

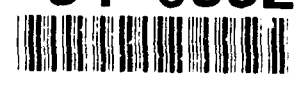
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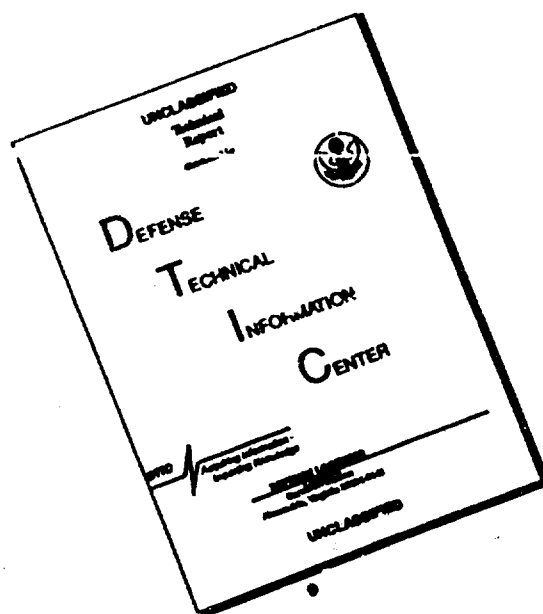
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FINAL REPORT - P.I.: Aaron Wold, Department of Chemistry, Brown University

Summary of work done under contract N000 14-77-C-0387 during contract period May 1, 1983 to April 30, 1986.

(See summaries from End-of-Year Reports dated Sept. 1983, 1984, 1985 and 1986 - partially reproduced below.)

From 1983 End-of-Year Report:

...Our program at present is concerned with the following problems:

1. The electrochemical generation of solvated electrons which might then be able to carry out reduction reactions at the cathode in a suitable cell. At present, the reduction of benzene to cyclohexane is being studied but we expect next year to attempt the reduction of CO_2 to methanol.
2. The study of the interaction between hydrogen and various metal oxides (e.g. Fe_2O_3 , V_2O_5 , RuO_2 , Rh_2O_3) on an inert support (e.g. gamma- Al_2O_3 , MgO , etc.) is being carried out in an attempt to understand the factors necessary to stabilize mixed valence states of the metal oxide.
3. It is hoped that knowledge gained from a study of the stabilization of transition metal oxides in a reducing atmosphere (by interaction of the transition metal with the support) will lead to more effective catalysts for the reduction of CO or CO_2 with hydrogen to form methanol or an other readily storable compound. The ability to reduce CO_2 with hydrogen at low temperature ($<300^\circ\text{C}$) would be of great interest to the Navy. Improved catalysts must be developed if this process is to take place efficiently at relatively low temperatures. A suitable reactor has been constructed so that reduction reaction products of CO-CO_2 with H_2 on the surfaces of various catalysts can be identified.

From the September, 1984 End-of-the-Year Report:

The program at Brown University has consisted of three efforts during the past year. They are as follows:

1. The electrochemical reduction of benzene in ethanol-HMPA solutions, as well as the addition of colloidal Ru particles which were used to increase the extent of benzene reduction.
2. The reduction of CO/H_2 using iron catalysts and the characterization of the active catalysts at maximum activity by means of x-ray diffraction analysis and Curie Point determination.
3. The extension of the H_2 reduction studies to CO_2 using rhodium catalysts dispersed on ZrO_2 .



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Our studies on the reduction of benzene by means of solvated electrons showed that under suitable conditions over 60% of the benzene is reduced at a current of 240 mA with an overall current efficiency greater than 36%. The addition of colloidal metal particles to solutions containing benzene - 21 mole % ethanol - 79 mole % hexamethylphosphoramide resulted in an additional conversion of 15% of the benzene to cyclohexadiene. This additional reduction took place by direct hydrogenation of the benzene at room temperature and 10 psi of hydrogen pressure.

Methanation studies, i.e., reduction of CO by H₂ have been carried out at 290°C in a microreactor with a H₂/CO ratio of 9/1.

The catalysts studied were iron(III) oxide, iron(II) diiron(III) tetroxide, and metallic iron. All catalysts at maximum activity contained Fe₅C₂. Deactivation of the catalysts was found to be due to excess graphitic carbon. Sustained catalytic activity was found to require the presence of iron(II) diiron(III) tetroxide, probably to serve as a source for continual renewal of the active catalyst surface.

Preliminary experiments carried out on the reduction of CO₂ with hydrogen using a metallic rhodium catalyst dispersed on zirconium oxide indicate that with a H₂/CO₂ ratio of 9:1, at ambient pressure and 246°C, 50% of the CO₂ is converted solely to methane.

Summary from September 1985 End-of-Year Report:

Single crystal boules of Cd_{1-x}Mn_xSe with x = 0.01, 0.05 and 0.10 have been grown by a modified Bridgman method using 5% excess selenium to lower the melting point. A technique has been developed for the growth of high quality, single grain boules with demonstrated uniform manganese distribution. Free carriers have been introduced in a controlled fashion by adding gallium to the melt and annealing crystal slices in cadmium vapor. Reproducible carrier concentrations from 2 x 10¹⁷ to 2 x 10¹⁸ cm⁻³ have been achieved. The group at the National Magnet Laboratory have studied the magnetoresistance near the metal-insulator transition for the compositions Cd_{0.99}Mn_{0.01}Se and Cd_{0.95}Mn_{0.05}Se.

Methanation studies have been carried out at 290°C in a microreactor with a H₂/CO ratio of 9/1. The catalysts studied were iron(III) oxide, iron(II) diiron(III) tetroxide and metallic iron. These were all prepared reproducibly from iron(III) nitrate. The catalysts were characterized by x-ray diffraction and magnetic analysis, both at maximum activity and after deactivation. All catalysts at maximum activity contained Fe₅C₂. Deactivation of the catalysts was found to be due to excess graphitic carbon. Sustained catalytic activity was found to require the presence of iron(II) diiron(III) tetroxide, probably to serve as a source for continual renewal of the active catalyst surface.

For members of the system $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$, a convenient, non-destructive method for monitoring the Mn uniformity is the shift with Mn concentration of an optical absorption edge near 700 nm. The shift has been measured as about 4.0 nm for each 1% Mn present in the sample. For 17 boules prepared the addition of Ga as a controlled impurity in the melt gave a range in carrier concentration from 2×10^{17} to 2×10^{18} . The standard deviation of the measured carrier concentration from those desired was $\pm 15\%$.

An investigation into the chemistry of catalyst-support interactions has resulted in the finding that up to 10% loading, catalyst-support interaction between Rh_2O_3 and ZrO_2 is strong. Whereas bulk Rh_2O_3 reduces in Ar/H_2 at 100°C , supported Rh_2O_3 on ZrO_2 is stable up to 350°C . The morphology of the support particles is also affected.

From September 1986 End-of-the-Year Report:

Research in the area of catalysis at Brown deals with the development of low temperature synthetic methods for the preparation of well-dispersed catalysts (Fe_2O_3 , Cr_2O_3 , Rh_2O_3 and NiO) on several oxide supports (ZrO_2 , TiO_2). Physical methods, such as x-ray diffraction, magnetic susceptibility and temperature programmed reduction, are used to study the interaction between the dispersed metal oxide and the support. For the specific system $\text{Rh}_2\text{O}_3/\text{ZrO}_2$, the solubility of rhodium oxide in the support was followed as a function of the structural changes of the ZrO_2 as well as the stabilization of the Rh_2O_3 towards reduction.

The extent of substitution of nickel into Fe_5C_2 was also studied since both nickel and iron are Fischer-Tropsch catalysts. The limit of substitution was determined for samples prepared under actual reactor conditions and was determined from both magnetic and x-ray analysis.

Finally, a thermomagnetic balance was constructed and was used to determine the nucleation and growth of catalytically active magnetic phases which can be correlated at the same time with the temperature programmed data.

During the course of the program it was shown that nickel can be substituted into Fe_5C_2 to the extent of 20 atomic percent. Samples were prepared by codecomposition of mixed nitrates followed by reduction at 290°C in a 9:1 $\text{H}_2:\text{CO}$ atmosphere. Confirmation of the limits of substitution was made by both magnetic and x-ray analysis.

Samples of well-dispersed hexagonal Rh_2O_3 on tetragonal ZrO_2 have been prepared by the codecomposition of the nitrates at 900°C . An increase in the stability of dispersed Rh_2O_3 compared to bulk Rh_2O_3 demonstrates that a solid solution was formed between the two oxides.

In addition to the information in the 1986 End-of-the-Year report...

(continued next page)

Samples of zirconium oxide containing 5-20 atomic percent chromium were prepared by double decomposition of the nitrates. X-ray diffraction analysis showed the products to be single phase. Magnetic susceptibility measurements were used to characterize the formal oxidation state of the chromium.

Samples of cubic ZrO_2 containing up to almost 10 atomic percent cobalt were prepared by codecomposition of the nitrate. Magnetic susceptibility measurements confirmed the limit of solubility and the presence of the cobalt as $Co(II)$. The reduction of the cobalt inserted in cubic zirconia took place at a considerably higher temperature than bulk cobalt oxide.

See Technical Reports 27 - 40

Technical Report 27. Dependence of Magnetic Properties on Structure in the Systems $NiMoO_4$ and $CoMoO_4$. August, 1983.

Technical Report 28. Homogeneity and Magnetic Susceptibility in Some Substituted Cadmium Spinels. November 1983.

Technical Report 29. Stability of Several Substituted Ferrites in a Reducing Atmosphere.

Technical Report 30. Preparation and Electronic Properties of MoS_2 and WS_2 Single Crystals Grown in the Presence of Cobalt. Sept. 1984.

Technical Report 31. Prepared by Dr. Arthur Ellis, Univ. of Wisconsin. Copy not available in our files. 1984.

Technical Report 32. The electrochemical Reduction of Benzene by Solvated Electrons in HMPA-Alcohol Solutions. Oct. 1984.

Technical Report 33. Use of Colloidal Ruthenium Particles in the Electrochemical Reduction of Benzene by Solvated Electrons. October 1984.

Technical Report 34. Methanation Studies I. Characterization of Some Iron Catalysts by X-ray Diffraction and Curie Point Determination. October 1984.

Technical Report 35. Single Crystal Growth of Cadmium Manganese Selenides with controlled Carrier Concentration. April 1985.

Technical Report 36. Stability of Several Iron and Rhodium Ternary Oxides in a Reducing Atmosphere. April 1985

Technical Report 37. Preparation and Characterization of Tetragonal ZrO_2 October 1985.

- Technical Report 38. Preparation and Characterization of Alumina Films by Sol Gel Method. January 1986.
- Technical Report 39. The Photoelectrochemical Properties of MoS₂ Single Crystals Grown in the Presence of Cobalt. January 1986.
- Technical Report 40. Preparation and Characterization of Dispersed Rh₂O₃ on Tetragonal ZrO₂. April 1986.

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