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Slurry methanol synthesis from CO_2 hydrogenation over micro-spherical SiO_2 support Cu/ZnO catalysts

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ABSTRACT

The micro-spherical SiO_2 support is prepared by the spray-drying method, and then a series of SiO_2 supported Cu/ZnO-based catalysts with different percentage of Cu and ZnO are synthesized by ammonia-evaporation method. The Cu and ZnO loadings play a critical role on the physicochemical properties and catalytic performance of catalysts. The results show that Cu and Zn cations can be deposited into the pores of the micro-spherical SiO_2 with well-distributed when the metal loadings are below 47.91 wt%. In addition, the specific surface area of catalysts increases with increasing loadings due to the formation of porous structure inside SiO_2 support, while it decreases when the metal loading is above 47.91 wt%. According to XRD, XPS, XAES and CO adsorption *in situ* FTIR analysis, both Cu^+ and Cu° species exist on the reduced surface of $Cu/ZnO/SiO_2$ catalysts. The catalytic performance for slurry methanol synthesis from CO_2 hydrogenation is examined. The $Cu/ZnO/SiO_2$ catalyst exhibits an optimum catalytic activity when the metal loading reaches to 28.23 wt%. However, the CO_2 conversion changes slightly with a further increase of metal loadings, because the pore of support is blocked and the reducibility of catalysts is decreased significantly with incorporation of excess metal compounds into SiO_2. In addition, the methanol selectivity enhances with increasing metal loadings due to the decrease of the proportion of Cu^+ species.

1. Introduction

It is well known that CO_2 is not only one of the main greenhouse gases, but also an economical, safe and renewable C1 feed stock. Capturing CO_2 and converting it into value-added chemicals and fuels using renewable energy is of great importance to sustainable development and has attracted considerable attention [1–5]. Catalytic hydrogenation of CO_2 using H_2 produced from renewable energy sources, such as solar, wind, biomass and so on, is considered as a practical route for the sustainable production of methanol, lower olefins and higher hydrocarbons [6–10]. Among all, most of researches focused on catalytic conversion of CO_2 to methanol because methanol is an important raw material in the chemical industry and can be utilized directly as a fuel additive or a clean fuel [11–16]. Therefore, CO_2 hydrogenation to methanol is supposed to be one of the economic ways to alleviate the global warming and result in production of fuels and valuable chemicals.

Up to now, the vast majority of research interests focused on the methanol synthesis which was carried out in a fixed bed reactor, however, less attention has been paid to methanol synthesis in the slurry phase reactor. The slurry phase methanol synthesis has been known as a potential process for large-scale methanol production since it provides many advantages over fixed bed reactors, such as high heat and mass transfer rates, high productivity of unit reactor volume, convenient on-line catalyst addition and withdrawal, simple construction and low operation cost [17–19]. The catalysts used in the methanol synthesis are mainly copper-based catalysts (such as Cu/ZnO, $Cu/ZnO/Al_2O_3$, $Cu/ZnO/Al_2O_3/ZrO_2$, $Cu/ZnO/SiO_2$ and so on), which are usually prepared by co-precipitation method [20–24]. However, catalyst attrition, causing downstream filter plugging or increased slurry viscosity, has kept back the use of above catalysts prepared by conventional drying method for slurry phase methanol synthesis [25]. Herein, efforts have been put forth to increase the mechanical and attrition strength of catalysts. Spray-drying method was employed after

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Table 1
Component contents of as-prepared *x*CZ/S catalysts.

Catalysts	CuO (wt%)	ZnO (wt%)	SiO_2 (wt%)	Cu/Zn	Cu + ZnO (wt%)
10CZ/S	8.2	3.4	88.4	2.43	10.03
20CZ/S	15.4	6.5	78.1	2.42	18.97
30CZ/S	22.9	9.5	67.6	2.47	28.23
50CZ/S	37.6	16.7	45.7	2.30	47.91
60CZ/S	45.4	20.4	34.3	2.28	58.23

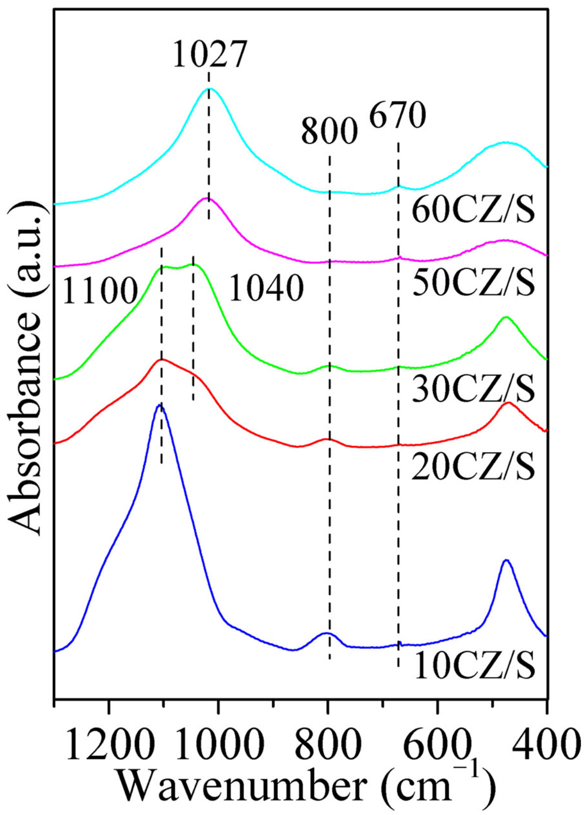

Fig. 1. IR spectra of the calcined *x*CZ/S samples.

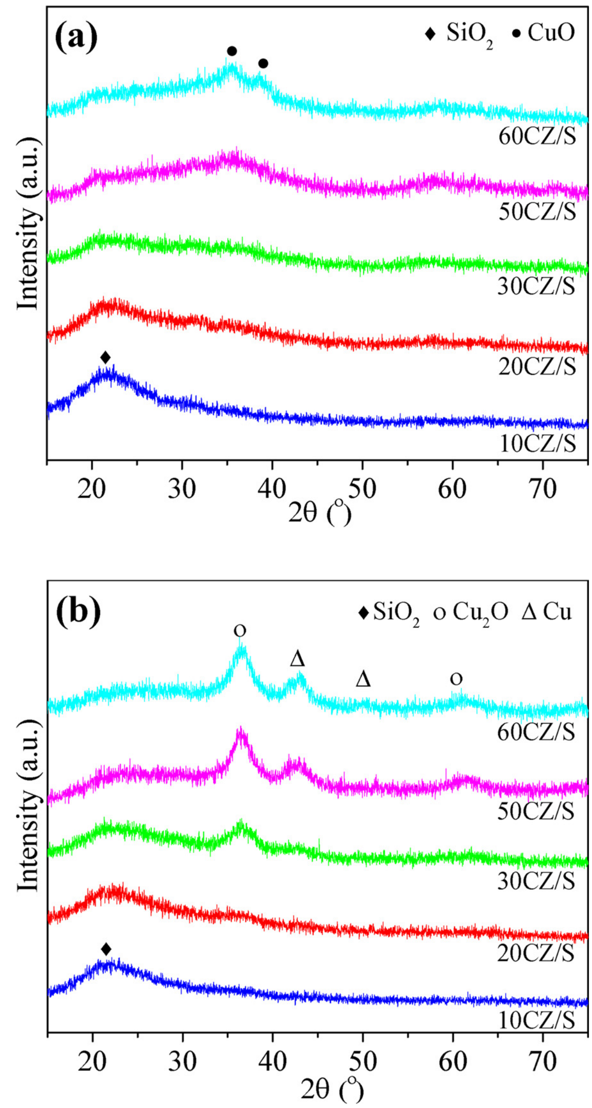

Fig. 2. XRD patterns of *x*CZ/S samples after (a) calcination and (b) reduction.

the co-precipitation process to prepare micro-spherical particles with improved physical strength as well as strong stability, and a binding additive such as silica sol, alumina sol was usually added [18,19,26]. Nevertheless, the catalyst prepared by this method has a small specific surface area and limited pore volume. Moreover, the introduced additive sometimes does not work, on the contrary, it would restrict the chemical composition and functionality of Cu-based nanocatalysts.

SiO_2 as a support is widely used in the methanol synthesis since it possesses high thermal stability and good compatibility with other materials [27–31]. Besides, mesoporous SiO_2 (*m*-SiO_2) favors metal dispersion and diffusion due to the higher specific surface area and enriched porosity. In order to enhance the pore volume and the availability of functional components of Cu-based catalysts, micro-spherical SiO_2 support with good attrition resistance was employed. In our present work, the micro-spherical SiO_2 was prepared by the spray-drying method, and then a series of SiO_2 supported Cu/ZnO-based catalysts with different percentage of Cu and ZnO loading were synthesized by ammonia-evaporation method. After calcination and reduction, the highly dispersed Cu/ZnO/SiO_2 catalysts were obtained and tested for methanol synthesis from CO_2 hydrogenation in a slurry phase reactor. The main focus is the effects of the total Cu and ZnO loading on the physicochemical and catalytic properties of the micro-spherical SiO_2 supported Cu/ZnO-based catalyst.

2. Experimental

2.1. Preparation of catalysts

The Cu/ZnO/SiO_2 catalysts for slurry phase methanol synthesis were prepared as follows. Firstly, micro-spherical support SiO_2 with good attrition resistance was synthesized by the spray-drying method (The mixtures that contain a desired amount of aerosil, silica sol and deionized water were spray-dried, and the micro-spherical support SiO_2 was obtained after calcination), and then the Cu^{2+} and Zn^{2+} ions were deposited on SiO_2 support by ammonia-evaporation (AE) methods [32,33]. Typically, an aqueous solution (1000 mL) containing a certain amount of $CuCO_3$. $Cu(OH)_2$, $3Zn(OH)_2.2ZnCO_3$ (Cu/Zn molar ratio of 7/3) and ammonia solution (25 wt%) was placed in a three-necked flask. Then, the as-prepared SiO_2 (20 g, 100–200 mesh) was added with vigorous stirring to obtain a homogeneous suspension. Subsequently, the mixture was kept under stirring at 363 K for 12 h to allow for the evaporation of ammonia along with the deposition of metal species on SiO_2, and meanwhile nitrogen (200 mL min^{-1}) was flushed through the system. After the precipitation, the precipitate was obtained by centrifugation, washed several times with distilled water and dried at 373 K for 12 h, followed by calcination at 623 K in air for 4 h. The as-obtained samples were denoted as *x*CZ/S (*x* represents the total weight