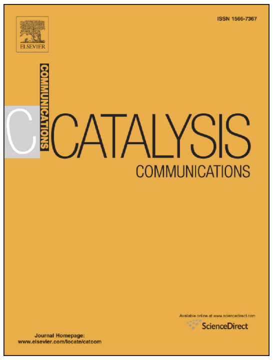

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Morphology effect of nanostructure ceria on the Cu/CeO$_2$ catalysts for synthesis of methanol from CO$_2$ hydrogenation

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Abstract: Three kinds of CeO_2 with different nanostructures were prepared by a controlled hydrolysis method, and Cu/CeO_2 catalysts were prepared by an incipient wetness impregnation method. The catalytic activity of Cu/CeO_2 catalysts was evaluated by the methanol synthesis from CO_2 hydrogenation. It was observed that the support morphology greatly affected the activity and selectivity of methanol synthesis from CO_2 hydrogenation. The nanorod CeO_2 supported Cu/CeO_2 catalyst by the exposure of (100) and (110) faces showed the strongest interaction between CuO and CeO_2, highest CuO dispersion and the highest catalytic activity with methanol yield of 1.9% at 240^{o}C and 2MPa.

Key words: Morphology effect, CO_2 Hydrogenation, Methanol, Cu/CeO_2 catalyst

1. Introduction

The conversion of CO_2 into value-added chemicals has received considerable attention because CO_2 is both a major greenhouse gas and a cheap C1 resource [1]. Methanol is a key commodity chemical, which has been widely used for the production of a number of chemical intermediates [2]. It would be attractive if the distributed and produced in small-scale devices H_2 reacted with CO_2 to produced methanol, the later can be easily stored and transported, and used for further processing [3]. Currently, methanol is industrially synthesized from H_2, CO_2, and CO at high pressure (50~100 atm) and high temperature (200~300^oC) over $Cu/ZnO/Al_2O_3$ catalyst [4]. The methanol synthesis from CO_2 hydrogenation ($CO_2+3H_2 \rightarrow CH_3OH + H_2O$) is a challenging task because of the chemical inertness of CO_2 [5]. Due to the inertness of CO_2, the CO_2 conversion was usually low. Except methanol, other hydrogenated products such as higher alcohols and hydrocarbons were also produced [6]. In addition, the relatively high concentration of CO_2 and H_2 also promoted the reverse water gas shift reaction ($CO_2+H_2 \rightarrow CO+H_2O$) to give CO [4, 5]. Therefore, the effective synthesis of methanol is still a great challenge.

The catalysts for CO_2 hydrogenation to methanol mainly focus on Cu, Pd [7, 8] and other hybrid catalyst, such as Ni-Ga [9], Pt-Co [10]. Cu based catalysts have received great interest for the synthesis of methanol from CO_2 hydrogenation, as the low cost of the Cu catalysts would reduce the industrial production cost. CeO_2 is one of the most important oxides in heterogeneous catalysis due to its high redox ability. There are some literatures which use of CeO_2 as a support in CO_2 hydrogenation process for methanol production [11-12]. Fan et.al reported the strong metal support interaction (SMSI) between Pd and CeO_2, which greatly improved the selectivity and lifetime for methanol synthesis form CO_2 hydrogenation [12]. Graciani et al [4] found that the Cu-ceria interface was active site for synthesis of methanol. The metal and oxide interface afforded special path way for CO_2 to methanol conversion.

CeO_2 with various uniform and well defined morphologies has been successfully prepared through controlled conditions. The effect of the morphology of the CeO_2 support was also observed on catalytic performance over water-gas shift (WGS), steam reforming of methanol (SRM) and other reaction [13-15]. In addition, the support morphology also affects the activity and selectivity of methanol synthesis from CO_2 hydrogenation. Shik C. Tsang et al. [16] found the exposed polar (002) face in platelike ZnO showed a much stronger material synergy with copper than other crystal facets, which gave higher selectivity towards methanol from CO_2 hydrogenation. However, there was no report on the morphology effect of CeO_2 over methanol synthesis from CO_2 hydrogenation. In this paper, three kinds of CeO_2 with different nanostructures were prepared by a controlled hydrolysis method. The Cu/CeO_2 catalysts were prepared by an incipient wetness impregnation method and applied in methanol synthesis from CO_2 hydrogenation.

2. Experimental Section

2.1 Catalyst preparation

2.1.1 Preparation of CeO_2 support with different shapes

Different shapes of nanoscale ceria (nanorods, nanocubes and nanoparticles) were prepared via a controlled hydrolysis method according to the known procedures with some modifications [17]. Typically, $Ce(NO_3)_3.6H_2O$ (4.34 g) was firstly dissolved in deionized water (10 ml), then KOH (2.8 g) in 50 mL of deionized water was added dropwise into $Ce(NO_3)_3$ solution at room temperature. After the complete addition, the mixture was magnetically stirred for 2 h. Then the mixture was introduced into a stainless steel autoclave and kept at 100 ^{o}C or 180 ^{o}C for 24 h. The precipitants were further separated, washed and dried at 100^{o}C for 24 h. Finally, the as-made powder was calcined in air at 400 ^{o}C for 4 h to obtain CeO_2 with nanorods with the hydrothermal temperature of 100 ^{o}C and nanocubes with the hydrothermal temperature of 180 ^{o}C. The procedures for the preparation of CeO_2 nanoparticles were almost the same as those for the preparation of nanorods CeO_2 except the crystallization temperature was changed to 100 ^{o}C and 0. 28 g of KOH was used.

2.1.2 Preparation of CuO/CeO$_2$ catalysts

CuO/CeO_2 catalysts were prepared by an incipient wetness impregnation (IMP) method. $Cu(NO_3)_2$ was used as the precursor. The calculated Cu loading of 5wt.%. Then the mixture was dried overnight at 100^{o}C and calcined in air at 400 ^{o}C for 4 h to get the CuO/CeO_2 catalysts.

2.2 Catalysts characterization

The X-ray diffraction (**XRD**) patterns were determined using a Bruker-D8 diffractormeter with monochromatized Cu-Kα radiation (λ = 1.54056 Å) operated at 40 kV and 40 mA and collected by a Vantec-1 detector.

BET surface area of the CeO_2 was determined by physisorption of N_2 at 77 K by using a quantachrome Autosorb-1-C-MS instrument. About 200 mg sample were degassed in vacuum at 623 K for 3 h prior to the measurements to remove pre-adsorbed components. The specific surface area was determined from the linear portion of the Brunauer–Emmett–Teller (BET) plot.

Transmission electron microscopy (**TEM**) images of the catalyst samples were obtained with a FEI Tecnai G20 instrument. The samples were prepared by directly suspending the catalyst in ethanol with ultrasonic treatment. A copper microscope grid covered with perforated carbon was dipped into the solution and then dried.

H_2-temperature processed reduction (**H_2-TPR**) was experiments were carried out using AMI-200 from Zeton Altamira Company. The sample (50 mg) in a quartz reactor was purged with 30 ml/ min Ar while heating at a ramp rate of 10 °C /min to 150°C and maintaining that temperature for 1 h to remove traces of water. After cooling to 50°C, the sample was reduced in a flow of 10 vol.% H_2/Ar (30 ml/min) while heating from 50 °C to 800 °C at a rate of 10 °C /min.

2.3 Typical procedure for CO_2 hydrogenation reaction

All catalytic tests were performed in fixed-bed flow reactor (stainless steel having a length of 47cm and inside diameter of 1/4 inch). The reactor system was equipped with a programmable temperature controller. Typically, the Cu/CeO_2 catalyst (0.1 g) was first reduced at 400 °C (1 °C/min) for 2 h with H_2 flow rate of 5 mL/min at atmosphere pressure prior to methanol synthesis. The reactor was then cooled down to 100°C and the gas mixture (25% CO_2+75% H_2, 5 mL/min) was introduced continuously for a certain time at different temperatures (240 ~300 °C) and 2MPa. The GHSV = 3 L $h^{-1}g_{cat}^{-1}$.The gas products were analyzed by Agilent GC 7890B on line (thermal conductivity and flame ionization detectors). The liquid product was collected in cold trap and analyzed by 4890 gas chromatography (flame ionization detectors) off line. The conversion and selectivity reaction parameters are defined as:

$$X_{CO2} = \frac{n_{CO2,in} - n_{CO2,out}}{n_{CO2,in}}$$

$$\text{Selectivity} = \frac{n_{product,out}}{n_{CO2,in} - n_{CO2,out}}$$

3. Results and Discussion

Firstly, CeO_2 with different morphologies prepared with different conditions were characterized by TEM technology, and the results are shown in Fig. S1. CeO_2 nanorods were clearly observed in Fig. S1a, which had a uniform width of 10±3 nm with a length of 80–150 nm. High resolution TEM (HRTEM) images of Fig. S1b and Fig. S1c revealed CeO_2 nanorods exposed (100) and (110) faces. As shown in Fig. S1 d, CeO_2 prepared at the hydrothermal temperature of 180 ^oC showed nanocubes structure with a side-size of 50-110 nm. HRTEM images of CeO_2 nanocubes exposed (100) face (Fig. S1e). The change of crystallization temperature and the concentration of KOH produced CeO_2 nanoparticles with a uniform diameter 21±3 nm (Fig. S1f), exposing diverse faces in which the thermodynamically stable (111) faces are predominant. TEM results indicated that the CeO_2 shape greatly affected by the preparative conditions, especially the crystallization temperature and substrate concentration. Torrente-Murciano et al. [15] also found that the morphological phase of CeO_2 was related with the base concentration and temperature during the hydrothermal synthesis. At low temperature and base concentration, the dissolution/recrystallization rate was slow, resulting in the formation of ceria nanoparticles. With the increasing of base concentration, the chemical potential accelerated the anisotropic growth of the $Ce(OH)_3$ nuclei, forming ceria nanorods. Increasing the hydrothermal temperature further, the $Ce(OH)_3$ nuclei are condensed to ceria, nanocubes morphology formed.

The morphology of CuO/CeO_2 catalysts was also characterized by TEM technologies. As shown in Fig. S2, the morphologies of CeO_2 were remained after doping of CuO nanoparticles on the surface of CeO_2. It was observed that CuO nanoparticles were almost homogenously dispersed on the surface of the CeO_2 supports without apparent aggregation.

H_2-TPR profiles were performed to study the redox ability of the three kinds of CeO_2, and were shown in Fig.1a. All the three CeO_2 had two reduction peaks. The lower temperature reduction peak belongs to the reduction of surface oxygen in CeO_2, and the higher reaction temperature reduction peak belongs to the reduction of bulk oxygen [18]. The reduction temperature of surface oxygen increased in an order of CeO_2 nanoparticles, CeO_2 nanocubes and CeO_2 nanorods. The reduction temperature and reduction peak area are summarized in Table 1. The H_2 consumption of surface oxygen for CeO_2 nanorods was closed to that for CeO_2 nanocubes, which were 110 and 102 μmol, respectively. The number was 83 μmol for CeO_2 nanoparticles. The BET surface area of the CeO_2 was also shown in Table 1, the surface area was 56, 69, 77 m^2/g for CeO_2 nanorods, nanocubes and nanoparticles. The CeO_2 nanorods had the smallest surface area but the highest surface oxygen content. H_2-TPR profiles of CuO/CeO_2 catalysts are show in Fig.1b. A main reduction peak at 179 ^oC together with a peak at 154^oC were observed for 5% CuO/CeO_2 nanoparticles, which were attributed to the reduction of CuO and ceria on the interface of CuO-CeO_2.[19]. The reduction temperature increased to 251 ^oC and 309 ^oC for 5% CuO/CeO_2 nanocubes and 5% CuO/CeO_2 naorods catalysts, respectively. Compared to the bulk CeO_2, the reduction temperature of the catalyst decreased obviously due to the strong interaction between metal and support (SMSI) effect, high calcination temperature will improve this effect [20]. Cu can effectively activate the surface Ce-O bond and promoted the surface reduction of CeO_2. Araiza et al. [21] studied the CuO supported on different morphology CeO_2, and also found the CuO/CeO_2-rod had the highest temperature of main reduction peak. As CeO_2 nanocubes has exposed (100) crystal planes and CeO_2 nanorods has exposed (100) and (110) crystal planes, it is likely that the Cu precursor preferentially interacts with the (110) crystal planes of CeO_2 nanorods.

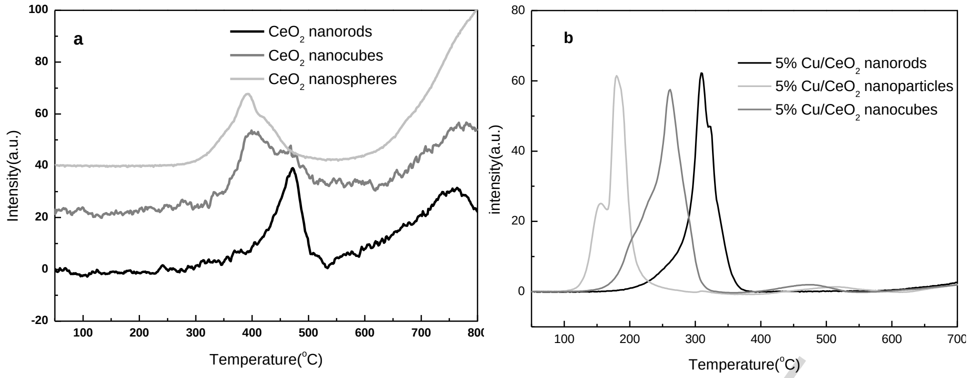

Fig. 1 H_2-TPR of CeO_2 support and 5% CuO/CeO_2 catalysts

Table 1. The surface area from BET experiment and reduction temperature, H_2 consumption of CeO_2 samples summarized in H_2-TPR experiment

	surface area (m^2/g)	Surface oxygen reduction temperature (°C)	Surface oxygen H_2 consumption(μmol)
CeO_2 nanorods	56	472	110
CeO_2 nanocubes	69	399	102
CeO_2 nanoparticles	77	391	83

XRD patterns of the three as-prepared CuO/CeO_2 catalysts were shown in Fig. 2. Diffraction peaks with 2θ at 28.6, 33.1, 47.5, 56.3, 59.1° are indexed to the (111), (200), (220), (311) and (222) planes of face-centered cubic CeO_2 with a fluorite structure (PDF#34-0394). The CeO_2 crystallite sizes were calculated from the XRD peak widths using the Scherrer equation. The diameters were 16, 13 and 11 nm for CeO_2 nanocubes, nanoparticles and nanorods, respectively. The diffraction peaks with 2θ at 35.5 and 38.7 ° were ascribed to (002) and (111) planes of CuO (PDF#45-0397) in 5% CuO/CeO_2 nanoparticles. However, there were no diffraction peaks of CuO in 5% CuO/CeO_2 nanorods and nanocubes catalysts, which indicated that small sized CuO nanoparticles were homogeneously dispersed in 5% CuO/CeO_2 nanorods and naocubes catalysts.

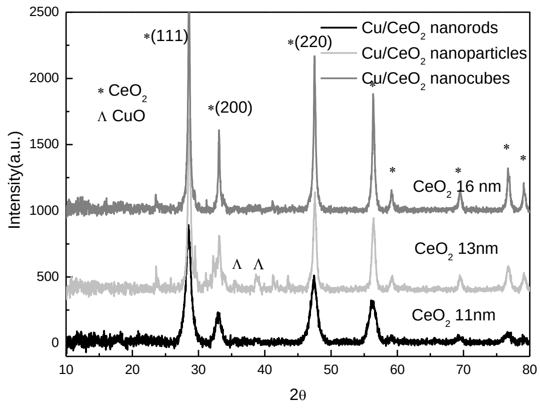

Fig.2 XRD profiles of 5%CuO/CeO_2 catalysts

The H_2-TPR and XRD results show clearly that the tendency of reduction temperature of CuO/CeO_2 catalysts was the same as the CeO_2 support (nanorods > nanocubes > nanoparticles), but not consistent with the particle size of CuO (CuO/CeO_2 nanocubes > CuO/CeO_2 nanoparticles >CuO/CeO_2 nanorods). That means the morphology effect of support was larger than the particle size effect of CuO in our catalysts. H_2-TPR experiments also indicated the interaction and reduction of the CuO with the CeO_2 support vary with the morphology and exposed crystal planes of the CeO_2 support. The CeO_2 nanorods, which exposed (100) and (110) faces showed the highest Cu dispersion and interaction between CuO and CeO_2.

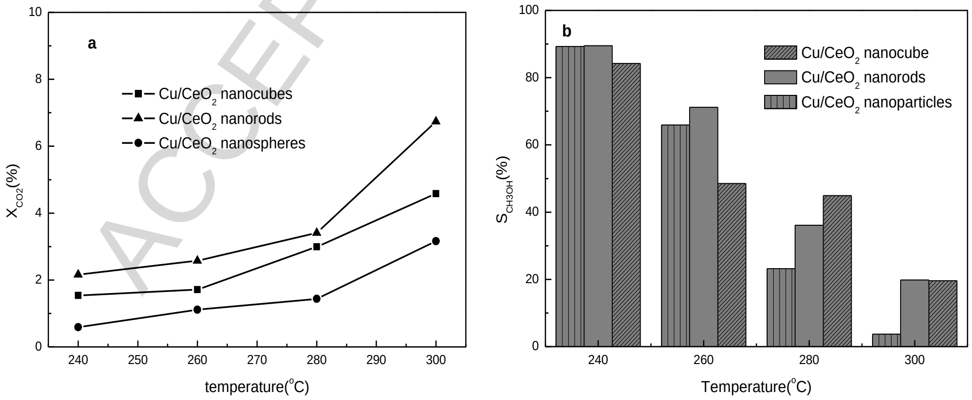

Fig. 3. The temperature effect on CO_2 conversion and methanol selectivity of Cu/CeO_2 catalysts

The effect of the reaction temperature on CO_2 conversion was studied and the results are shown in Fig.3a. The catalytic activity of the three Cu/CeO$_2$ catalysts increased with the increase of the reaction temperature. However, the highest CO$_2$ conversion was only 6.7% for Cu/CeO$_2$ nanorod catalyst at 300 ^{o}C The CO$_2$ conversion was according the followed sequence, conv. Nanorods > conv. Nanocubes > conv. Nanoparticles, which was consistant with the H$_2$-TPR of Cu/CeO$_2$ catalysts. The Cu/CeO$_2$ nanorods had the strongest interaction between CuO and CeO$_2$, highest CuO dispersion and largest CO$_2$ conversion. Fig. 3b showed the methanol selectivity. The methanol selectivity decreased sharply with the increase of the reaction temperature. For instance, the methanol selectivity of Cu/CeO$_2$ nanorod catalyst was 89.5% at 240^{o}C, and that sharply decreased to 19.8% at 300^{o}C. The highest methanol yield was 1.9% over Cu/CeO$_2$ nanorods catalysts at 240 ^{o}C and 2 MPa. The other by-product were CH$_4$ and CO. At lower temperature (240^{o}C), the main side reaction was methanation reaction ($CO_2+4H_2 \rightarrow CH_4+2H_2O$), and at higher temperature (260, 280, 300^{o}C), the reverse WGS reaction ($CO_2+H_2 \rightarrow CO+H_2O$) activity increased sharply due to Cu based catalysts was also a good WGS or reversed WGS catalyst [22].

Conclusions

In conclusion, three nanostructure Cu/CeO$_2$ catalysts with different morphology were prepared and applied in CO$_2$ hydrogenation to methanol. The Cu/CeO$_2$ nanorods catalyst showed the highest methanol yield of 1.9% at 240 ^{o}C and 2MPa. H$_2$-TPR and XRD results indicated CuO/CeO$_2$ nanorods had the strongest interaction between CuO and CeO$_2$, highest CuO dispersion and largest CO$_2$ conversion.

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Highlights

- Three Cu/CeO_2 catalysts were applied in CO_2 hydrogenation to methanol reaction.
- Support morphology greatly affected the catalyst activity of CO_2 hydrogenation.
- The Cu/CeO_2 nanorods gave the highest methanol yield of 1.9% at 240°C and 2MPa.