The Influence of Temperature and Pressure Variation on the Reactivity of Multimetallic-Zeolite Hybrid Catalyst for Methanol Synthesis from Carbon Dioxide

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Abstract. The potential of Cu/Zn/Al/Zr – ZSM-5 zeolite hybrid catalyst, prepared by using the newly-improved technique, namely ultrasonic spray precipitation (USP) is being explored in converting CO2 into methanol. In this study, the effect of reaction temperature (400–560K) and pressure (20–50 bar) towards catalytic activity were investigated. This technique had influenced the formation of ultrafine particles (75 nm) with relatively high BET surface area (167 m² g⁻¹) and both Cu surface area (12.5 m² g⁻¹) as well as Cu dispersion (8.88 %). TPD profile of H2 and CO2 revealed that this catalyst possess a multiple adsorption states at low (353–383 K) and high (653–858 K) temperature region. Reactivity – wise, an increment of pressure had improved the CO2 conversion and methanol selectivity with maximum value of 35.5 % and 28 %, respectively. In contrast, the exothermic nature of CO2 hydrogenation reaction had retarding both CO2 conversion and methanol selectivity at temperature higher than 523 K with the highest value for both were 36.3 % and 20.7 %, respectively.

1. Introduction

Issues on global warming that associated with man-made CO2 emission have attracted considerable attention as the current global concentration of CO2 has reached an alarming level of 400 ppm [1]. The area of CO2 mitigation and sequestration has progressively being explored to overcome such problem. The idea of consuming CO2 by means of catalytic hydrogenation reaction process to form valuable chemicals such as methanol and dimethyl ether is considered to be a promising one [2]. Catalyst development for this reaction constitutes a major challenge due to thermodynamic limitation [3], therefore a modified copper-based catalysts are found to be feasible to catalysed the reaction [4].

While much attention have been given in optimizing the catalyst formulation particularly on the elemental composition aspect, preparation technique has also becoming an important scope of studies in recent years based on the fact that the nature of precursors during catalyst formation step play a critical role in the final structure and catalytic performance [5]. Co-precipitation is regarded as the most common and widely used technique in producing multi- elemental catalysts. Despite of its proven effectiveness, different preparation techniques could be explored to overcome some potential weaknesses possessed by conventional drop-wise titration of co-precipitation method. Critical catalyst microstructural...
properties such as surface area, pore size and its volume, as well as accessible active sites that determined the activity, selectivity, deactivation resistance and durability are among of the subjects to be improved by adopting unconventional preparation methods. Some studies have employed sol-gel method that improved the total and metal surface area that lead to high activity [11], while others have claimed better elemental distribution when employed the co-precipitation-deposition method under ultrasound irradiation [6-8].

In the present study, an improvised technique namely Ultrasonic Spray Precipitation (USP) was employed. In this technique, metal precursors solution was introduced into the precipitant by spraying action under ultrasonic irradiation rather than conventional drop-wise titration. From the thermodynamic point of view, particle size of the dried precipitate is significantly influenced by the generation rate as well as growth rate of the crystal nucleation, which also related with the super-saturation state of the solution [9]. Hence, in order to dictate the formation of uniform and ultrafine particles, a large numbers of crystal nucleus should be generated and grown simultaneously. This only can be achieved by providing a micro-droplet precursors to be reacted with precipitant. The physicochemical properties of prepared catalyst were characterized by SEM, BET surface area, N₂O chemisorption, H₂-TPR, CO₂-TPD and H₂-TPD analyses while the catalytic performance in CO₂ hydrogenation reaction at various temperature and pressure were tested using a fixed-bed reactor.

2. Methodology

2.1. Catalyst Preparation

In hybrid catalyst formulation, it comprises of two functional components, namely the methanol synthesis (MS) and the methanol dehydration (MD) catalyst. MS catalyst is a modified formulation based on the similar elemental component to that of an industrial methanol synthesis catalyst comprising copper, zinc and aluminum with an addition of zirconium while ZSM-5 zeolite is served as the MD catalyst. The elemental composition of Cu:Zn:Al:Zr was kept at 4:3:1:2 ratio while ZSM-5 zeolite was made equal to Cu loading.

Typically, an aqueous solution mixture of Cu, Zn, Al and Zr nitrate was titrated into Na₂CO₃ solution that contained a pre-dispersed ZSM-5 zeolite. In USP technique, the introduction of metal nitrate solution into Na₂CO₃ – ZSM-5 zeolite mixture was by means of spraying action using the customized apparatus setup (Figure 1). Pneumatic spraying tool (0.3 mm nozzle) dispersed the metal precursor solution into micro – size droplets. A controlled pneumatic supply ensures an appropriate impact momentum of the sprayed droplets as well as constant precursor delivery. The mixing chamber was submerged in thermostatic bath with ultrasonic generator (37 kHz) that provide heat and ultrasonic energy in assisting the mixing and precipitation process. During precipitation, temperature and pH were maintained at 333 K and 7.0, respectively. The precipitate was aged for 3 h and then filtered and washed multiple times with deionized water. Subsequently, it was dried overnight at 388 K, crushed and sieved (45 – 63 μm), and calcined in air at 623 K for 4 h. The synthesized catalyst was denoted as “CZAZ-Z”.

![Figure 1. Ultrasonic Spray Precipitation (USP) apparatus setup. (A) metal precursors feed (B) pneumatic inlet (C) ultrasonic generator (D) precipitant – zeolite mixture](image-url)
2.2. Characterization of Catalysts

The visual surface morphology of catalyst was investigated using FEI Quanta FEG 650 FE-SEM at an accelerating voltage of 15 kV and working distance at 6.6 mm with LFD detector. The structural analysis was performed using Micromeritics ASAP 2020 which based on multipoint nitrogen adsorption-desorption principle. Prior to analysis, sample was degassed at 423 K for 3 h. The bulk surface area was calculated using the Brunauer-Emmett-Teller (BET) method.

The measurement of Cu surface area and dispersion were carried out by method namely dissociative N2O adsorption using Micromeritics Autochem II 2920 instrument. The catalyst sample (50 mg) was firstly pre-treated with pure He flow (50 ml/min) at 393 K for 10 min before being reduced in a 10 % H2–Ar (50 ml/min) at 603 K. The amount of H2 consumption was denoted as X. Then the reduced sample was cooled to 338 K under He purging. N2O was then introduced to the sample (85 ml/min) for 1 h to ensure complete oxidation of metallic Cu. The excess N2O was flushed out with He while cooling to ambient temperature. Finally, the reducing gas was introduced again at 603 K and the respective H2 consumption was denoted as Y. Determination of Cu surface area and dispersion were calculated by the Equations (1) and (2):

\[
D_{\text{Cu}} = \frac{2Y}{X} \times 100\%
\]

\[
S_{\text{Cu}} = \frac{2\eta H_2 \times NA}{1.4 \times 10^{19} \times W} \text{ (m}^2 \text{g}^{-1})
\]

where \(D_{\text{Cu}}\) is the Cu dispersion, \(W\) is the catalyst weight, \(S_{\text{Cu}}\) is Cu surface area per gram catalyst, \(\eta H_2\) molar number of consumed H2, \(NA\) is Avogadro’s constant \((6.23 \times 10^{23} \text{ atoms mol}^{-1})\), and \(1.4 \times 10^{19}\) is the number of Cu atoms per square meter.

2.3. Catalyst Reactivity

The catalytic reactivity at different temperature and pressure conditions were tested in a micro-tubular fixed–bed reactor (9 mm i.d. x 300 mm). Prior to each test, 250 mg of catalyst sample was loaded between two layers of quartz wool on the 20 microns inner porous plate bed. It was firstly reduced at 503 K in H2 flow for 1 h. After purging, the reacting gases (CO2/H2/He at 1/3/2 ratio and 10,000 h-1 GHSV) were continuously fed into the reactor at a desired temperature and pressure. The product stream was analysed after 5 h reaction time by an on-line gas chromatography (GC) equipped with multi–column (DB-1, Hayesep Q and Molsieve) separation system connected to TCD and FID detector. The CO2 conversion and product selectivity were calculated by an internal standardisation method.

3. Results and Discussion

3.1. Physicochemical Properties

Surface morphology of the catalyst was investigated using SEM (Figure 2). It can be observed that this catalyst possesses a uniform, dense-stacking structure and considerably finer particles. Furthermore, less agglomeration can be noticed whereby an individual spherical-shape particles were fairly distributed and well-covered by much finer ZSM-5 zeolite particles without compromising the porosity of the structure to ensure high surface area. These morphological characteristics were believed be the effect of ultrasonic irradiation action during co-precipitation stage that favours a better mixing effect among precursors which also enhancing their distribution onto the zeolite framework [9]. This is based on the fact that sono-crystallization induces rapid nucleation that generally yields smaller crystals of a more narrow size distribution [10].
These morphological findings were supported by crystallite size (dc) determination based on Scherrer Equation (Table 1) which revealed a lowly 75 nm. In line with this trend, the bulk surface area (SABET) also shown a remarkable value of 167 m²g⁻¹ which comparable with typical methanol synthesis catalysts [16]. Based on the fact that copper species is the active metal for this catalyst, its accessible surface area (SAcu) and dispersion (DCu) would be really critical in determining the reactivity during reaction. Both parameters were notably high considering a copper content in the catalyst sample was only about 20 % (w/w).

| Sample  | SABET (m² g⁻¹) | SAcu (m² g⁻¹) | DCu (%) | dc (nm) |
|---------|----------------|---------------|---------|---------|
| CZAZ-Z  | 167            | 12.52         | 8.88    | 75      |

3.2. Reactivity

Methanol synthesis via rich CO₂ feedstock proceeds with this main reaction (1):

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$  \hspace{1cm} (3)

$$CO_2 + H_2 \rightarrow CO + H_2O$$  \hspace{1cm} (4)

However, the typical copper-based catalysts are less active due to thermodynamic limitation associated with more stable CO₂ [13]. Based on thermodynamic theoretical calculations [11], when the reactants contain only CO₂, the equilibrium yield of CO has always a positive value, implying that CO is an inevitable product through reverse water gas shift (RWGS) reaction (2).
As the reaction proceeds further, CO formation may change its direction of reaction (2). Under such conditions, CO$_2$ becomes a reactant of reaction (1) and a product in reaction (2). Hence the CO equilibrium constant becomes a negative value, implying that some CO are converted into CO2 and further hydrogenated to methanol. This competing reaction could reduce methanol selectivity while adding more CO and H$_2$O by-products [11]. Therefore, the Cu-Zn- Al-Zr–ZSM5 zeolite hybrid catalyst prepared by USP technique in this study had shown promising results in terms of its reactivity towards both reaction temperature and pressure effects.

Figure 3 illustrates the CO$_2$ conversion and methanol selectivity trend when the reaction was subjected to temperature variation (at 30 bar). The conversion of CO$_2$ increases at lower temperature range between 470 – 520 K and begin to fall beyond 520 K after reaching the highest value of 36.3 %. So does the methanol selectivity which start to decrease after 500 K at 20.7 %. A previous study concluded that hydrogenation of CO$_2$ on copper-based catalysts is faster and begin at low temperature [12,13]. Inversely, an opposite trend was observed during pressure-dependent reactions (at 500 K). Between 20 – 50 bar range, both CO2 conversion and methanol selectivity increased progressively and peaked at 35.5 % and 28 %, respectively. Analysis of by-products (H$_2$O and CO) revealed that RWGS reaction generally remain dominant over the main reaction, resulting in high CO selectivity (above 60 %) in the product stream. However, based on the above trends, CO$_2$ conversion and methanol selectivity could be increased by applying reaction pressure beyond 50 bar (at T < 520 K) while also inhibiting CO selectivity at certain extent.

4. Conclusions
The introduction of ultrasonic spray titration (USP) technique has improved the multi-elemental interaction as well as particle formation of the catalyst during the precipitation stage of preparation. It leads to a finer and more uniform particles that contributed to a better reducibility, gas adsorption–desorption characteristics, total bulk surface area as well as an accessibility of active metal sites. Reactivity wise, CO$_2$ conversion and methanol selectivity increases significantly with increasing pressure but decreases strongly at temperature beyond 520 K. This trend in lines with thermodynamic fact that CO$_2$ reaction is exothermic, thus favours high pressure and low temperature condition.

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