Research on

CATALYSIS

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CATALYSIS IS A developing science which plays a critically important role in the gas, petroleum, chemical, and emerging energy industries. It combines principles from the diverse disciplines of kinetics, chemistry, materials science, surface science, and chemical engineering. Catalysis research at universities is typically pursued in departments of chemical engineering and chemistry, although some of the most successful centers of catalysis research employ surface scientists, material scientists, and physicists as well.

Catalysis research at Brigham Young University (BYU) had its beginning about eleven years ago when Professor Bartholomew joined the chemical engineering faculty and has since evolved into an interdisciplinary program referred to as the BYU Catalysis Laboratory. The Catalysis Laboratory currently involves three faculty, two postdoctoral fellows, two visiting scholars, and fifteen students in basic investigations of heterogeneous catalysts.

OBJECTIVES AND PHILOSOPHY

The long term objectives of the laboratory are to:

- **Pursue basic research in the following catalysis-related areas: adsorption, supported metal catalysis, catalyst preparation, catalyst characterization, and catalyst deactivation.**
- **Obtain a basic understanding of catalyst functions in energy- and air pollution-related processes such as methanation, Fischer-Tropsch synthesis and nitric oxide reduction which can be used by industry to develop new and better catalyst technology.**
- **Develop new and improve existing methods and tools for catalyst study, e.g. adsorption techniques, calorimetry, infrared and Moessbauer spectroscopies.**
- **Train and educate 10-15 students on a continuous basis in the science and art of catalysis research.**

Our guiding philosophies are that a basic understanding of these relationships will lead to the development of better catalyst technology and that university laboratories are best suited to carry out fundamental investigations . . .

The emphasis in our laboratory is on basic research relating the physical and chemical properties of catalysts to their activity and selectivity properties. Our guiding philosophies are (i) that a basic understanding of these relationships will lead to the development of better catalyst technology, and (ii) that university laboratories are best suited to carry out fundamental investigations of catalysts and catalytic reactions while industry is better equipped to undertake catalyst screening and development activities. We subscribe to the "multitool approach"; namely, utilizing as many scientific techniques as can be usefully applied to the study of a particular catalyst or catalytic reaction.

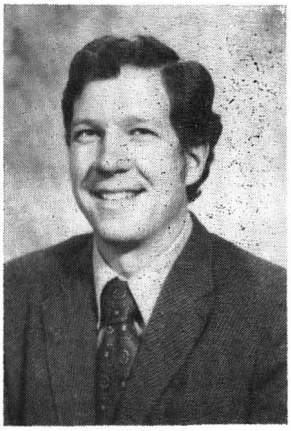
RECENT AND CURRENT RESEARCH ACTIVITIES

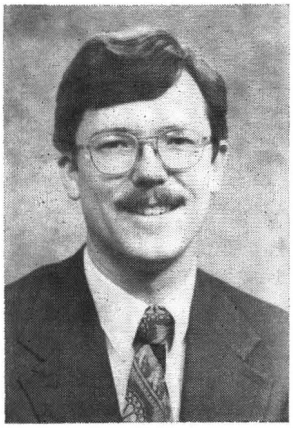
Work over the past five years has focussed on preparation, characterization, activity/selectivity, deactivation, and kinetic studies of cobalt, nickel, and iron catalysts in methanation and Fischer-Tropsch synthesis. Publications of the Catalysis

TABLE 1

Current Laboratory Research Projects

1. **Investigation of Boron Promoted Cobalt and Iron Catalysts in Fischer-Tropsch Synthesis: Sponsors, DOE Fossil Energy, Pittsburgh Energy Technology Center**
2. **Effects of Support on Adsorption, Activity/Selectivity and Electronic Properties of Cobalt: Sponsor, DOE Basic Energy Sciences, Division of Chemical Sciences**
3. **Investigation of Carbonyl-Derived Fischer-Tropsch Catalysts: Sponsor, Atlantic Richfield Co.**
4. **Carbon Deposition on Fluidized Bed Methanation Catalysts: Sponsor, BCR**
5. **Mathematical Modeling of Methanation on Monolithic Nickel Catalysts: Sponsor, BYU**
6. **Infrared and Reaction Studies of Rhodium and Rhodium-Molybdenum Nitric Oxide Reduction Catalysts: Sponsor, BYU**





Calvin H. Bartholomew received his BS degree from Brigham Young University and his MS and PhD degrees in chemical engineering from Stanford University. He spent a year at Corning Glass Works as a Senior Chemical Engineer in Surface Chemistry Research and a summer at Union Oil as a visiting consultant. In 1973 he joined the chemical engineering department at Brigham Young University and was recently promoted to professor. He has authored over 60 scientific papers and 3 major reviews in the fields of heterogeneous catalysis and catalyst deactivation. Active in both teaching and research, he has also consulted with 12 different companies and is currently President of the California Catalysis Society. His major research and teaching interests are heterogeneous catalysis (adsorption, kinetics, and catalyst characterization), Moessbauer spectroscopy, and air pollution chemistry. **(L)**

William C. Hecker received his BS and MS degrees from Brigham Young University and his PhD degree from the University of California, Berkeley (1982). He has considerable industrial experience, having worked for Chevron Research, Occidental Research, Dow Chemical, Exxon, and Columbia Gas Systems. His research and teaching interests include heterogeneous catalysis, chemical kinetics, heat transfer, and infrared spectroscopy. **(R)**

Laboratory since 1982 are listed in the References section to this paper. A complete list of publications and areas of current investigation may be had by contacting the authors. Recent investigations have considered metal boride catalyst preparation chemistry; adsorption of CO, H_2 and H_2S on nickel, cobalt, and iron and of O_2 on reduced and sulfided molybdenum catalysts; activities and selectivities of cobalt, iron and nickel in CO and CO_2 hydrogenation reactions; kinetics of CO and CO_2 methanation on nickel; interactions of cobalt, iron, and nickel with various supports; activities of monolithic nickel catalysts; and deactivation of nickel catalysts by sulfur poisoning, carbon deposition or sintering. Current research projects (Table 1) are directed toward the understanding of activity and selectivity properties of boron-promoted and carbonyl-derived cobalt and iron catalysts in Fischer-Tropsch synthesis; effects of support and dispersion on the adsorption, activity, and selectivity properties of cobalt; mathematical modeling of CO hydrogenation on cobalt, iron, and nickel catalysts; and infrared/reaction studies of NO reduction on Rh and Rh-Mo catalysts.

From the above brief description it is apparent that BYU's efforts in catalysis are diverse in terms of the reactions and catalyst types studied (i.e., methanation, Fischer-Tropsch, NO reduction; metals, oxides, and sulfides). Nevertheless, the experimental approach in most of these studies has a common feature, namely an emphasis on the characterization of these systems using adsorption techniques and spectroscopy combined with laboratory reactor studies to determine specific activity/selectivity properties. The breadth of research interests in the Catalysis Laboratory is further illustrated by the previous work with nickel methanation catalysts which included studies of CO and H_2 adsorption stoichiometry, activity/selectivity properties for CO_2 and CO methanation, CO and CO_2 methanation kinetics, metal-support interactions, TPD of H_2 desorption for nickel on different supports, sulfur poisoning, carbon deposition, sintering of nickel on different supports and modeling of monolithic Ni reactors.

The following brief description of four recent or ongoing studies illustrates the nature of catalysis research at BYU. The first example concerns a study of O_2 adsorption on unsupported MoS_2, carried out by Bernardo Concha (M.S. candidate) under the direction of Professor Bartholomew. Oxygen adsorption uptakes and methanation activities were determined for a series of MoS_2 catalysts having a range of surface areas. The excellent linear correlation of the data (Fig. 1) indi-

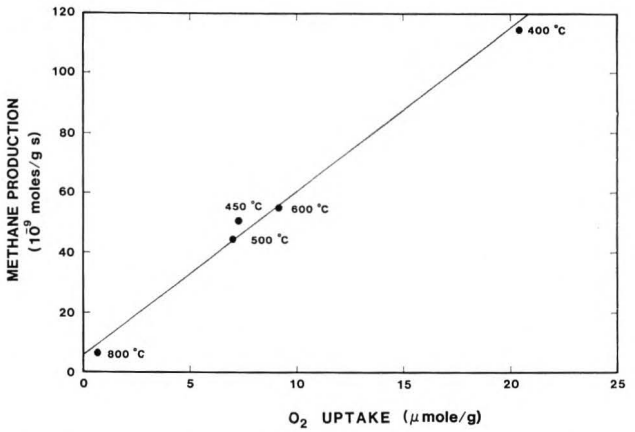


FIGURE 1. Oxygen uptake of MoS_2 catalysts after reaction for 15-20 h versus steady-state methane production (sulfiding temperatures are designated for each catalyst). (Paper Ref. 10)

to the number of oxygen adsorption sites. These results have important application in the development of techniques for characterizing sulfide hydrotreating catalysts used to remove sulfur from sour petroleum and synthetic crude feedstocks.

The second example is the result of a joint effort by Professors Bartholomew, Brewster, and Philip J. Smith in cooperation with PhD candidates Edward Sughrue and Philip R. Smith to model both pellet and monolithic, fixed bed methanators. This state-of-the-art model includes complete kinetic rate expressions for CO and CO_2 methanation reactions, for the water-gas-shift reaction, and for inhibition by steam. It also incorporates the appropriate reaction rate terms to account for pore diffusion, heat transfer, and external mass transfer. Using this model it is possible to predict reactor temperature profiles and conversion-temperature profiles in good agreement with experimental data for pellet or monolithic packed bed methanators (see Fig. 2).

The third example, an ongoing study conducted by Bruce Breneman (MS candidate) and Huo-Yen Hsieh (PhD candidate) under the direction of Professor Hecker, involves the use of infrared spectroscopy to investigate NO reduction catalysts. (NO reduction is an important function of auto emissions catalysts.) A series of supported rhodium catalysts have been prepared using various preparation techniques and various amounts of molybdenum in an effort to improve their activity and selectivity. Activity/selectivity measurements and two types of IR measurements are made on each catalyst. In the first type, the quantity and stoichiometry of various adsorbate molecules (e.g. CO) adsorbed on the catalyst surface at room temperature are determined. This

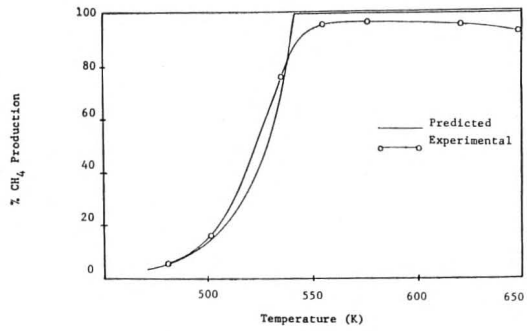


FIGURE 2. Comparison of experimental conversion-temperature profile for 3% Ni/Al_2O_4/monolith with model calculations. (E. L. Sughrue, Ph.D. Dissertation, Brigham Young Univ., 1983)

cates that hydrogenation activity is proportional information is used to determine useful correlations with activity and selectivity. In the second type, IR spectra are obtained under reaction conditions and reveal important information regarding the state of the catalyst surface and the nature of the reaction intermediates. This information is important in determining reaction mechanisms.

The fourth study, carried out by Robert Reuel (MS graduate) under the direction of Professor Bartholomew, involved the measurement of specific activities and product selectivities of cobalt on different supports. These catalysts were found to have a range of cobalt dispersions (fractions of cobalt atoms exposed to the surface) which varied over 2 orders of magnitude. While preparation, support, and cobalt loading influenced the activity and selectivity properties, these data were best correlated with dispersion (see Figs. 3 and

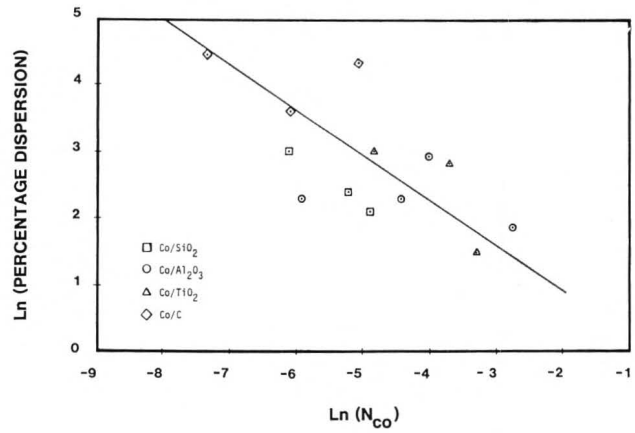


FIGURE 3. Percentage dispersion (percentage of atoms exposed to the surface) versus CO turnover frequency (rate of CO conversion per site per second) at 225°C for supported cobalt catalysts. (Paper Ref. 20)

4). These results indicate that the specific activity of cobalt and its selectivity to high molecular weight products both decrease with increasing dispersion.

One important dimension of scientific work is the careful technical communication of the results. It is, in our opinion, the necessary finishing touch to any project. The laboratory has been reasonably productive in this regard. For example, during a two-year period from 1981 to 1983, the personnel of the laboratory participated in 8 different projects, published 42 papers and reports, completed 7 theses and dissertations, and presented 26 papers and seminars.

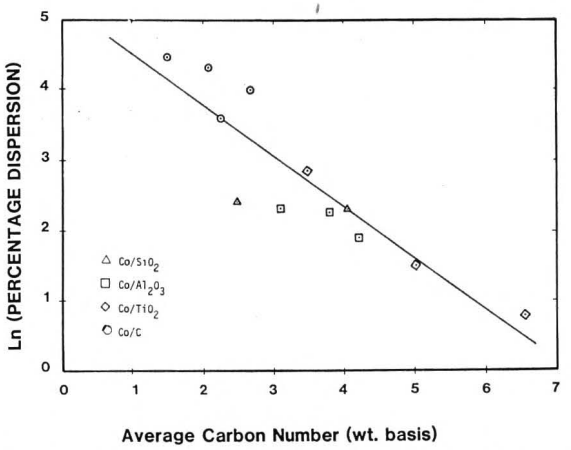


FIGURE 4. Average carbon number of hydrocarbons produced at 225°C and 1 atmosphere for 3 and 10 wt.% supported cobalt catalysts as a function of dispersion. (Paper Ref. 20)

EDUCATIONAL OPPORTUNITIES

The most important objective of our research is to educate and train students in the science and art of catalysis research. This is accomplished at BYU in a number of ways: through participation in research projects and special courses, by participation in the biweekly catalysis seminars, and by attendance at regional and national meetings. In addition to our basic graduate course on kinetics and catalysis (see *Chem. Eng. Ed.*, Fall, 1981), advanced graduate courses are offered biyearly on special topics related to catalysis, e.g., catalyst deactivation, industrial catalysis, and reactor design. The laboratory is host to roughly 10-12 visitors each year of whom about 5-6 present seminars. Graduate students are also provided with opportunities to attend and present papers at regional and national catalysis meetings.

RESEARCH FACILITIES

The Catalysis Laboratory is located in the Clyde Building, which houses the engineering disciplines. It presently includes 6 laboratories (3,000 ft²) and the basic equipment listed in Table 2 to carry out adsorption, reaction, infrared, and Moessbauer spectroscopy studies. Our facilities for studying adsorption processes (two vacuum systems, one flow system, a TGA system, and two TPD systems) are scarcely equalled even by industrial laboratories. The temperature-programmed-desorption (TPD) systems have proven to be particularly valuable in determining the states and energetics of H_2 and CO adsorptions on cobalt, iron, and nickel catalysts. The Moessbauer spectrometer has been extremely useful in determining phase composition and oxidation states of iron in Fischer-Tropsch catalysts while our new FTIR infrared spectrometer is proving its worth in the study of NO adsorption and reactions on Rh catalysts. Having this variety of adsorption, reaction and spectroscopic techniques at our disposal makes it possible for us to pursue the multitool approach.

SOURCES OF RESEARCH SUPPORT

The Catalysis Laboratory has weathered the recent turbulent times of increased competition and declining federal support through diversification of funding from both industry and government agencies (see Table 2 and acknowledgments). We presently receive about $200,000-$250,000 in yearly support from sources outside the university. A new fund raising effort, the Industrial Affiliates program, was initiated about two years ago. The objectives of this program are to establish closer ties with our industrial col-

TABLE 2

Facilities and Equipment of the BYU Catalysis Laboratory

CATALYSIS LABORATORY

- **Six laboratories—3,000 ft² with catalyst preparation areas and preparation equipment[a]**
- **Three lab reactors including a Berty Autoclave reactor**
- **Two vacuum adsorption systems**
- **One flow adsorption system**
- **Five chromatographs—including HP-5830 and Sigma I systems**
- **TGS-2 thermogravimetric balance**
- **Two TPD/TPR systems with mass spectrometer and TC detection**
- **Moessbauer spectrometer system**
- **Nicholet 5-MX FTIR infrared spectrometer system[b]**
- **Sage II, 68000 computer system[b]; 2 Macintosh and one Lisa II-5 computers[c]**
- **Vacuum Atmospheres HE-43-2 Dri-Lab glove box[b]**

UNIVERSITY

- **Six large computers (several VAX 750 and 780 systems, IBM-4341)**
- **Transmission electron microscopes (Botany): Phillips EM-400 (with EDAX) and Hitachi HU-11E. (Both microscopes have been used for catalyst work; TEM sample preparations have been developed.)**
- **Calorimeters (The Thermochemical Institute)**
- **GC-MS (Chemistry)**
- **X-ray fluorescence spectroscopy (Chemistry)**

[a]Three new laboratories added in 1982-83.
[b]Equipment added in 1983.
[c]Equipment added in 1984.

leagues and obtain fellowship support for graduate students through annual subscriptions of $5,000-$15,000. Affiliates of our program receive advance copies of our publications and a special annual study on some aspect of catalysis. Thus far, three companies (Atlantic Richfield Co., Phillips Petroleum Co., and Union Oil Co. of California) have joined our program.

SUMMARY

Catalysis at BYU is a growing cooperative effort of faculty and students engaged in diverse areas of basic research in heterogeneous catalysis. While the Catalysis Lab is unusually productive in terms of publications, its most important products are students well trained in the multitool, multidisciplinary approach to catalysis research. Looking ahead, members of the laboratory are hoping to expand into other areas of catalysis research including homogeneous catalysis and surface science with the addition of a senior scientist in each of these areas. □

ACKNOWLEDGMENTS

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