Synthesis and Characterization of Hybrid Catalyst on SBA-15 Support for CO₂ Hydrogenation Reaction

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Abstract. Mesoporous silica (SBA-15) was prepared using P123, hydrochloric acid (HCl) and tetraethyl orthosilicate (TEOS). Hybrid catalysts comprising Cu/ZnO/Fe/K/Rh and Cu/Al/Fe/K/Rh on SBA-15 support were prepared by a wet impregnation method. The morphology and surface area of catalysts were characterized by using field emission scanning electron microscopy (FESEM) and Brunauer-Emmet-Teller (BET) techniques, respectively. These catalysts were evaluated in a microactivity fixed-bed reactor for CO₂ conversion at 3 MPa, 523.15 K and gas flow rate of 48 ml/min. The Cu/ZnO/Fe/K/Rh and Cu/Al/Fe/K/Rh hybrid catalysts were tested at two different GHSV. The lower GHSV of 5760 ml/g.hr exhibited higher CO₂ conversion of 6.21% and 6.92% as compared to those of higher GHSV of 14,400 ml/g.hr with 1.21% and 2.22% CO₂ conversion.

1. INTRODUCTION

The discovery of mesoporous silica material has showed an interesting application in sensor design, drug delivery, optical devices, separation and catalysis whereby its well-ordered structure and high surface area can allow the accessibility of active materials to be attached through the channel [1]. The ease in structure functionalization and ability to control the pore size further enhances its versatility that can be suited in different applications. To date, there is a variety of highly ordered mesoporous silica materials that is being used as a catalyst support and one of them is SBA (Santa Barbara USA). SBA-15 is well-known for its high surface area which range from 400 – 900 m²/g and its various tunable shapes such as fibers, sponge-like membranes, rod-like powders and spheres which have arouse specific interest in catalytic applications [1], [2]. The major challenges to adopt SBA-15 as a catalyst support started from the step to control the morphology itself. This is because properties of mesoporous silica are influenced by several important factors which includes the condensation rate of silica species, shape of surfactant micelles, acidity of the solution, stirring, drying and aging rate.

Herein, we report a facile method of synthesizing hollow tubular mesoporous silica (SBA-15) with high surface area and implementing the synthesized SBA-15 as a catalyst support to form hybrid catalysts for CO₂ hydrogenation reaction.
2. METHODOLOGY

2.1. Synthesis of SBA-15
5g Pluronic 123 were dissolved in 37.5 mL distilled water in a 500 mL PP bottle and it was placed in a regulated oil bath on a hotplate stirrer. 150 mL 2M HCl solution was then added to the mixture and stirred for 3 h at 40°C. 10.625 g TEOS was added dropwise into the mixture and then stirred for 24 h at 40°C. Then the bottle containing the mixture was placed in an oven at 95°C for 48 h. The slurry was filtered and washed with 1125 mL DI water and 110 mL ethanol. The precipitate was dried overnight in an oven at 90°C, ground to fine powder and calcined at 600°C for 6 hrs [3,4].

2.2 Impregnation of metal on SBA-15
The catalysts were synthesized by wet impregnation method using either aqueous solution of copper, zinc and iron nitrates or copper, aluminum and iron nitrates with ratio of 1:1:3. The promoting agent (nitrate salt of K, Rh) was added to the solutions of Cu/ZnO/Fe and Cu/Al/Fe nitrates with the total metal loading of 15.14%. The precursor solution was added dropwise into the beaker containing SBA-15 support and stirred for a few minutes. pH was measured and altered to pH7/pH4 according to the catalyst formulation. The catalyst was stirred for 24 hr. Then it was washed with DI water and dried in an oven at 120°C for 12 hr. The catalyst was then calcined in a muffle furnace at 350°C for 4 hr.

2.3 Catalyst Characterization
Morphologies of the samples were observed on Hitachi-8020 field emission scanning electron microscope (FESEM). Surface analyzer and porosimetry system (ASAP) isotherms of the catalysts was plotted using Micromeritics ASAP 2020 to analyze their surface area and pore size distribution. 0.3 g of catalyst was degassed in liquid nitrogen at temperature of 77.0 K for 4 h before being analyzed. Their specific Brunauer, Emmett, and Teller (BET) surface areas and Barret-Joyner-Halenda (BJH) pore size distributions methods were obtained via nitrogen adsorption-desorption isotherms.

2.4 Catalyst Performance Evaluation
Catalyst performance evaluation was performed in a micro-activity fixed bed reactor (Microactivity Reference PID-Eng). Prior to reaction, 0.2 g of calcined catalyst was reduced in 5 vol% of H2 in Argon gas at 20 mL min−1 and 523 K for 4 hours. The hydrogenation reaction was performed at 3 MPa, 523.15 K, and the gas feed ratio of CO2 to H2 was 1:3 with total flow rate of 48 mL/min for 5 hours. The reactor effluents were analyzed by gas chromatograph (Agilent 6890) equipped with TCD detector for analysis of H2 and CO2, and with FID detector for alcohols and other hydrocarbons analysis [5]. CO2 conversion, products selectivity, space time yield and yield were calculated using Eq. 1 2, 3,4 respectively.

\[
CO_2 \text{ conversion (\%) = } \frac{\text{Mole of CO}_2 \text{ in} - \text{Mole of CO}_2 \text{ out}}{\text{Mole of CO}_2 \text{ in}} \times 100\% 
\]

(1)

\[
Product \text{ selectivity (\%) = } \frac{\text{Mole of product } X \text{ produced}}{\text{Total mole of products}} \times 100\% 
\]

(2)
Space time yield (STY) = \frac{\text{Moles product } X \times V_{CO_2} \times MW_{\text{product } X}}{\text{moles}_{CO_2 \text{in}} \times \text{total amount of catalyst} \times MV} \quad (3)

*Where $V_{CO_2}$ is the CO$_2$ volumetric flow (mL/min), $MW_{\text{product } X}$ is the molecular weight of product (g/mol) and MV is the molar volume of ideal gas, 22400 mL/mol.

\[
\text{Yield} = \text{Conversi} \times \text{Selectivity} \quad (4)
\]

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GHSV = \frac{\text{Volume of feed gas } \left( \frac{\text{mL}}{\text{h}} \right)}{\text{Total amount of catalyst } (g) \times \text{hour } (h)} \quad (5)
\]

3. RESULTS AND DISCUSSION

3.1 Morphological and Textural Properties of Sample

FESEM images with 5000 magnification of SBA-15, Cu/ZnO/Fe/K/Rh/SBA-15 and Cu/Al/Fe/K/Rh/SBA-15 are shown in Figure 1. Based on FESEM analysis, there is no significant difference observed for bare support and the hybrid catalysts. The samples exhibit short rods with capsule like morphology, similar to that reported by Wang et al. [6].

![FESEM image of sample](a)
Figure 1. FESEM images of (a) SBA-15, (b) Cu/ZnO/Fe/K/Rh/SBA-15, (c) Cu/Al/Fe/K/Rh/SBA-15

The textural properties such as the catalyst surface area (SBET), pore volume (VP) and pore diameter (DBJH) are shown in Table 1. It is typical for catalyst support like mesoporous SBA-15 silica material to have relatively large BET surface area [7]. However, the surface areas were found to decrease to 548.70 m²/g and 394.51 m²/g, respectively in the presence of Cu/ZnO/Fe/K/Rh and Cu/Al/Fe/K/Rh as compared to the unloaded SBA-15 of 596.99 m²/g. The decrease in the surface areas might be due to partial blockage of the pores by the loaded metallic species [8]. It was observed that, the BET surface area and pore diameter decreased signifying the active metals filling the empty pores. Meanwhile, the pore volume is having the opposite trend although the value is invariant as the difference is only 0.01 cm³/g.

Table 1. Textural properties of the sample

| Sample                  | $S_{\text{BET}}$ (m²/g) | Mesoporous volume, VP (cm³/g) | Pore size distribution diameter, $D_{\text{BJH}}$ (nm) |
|-------------------------|-------------------------|-------------------------------|---------------------------------|
| SBA-15                  | 596.99                  | 0.01                          | 6.32                            |
| Cu/ZnO/Fe/K/Rh/SBA-15  | 548.70                  | 0.02                          | 5.71                            |
| Cu/Al/Fe/K/Rh/SBA-15   | 394.51                  | 0.02                          | 5.63                            |

Figure 2 shown nitrogen adsorption-desorption isotherm for SBA-15, Cu/ZnO/Fe/K/Rh/SBA-15 and Cu/Al/Fe/K/Rh/SBA-15. SBA-15 bare support corresponded to Type 1V isotherm and recognized as type H₂ hysteresis loop according to the IUPAC classification. This indicate that it is a mesoporous material with pores of cylindrical geometry and nonuniform pore size distributions. The Cu/ZnO/Fe/K/Rh/SBA-15 and Cu/Al/Fe/K/Rh/SBA-15 corresponded to a typical Type IV isotherm exhibiting hysteresis loop of type H1 which is associated with solids made up of agglomerates of spheroidal particles with uniform size and shape [9].
3.2 Catalyst Performance

The catalytic performance of Cu/ZnO/Fe/K/Rh/SBA-15 and Cu/Al/Fe/K/Rh/SBA-15 hybrid catalysts were tested in CO₂ hydrogenation reaction via micro-activity fixed-bed reactor at temperature of 523.15 K, pressure of 3 MPa, and feed gas volume CO₂ to H₂ ratio of 1:3. Figure 3 (a) and (b) show the activity of the catalysts by CO₂ conversion at two different GHSV. The results showed that, the lower GHSV exhibits higher CO₂ conversion for both hybrid catalysts of 6.21% and 6.92% respectively. The longer contact time of the feed gas onto the catalyst resulted in higher CO₂ conversion.

The product distribution, which is represented by selectivity obtained from CO₂ hydrogenation, is shown in Figure 4 (a) and (b). Methane was the main product for the CO₂ hydrogenation reaction in the presence of both hybrid catalysts of 69.76% and 42.27% at GHSV 5760 mL/g.h. This results are similar to that reported by Inui et al. [10]. Other products detected were methanol, methyl formate and ethanol. However, the catalyst containing Al exhibits higher methanol selectivity of 38.64% at GHSV 5760 mL/g.h as compared to that of ZnO formulation of 1.19% with the same GHSV. This preliminary result indicate that Al increased the oxygenate formation.
Figure 3. CO₂ conversion of hybrid catalysts on SBA-15 support
4. CONCLUSIONS
The synthesis and characterization of hybrid catalysts on SBA-15 support have been carried out. The catalysts performance in CO\textsubscript{2} hydrogenation reaction has been investigated. The SBA-15 support exhibits short rods with capsule-like morphology with high surface area. The loaded metal catalyst to the bare support resulted in a decrease of the BET surface area. Hybrid Cu/Al/Fe/K/Rh/SBA-15 catalyst exhibited higher activity in terms of CO\textsubscript{2} conversion as compared to that of Cu/ZnO/Fe/K/Rh/SBA-15 catalyst.

5. ACKNOWLEDGEMENTS
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