, ZnO-ZrO_2 solid solution catalyst, which can achieve methanol selectivity up to 86%～91% with CO_2 single-pass conversion over 10% under the similar industrial conditions. The solid solution structure affords dual active site for H_2 activation by Zn site and CO_2 activation by its neighboring Zr site respectively, and is responsible for the excellent catalytic performance.

Keywords: CO_2 hydrogenation, methanol synthesis, ZnO-ZrO_2 solid solution.

1. Introduction

Methanol synthesis via CO hydrogenation has been industrialized for about 50 years using $CuZnOAl_2O_3$ catalyst, which also seems like the best catalyst for methanol synthesis for CO_2 hydrogenation. However, methanol selectivity on $CuZnOAl_2O_3$ from CO hydrogenation is near 99%, while that from CO_2 hydrogenation is less than 60% caused by reverse water gas shift reaction (RWGS). The even more severe problem is the rapid deactivation caused by produced water, which accelerates the sintering of Cu active component during the CO_2 hydrogenation. Therefore, new catalyst is needed to develop to realize the process of CO_2 hydrogenation to methanol with high selectivity of methanol.

2. Experimental

ZnO-ZrO_2 catalyst was synthesized by the co-precipitation method. The activity tests of the catalysts for CO_2 hydrogenation to methanol were carried out in a tubular fixed-bed continuous-flow reactor equipped with gas chromatography (GC). The XRD results were collected on a Philips PW1050/81 diffractometer operating in Bragg-Brentano focusing geometry and using Cu Kα radiation (λ = 1.5418 Å) from a generator operating at 40 kV and 30 mA. TEM images were obtained with a JEM-2100 microscope, 200 kV. Element mappings were obtained with a JEM-ARM200F microscope. The CO_2 -TPD of the catalysts was conducted with an adsorption/desorption system and conducted from 50 C to 600 ^oC. H_2–D_2 exchange experiments were carried out in a flow reactor at 280 ^oC. The formation rate of HD was measured by mass signal intensity.

3. Results and discussion

ZnO-ZrO_2 solid solution catalyst can achieve methanol selectivity up to 86%～91% with CO_2 single-pass conversion over 10% under the reaction conditions of 5.0 MPa, 24000 mL/(g h), H_2/CO_2 =3/1～4/1, 320～315 ^oC (Fig. 1A). ZnO phase was not observed in XRD when adding ZnO (5–33%) into ZrO_2, but leads to the phase change of ZrO_2 from monoclinic to tetragonal. The (011) of ZrO_2 shifts to a higher angle when Zn concentration is increased, indicating that ZnO-ZrO_2 is in a solid solution state with Zn incorporated into the ZrO_2 lattice matrix when ZnO contents in the range below 50% (Fig. 1B-D). Their CO_2-TPD experiments show that most of the CO_2 adsorbed by 13%ZnO-ZrO_2 is on Zr sites, however, H_2-D_2 experiments suggest that there is a strong synergetic effect in the H_2 activation between the two sites, Zn and Zr. The solid solution structure affords dual active site for H_2 activation by Zn site and CO_2 activation by its neighboring Zr site respectively, and is responsible for the excellent catalytic performance. propose a mechanism of the direct hydrogenation of CO_2 likely via a formate intermediate, rather than consecutive RWGS and CO hydrogenation on ZnO-ZrO_2 solid solution catalyst. HCOO* and H_3CO* species were observed and identified by *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Their further isotopic experiments demonstrate that the surface HCOO* and H_3CO^* species can be hydrogenated to methanol (Fig. 1E-F).

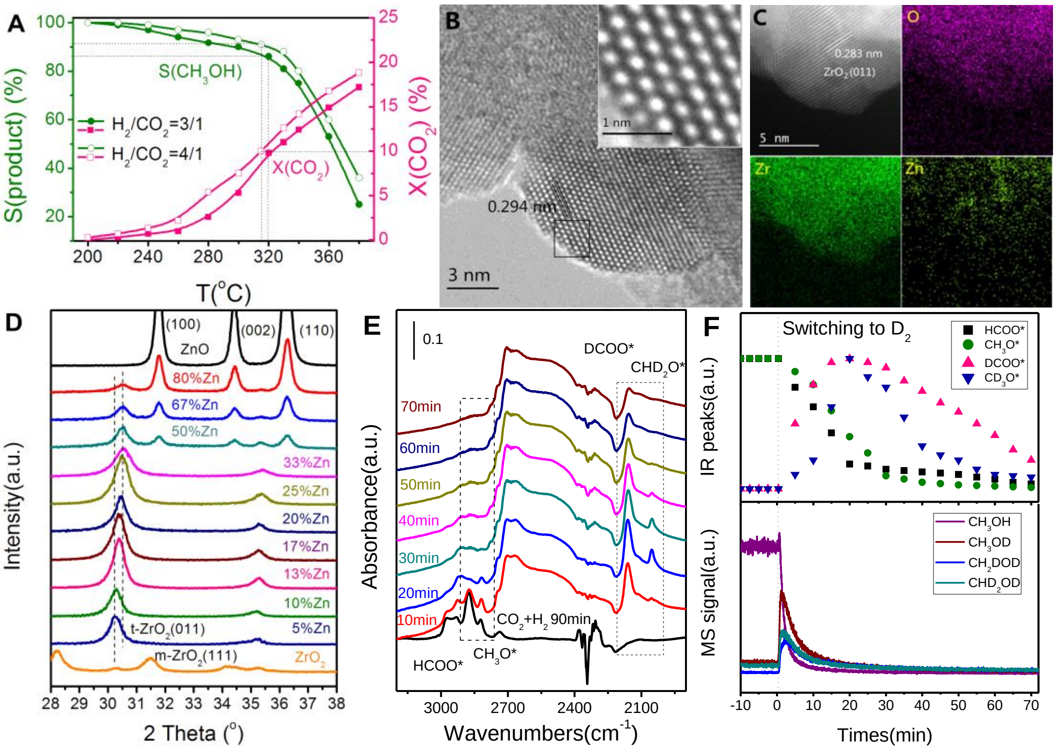

Figure 1. (A) The catalytic performance at the reaction temperatures from 200 to 380 °C with H_2/CO_2 = 3/1 and 4/1. (B) HRTEM and (C) Aberration-corrected STEM-HAADF images and element distribution of 13%ZnO-ZrO_2. (D) XRD patterns of ZnO-ZrO_2. (E) *In-situ* DRIFT spectra of surface species from CO_2 +H_2 and subsequently switched to D_2. (F) DRIFT-MS of CO_2 + H_2 and subsequently switched to D_2.

4. Conclusions

ZnO-ZrO_2 binary metal oxide solid solution catalyst was discovered for highly selective and stable hydrogenation of CO_2 to methanol, which is of interest to both industry and academia. The high selectivity and stability of the ZnO-ZrO_2 catalyst show potential application in carbon capture and utilization (CCU). The dual active sites nature of the solid solution catalyst offers a new opportunity in fine-tuning catalytic activity and selectivity of a wide range of catalysis

References

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