

CATALYTIC HYDROGENATION OF CO: CATALYSIS ON WELL-CHARACTERIZED SURFACES

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The purpose of these studies is to explore the molecular ingredients necessary to produce organic molecules (alkenes, oxygen or nitrogen containing molecules, alkanes) selectively from CO and H₂. We utilize small area (~1cm²) single crystals or polycrystalline compounds as catalysts. Our reactors permit surface analysis in uhv by LEED, AES, XPS and TDS and can be used to measure reaction rates and product distributions in the pressure range of 1-50 atm in a flow or batch mode. This way, the kinetic parameters of the reaction can be correlated with the surface structure, surface composition and oxidation states of surface atoms.

RESULTS

1) The Effect of the Rhodium Ion Oxidation State on the Product Distribution in the CO/H₂ Reaction.

Mark Logan and G.A. Somorjai

Metallic rhodium produces mostly methane and the reaction rate exhibits a deuterium isotope effect. Rhodium oxide and lanthanum rhodate (LaRhO₃) produce oxygenated molecules ethanol, methanol and acetaldehyde. The presence of both, metallic and +3 formal oxidation states of rhodium are needed to form these molecules. While CO dissociation and hydrogenation are efficient processes on the metal, CO insertion (carbonylation) that is required for the production of oxygenated molecules in the property of Rh³⁺ ions. Test reactions with ethylene in the presence of CO and H₂ clearly show this as ethane is produced over the metal and propionaldehyde over Rh₂O₃.

FeRhO₃ produces mostly ethylene from CO and H₂. This desirable reaction is under detailed investigation at present.

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2) Thorium Oxide: A New Catalyst for Methanol Production from CO and H₂.

Joseph Maj, Carlos Colmenares and G.A. Somorjai

High surface area (~120 m²/g) thoria catalysts were prepared by precipitation of thorium oxycarbonate from thorium nitrate solutions using ammonium carbonate solutions followed by calcination at 520K. The reaction was carried out at a pressure of 5.4 MPa and a flow rate of 1.8 m³/h-kg. Experimental results are displayed in Figures 1 and 2. The thoria catalysts are highly active for methanol synthesis at a CO conversion of 3%. In addition to methanol the formation of isobutanol and isobutane are also observed. The measured activation energy for methanol production is 45 kJ/mole.

3) Studies of Molybdenum and Rhenium for CO Hydrogenation.

Eric Garfunkel, Andrew Gellman and G.A. Somorjai

The (100) Crystal Face of molybdenum and a polycrystalline foil were used in these studies. Mostly methane and ethane are produced over the clean metal surface and there is a rapid carbon build-up on the surface that slows down the reaction. In the presence of a partial monolayer of sulfur the formation of ethane predominates while the production of methane is inhibited. It appears that sulfur addition renders Mo selective for ethane production.

Rhenium produces methane almost exclusively at atmospheric pressures of CO and H₂. Studies are in progress to alter the oxidation states of these metals by oxidation and sulfide formation to explore their effects on the product distribution during the hydrogenation of CO.

4) The Effects of Alkali Metal Addition to Transition Metals during the CO/H₂ Reaction.

Eric Garfunkel, John Crowell and G.A. Somorjai

TDS and HREELS studies explored the coadsorption of potassium and potassium oxide with CO. The presence of the alkali metal increases the heat of adsorption of CO on Rh and Pt by 12 kcal/mole. The molecule

shifts its location from the top site to primarily onto the bridge sites and there is a $\sim 300 \text{ cm}^{-1}$ decrease in the C=O stretching frequency with increasing potassium coverage. This indicates a weakening of the CO double bond to a bond order of $\sim 1-1/2$ bond.

The addition of potassium to iron foils increases the production of higher molecular weight hydrocarbons and decreases the formation rate of methane. The total CO/H₂ reaction rate is decreased in the presence of the alkali metal. These observations are consistent with the observations that potassium facilitates CO dissociation and decreases the rate of hydrogenation of the carbon containing reaction intermediates.

PUBLICATIONS in 1982-83

1. The Formation of Oxygen-Containing Organic Molecules by the Hydrogenation of Carbon Monoxide Using a Lanthanum Rhodate Catalyst (with P.R. Watson), J. Catal. 74, 282-295 (1982).
2. Electron Spectroscopy Studies of the Clean Thorium and Uranium Surfaces. The Chemisorption and Initial Stages of Reaction with O₂, CO, and CO₂ (with W. McLean, C.A. Colmenares, and R.L. Smith), Phys. Rev. B 25(1), 8 (1982).
3. The Composition and Structure of Oxide Films Grown on the (110) Crystal Face of Iron (with M. Langell), J. Vac. Sci. & Technol. 21, (3) 858 (1982).
4. The Strong Influence of Potassium on the Adsorption of CO on Platinum Surfaces: A TDS and HREELS Study (with E.L. Garfunkel and J.E. Crowell), J. Phys. Chem. 86, 310 (1982).
5. The Interaction of CO, CO₂, and D₂ with Rhodium Oxide (Rh₂O₃.5H₂O): Its Reduction and Catalytic Stability (with P.R. Watson), J. Phys. Chem. 86, 3993 (1982).
6. The Chemisorption of CO and CO₂ on Gold Supported ThO₂ Films, (with W. McLean, C.A. Colmenares and R.L. Smith), J. Phys. Chem., 87, 788 (1983).
7. The Coadsorption of Potassium and CO on the Pt(111) Crystal Surface: A TDS, HREELS and UPS Study, (with J.E. Crowell and E.L. Garfunkel), Surf. Science, 121, 303-320 (1982).

FUTURE RESEARCH

Our studies will proceed in two directions: 1) The oxidation state of the transition metal ions will be correlated with the selectivity and product distribution of the CO/H₂ reaction. The compounds of the following transition metals will be studied; rhodium, palladium, molybdenum, rhenium and iron. 2) Iron, rhenium and molybdenum will catalyze the reactions of both CO and N₂ with hydrogen. CO, N₂ and H₂ will be used in combination in an attempt to produce nitrogen containing organic molecules.

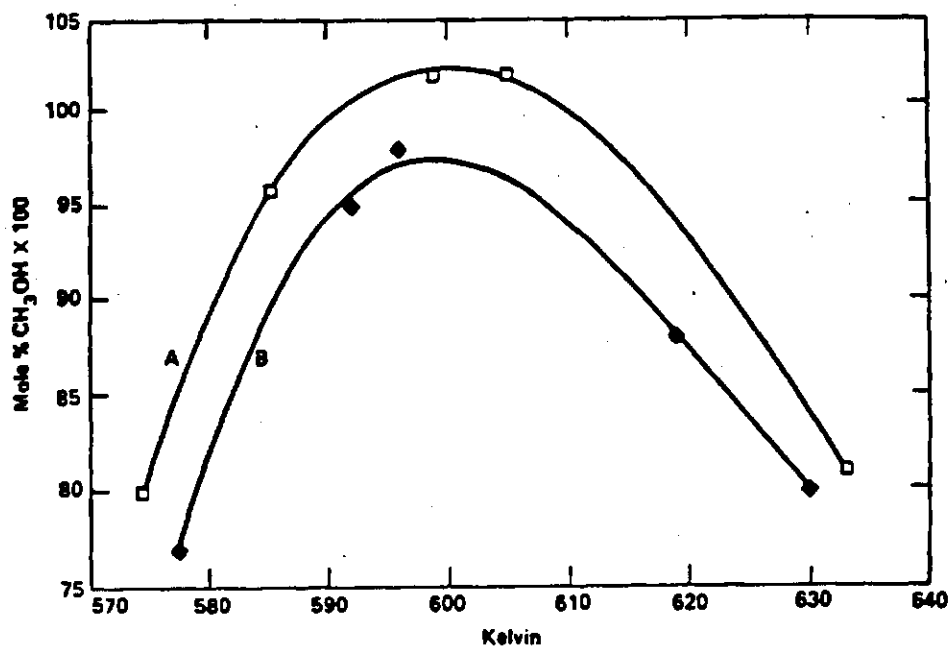


Figure 1. Mole percent methanol in reactor effluent vs. temperature for thoria catalysts precipitated from (A) $(\text{NH}_4)_2\text{CO}_3$ and (B) Na_2CO_3 .

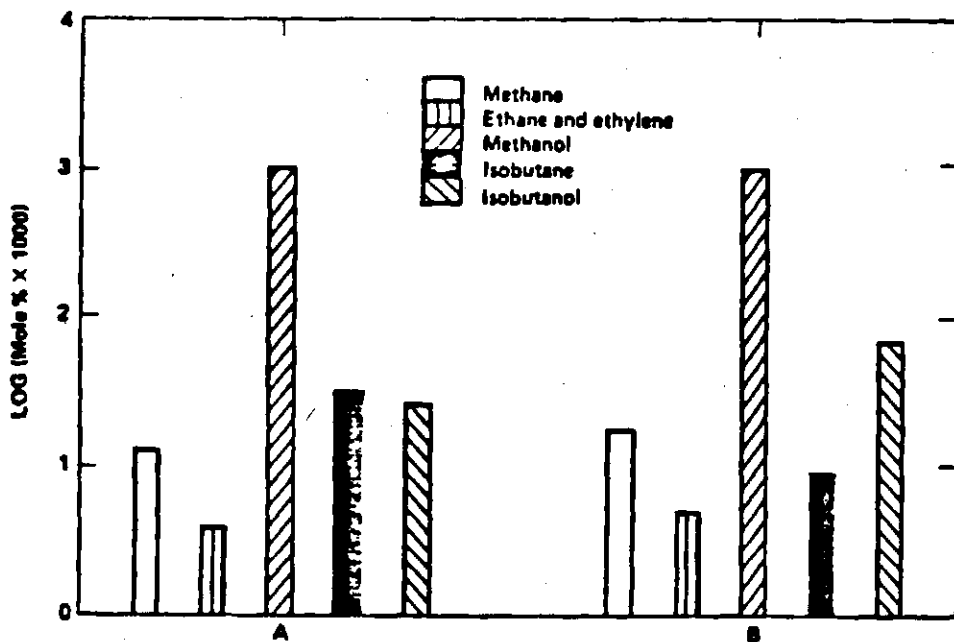


Figure 2. Product distribution (mole percent in reactor effluent) for thoria catalysts at 600 K and 5.4 MPa precipitated with (A) $(\text{NH}_4)_2\text{CO}_3$ and (B) Na_2CO_3 .