



Methanol synthesis catalyst manufacturing using the green solid-state method

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ABSTRACT

In this research study, methanol synthesis catalysts were manufactured with various mole ratios of metal carbonates (zinc, copper and aluminum carbonate) and ammonium hydrogen carbonate via a green solid-state method that employed a ball mill apparatus. Some parameters for the catalyst preparation, such as Al mole percent, Cu/Zn mole ratio, rotations milling speeds and aging time, were optimized to obtain the maximum catalyst activity. The prepared catalysts were compared with the best quality industrial catalyst under the same temperature and pressure condition in a titanium tabular fixed bed reactor. This novel method has many advantages in comparison to the conventional method. The main advantage of the solid-state method is that the methanol synthesis catalyst can be produced without using solvent. Furthermore, this new method reduces operating costs due to the elimination of the filtration and washing steps. Methanol synthesis catalytic activity was maximized at an optimized mole ratio of Cu/Zn of 1.9234 and an Al mole percent of 8 at the maximum grinding speed (450 rpm) during an aging time of 30 min, which showed higher activity (240 gCH₃OH/kg cat.h) in comparison with an industrial catalyst sample (218 gCH₃OH/kg cat.h). The production of a green catalyst, which requires less water and results in higher catalyst activity, can be widely used for methanol synthesis catalytic applications.

1. Introduction

Methanol is the most important chemical feedstock used in chemical industries. Cu/ZnO/Al₂O₃ catalysts are chosen for methanol synthesis from syngas containing a CO, CO₂ and H₂ gas mixture [1]. A ternary Cu/ZnO/Al₂O₃ catalyst is extensively used in commercial productions [2], steam reforming [3], the production of propylene from methanol [4] co-precipitation [5], impregnation [6], and sol-gel [7]. Solid state methods are employed for the preparation of methanol synthesis catalysts [8]. Cu/ZnO/Al₂O₃ catalysts were prepared by the co-precipitation method for methanol synthesis which was considered an important

industrial preparation method after the publication of a key patent relating to ICI in 1968 [9]. There have been a number of patents in regard to methanol synthesis catalysts and its characterization in past decades [10-13]. Cu/ZrO₂ catalysts are considered to be the most profitable catalyst due to their high activity and stability from the hydrogenation of CO/CO₂ gases [14]. In another study, Nitta and coworkers showed that an amount of zinc oxide was essential for promoting copper dispersion and catalyst activity of the copper-based catalyst [15]. Many researchers reported that the addition of a suitable promoter to the copper-based catalysts increased the catalyst activity and specific surface area [16-18]. However, the promoted catalyst with

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zirconium and magnesium oxides showed a high initial activity among the other metal oxides [19,20]. In fact, the copper/zinc-based catalysts with promoters like Ce [21], Ga [22], Mn [23], Zr [24] and Si [25] beneficially affected the copper dispersion, catalytic activity and stability. Another group of researchers led by Meshkini et al. improved the activity of the methanol synthesis catalyst by the addition of different promoters like Mg, Ca, chromium or zirconium oxides to the Cu/ZnO/Al₂O₃ catalysts in which the Mg promoter enhanced the catalyst activity [26]. The composition of the precursor phases has a strong influence on catalytic properties and its final catalyst activity [27-31]. Alternatively, Rosa site and Aurichalcite phases that form in the oxidation zones during the period of aging time improved the methanol catalyst activity [32]. The pH of the solution, aging temperature and time had a significant influence on the formation of precipitates during the preparation [33]. Aging and calcination temperature played an important role on physicochemical properties to control the quality of the catalyst [34-36]. In most conventional catalysts, sodium carbonate or sodium bicarbonate are used as the precipitant agents, which requires at least three-stage washing with large amounts of hot distilled water for removing the sodium. Therefore, this method was not economical [21]. Shi et al. prepared a Cu-ZnO catalyst via a solid-state combustion method with the mixture of metal nitrates and citric acid [37]. CuO/ZnO/ZrO₂ catalysts were prepared by using the solid-state method between hydrated metal salts and citric acid [37]. In the present study, ternary Cu/ZnO/Al₂O₃ catalysts were prepared by the solid-state method at various rotation milling speeds, Cu/Zn mole ratios, and Al mole percents. Then, the prepared catalysts were investigated and compared with the best quality industrial catalyst to improve the methanol production. In this new method, the washing step was eliminated due to the reduction in water consumption and pollution as well as implementation time. The aim of the present work was to investigate the effect of this new solid-state technique on the catalyst's performance.

2. Materials and methods

2.1. Design of experiments

Experimental design is a well-known statistical technique. A factorial design is a method consisting of two or more factors that allow the researcher to determine the effect of several factors on the response [38,39]. In this study, the factorial method was chosen to optimize the preparation parameters by employing MINITAB software that reduced the time, the number of experiments, and the process cost. Table 1 lists the catalyst preparation conditions through the green solid-state method.

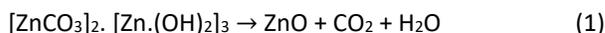
Table 1. Catalysts preparation condition by green solid-state method

Catalytic samples	Aging time (min)	Rotation milling (rpm) speed	Al Mole %	Mole Ratio Cu/Zn
1	120	300	8	1.83
2	420	300	8	2.5
3	420	300	15	1.83
4	120	300	15	2.5
5	420	450	8	1.83
6	120	450	8	2.5
7	120	450	15	1.83
8	420	450	15	2.5

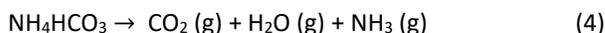
The samples were designed as a number of tests under various preparation conditions for all of the Cu/ZnO/Al₂O₃ catalysts.

2.2. Materials

The blue-green copper (II) carbonate solid (65%) was made from CuCO₃. Cu (OH)₂, white zinc (II) carbonate crystal (23%) were made from [ZnCO₃]₂ with [Zn.(OH)₂]₃ as an active site (Sigma-Aldrich, USA) and aluminum (III) carbonate Al₂(CO₃)₃ (12%) as a thermal stabilizer (Meryer, Shanghai). In this new method, ammonium hydrogen carbonate with the formula NH₄HCO₃ (Sigma-Aldrich, USA) was used in place of the sodium carbonate or bicarbonate which is utilized in the conventional method. Theoretically, metal carbonates can be converted into metal oxides, carbon dioxide and water by the following three reactions:



Ammonium hydrogen carbonate naturally decomposes via the following reaction:



These reactions are endothermic. Therefore, heat must be supplied in order to maintain the optimum reaction temperature; the heat can be provided through ball mill rotation at room temperature and ambient pressure.

2.3. Catalyst preparation

A series of ternary Cu/ZnO/Al₂O₃ samples were prepared by using the green solid-state method from their solid carbonate salts. Firstly, 25 grams of metal carbonates were mixed with ammonium hydrogen carbonate, and then crushed by continuous stirring in a ball mill for 10 min at a certain milling speed. After initial mixing, the component was kept at ball mill in a zirconium oxide milling jar for a long period of time. A large amount of gases such as H₂O, NH₃ and CO₂ were emitted through the decomposition of the

metals. Then, the gases were liberated by blowing air for 60 min. In this work, the filtration and washing processes were not required. After grinding, the precursors were dried overnight in a vacuum oven at 110 °C. The dried precursors were calcined in a tubular furnace under a continuous air flow at 350 °C with the temperature rising at a rate of 3 °C/min for 4 hr until the hydroxy carbonate precursors changed to a metal oxides form.

2.4. Reactor test

The methanol catalytic activity for CO/CO₂ hydrogenation was carried out in a continuous titanium tubular flow fixed-bed reactor. 5.2 grams of catalyst particles (16-25 mesh size) was loaded between two layers of silicon carbide in the reactor. The reaction conditions were 50 bar, 240 °C, and a space velocity of 6000 hr⁻¹ with a mixture of hydrogen and carbon oxides. The temperature was raised from room temperature to 240 °C under atmospheric pressure due to control of the central temperature. Thereafter, the pressure was increased consecutively to 50 bar. Prior to each run, the calcined powder was diluted before the reactor test with 2% wt silicon carbide and formed into a tablet. Then, the catalysts were pre-treated with H₂/ N₂ in a mixture of 5 to 100%vol. of hydrogen in nitrogen with a gradual increase in the percentage of hydrogen to 490 ml min⁻¹ for 10 to 14 hr at atmospheric pressure. The catalysts were kept overnight in order to complete the reduction. The composition of the syngas (mole percentage) is given in Table 2.

Table 2. The composition and flow rate of the feed gas

Component	Mole (%)	Flow rate (ml/min)
CO	6	15
CO ₂	6	15
H ₂	88	220

The reactor effluent was analyzed by on-line gas chromatographs equipped with a thermal conduction detector (TCD) for the analysis of CO and CO₂ as well as a flame ionization detector (FID) for the analysis of methanol. The reactor stream was analyzed after 1 hr, which was enough to reach a steady state. The methanol activity was calculated and compared with the best quality industrial catalyst under the same industry operating conditions. The methanol activity was expressed by space time yield.

3. Results and discussion

3.1. Role of solid state method for catalyst preparation

In the preparation of a conventional catalyst, a buffer solution such as sodium carbonate or bicarbonate is added drop-wise into the solution of metal carbonates to adjust the slurry pH in the range 7 to 7.5. The precipitate is then filtered out and washed three-times with hot distilled water

to remove the sodium after the aging time. Otherwise, the impurity would produce alcohols after calcinations in the reactor. Still, the water consumption remains high enough to cause environmental problems. In addition, the conventional co-precipitation method runs at a high temperature and is mixed at a desired pH value which requires additional instrumentation for controlling pH by adjusting the flow rate. The new method offers many advantages over the conventional co-precipitation method such as using less energy and time due to the elimination of the washing and filtration steps. The conventional catalyst is usually made by either the co-precipitation of metal salts (nitrate, sulfate, or acetate) or the impregnation of metal salt [40], but metal carbonates have been used in this novel method. Baoshan and coworkers have shown that the absence of sodium carbonate reduced the concentration of methyl formate in the liquid-phase methanol synthesis process [41]. In this new method, ammonium hydrogen carbonate with the formula NH₄HCO₃ was used instead of sodium carbonate or bicarbonate for solving the negative effects of sodium during the reactor test. It was also possible to use different types of raw materials such as metal oxides and hydroxides or ammonium carbonate and bicarbonate as the precipitant and reducing agent in this condition. Thus, we suggest this new method for methanol synthesis from syngas using a Cu/ZnO/Al₂O₃ catalyst by means of metal carbonates with ammonium hydrogen carbonate.

3.2. Factorial experiments

Figure 1 shows the effect of the preparation parameters on the activity of the prepared samples to achieve the optimized preparation condition. A significant increase in catalyst activity or space time yield was observed, denoted by the letter y, with a decreasing aging time from 120 to 30 min. The catalytic samples with a Cu/Zn mole ratio of 1.9234 and an Al mole percent of 8, which were aged for 30 min, gave the best catalyst activity (240 gCH₃OH/kg cat.h) at the maximum rotation milling speed (450 rpm).

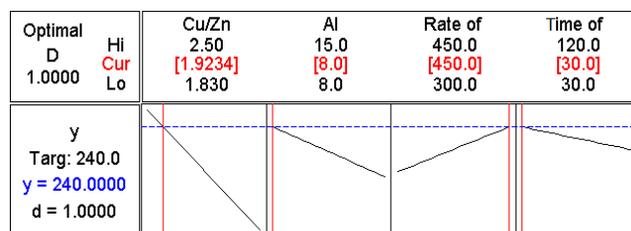


Fig. 1. Effect of preparation parameters on catalyst activity

Figure 2 presents the space time yield of methanol at the fixed aging time (120 min) and milling speed (450 rpm) versus different mole ratios of Cu/Zn and Al mole percent. The methanol activity or space time yield increased to 220 grCH₃OH/ (kg cat.hr), which showed even better results than the industrial catalyst.

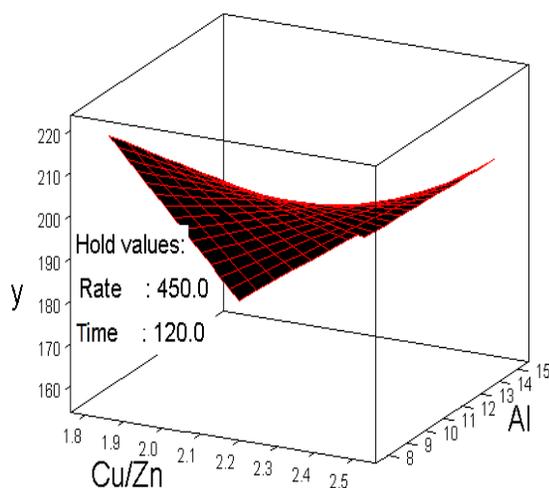


Fig. 2. Methanol catalyst activity at various Al and Cu/Zn mole ratio at certain condition (rotation milling speed: 450 rpm, aging time: 120 min).

3.3. Activity test

All catalysts were compared with the best quality commercial catalyst, which was purchased from Merck, Germany. Table 3 shows the space time yield (catalyst activity) of the reactor test for all samples in comparison to the commercial catalyst. The highest catalyst activity was observed at 218 g CH₃OH/kg cat.hr, while the commercial catalyst displayed the same value. But catalyst 4 was about 45% lower in comparison with catalyst 5 and the commercial catalyst. Table 4 shows the catalyst condition with the best performance, which was optimized by the fractional factorial results of eight primary catalytic samples. This new catalyst exhibited higher activity (space time yield) than the commercial catalyst. The process employed in the present work was particularly useful because it offered a faster start-up than the conventional catalyst.

Table 3. Final result of reactor test in comparison with commercial catalyst

Experiment	1	2	3	4	5	6	7	8	Commercial catalyst
Space time Yield (gCH ₃ OH/kgcat.hr)	204	195	194	124	218	135	198	202	218

Table 4. The optimized condition and final result of reactor test for preparing best catalyst

Experiment	Aging time (min)	Grinding speed (rpm)	Al Mole %	Cu/Zn Mole Ratio	Space time Yeild (gCH ₃ OH/kg cat.h)
9	30	450	8	1.93	240

4. Conclusions

A series of Cu/ZnO/Al₂O₃ catalysts were prepared with metal carbonate salts and ammonium hydrogen carbonate by using the solid-state method in a ball mill at different preparation condition. Aging time, rotation milling speed, Cu/Zn mole ratio, and Al mole percent were the influential parameters that affected the activity of the ternary Cu/ZnO/Al₂O₃ catalyst for the hydrogenation of syngas to methanol. The methanol activity of the optimized catalyst showed the highest activity (240 gCH₃OH/kg cat.hr) in comparison to the commercial catalyst (218 gCH₃OH/kg cat.hr) that was prepared by the conventional co-precipitation method. The mechanical milling method employed in the preparation of the methanol catalyst was considered as a low-cost (saving energy) and simple method (saving time) in which the washing steps by hot water was eliminated. Also, this novel method was wastewater free and can be categorized as a green reaction. This method

was highly effective for the production of methanol from dry precursor salts.

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