Preparation of high performance nano-sized Cu/ZnO/Al$_2$O$_3$ methanol synthesis catalyst via aluminum hydrous oxide sol

Mohsen Bahmani [a,b], Bahman Vasheghani Farahani [a,*], Saeed Sahebdelfar [b]

[a] Chemistry Department, Faculty of Science, Imam Khomeini International University, P.O. Box 288 Qazvin 34149, Iran
[b] Catalyst Research Group, Petrochemical Research and Technology Company, National Petrochemical Company (NPC-RT), P.O. Box 14965/115, Tehran, Iran

ARTICLE INFO

ABSTRACT

Ternary Cu/ZnO/Al$_2$O$_3$ methanol synthesis catalysts were synthesized by co-precipitation of copper and zinc hydroxycarbonates in the presence of various aluminum hydrous oxide sol preparation methods from sodium aluminate and aluminum nitrate as aluminum oxide sources. The catalysts were characterized at various stages of preparation by nitrogen adsorption-desorption, X-ray diffraction, transmission electron microscopy, temperature programmed reduction and N$_2$O chemisorption techniques. The TPR profiles of calcined precipitates were deconvoluted into three peaks which were assigned to the reduction of copper oxide species exhibiting different crystallite size and/or different interactions with zinc oxide. All catalysts were tested for methanol synthesis activity in a fixed-bed reactor under conditions similar to that of commercial operation (503 K, 50 bar and GHSV of 17250 h^{-1}), using H$_2$, CO, and CO$_2$ (80/12/8 molar ratio) mixture as the feed. The experimental results illustrated that the catalyst synthesized based on aluminum hydrous oxide sol prepared by peptization of aluminum hydroxide exhibited higher specific surface area, copper dispersion and catalytic activity for methanol synthesis. The catalysts thus prepared were shown to have less hydrotalcite-like phase, stronger interdispersion between Cu and ZnO and well-dispersed Cu nanoparticles with improved stability and activity in methanol synthesis from syngas.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Methanol is produced on industrial scale from synthesis gas mixtures (CO/CO$_2$/H$_2$) over a Cu/ZnO/Al$_2$O$_3$ catalyst at typical reaction conditions of 230–280 °C and 50–100 bar [1] with a worldwide production over 50 million metric tons per year [2]. Methanol is chiefly used as solvent and raw material. It is also of interest as a potential energy carrier in the future and a bulk chemical for fixation of the captured CO$_2$ [3].

Industrial Cu/ZnO-based catalysts are prepared by co-precipitation method [4] which creates precursors with a definite stoichiometry capable of transformation into a porous and homogeneous aggregates of Cu and ZnO nanoparticles (NPs) component [5]. Nearly spherical Cu NPs of a size around 10 nm and ZnO NPs which are arranged in an alternating manner forming porous aggregates with relatively large Cu exposed surface area of up to about 40 m^{2}g^{-1} are produced [2].

In recent years, the role of methanol as a basic chemical has strongly increased, and therefore further development of the ternary Cu/ZnO/Al$_2$O$_3$ catalyst for methanol synthesis has become more important [6]. It is widely accepted that ZnO acts both as an electronic and structural promoter exhibiting a major influence on the catalytic activity, while alumina or other refractory oxides mainly increase the long-term stability as structural promoter of the ternary catalyst system [7]. Eliminating any of the constituting components severely reduces the performance of the catalyst system. Consequently, the interest in ternary CuO/ZnO/Al$_2$O$_3$ system as catalytic materials remains very high [8]. The precipitation conditions such as the concentration of initial solutions [9,10], precipitation temperature, pH of precipitation, addition of promoters [11–13] and the duration of aging of precursor precipitate play a significant role on the performance of the catalyst [14–16]. The activity and stability of the catalyst could be enhanced by using an appropriate support [17–19] and also by applying novel preparation methods [20–22].

Although many works has been done to improve the performance of methanol synthesis catalysts [23,24], the influence of using some novel sol and colloidal primary solutions as alternatives to true solutions to prepare the catalyst and their influence

Table 1
Ternary Cu/ZnO/Al$_2$O$_3$ catalyst names prepared with different initial solutions.

Catalyst[a]	Aluminum source solution	Tyndall effects[b]
CZ_AN	Aluminum Nitrate (AN)	None
CZ_AN + AH	Aluminum Nitrate (AN) partially neutered by Ammonium Hydroxide (AH) n (AN)/n (AH) = 2.5	Yes
CZ_SA	Sodium Aluminate	Yes
CZ_SA + NA	Sodium Aluminate (SA) Acidified by Nitric Acid (NA) n (SA)/n (NA) = 2.5	Yes (great)

[a] The sample designating are: AN stands for Aluminum Nitrate, AH stands for Ammonium Hydroxide, SA stands for Sodium Aluminate, NA stand for Nitric Acid.
[b] See Supplementary Fig. S1.

on catalytic activity, selectivity and stability have not yet been fully recognized. Aluminum hydrous oxide sols could be obtained by the addition of NH$_3$ to the solution of an aluminum salt and also by peptization of an aluminum hydroxide precipitate [25,26].

This work focuses on using some novel primary solution based upon sol and colloidal systems for the preparation of the ternary Cu/ZnO/Al$_2$O$_3$ catalyst and investigating their effect on the activity and stability of the catalyst for methanol synthesis. The catalysts were characterized by various relevant techniques and their catalytic performance was related to their structural and chemical properties.

2. Experimental

2.1. Precursor solutions preparation

To prepare the catalysts, four different mixed copper, zinc and aluminum nitrate solutions were made according to the following procedures as summarized in Table 1. The nominal Cu:Zn:Al molar ratios of all solutions were 60:30:10.

2.1.1. Copper, zinc nitrate and aluminum nitrate solutions (CZ_AN)

Solutions of 1.0 mol/L copper nitrate, 1.0 mol/L zinc nitrate, (prepared separately by dissolving basic copper carbonate and zinc oxide in appropriate amount of nitric acid solution, respectively) and 1.0 mol/L aluminum nitrate (AN) (prepared by dissolving aluminum nitrate nonahydrate in demineralized water) were mixed to obtain the ternary mixed metal nitrate true solution.

2.1.2. Copper, zinc nitrate and aluminum nitrate (AN) solution partially neutered by aqueous ammonia ("ammonium hydroxide", AH) sol (CZ_AN + AH)

First aluminum nitrate nonahydrate was dissolved in demineralized water to prepare 1.0 mol/L solution. Then 2.5 mol/L aqueous ammonia solution was added to achieve NH$_{3(aq)}$/Al(NO$_3$)$_3$ molar ratio of 2.5. During addition of ammonia solution, aluminum hydroxide precipitate was observed which re-dissolved by completing addition of ammonia solution and a clear solution without precipitate was obtained. By this route, the (AN + AH) sol was prepared (Supplementary Fig. S1). Finally, the sol was added dropwise to 1.0 mol/L copper nitrate and 1.0 mol/L zinc nitrate mixed solution.

2.1.3. Copper, zinc nitrate solutions and sodium aluminate sol (CZ_SA)

In this and in the following solutions, sodium aluminate (SA) was used as the source of aluminum in the catalysts. First sodium aluminate was dissolved in demineralized water to prepare 1.0 mol/L solution and stirred for 20 min to obtain the sodium aluminate sol (Supplementary Fig. S1). After that, appropriate amount of this solution was added dropwise to a mixture of 1.0 mol/L copper nitrate and 1.0 mol/L zinc nitrate solution. During addition of the sodium aluminate (a basic solution), small amount of white precipitate formed, most of which slowly re-dissolved, although a completely clear solution without precipitate was not obtained.

2.1.4. Copper, zinc nitrate solutions and acidified sodium aluminate sol (CZ_SA + NA)

For preparation of the fourth precursor solution, first appropriate amount of 1.0 mol/L sodium aluminate solution was prepared. Then 56% nitric acid (NA) was added to achieve HNO$_3$/NaAlO$_2$ molar ratio of 2.5. During addition of HNO$_3$, gelation and formation of aluminum hydroxide precipitate was observed which re-dissolved by completing slow addition of nitric acid and heating. After that, aluminum hydrous oxide sol was formed (Supplementary Fig. S1). Finally, the sol was added dropwise to a mixture of 1.0 mol/L copper nitrate and 1.0 mol/L zinc nitrate solution.

2.2. Synthesis of catalysts

A series of ternary Cu/ZnO/Al$_2$O$_3$ catalyst samples were prepared by co-precipitation method using the above primary solutions. The mixed copper, zinc and aluminum nitrate solutions (Table 1) and a solution of Na$_2$CO$_3$ as a precipitant were pumped into a stirred and heated glass reactor containing 250 ml of demineralized water. During precipitation process, the metal nitrate solution was pumped continuously at a constant flow rate, while the temperature was controlled. The sodium carbonate solution was added with controlled flow rate to maintain a constant pH = 6.5, monitored by a CONSORT R305 pH meter. The precipitation was stopped when 2.0 l of metal nitrate solution was added. The resulting precursor was aged until a pH drop along with a color change from blue to green was observed. After aging, the precipitate (copper-zinc hydroxycarbonate precursors) was filtered, washed and then dried overnight at 105 °C. The amount of residual sodium in the catalyst was checked by the analysis of decanted water from the last washing step for sodium content which was typically below 60 ppm. Finally, the dried precipitate was calcined at 320 °C in a tubular furnace under air flow for 3.5 h (3 °C/min). The catalyst names and their initial constituent mixed copper, zinc and aluminum solution are given in Table 1.

2.3. Catalyst characterization

Nitrogen adsorption/desorption measurements were carried out using a NOVA Quantachrome 2200 High-Speed Gas Sorption Analyzer, version 7.11. Before analysis, the samples were pretreated under N$_2$ gas flow at 150 °C for 1.5 h. The isotherms were recorded at 77 K. The BET surface area was calculated from multipoint adsorption data in the relative pressure interval from 0.05 to 0.25. The total micropore and mesopore volume (V_p) was determined using the t-plot method [27]. The pore size distribution of the catalysts was determined by the BJH model applied to the adsorption branch of the isotherms.

X-ray diffraction (XRD) patterns of calcined catalysts were recorded on a BrukerD8 Advance X-ray diffractometer using Ni filtered CuKα_1 radiation. The diffraction patterns were collected in the 2θ range from 10° to 70°. The crystallite size of CuO in calcined catalyst was estimated from the full width at half maximum (FWHM) of the basic CuO XRD peaks [2θ = 38.8°, (111) + (200)] using the Scherrer equation (Eq. (1)).

$$Crystallite\ Size\,(nm) = \frac{k\lambda}{\beta cos\theta} \tag{1}$$

where k is a constant which is 0.9 for spherical particles, λ X-ray wavelength (1.5406 Å), and β is the FWHM in radians.