



## Cu/Zn<sub>x</sub>Al<sub>y</sub>O<sub>z</sub> supported catalysts (ZnO: Al<sub>2</sub>O<sub>3</sub> = 1, 2, 4) for methanol synthesis

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### ABSTRACT

The main goal of this work was determination of the dependence of the physicochemical properties of Cu/support catalysts (ZnO, Al<sub>2</sub>O<sub>3</sub>, ZnAl<sub>2</sub>O<sub>4</sub>, ZnAlO<sub>2.5</sub>, Zn<sub>2</sub>AlO<sub>3.5</sub>) with their activity in methanol synthesis. The formation of spinel ZnAl<sub>2</sub>O<sub>4</sub> structure during calcination process was proved by XRD technique. The mechanism of methanol synthesis was discussed. Activity tests show that the most active catalyst was system supported on binary oxide ZnAl<sub>2</sub>O<sub>4</sub>.

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### 1. Introduction

Methanol is industrially produced from synthesis gas CO/CO<sub>2</sub>/H<sub>2</sub> under rather low temperature and high pressure conditions over a ternary CuO–ZnO–Al<sub>2</sub>O<sub>3</sub> catalysts [1]. During the last decades, CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH has gained wide interest as a mean to contribute to reduction of CO<sub>2</sub> emissions. Furthermore the direct conversion of CO<sub>2</sub> and hydrogen to CH<sub>3</sub>OH has already been demonstrated with higher selectivity than CO and lower reaction temperature [2]. However, there is still controversy concerning the mechanism of methanol synthesis [3,4]. Some authors claimed that carbon monoxide is the main source for methanol synthesis. But this viewpoint cannot explain the remarkable improvement of activity after CO<sub>2</sub> introduction [5]. Saussey [6] and Fujita [7] claimed that methanol synthesis carried out from CO and CO<sub>2</sub> hydrogenation has different mechanisms. Fujita thought that during methanol synthesis running from CO and H<sub>2</sub> mixture, zinc formate was formed first, followed by hydrogenated to zinc methoxy and then reacted with surface hydroxyl species to form methanol. Whereas, CO<sub>2</sub> hydrogenation lead to both zinc formate and copper formate formation on the catalyst surface, then these formates are hydrogenated to methoxide, and hydrolyzed to methanol. Qi Sun [8] suggested that methanol was formed directly from CO<sub>2</sub> hydrogenation both for CO<sub>2</sub> and for CO/CO<sub>2</sub> hydrogenation, and b-HCOO<sup>-</sup> species were the key intermediate.

The rate-limiting step was hydrogenation of bidentate formates surface species.

Many studies and discussions about the role of copper during hydrogenation of CO or CO<sub>2</sub> are available in literature. Particle size, surface area, metallic copper surface area and composition of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst are important factors influencing on the catalytic process. Chinchin et al. proposed a linear relationship between the catalytic activity in methanol synthesis and metallic copper surface area of the catalyst [9,10]. Fujitani et al. [11] reported that the activity of methanol synthesis from CO increases with the concentration of Cu<sup>+</sup> sites. The Cu<sup>+</sup> as well as Cu<sup>0</sup> could possibly be active species during methanol synthesis from CO<sub>2</sub>, where carbonate, formate and methoxy species may be intermediates.

Lavalley et al. [12] reported that methanol is formed via an active formate species adsorbed on metallic copper, which depends on the copper dispersion and the ability of the mixed oxide phases (Cu–ZnO) to generate and store active hydrogen.

Additionally, activity of copper based catalysts can be improved by mixtures of metal oxides MO<sub>x</sub> (M: Cr, Zn, Al) which were usually produced by co-precipitation or impregnation methods. Catalysts containing these metal oxides have been found to be more active than the individual component [13–16]. In addition some transition metals have been used as promoters to modify the activity of Cu–ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts in methanol synthesis [16].

Various methods for Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts preparation which allow to achieve large copper surface, fine particle size and optimized compositions leading to high catalytic activity and selectivity of methanol synthesis through CO or/and CO<sub>2</sub> hydrogenation were investigated. Tanaka and co-workers [17] prepared Cu/ZnO catalyst from a solution of copper and zinc nitrates dissolved in ethylene

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glycol. They found that the selectivity to methanol was highest when the ratio of Cu/ZnO was 1. Deng et al. [18] reported that catalytic activity of methanol synthesis through CO<sub>2</sub> hydrogenation increasing with increasing of the metallic surface area for Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> system until it reaches a maximum at Cu/ZnO = 8 and then decreases at higher molar ratio.

In the present work copper supported catalysts containing 20 wt.% Cu (Al<sub>2</sub>O<sub>3</sub>, ZnAl<sub>2</sub>O<sub>4</sub>, ZnAlO<sub>2.5</sub>, Zn<sub>2</sub>AlO<sub>3.5</sub>, ZnO) were prepared by conventional impregnation method. The main goal of this work was investigation the influence of support composition on the structure of the catalyst and its catalytic activity in methanol synthesis from CO<sub>2</sub>/H<sub>2</sub>. The physicochemical properties of the catalysts were examined by BET, XRD, DRIFT, TPR-H<sub>2</sub> methods. Catalytic activity test in methanol synthesis by CO<sub>2</sub> hydrogenation were carried out under elevated pressure (4 MPa) in fixed bed reactor.

## 2. Experimental

### 2.1. Catalysts preparation

Copper supported catalysts Cu/Zn<sub>x</sub>Al<sub>y</sub>O<sub>z</sub> were prepared by wet aqueous impregnation method. Binary oxides of Zn<sub>x</sub>Al<sub>y</sub>O<sub>z</sub> (molar ratio Zn: Al = 0.5, 1, 2) were prepared by co-precipitation. Aqueous solutions of 1 M zinc acetate and 1 M aluminium nitrate were mixed in appreciate quantity under vigorous stirring at 80 °C. A concentrated ammonia solution was then added by dropwise addition until the pH reached values between 10 and 11 and the mixtures were stirred for another 30 min. The resulting fine precipitates were washed two times in deionized water and then dried at 120 °C for 15 h and subsequently calcined for 3 h in air at 600, 700 and 900 °C, respectively. Choice of the first temperature calcination was prescribed by necessity of spinel structure creation and for removal of the acetate precursor from catalytic systems. Higher temperature calcination was imposed to investigate of the phase composition during the calcination process.

Metal phase (Cu) was introduced on support surface by wet impregnation method with an aqueous solution of its nitrate and then the supported catalysts were dried at 120 °C and finally calcined for 4 h in air at 400 °C for removal of nitrates and at 700 °C for elucidate the interaction between support and active phase. Copper loading was 20 wt.% in all cases.

### 2.2. Methods of catalysts characterization

#### 2.2.1. Specific surface area and porosity (BET)

The specific surface area and porosity of the catalysts and their supports were determined with automatic sorptometer Sorptomatic 1900. Samples were prepared at 250 °C and 12 h evacuation followed by low temperature nitrogen adsorption-desorption measurements were carried out using BET, liquid N<sub>2</sub> method.

#### 2.2.2. Temperature programmed reduction (TPR-H<sub>2</sub>)

The TPR-H<sub>2</sub> measurements were carried out in an automatic TPR system AMI-1 in the temperature range 25–900 °C with linear heating rate 10 °C/min. Samples (weight about 0.1 g) were reduced in hydrogen stream (5% H<sub>2</sub>–95% Ar) with the gas volume velocity of 40 cm<sup>3</sup> per minute. The hydrogen consumption was monitored by a thermal conductivity detector.

#### 2.2.3. XRD measurements

Room temperature powder X-ray diffraction patterns were collected using a PANalytical X'Pert Pro MPD diffractometer in Bragg-Brentano reflecting geometry. Copper CuK<sub>α</sub> radiation from a sealed tube was utilized. Data were collected in the range 5–90° 2θ with step 0.0167° and exposition per one step of 27 s. Due to the fact that raw diffraction data contain some noise, the background

**Table 1**

BET surface area measurements and average pore size for supports: ZnAl<sub>2</sub>O<sub>4</sub>, ZnAlO<sub>2.5</sub>, Zn<sub>2</sub>AlO<sub>3.5</sub>, Al<sub>2</sub>O<sub>3</sub> and ZnO calcined 3 h in air at various temperatures.

Support	Calcination temperature (°C)	Specific surface area (m <sup>2</sup> /g)	Average pore size (Å)
Al <sub>2</sub> O <sub>3</sub>	400	237	27
ZnAl <sub>2</sub> O <sub>4</sub>	600	63	30
ZnAlO <sub>2.5</sub>	600	60	42
Zn <sub>2</sub> AlO <sub>3.5</sub>	600	19	55
ZnO	400	37	–

during the analysis was subtracted using Sonneveld, E.J. and Visser algorithm. The data was then smoothed using cubic polynomial. All calculations were done with X'Pert HighScore Plus computer program.

#### 2.2.4. Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS)

Infrared spectra were recorded with a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector. Before analysis the sample was reduced at 300 °C in gas reduction mixture (5% H<sub>2</sub>–95% Ar for 1 h). A resolution of 4.0 cm<sup>-1</sup> was used throughout the investigation. 64 scans were taken to achieve a satisfactory signal to noise ration. The background spectrum was collected at 50 °C after reduction. Then the reduction mixture was shifted to a reaction mixture of approximately 20% CO<sub>2</sub> and 80% H<sub>2</sub>. Reaction was carried out in temperature range 50–280 °C under atmospheric pressure. Spectra were taken in each temperature after 10 min in reaction mixture flow.

#### 2.2.5. Catalytic activity test

Carbon dioxide hydrogenation tests were carried out in a fixed bed reactor using a gas mixture of H<sub>2</sub> and CO<sub>2</sub> with molar ratio 3:1, respectively. The process was carried out under elevated pressure (4 MPa) at 180 and 260 °C. Before activity tests, the catalysts were pre-reduced for 2 h in a flow of 5% H<sub>2</sub>–95% Ar at 300 °C under atmospheric pressure. The catalysts were cooled to the reaction temperature of 260 °C and then the inlet flow was switched to reaction mixture. The steady-state activity measurements were taken after at least 12 h on the stream. The analysis of the reaction products were carried out by an on-line gas chromatograph equipped with FID detector and 10% Carbowax 1500 on Graphpac column. The CO and CO<sub>2</sub> concentrations were monitored by GC chromatograph equipped with TCD detector (120 °C, 130 mA), and Carboxphere 60/80 (90 °C) column. CO conversion was calculated by the following equation:

$$\text{CO}_2 \text{ conv.} = \left[ \frac{(\text{CO}_2 \text{ in feed} - \text{CO}_2 \text{ in effluent})}{(\text{CO}_2 \text{ in feed})} \times 100 \right]$$

The selectivity of the products were calculated as follows:

$$P_i \text{ selectivity} = \left( \frac{P_i \text{ yield}}{\sum P_i \text{ yield}} \right) \times 100$$

$P_i$  is the mol number of every product.

## 3. Results and discussion

The BET results embracing surface area and dominant pore size of the calcined at various temperature supports (Al<sub>2</sub>O<sub>3</sub>, ZnO, ZnAl<sub>2</sub>O<sub>4</sub>, ZnAlO<sub>2.5</sub>, Zn<sub>2</sub>AlO<sub>3.5</sub>) are shown in Table 1. The individual Al<sub>2</sub>O<sub>3</sub> calcined at 400 °C had the largest specific surface area of 237 m<sup>2</sup>/g compared to the ZnO sample which had the lowest surface area of 37 m<sup>2</sup>/g. The binary oxides ZnAl<sub>2</sub>O<sub>4</sub> and ZnAlO<sub>2.5</sub> showed intermediate specific surface area of about 60 m<sup>2</sup>/g. On the

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