IV. DOUBLE-BED $Cs/Cu/ZnO/Cr_2O_3$ CATALYST FOR HIGHER ALCOHOL SYNTHESIS

Catalytic Testing Results

A comparison of the results of the single-bed copper-based catalyst at high temperature (described in the previous section) with the copper-free catalyst reported by Beretta et al. [1996] suggested that the former could be effectively used as the bottom bed in a double-bed configuration. The relative stability of the cesium-doped copper-based catalyst at high temperatures, along with its high selectivity toward isobutanol synthesis, indicated that this catalyst could be used to improve upon the previous double-bed experiment by increasing the isobutanol yield. Indeed, the single-bed study of the copper-based catalyst demonstrated that this catalyst was more active toward isobutanol production at lower temperatures (613 and 643K) than the copper-free catalyst at high temperature (678K). In order to maximize isobutanol production, the copper-based catalyst was utilized in a double-bed configuration. In this manner, the temperatures of the two beds of equal volume could be controlled separately in order to achieve higher isobutanol productivity. Figure 20 shows the distribution of major products at two different bottom-bed temperatures (613 and 643K). It is seen that the space time yields of these products were lower at the higher bottom-bed temperature. As a group, the linear, primary alcohols showed the strongest temperature dependence. The remaining products (branched primary alcohols, secondary alcohols, and hydrocarbons) exhibited a weaker dependence upon temperature.

Table 9 lists all of the products observed under the HAS conditions specified in Figure 20. As can be seen, at the higher bottom-bed temperature of 643K, small amounts of butanol and pentanol were also produced. CO conversion, also listed in Table 9, was disfavored at the higher bottom-bed temperature. With the bottom-bed temperature maintained at 613K, CO conversion was 8.5%, but it decreased to 6.2% when the bed temperature was increased to 643K.

This experiment shows that by modifying the double-bed higher alcohol synthesis by using the $Cs/Cu/ZnO/Cr_2O_3$ catalyst in both beds but at different temperatures, isobutanol productivity increased significantly, as did the production of methanol. When the copper-based catalyst was used as the bottom bed and maintained at 340°C, isobutanol STY was 202 g/kg cat/hr, compared to 125 g/kg cat/hr (see Table 6) when the bottom bed consisted of the copper-free catalyst at 678K, an increase of 62%. Similarly, methanol production was greatly increased by the copper-containing bottom bed, reaching a value of 574 g/kg cat/hr. Product distribution was influenced by the temperature of the copper-based bottom bed. High yields of methanol are expected at the lower reactant temperature due to equilibrium constraints at higher temperatures. Lower temperature is also expected to increase the overall productivity of the copper-based catalyst. This was

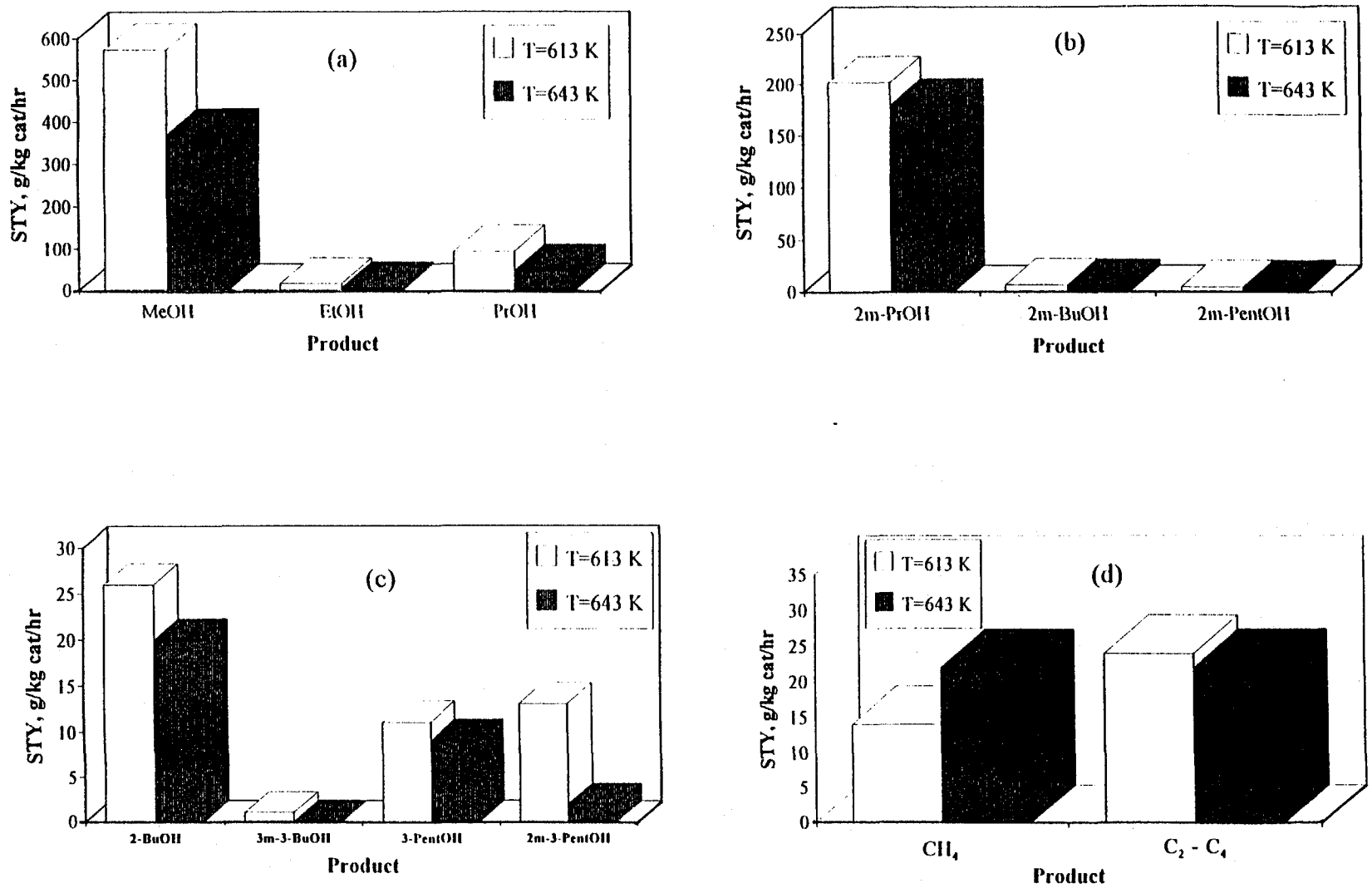

Figure 20. Product distribution over the double-bed 3 mol % Cs-Cu/ZnO/Cr_2O_3 (both beds) catalyst with $T_{top\ bed}$ = 598K, H_2/CO = 0.75 and GHSV = 18,375 l(STP)/kg cat/hr at a reaction pressure of 7.6 MPa with bottom-bed temperatures of 613 and 643K for (a) primary alcohols, (b) branched alcohols, (c) secondary alcohols, and (d) hydrocarbons.

TABLE 9. Higher alcohol synthesis over two portions of the 3 mol% $Cs/Cu/ZnO/Cr_2O_3$ catalyst held in a double-bed configuration, where the top bed (1 g) was held at 598K and the lower bed (1 g) was maintained at 613 or 643K.
The synthesis gas consisted of $H_2/CO = 0.75$ at 7.6 MPa with GHSV = 18,375 l(STP)/kg cat/hr. The productivities of aldehydes and ketones have been added to those of the corresponding primary and secondary alcohols. Abbreviations used are Me = methyl, Et = ethyl, Pr = propyl, Bu = butyl, Pent = pentyl, 2m = 2-methyl, 3m = 3-methyl, and HC = hydrocarbon.

	Top = 598K Bottom = 613K (g/kg cat/hr)	Top = 598K Bottom = 643K (g/kg cat/hr)
MeOH	574	369
EtOH	15	5
PrOH	93	47
BuOH	0	1
PentOH	0	1
2m-PrOH	202	180
2m-BuOH	7	6
2m-PentOH	5	5
2-BuOH	26	20
3m-2-BuOH	1	0
3-PentOH	11	9
2m-3-PentOH	13	2
CH_4	14	22
C_2-C_4 HC	24	22
%CO Conv. (CO_2-free)	8.5	6.2

reflected in the CO conversion level, which increased from 6.2 to 8.5% when the reaction temperature was decreased. With the copper-based bottom bed, the selectivity of isobutanol among the other 2-methyl alcohols was greatly increased, as well.

Conclusions

This study used the recently demonstrated concept of employing two sequential catalysts at different reaction temperatures to enhance the productivity of isobutanol from synthesis gas. It was shown that the $Cs/Cu/ZnO/Cr_2O_3$ catalyst could be utilized to advantage as the second-bed catalyst at 613-643K instead of the previously used copper-free $Cs-ZnO/Cr_2O_3$ catalyst at the higher temperature of 678K. High space time yields of *202 g/kg cat/hr for isobutanol* and high selectivity toward isobutanol/methanol mixtures were achieved by coupling two beds of the $Cs/Cu/ZnO/Cr_2O_3$ catalyst at different reaction temperatures in a double-bed configuration. The isobutanol/methanol mass ratios were about 0.35 and 0.5 for the lower bed temperatures of 613 and 643K, respectively. The selectivity of the isobutanol and methanol products was notable. At the lower bed temperature of 613K, 67% of the C in the products shown in Table 9 was in the isobutanol and methanol products. If n-propanol is included along with isobutanol and methanol, then 80% of the carbon found in the alcohol and hydrocarbon products was obtained in these three alcohols.

ACKNOWLEDGEMENTS

Alessandra Beretta thanks the Council for International Scholar Exchange for receipt of a Fulbright Fellowship during her stay at Lehigh University. Marie Johansson assisted in the characterization of catalysts. Maria Burcham and Marie Johansson thank Unilever Research U.S. for partial support *via* Research Fellowships. Adrian Perry contributed to the project as a summer undergraduate researcher.

Present addresses of co-workers on this research project are:

Dr. Alessandra Beretta, Dipartimento di Chimica Industriale e Ingegneria Chimica "G. Natta," Piazza Leonardo da Vinci 32, Politecnico di Milano, 20133 Milano, Italy.

Maria Burcham, Department of Chemistry, S. B. Mudd Bldg., 6 Packer Avenue, Lehigh University, Bethlehem, PA 18015.

Dr. Yeping Cai, Zettlemoyer Center for Surface Studies, Sinclair Laboratory, 7 Asa Drive, Lehigh University, Bethlehem, PA 18015.

Dr. Marie Johansson, STC Technolgies, Inc., 1745 Eaton Avenue, Bethlehem, PA 18018-1799.

Dr. Biswanath Roy, Department of Chemical Engineering, Iacocca Hall, 111 Research Drive, Lehigh University, Bethlehem, PA 18015.

Dr. Qun Sun, Dupont CR&D, Experimental Station, P.O. Box 80356, Wilmington, DE 19880-0356.

LIST OF PUBLICATIONS TO-DATE

- **Publications Based on the Research Carried out During this Project**:

"Higher Alcohol Synthesis Over Cs-Doped Cu/Zn/Cr Oxide Catalysts: Effect of Reaction Temperature on the Product Distribution and Catalyst Stability," A. Beretta, Q. Sun, R. G. Herman, and K. Klier, Preprints, Div. Fuel Chem., ACS, **40(1)**, 142-147 (1995).

"Synthesis of 2-Methylpropan-1-ol/Methanol Mixtures From H_2/CO Synthesis Gas Over Double-Bed $Cs/Cu/ZnO/Cr_2O_3$ and $Cs/ZnO/Cr_2O_3$ Catalysts," A. Beretta, Q. Sun, R. G. Herman, and K. Klier, J. Chem. Soc., Chem. Commun., 2525-2526 (1995).

"Catalytic Synthesis of Methanol, Higher Alcohols and Ethers," K. Klier, A. Beretta, Q. Sun, O. C. Feeley, and R. G. Herman, in "*Proc. of the Workshop on Environmental Catalysis: The Role of IB Metals*," Osaka, Japan, Osaka National Research Institute, AIST-MITI, 6-15 (1995).

"Production of Methanol and Isobutanol Mixtures Over Double-Bed Cs-Promoted $Cu/ZnO/Cr_2O_3$ and ZnO/Cr_2O_3 Catalysts," A. Beretta, Q. Sun, R. G. Herman, and K. Klier, Ing. Eng. Chem. Res., **35**, 1534-1542 (1996).

"Surface Acidity (Brønsted and Lewis) by High Resolution X-Ray Photoelectron Spectroscopy," M. Johansson and K. Klier, Catal. Lett. (1996); in press.

"High Pressure Methanol Synthesis Over Zirconia Supported Copper Catalysts," Y. Cai, M. M. Burcham, B. Roy, R. G. Herman, and K. Klier, J. Catal., manuscript under revision.

"Higher Alcohol Synthesis Over Cesium-Promoted $Cu/ZnO/Cr_2O_3$ and ZnO/Cr_2O_3 Catalysts in a Double Bed Reactor Configuration at High Temperatures and Pressures," M. M. Burcham, Y. Cai, R. G. Herman, and K. Klier, Ing. Eng. Chem. Res., manuscript under revision.

- **Recent Publications Resulting From the Ether Synthesis Research carried out during the Previous Research Period**:

"Coupling of Alcohols to Ethers: the Dominance of the Surface S_N2 Reaction Pathway," K. Klier, Q. Sun, O. C. Feeley, M. Johansson, and R. G. Herman, in "*11th Intern. Congr. Catal.-40th Ann.*," (Studies in Surface Science and Catalysis), **101A**, ed. by J. W. Hightower, W. N. Delgass, E. Iglesia, and A. T. Bell, Elsevier, Amsterdam, 601-610 (1996).

"Kinetic Evaluation of the Direct Synthesis of Ethers from Alcohols over Sulfonated Resin Catalysts," L. Lietti, Q. Sun, R. G. Herman, and K. Klier, Catal. Today, **27**, 151-158 (1996).

"Chirality Inversion in HZSM-5 and Nafion-H Solid Acid-Catalyzed Synthesis of Ethers from Alcohols *via* Surface S_N2 Reaction," Q. Sun, R. G. Herman, and K. Klier, J. Chem. Soc., Chem. Commun., 1849-1850 (1995).

"Selective Isotopic Oxygen Incorporation into C_5 and C_6 Ethers *via* Solid Acid Catalyzed Reaction of Methanol and Ethanol with Isobutanol," O. C. Feeley, Q. Sun, R. G. Herman, M. Johansson, L. Lietti, and K. Klier, Catal. Letters, **35**, 13-22 (1995).

"Mechanistic Studies of the Pathways Leading to Ethers *via* Coupling of Alcohols," Q. Sun, L. Lietti, R. G. Herman, and K. Klier, Preprints, Div. Fuel Chem., ACS, **40(1)**, 138-141 (1995).

REFERENCES

Amenomiya, Y. Methanol Synthesis from Carbon Dioxide and Hydrogen. II. Copper-based Binary and Ternary Catalysts. *Appl. Catal.* **1987**, *30*, 57-68.

Anderson, R. B.; Feldman, J.; Storch, H. H. Synthesis of Alcohols by Hydrogenation of Carbon Monoxide. *Ind. Eng. Chem.* **1952**, *44*, 2418-2424.

Bart, J. C. J.; Sneeden, R. P. A. Alcohols from Synthesis Gas--A Status Report. *Catal. Today* **1987**, *2*, 1-124.

Bartley, G. J. J.; Burch, R.; Chappell, R. J. Investigation of the Dispersion of Supported Copper Catalyst by Oxygen Adsorption and Nitrous Oxide Decomposition. *Appl. Catal.* **1988**, *43*, 91-104.

Bartley, G. J. J.; Burch, R. Support and Morphological Effects in the Synthesis of Methanol over Cu/ZnO, Cu/ZrO_2, and Cu/SiO_2 Catalysts. *Appl. Catal.* **1988**, *43*, 141-153.

Beretta, A.; Tronconi, E.; Forzatti, P.; Lietti, L; Pasquon, I. Synthesis of Oxygenates from CO/H_2 for Reformulated Gasolines. In *Proceedings of the 27th ISATA Conference;* Dedicated Conference on the Electric, Hybrid and Alternative Fuel Vehicle; Aachen, Germany; Oct 31-Nov 4, **1994**; pp 229-307.

Beretta, A.; Sun, Q.; Herman, R. G.; Klier, K. Synthesis of 2-Methylpropan-1-ol/Methanol Mixtures From H_2/CO Synthesis Gas Over Double-Bed Cs/Cu/ZnO/Cr_2O_3 and Cs/ZnO/ Cr_2O_3 Catalysts. *J. Chem. Soc., Chem. Commun.* **1995**, 2525-2526.

Beretta, A.; Sun, Q.; Herman, R. G.; Klier, K. Production of Methanol and Isobutyl Alcohol Mixtures over Double-Bed Cesium-Promoted $Cu/ZnO/Cr_2O_3$ and ZnO/Cr_2O_3 Catalysts. *Ind. Eng. Chem. Res.* **1996**, 35, 1534-1542.

Bogdan, C. E.; Nunan, J. G.; Santiesteban, J. G.; Herman, R. G.; Klier, K. Deactivation Studies of the Cs/Cu/ZnO and Alkali/MoS_2 Alcohol Synthesis Catalysts. In *Catalysis-1987*; Ward, J. W., Ed.; Elsevier: Amsterdam; **1988**; pp 745-760.

Bowker, M.; Hadden, R. A.; Houghton, H.; Hyland, J. N. K.; Waugh, K. C. The Mechanism of Methanol Synthesis on Copper/Zinc Oxide/Alumina Catalysts. *J. Catal.* **1988**, *109*, 263-273.

Boz, I.; Sahibdaza, M.; Metcalfe, I. S. Kinetics of the Higher Alcohol Synthesis over a K-promoted $CuO/ZnO/Al_2O_3$ Catalyst. *Ind. Eng. Chem. Res.* **1994**, *33*, 2021-2028.

Breman, B. B.; Beenackers, A. C. C. M.; Oesterholt, E. A. Kinetic Model for the Methanol-Higher Alcohol Synthesis from $CO/CO_2/H_2$ over Cu/ZnO-Based Catalysts Including Simultaneous Formation of Methyl Esters and Hydrocarbons. *Chem. Eng. Sci.* **1994**, *49*, 4409-4428.

Bridger, G. W.; Spenser, M. S. Methanol Synthesis. In *Catalyst Handbook*, 2nd. Ed.; Twigg, M. V., Ed.; Wolfe Publ. Ltd.: Frome, England; **1989**; pp 441-468.

Bridgewater, A. J.; Wainwright, M. S.; Young, D. J.; Orchard, J. P. Methanol Synthesis over Raney Copper-Zinc Catalysts. III. Optimization of Alloy Composition and Catalyst Preparation. *Appl. Catal.* **1983**, *7*, 369-382.

Brown, D. Development of Alternative Fuels and Chemicals From Synthesis Gas. In *Proceedings of Coal Liquefaction and Gas Conversion Contractors Review Conference*; U.S. Department of Energy-PETC: Pittsburgh, PA; Sept **1993**; Vol. II, pp 789-813.

Bulko, J. B.; Herman, R. G.; Klier, K.; Simmons, G. W. Optical Properties and Electronic Interactions of Microcrystalline Cu/ZnO Catalysts. *J. Phys. Chem.* **1979**, *83*, 3118-3122.

Burch, R.; Golunski, S.E.; Spencer, M.S. The Role of Copper and Zinc Oxide in Methanol Synthesis Catalysts. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 2683-2691.

Busetto, C.; Del Piero, G.; Manara, G.; Trifiro, F.; Vaccari, A. Catalysts for Low-Temperature Methanol Synthesis. Preparations of Cu-Zn-Al Mixed Oxides via Hydrotalcite-like Precursors. *J. Catal.* **1984**, *85*, 260-266.

Bybell, D. G.; Deutsch, P. P.; Herman, R. G.; Himelfarb, P. B.; Nunan, J. G.; Young, C.-W.; Bogdan, C. E.; Simmons, G. W.; Klier, K. Promotion by Cs(I) and Poisoning by Tl(I) of the Cu/ZnO Catalysts for Methanol Synthesis and the Water Gas Shift Reaction. *Preprint, Div. Pet.Chem., ACS* **1986**, *31(1)*, 282-290.

Calverley, E. M.; Anderson, R. B. Synthesis of Higher Alcohols over Promoted Copper Catalysts. *J. Catal.* **1987**, *104*, 434-440.

Campos-Martin, J. M.; Guerrero-Ruiz, A.; Fierro, J. L. G. Structural and Surface Properties of $CuO-ZnO-Cr_2O_3$ Catalysts and Their Relationship with Selectivity to Higher Alcohol Synthesis, *J. Catal.*, **1995**, *156*, 208-218.

Chinchen, G. C.; Denny, P. J.; Parker, D. G.; Short, G. D.; Whan, D. A.; Spencer, M. S.; Waugh, K. C. The Activity of $Cu-ZnO-Al_2O_3$ Methanol Synthesis Catalysts. *Preprint, Div. Fuel. Chem., ACS* **1984**, *29(5)*, 178-188.

Denise, B; Sneeden, R. P. A. Oxide-Supported Copper Catalysts Prepared from Copper Formate: Differences in Behavior in Methanol Synthesis from Carbon Monoxide/Hydrogen and Carbon Dioxide/Hydrogen Mixtures. *Appl. Catal.* **1986**, *28*, 235-239.

Denise, B.; Sneeden, R. P. A.; Beguin, B.; Cherifi, O. Supported Copper Catalysts in the Synthesis of Methanol: Nitrous Oxide Titrations. *Appl. Catal.* **1987**, *30*, 353-363.

Denise, B.; Cherifi, O.; Bettahar, M. M.; Sneeden, R. P. A. Supported Copper Catalysts Prepared from Copper(II) Formate: Hydrogenation of Carbon Dioxide Containing Feedstocks. *Appl. Catal.* **1989**, *48*, 365-372.

Elliott, D. J.; Pennella, F. Mechanisms of Ethanol Formation from Synthesis Gas over $CuO/ZnO/Al_2O_3$. *J. Catal.* **1988**, *114*, 90-99.

Fleisch, T. H.; Mieville, R. L. Studies of the Chemical State of Cu during Methanol Synthesis. *J. Catal.* **1984**, *90*, 165-172.

Friedrich, J. B.; Wainwright, M. S.; Young, D. J. Methanol Synthesis over Raney Copper-Zinc Catalysts. I. Activities and Surface Properties of Fully Extracted Catalysts. *J. Catal.* **1983** *80*, 1-13.

Forzatti, P.; Tronconi, E. Higher Alcohol Synthesis. *Catal. Rev. Sci. Eng.* **1991**, *33*, 109-168.

Fox, J. M. The Different Catalytic Routes for Methane Volorization: An Assessment of Processes for Liquid Fuels. *Catal. Rev. Sci. Eng.* **1993**, *35*, 169-212.

Frolich, P. K.; Cryder, D. S. Catalysts for the Formation of Alcohols from Carbon Monoxide and Hydrogen. VI. Investigation of the Mechanism of Formation of Alcohols Higher than Methanol. *Ind. Eng. Chem.* **1930**, *22*, 1051-1057.

Gasser, D.; Baiker, A. Hydrogenation of Carbon Dioxide over Copper-Zirconia Catalysts Prepared by *in-situ* Activation of Amorphous Copper-Zirconium Alloy. *Appl. Catal.* **1989**, *48*, 279-294.

Herman, R. G.; Klier, K.; Simmons, G. W.; Finn, B. F.; Bulko, J. B.; Kobylinski, T. P. Catalytic Synthesis of Methanol from CO/H_2. I. Phase Composition, Electronic Properties, and Activities of the $Cu/ZnO/M_2O_3$ Catalysts. *J. Catal.* **1979**, *56*, 407-429.

Herman, R. G. Classical and Non-Classical Routes for Alcohol Synthesis. In *New Trends in CO Activation*; Guczi, L., Ed.; Elsevier: Amsterdam; **1991**; pp 265-349.

Herman, R. G.; Klier, K.; Feeley, O. C.; Johansson, M. A. Synthesis of Oxygenates From H_2/CO Synthesis Gas and Use as Fuel Additives. *Preprints, Div. Fuel Chem., ACS*, **1994**, *39(2)*, 343-349.

Herman, R. G.; Lietti, L. Controlling Factors in the Synthesis of Higher Alcohols over Alkali-Promoted Low-Temperature Cu/Zn/(Cr or Al) and High Temperature Zn/Cr Catalysts. In *Proc. of the 11th International Pittsburgh Coal Conference*; Chiang, S.-H., Ed.; **1994**; Vol. 1, 68-73.

Himelfarb, P. B.; Simmons, G. W.; Klier, K.; Herman, R. G. Precursors of the Copper-Zinc Oxide Methanol Synthesis Catalysts. *J. Catal.* **1985**, *93*, 442-450.

Hindermann, J. P.; Hutchins, G. J.; Kiennemann, A. Mechanistic Aspects of the Formation of Hydrocarbons and Alcohols from CO Hydrogenation. *Catal. Rev. Sci. Eng.* **1993**, *35*, 1-127.

Hoppener, R. H.; Doesburg, E. B. M.; Scholten, J. J. F. Preparation and Characterization of Stable Copper/Zinc Oxide/Alumina Catalysts for Methanol Synthesis. *Appl. Catal.* **1986**, *25*, 109-119.

Hu, X.-D.; Foley, H. C.; Stiles, A. B. Design of Alcohol Synthesis Catalysts Assisted by a Knowledge-Based Expert System. *Ind. Eng. Chem. Res.* **1991**, *30*, 1419-1427.

Johansson, M. A. Analysis of Solid Acid Catalysts: By Catalytic Reactions and by High Resolution X-Ray Photoelectron Spectroscopy (HR-XPS). Ph.D Dissertation, Department of Chemistry, Lehigh University, **1995**.

Kanoun, N.; Astier, M. P.; Pajonk, G. M. Catalytic Properties of new Copper Based Catalysts Containing Zr and/or V for Methanol Synthesis from a Carbon Dioxide and Hydrogen Mixture. *Catal. Lett.* **1992**, *15*, 231-235.

Keim, W.; Falter, W. Isobutanol from Synthesis Gas. *Catal. Lett.* **1989**, *3*, 59-64.

Klier, K. Methanol Synthesis. *Adv. Catal.* **1982**, *31*, 243-313.

Klier, K.; Chatikavanij, V.; Herman, R. G.; Simmons, G. W. Catalytic Synthesis of Methanol from CO/H_2. IV. The Effects of Carbon Dioxide. *J. Catal.* **1982**, *74*, 343-360.

Klier K.; Herman R. G.; Young C.-W. Direct Synthesis of 2-Methyl-1-Propanol. *Preprints, Div. Fuel Chem., ACS* **1984**, *29(5)*, 273-280.

Klier, K.; Herman, R. G.; Nunan, J. G.; Smith, K. J.; Bogdan, C. E.; Young, C.-W.; Santiesteban, J. G. Mechanism of Methanol and Higher Oxygenates Synthesis. In *Methane Conversion*; Bibby, D. M; Chang, C. D.; Howe, R. F.; Yurchak, S., Eds.; Elsevier: Amsterdam, **1988**; pp 109-125.

Klier, K.; Herman, R. G.; Johansson, M. A.; Feeley, O. C. Synthesis of C_5 Ethers From Methanol and 2-Methyl-1-Propanol (Isobutanol). *Preprints, Div. Fuel Chem., ACS* **1992**, *37(1)*, 236-246.

Klier, K.; Herman, R. G.; Himelfarb, P. B.; Young, C.-W.; Hou, S.; Marcos, J. A. C-C Bond Formation *via* β-Addition with Oxygen Retention Reversal in Oxygenate Synthesis. In *New Frontiers in Catalysis*; Guczi, L., Solymosi, F., Telenyi, P., Eds.; Elsevier: Amsterdam; **1993a**; pp 1441-1452.

Klier, K.; Herman, R. G.; Feeley, O. C.; Johansson, M. A.; Menszak, J. High Octane Ethers from Synthesis Gas-Derived Alcohols. In *Proc. Coal Liquefacion and Gas Conversion Contractors Review Conference*; U. S. Dept. of Energy-PETC: Pittsburgh, Sept. **1993b**; Vol. II, pp 739-763.

Koeppel, R. A.; Baiker, A.; Schild, C.; Wokaun, A. Effect of Preparation Variables on Catalytic Behaviour of Copper/Zirconia Catalysts for the Synthesis of Methanol from Carbon Dioxide. In *Preparation of Catalysts V*; Poncelet, G., Jacobs, P. A., Grange, P., Delmon, B., Eds.; Elsevier: Amsterdam; **1991**, pp 59-68

Koeppel, R. A.; Baiker, A. Copper/Zirconia Catalysts for the Synthesis of Methanol from Carbon Dioxide. Influence of Preparation Variables on Structural and Catalytic Properties of Catalysts. *Appl. Catal. A* **1992**, *84*, 77-102.

Kung, H. H. Methanol Synthesis. *Catal. Rev. Sci. Eng.* **1980**, *22*, 235-259.

Lietti, L.; Tronconi, E.; Forzatti, P. Mechanistic Aspects of the Higher Alcohol Synthesis over K_2O-Promoted ZnCr Oxide: Temperature-Programmed Reaction and Flow Experiments of C_3, C_4, and C_5 Oxygenates. *J. Catal.* **1992**, *135*, 400-419.

Mehta, S.; Simmons, G. W.; Klier, K.; Herman, R. G. Catalytic Synthesis of Methanol from CO/H_2. II. Electron Microscopy (TEM, STEM, Microdiffraction, and Energy Dispersive Analysis) of the Cu/ZnO and $Cu/ZnO/Cr_2O_3$ Catalysts. *J. Catal.* **1979**, 57, 339-360.

Minahan, D. M.; Nagaki, D. A. Heterogeneous Catalytic Process for Alcohol Fuels from Syngas. In *Proc. Coal Liquefacion and Gas Conversion Contractors Review Conference*; U. S. Dept. of Energy-PETC: Pittsburgh; Sept. **1994**; Vol. I, 265-279.

Miyata, S. Anion-Exchange Properties of Hydrotalcite-Like Compounds. *Clays and Clay Miner.* **1983**, *31*, 305-311.

Natta, G. Methanol Synthesis. In *Catalysis*; Emmett, P. H., Ed.; Reinhold: New York; **1955,** Vol III, pp 349-411.

Natta, G. ;Colombo, U.; Pasquon, I. Higher Alcohols. In *Catalysis*; Emmett, P. H., Ed.; Reinhold: New York, **1957**; Vol. V, Chapter 3, pp 131-174.

Nitta, Y.; Fujimatsu, T.; Okamoto, Y.; Imanaka, T. Effect of Starting Salt on Catalytic Behavior of Cu-ZrO_2 Catalysts in Methanol Synthesis from Carbon Dioxide. *Catal. Lett.* **1993**, *17*, 157-165.

Nunan, J.; Klier, K.; Herman, R. G. Selective Coupling of Methanol and 2-Methylpropan-1-ol to give 1-Methyoxy-2-Methylpropane (Methyl Isobutyl Ether). *J. Chem. Soc., Chem. Commun.***1985**, 676-678.

Nunan, J. G.; Klier, K.; Young, C. W.; Himelfarb, P. B.; Herman, R. G. Promotion of Methanol Synthesis over Cu/ZnO Catalysts by Doping with Caesium. *J. Chem. Soc., Chem. Commun.* **1986**, 193-195.

Nunan, J. G.; Bogdan, C. E.; Klier, K.; Smith, K. J.; Young, C.-W.; Herman, R. G. Methanol and C_2 Oxygenate Synthesis over Cesium Doped Cu/ZnO and Cu/ZnO/Al_2O_3 Catalysts: A Study of Selectivity and ^{13}C Incorporation Patterns. *J. Catal.* **1988**, *113*, 410-433.

Nunan, J. G.; Bogdan, C. E.; Klier, K.; Smith, K. J.; Young, C.-W.; Herman, R. G. Higher Alcohol and Oxygenate Synthesis over Cesium-Doped Cu/ZnO Catalysts. *J. Catal.* **1989a**, *116*, 195-221.

Nunan, J. G.; Bogdan, C. E.; Herman, R. G.; Klier, K. Efficient Carbon-Carbon Bond Formation in Ethanol Homologation by CO/H_2 with Specific C_1 Oxygen Retention over Cs/Cu/ZnO Catalysts. *Catal. Lett.* **1989b**, *2*, 49-56.

Nunan, J. G.; Herman, R. G.; Klier, K. Higher Alcohol Synthesis over Cs/Cu/ZnO/M_2O_3 (M = Al, Cr) Catalysts. *J. Catal.* **1989c**, *116*, 222-229.

Nunan, J. G.; Himelfarb, P. B.; Herman, R. G.; Klier K.; Bogdan, C. E.; Simmons, G. W. Methanol Synthesis Catalysts Based on Cs/Cu/ZnO/M_2O_3 (M = Al, Cr, Ga): Genesis from Coprecipitated Hydrotalcite-like Precursors, Solid-State Chemistry, Morphology, and Stability, *Inorg. Chem*, **1989d**, *28*, 3868-3874.

Paggini, A.; Sanfilippo, D.; Pecci, G.; Dybkjaer, I. Implementation of the Methanol Plus Higher Alcohols Process by Snamprogetti, Enichem, Haldor Topsoe A/S MAS Technology. *Proc. 7th Int. Symp. Carbur. Alcohols,* **1986**, 62-67.

Reichle, W. T. Catalytic Reactions by Thermally Activated, Synthetic, Anionic Clay Minerals. *J. Catal.* **1985**, *94*, 547-557.

Reichle, W. T. Anionic Clay Minerals. *Chem. Tech.* **1986**, *16(1)*, 58-63.

Rogerson, P. L. The ICI Low-Pressure Methanol Process. In *Handbook of Synfuels Technology*; Meyers, R. A., Ed.; McGraw-Hill: New York; **1984**, 2-45.

Sanfilippo, D. Dehydrogenation in a Fluidized Bed: An East-West Collaboration. *Chem. Tech.* **1993**, *23(8)*, 35-39.

Schild, C.; Wokaun, A.; Baiker, A. On the Mechanism of Carbon Monoxide and Carbon Dioxide Hydrogenation Reactions on Zirconia-Supported Catalysts: A Diffuse Reflectance FTIR Study. Part I. Identification of Surface Species and Methanation Reactions on Palladium/Zirconia Catalysts. *J. Mol Catal.* **1990**, *63*, 223-242.

Schild, C.; Wokaun, A.; Baiker, A. On the Mechanism of Carbon Monoxide and Carbon Dioxide Hydrogenation Reactions on Zirconia-Supported Catalysts: A Diffuse Reflectance FTIR Study. Part II. Surface Species on Copper/Zirconia Catalysts: Implications for Methanol Synthesis Selectivity. *J. Mol. Catal.* **1990**, *63*, 243-254.

Schild, C.; Wokaun, A.; Koeppel, R.; Baiker, A. XRD and Raman Identification of the Zirconia Modifications in Copper/Zirconia and Palladium/Zirconia Catalysts Prepared from Amorphous Precursors. *J. Catal.* **1991**, *130*, 657-661.

Smith, K. J.; Herman, R. G.; Klier, K. Kinetic Modelling of Higher Alcohol Synthesis over Alkali-Promoted Cu/ZnO and MoS_2 Catalysts. *Chem. Eng. Sci.* **1990**, *45*, 2639-2646.

Smith, K. J.; Young, C.-W.; Herman, R. G.; Klier, K. Development of a Kinetic Model for Alcohol Synthesis over a Cesium-Promoted Cu/ZnO Catalyst. *Ind. Eng. Chem. Res.* **1991**, *29*, 61-71.

Solymosi, F. Importance of the Electric Properties of Supports in the Carrier Effect. *Catal. Rev.* **1968**, *1*, 233-255.

Stiles, A. B.; Chen, F.; Harrison, J. B.; Hu, X.; Storm, D. A.; Yang, H. X. Catalytic Conversion of Synthesis Gas to Methanol and Other Oxygenated Products. *Ind. Eng. Chem. Res.* **1991**, *30*, 811-821.

Supp, E.; Quinkler, R. F. The Lurgi Low-Pressure Methanol Process. In *Handbook of Synfuels Technology*; Meyers, R. A., Ed.; McGraw-Hill: New York; **1984**, pp 2-113.

Takahama, T.; Oshima, H.; Ueno, A.; Kotera, Y. The Preparation of a Catalyst for the Ester Exchange Reaction Between Ethylene Glycol and DMT. *Appl. Catal.* **1983**, *5*, 59-64.

Tronconi, E.; Ferlazzo, N.; Forzatti, P.; Pasquon, I. Synthesis of Alcohols from Carbon Oxides and Hydrogen. 4. Lumped Kinetics for the Higher Alcohol Synthesis over a Zn-Cr-K Oxide Catalyst. *Ind. Eng. Chem. Res.* **1987**, *26*, 2122-2129.

Tronconi, E.; Forzatti, P.; Pasquon, I. An Investigation of the Thermodynamic Constraints in Higher Alcohol Synthesis over Cs-Promoted ZnCr-Oxide Catalyst. *J. Catal.* **1990**, *124*, 376-390.

Tronconi, E.; Lietti, L.; Groppi, G.; Forzatti, P.; Pasquon, I. Mechanistic Kinetic Treatment of the Chain Growth Process in Higher Alcohol Synthesis over a Cs-promoted Zn-Cr-O Catalyst. *J. Catal.* **1992**, *135*, 99-114.

Ueda, W.; Ohshida, T.; Kuwabara, T.; Morikawa, Y. Higher Alcohol Synthesis over Functionalized Solid-Base Catalysts from Methanol as a Building Block. In *New Frontiers in Catalysis*; Guczi, L., Solymosi, F., Telenyi, P., Eds.; Elsevier: Amsterdam; **1993**; pp 2821-2824.

Vedage, G.A.; Pitchai, R.; Herman, R. G.; Klier, K. Water Promotion and Identification of Intermediates in Methanol Synthesis. *Proc.8th Intern. Congr. Catal.*, **1984a**, *II*, 47-58.

Vedage, G. A.; Pitchai, R.; Herman, R. G.; Klier, K. Mechanism and Intermediates of Methanol Synthesis over the Cu/ZnO Catalyst in the Presence of Water and Carbon Dioxide. *Preprints, Div. Fuel. Chem., ACS* **1984b**, *29(5)*, 196-201.

Zhou, P. *Summary of the Higher Alcohol Synthesis Workshop*; U.S. Department of Energy-PETC: Pittsburgh, PA, Feb **1994**.