Hybrid Heterogeneous Catalysts for Hydrogenation of Carbon Dioxide

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Introduction

Anthropogenic emissions of carbon dioxide, a gas often associated with global warming, have increased considerably since the beginning of the industrial age.[1] In the U.S., stationary CO_2 sources, such as electricity generation plants, produce about one-third of the anthropogenic CO_2 generation. Reports[2] indicate that the power required to recover 90% of the CO_2 from an integrated coal-fired power-plant is about 10% of the power-plant capacity. This energy requirement can be reduced to less than 1% if the recovered CO_2 is applied to the production of synthetic fuels. However, the lack of efficient catalysts along with the costs of energy and hydrogen has prevented the development of technologies for direct hydrogenation of CO_2.[3] Although the cost of hydrogen for hydrogenating CO_2 is not economically attractive at present, the future production of hydrogen by nuclear power sources could completely change this scenario.[2] Still, an efficient catalyst will be essential for commercial application of those processes.

The objective of the work presented here was the development of hybrid catalysts for one-step carbon dioxide hydrogenation to liquid fuels. The hybrid catalysts, which were prepared by two novel techniques, included a copper/zinc oxide catalytic function distributed within an acidic zeolitic matrix. Results of catalyst activity and selectivity studies at atmospheric pressure are presented in this contribution.

Experimental

Catalysts were prepared by two novel techniques and under several different conditions to produce copper/zinc oxide/zeolite materials. Once synthesized, samples were pelletized and the fraction between 40-60 mesh was utilized for the experiments. Two hundred milligrams of catalyst were loaded in a U-tube stainless steel reactor and a flow of 100 cm^3/min of a 10:90 H_2:Ar mixture was passed through the catalyst bed while the temperature was increased from room temperature to 513 K at 1.8 K/min and held at 513 K for 15 h. A reactant gas mixture composed by 10 cm^3/min of CO_2 and 30 cm^3/min of H_2 was then passed through the catalyst bed and the reaction products monitored by on-line gas chromatographic analyses using an SRI Multiple Gas Analyzer #2 equipped with 3 columns (MoleSieve 13X, Hayesep-D, and MXT-1) and 3 detectors (TCD, FID, and FID-methanizer). This GC system allowed for quantification of inert gases, CO, CO_2, methanol, dimethylether, higher alcohols, water, and hydrocarbons up to C_{20}.

One hundred milligrams of a commercial syngas-to-methanol catalyst along with the same amount of a commercial zeolite catalyst was utilized under the same reaction conditions for comparison purposes. These catalysts were utilized either in two-layers (Com1) or mixed together (Com2).

Results and Discussion

Under the conditions applied in this study, the main reaction products were CO, CH_3OH, CH_3OCH_3, and H_2O. Methanol and dimethylether production rates and selectivities with respect to CO formation are presented in Figures 1 and 2, respectively. Although the activity of the synthesized catalysts did not surpass the commercial catalysts, the selectivity to oxygenates with respect to CO on most of the synthesized catalysts were better than on the commercial catalysts. For example, catalyst Hyb1 displayed similar methanol production rate and one order of magnitude higher selectivity to methanol than catalyst Com1. Catalyst Hyb4 and Hyb5 were prepared using the same method but under different synthesis conditions. The results confirmed the important influence of synthesis conditions on catalyst activity and selectivity.
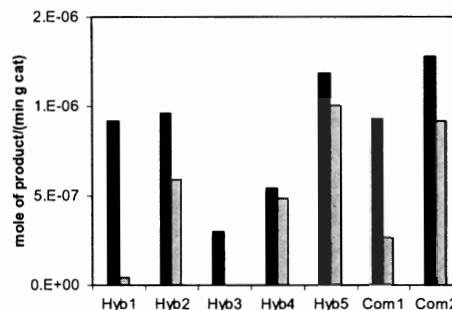

Figure 1. Production rates of methanol (black) and dimethylether (gray) at 157 min time on stream.
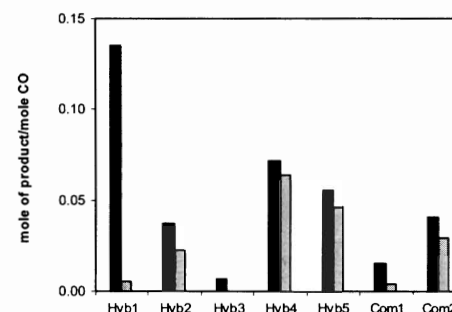

Figure 2. Catalyst selectivities for methanol (black) and dimethylether (gray) with respect to carbon monoxide formation at 157 min time on stream.

Conclusions

Novel zeolite supported copper/zinc oxide catalysts were synthesized by two different techniques and tested for the hydrogenation of CO_2. Catalyst selectivity to methanol and dimethyl ether with respect to CO was better with some of the hybrid catalysts than with a mixture of commercially available syngas-to methanol plus methanol-to gasoline catalysts.

References
(1) Xu, X. D.; Moulijn, J. A. *Energ. Fuel.* **1996**, *10*, 305-325.
(2) *Workshop Report to the Chemical Sciences Roundtable, NAS, 2001*, URL http://books.nap.edu/catalog/10153.html available on April 5, 2006.
(3) Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*(4), 953-996.