

Synthesis of CH₃OH fuel Extracted From Atmospheric CO₂

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Abstract: — As of today, CO₂ hydrogenation to methanol is a powerful alternative to renewable energy, which can mitigate both global warmings by CO₂ utilization and by reducing the usage of fossil fuels. Therefore, the conversion of CO₂ to methanol is one of the topmost research priorities all over the world. As the CO₂ sequestration process is expensive, there has been a quest for finding other alternative options. The CO₂ obtained can be converted and used to support various reactions by varying their ratios as per requirement. The catalyst Cu-ZrO₂-ZnO was preferred than Cu-ZrO₂ because of its conversion rate and stability in the reaction during the hydrogenation process.

Key words: Methanol, Cu-ZrO₂-ZnO—catalyst; Cu-ZrO₂-catalyst; hydrogenation; CO₂ sequestration; methanol selectivity.

I. INTRODUCTION

The effect of carbon emission on atmosphere has led to global warming. Removal of CO₂ from industrial sources or from the automobile emissions, with cutbacks in fossil fuel use, is essential to stabilize and possibly reduce overall CO₂ concentration in the atmosphere. Researches have been carried on capturing atmospheric CO₂ and using the same gas to convert CO₂ into CH₃OH by using various conversion methods. Among CO₂ hydrogenation products, CH₃OH is most attractive because it can be directly used as a liquid fuel for internal combustion engines and direct methanol fuel cells. Its industrial scale synthesis is based on syngas (CO, H₂, and CO₂) and Cu/ZnO/Al₂O₃-type heterogeneous catalysts under high pressure and elevated temperature (>200 °C). Similar Cu-based heterogeneous catalysts can also use solely CO₂ as a carbon source to produce CH₃OH. Besides heterogeneous catalysts, CH₃OH can be synthesized from CO₂ at mild temperature with metal-based homogeneous catalysts prepared by rational design. In this context, first CO₂ capture and subsequent conversion to fuels has started to attract considerable interest. Cu-ZrO₂-ZnO, Cu-ZrO₂ were used as catalysts. The enhanced activity of the Cu-ZrO₂ catalyst co-precipitated at lower temperatures (< ca. 320 K) by using zirconium sulfate was attributed to the increased dispersions. Therefore, the use of similar starting salts in the preparation of Cu-ZrO₂-ZnO catalysts is expected to improve the catalytic performance. In the present work, we have prepared a variety of Cu-ZrO₂-ZnO catalysts with varying compositions using different starting salts, and examined the catalytic behavior in the methanol synthesis.

II. EXPERIMENTAL PROCEDURE

Catalyst preparation: Two series of Cu-ZrO₂-ZnO catalysts, one containing 50 wt% of copper and another keeping the weight ratio of Cu to ZrO₂ at unity, were prepared by a co-precipitation method using different salts and 10% excess NaOH.

A typical procedure to do the catalyst is as follows:

An aqueous solution (25 cm³) of NaOH was rapidly added to a mixed solution of copper sulphate, zirconyl nitrate, and zinc sulphate in 100 cm³ of deionized water at 25°C while stirring vigorously. The precipitate was dried at 80°C for 15 min under gentle stirring, and then filtered and thoroughly washed with water. The precipitate was dried at 120°C for 20 h and crushed into a powder and calcinated at 210°C and the catalyst was obtained.

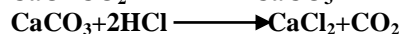
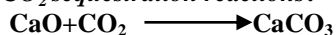
Hydrogenation procedure: The hydrogenation of CO₂ was carried out at a pressure of 9 bar using a continuous tubular flow fixed-bed micro-reactor. The catalyst sample (0.5 g) was mounted in a stainless steel reactor (i.e. = 6 mm length) and pre-reduced at 250°C for 1 h in a hydrogen flow of 100 cm³ min⁻¹ (NTP). After cooling to 140°C K the hydrogen flow was replaced with reactant gas (H₂/CO₂ = 3) flow of 40cm³ min⁻¹ (NTP) and then the pressure was increased gradually to 9bar. The reaction temperature was raised stepwise (30 min / step of 20°C) to 260°C. The product gas was analyzed at each reaction temperature by using gas chromatographs. Conversion of CO₂, typically in the range 0-20%, is defined as: (mol carbon dioxide converted to all products) / (mol carbon dioxide in the feed gas). The methanol selectivity is defined as:(mol methanol)/(mol carbon dioxide converted to all products).

CO₂ Sequestration

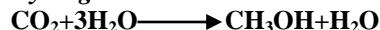
CO₂ gas sequestration was done with the usage of CaO which was exposed to automobile emission with CO₂ emission of 10%. This CaO was then subjected to AA (Atomic absorption spectroscopy) stating its closeness (i.e. =98mg/L for 100mg/L std specimen) to the standard CaCO₃ element. Then Kipp's apparatus was used to obtain the CO₂ gas; when reacted with 2M HCl solution liberating CO₂ as a bi-product. The reaction takes place as indicated in III.

III. REACTIONS

CO₂ sequestration reactions:

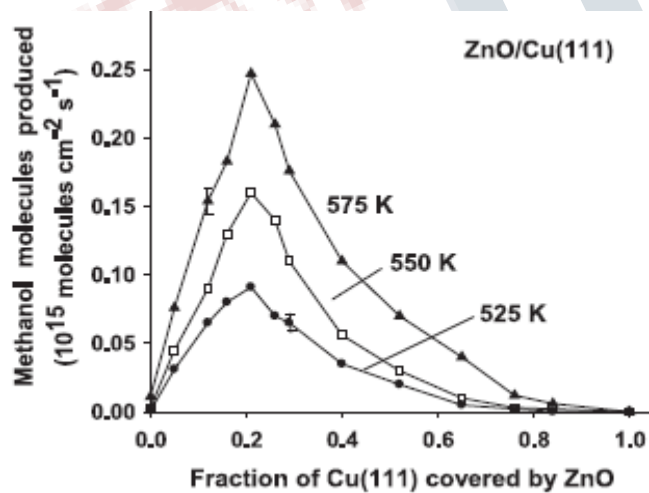


Hydrogenation reaction:

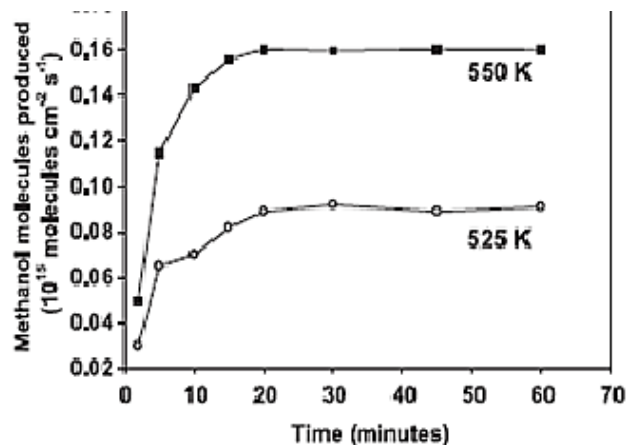


IV. TABULAR COLUMN

Fig A indicates the rate of conversion of CO₂ to methanol on Cu(111) as a function of the fraction of the metal surface covered by zinc oxide. Reaction conditions: T (temperature) = 525, 550, or 575 K; PH₂ (partial pressure of H₂) = 3 atm; PCO₂ (partial pressure of CO₂) = 1 atm.



[Fig A]



[Fig B]

Fig B indicates transformation of Zn to ZnO. Rate for the conversion of CO₂ to methanol on ZnCu(111) as a function of reaction time. Reaction conditions: T = 525 or 550 K, PH₂ = 3 atm, PCO₂ = 1 atm.

V. CONCLUSION

CO₂ gas was obtained with a yield of 42.5% using Kipp's apparatus. The catalysts used (Cu-ZrO₂-ZnO, Cu-ZrO₂) were economical & has good thermal stability. CO₂ conversion to methanol was found to be 13% max and min of 10.75%. Methanol conversion rate was good for Cu-ZrO₂-ZnO (13%). The methanol selectivity was 64% for Cu-ZrO₂-ZnO catalyst and was the best conversion rate obtained.

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