T/C

Department of Energy
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois 60439

MAY 6 1980

Dr. Louis C. Ianniello, ER-151
Materials Sciences Division
Office of Basic Energy Sciences
Mail Station J-309, GTN

MASTER

CONTRACT DE-AC02-78ER04993.A001 - NORTHWESTERN UNIVERSITY
(EXPIRATION DATE 7/31/80)

Enclosed are renewal documents in accordance with current DOE policy and procedures.

We will initiate contract closeout if we do not receive a completed DOE Form 799A at least 30 days prior to the expiration date of the contract.

Seymour Zirin, Supervisor
Acquisition and Assistance Unit

AA:MQ

Enclosures:
1. Renewal Proposal w/Budget (4 cys)
2. Financial Statement (1 cy)
3. Progress Report No. COO-4993-2 (3 cys)
4. Form DOE 538 (3 cys)

Office of Patent Counsel
MAY 1980

cc: Office of Patent Counsel, CORO - w/encl. 3 (1 cy)
Technical Information Center, Oak Ridge, TN.,
(THRU CORO OPC) - w/encl. 3, Form ERDA-427 and Form DOE 538 (1 cy ea)

(P-30D)

DISCLAIMER

Item 1

Report COO-4993-2

Progress Report

"Investigation of Dispersed Iron Alloy Catalysts in the Carbon Monoxide-Hydrogen Synthesis Reaction"

J. B. Butt and L. H. Schwartz
Northwestern University
Evanston, Il. 60201

MASTER

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

April, 1980

Report for the Period 8/1/79 - 7/31/80, DE-AC02-78ER04993

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

ep

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Endorsements: Co-Principal Investigators

Name:	John B. Butt	Lyle H. Schwartz
	JnB. Butt	L H Schwartz
Title:	Professor	Professor
Telephone:	(312) 492-7620	(312) 492-3606
Date:	4/22/80	4/21/80

Endorsements: Department Heads

Name:	J. S. Dranoff	M. Meshii
	JSDranoff	M. Meshii
Department:	Chemical Engineering	Materials Science & Engineering
Telephone:	(312) 492-7398	(312) 492-3213
Date:	4/22/80	4/22/80

Endorsements: University Official

Name:

Title:

Telephone:

Date:

Abstract

A series of Fe-Ni, Fe-Co, Fe-Cu and Fe-K catalysts supported on $S:O_2$ have been prepared, characterized, and investigated with respect to activity and selectivity in CO-H_2 synthesis. In addition, several silica supported iron nitrides have been prepared and characterized.

During the period encompassed by this report, our catalyst characterization activities have been directed toward the identification of the particle sizes and phases formed upon preparation, calcination, reduction and carburization. We have employed a combination of methods in doing these characterizations: transmission electron microscopy, x-ray diffraction, Mössbauer spectroscopy and temperature programmed oxidation-reduction. Study of the activity and selectivity of the catalyst series has been carried out in a differential reactor system in the range of 225-300°C with 3H:CO stoichiometry. We have also been developing a hydrogen uptake procedure for determining exposed surface in supported iron catalysts.

It has been found that the conditions of preparation strongly affect the nature of the resulting catalyst, both with respect to alloy homogeneity, metal particle size, and catalytic activity. For the Fe system in particular, standard methods of preparation via impregnation and calcination result in very large particle (ca. 80 nm) composites of smaller individual grains (ca. 10 nm). Characterization via x-ray or Mössbauer, however, reveals only the characteristic dimension of the granules and not of the composite particles.

A. Work Accomplished since last report to 1 April, 1980

This report of progress will be divided generally into four basic areas of effort. These are:

1) Thermogravimetric and other studies related to reducibility and relation to particle size.
2) Catalytic activity and selectivity measurements.
3) Transmission microscopy.
4) Iron nitride catalysts.

The catalysts involved in these studies are identified by the following codes: (all supported on Davison Grade 62 silica gel)

	Catalyst	Identification
1.	Fe-1	5 wt % Fe
2.	Fe-2	10 wt % Fe
3.	Ni-1	5 wt % Ni
4.	Fe-Ni-1	5 wt % metal, Fe:Ni=4:1
5.	Fe-Ni-2	5 wt % metal, Fe:Ni=1:1
6.	Fe-Cu-1	5 wt % metal, Fe:Cu=4:1
7.	Fe Co-1	5 wt % metal, Fe:Co=4:1
8.	Co-1	5 wt % Co
9.	Fe-K-1	5 wt % Fe, 1% K (sequential impregnation)

with the exception of Fe-K-1, all were prepared by co-impregnation, drying and calcination as described by us previously. (Amelse, et al., J. Phys. Chem, 82, 558 (1978); Unmuth, et al., J. Catal., 61, 242 (1980)).

Thermogravimetric and Related Studies

Thermogravimetric reducibility studies on Fe-1, Fe-2, Fe-Ni-1, Fe-Ni-2 and Fe-K-1 have shown that approximately 85% of the calcined oxide can be converted to the metallic state after H_2, 425°, 24h. The unreduced material is probably noncrystalline in nature due to the absence of any x-ray diffraction pattern. The activation energies for reduction of Fe-1 ($Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe$) were found to be 156 and 77.5 kJ/mol, somewhat higher than that corresponding to reduction of the bulk oxide (109 and 62 kJ/mol). The hematite reduction of Fe-2 was similar to that of bulk oxide, however the magnetite reduction gives a higher activation energy than for bulk oxide.

The Fe-K-1 catalyst underwent hematite reduction within the same temperature range as Fe-1, however the activation energy was much lower, 60 kJ/mol vs 156 kJ/mol. Magnetite reduction for this material occurred at higher temperatures compared to other Fe catalysts.

For the Fe-Ni-1 and -2, it was shown via Mössbauer and TPR that the oxide initially formed on calcination exists as separate oxides of Fe and Ni in intimate contact. Reduction proceeds via formation of a mixed spinel with a very wide composition range. The activation energies for these reductions are very close to those for Fe. X-ray profiles were very broad, indicative of small particle size and lattice broadening due to the mutual substitution of Fe in the FCC Ni lattice and Ni in the BCC Fe lattice.

It has been often reported that the relative area of the magnetic hyperfine and superparamagnetic peaks of a Mössbauer spectrum of α-Fe_2O_3 can be related to the particle size (or magnetic domain); these results have been supported by x-ray line broadening analysis. We have found, however, that for our silica supported samples this approach can lead to large errors. Using Warren-Averbach (line-shape) analysis of x-ray data, we have determined particle sizes on the order of one-half the size indicated by line broadening (Scherrer analysis), and it presently appears that the previously reported relationship between particle size and relative Mössbauer area is correct only in predicting the proper trend. It is not a quantitative measure.

We have also initiated some studies related to alternative methods of catalyst preparation to those used for the samples listed previously. A rapid heat treatment of the impregnated sample at (ca. 500°C, 1h) results in more highly dispersed catalysts (Fe) at the same metal loading. Initial studies of a 5% Fe/SiO_2 calcined at 500°C, 1 h. indicated the formation of a highly dispersed, non-aggregated oxide with an approximate particle size of 8 nm. (c.f. the section on transmission microscopy).

Catalytic Activity and Selectivity Measurements

Activity/selectivity studies have now been carried out on essentially all of the catalysts listed above. These have been conducted at atmospheric pressure, $3H_2$: CO stoichiometry, and for temperatures from 225-300°C. The catalysts have also been characterized by Mössbauer spectroscopy at three stages: i) after calcination, ii) after H_2, 425°, 24 h and iii) after use in catalysis of the synthesis reaction. Turnover frequencies for methane formation and total CO conversion up to C_5 were based on hydrogen uptake. The chemisorption technique, which consists of flow desorption from a catalyst which was cooled in hydrogen, provides reasonable agreement with particle sizes determined by transmission electron microscopy.

Olefins are believed to be the initial hydrocarbon products, and water the initial oxygen-containing product. In addition to exploring the tendancy to form higher hydrocarbons at a selected conversion, the conversion dependence of olefin saturation, and the water-gas shift reaction was examined.

Spectra of the calcined Fe-Ni catalysts indicate iron is present as α-Fe_2O_3. There is no indication of alloy formation in the oxide state, due to a lack of charge accomodation for Ni^{+2} in ferric oxide. Hence, calcination produces segregation. Upon reduction, both the Fe-Ni and Fe-Co systems form inhomogeneous alloys. Fe-Ni separated into BCC-iron rich and FCC-nickel rich phases. The Fe-Co catalyst exhibits broad Mössbauer absorption lines indicating varying composition.

Upon introduction of the reactant mixture, the Fe, Fe-K, and Fe-Cu catalysts carburize completely. Fe catalysts carburize forming a mixture of ϵ and ϵ' carbides at 250°C. Cu and K show little influence on the carbide crystal structure, with the Fe-Cu catalyst indicating a slightly higher ϵ to ϵ' ratio in a room temperature spectrum. The Fe-Ni catalysts do not carburize under Co and H_2. Neither does the Fe-Co catalyst.

Cooling air-passivated reduced and carburized Fe catalysts to liquid He temperature reveals the prescence of oxyhydroxides which are the passivation products. These compounds are not detected in room temperature Mössbauer spectra due to their low Néel temperature and small room temperature recoil free fraction.

The Fe, Fe-K, and Fe-Cu catalysts show an increase in activity as they carburize. Surface carbon formed by Co decomposition initially has two paths. It can diffuse into the bulk and form carbides, or it can be incorporated into hydrocarbon products. Carbide formation is evidently rapid with respect to hydrocarbon formation. Thus initial activity is low.

Another indication that carbide formation is rapid with respect to hydrocarbon formation is that the initial rate of Co consumption forming hydrocarbons and carbide is greater than the steady state rate of Co consumption. Thus, we favor hydrogenation of surface carbon rather than C-O bond rupture as the slow step in the synthesis. Iron carburizes faster in Co and H_2 than in pure Co. Hydrogen is believed to assist in oxygen removal, which is believed to be the slow step.

Olefins preferentially hydrogenate instead of being incorporated into growing chains, as evidenced by a rapid decrease in the $C_2^=/c_2$ and $C_3^=/c_3$ ratio as conversion is increased, while the fraction of CH_2, shows little change. The Fe, Fe-K, and Fe-Cu catalysts show a gain in their ability to hydrogenate olefins as they carburize.

Water is believed to be the initial oxygen-containing product over Fe, Fe-K, and Fe-Cu catalysts, since a plot of CO_2/H_2O ratio versus conversion extrapolates to the origin. This extrapolation cannot be made for Co and Fe-Ni catalysts which do not exhibit good shift activity.

A favorable synergistic effect is observed upon alloying Fe with Co. This catalyst showed the highest olefin/paraffin ratio, and a shift activity which is superior to iron, even though Co is a poor shift catalyst. Fe-K catalysts were found to be the best all around, showing high activity, the greatest tendancy to form higher hydrocarbons, and shift activity only slightly behind the Fe-Co catalyst. Co-impregnation is slightly superior to sequential impregnation in forming this catalyst.

Studies by Transmission Electron Microscopy (TEM)

Transmission microscopy has been used to examine the following samples in the forms indicated:

1) Fe-1; oxide, reduced, reoxidized, reduced, carburized;
   special pretreatments
2) Ni-1; oxide, reduced
3) Co-1; oxide
4) Fe-Ni-1; oxide
5) Fe-Ni-2; oxide
6) Fe-Cu-1: oxide, reduced, carburized

Ground samples were supported in a carbon coated "holey" Formvar film, and were examined in a JEOL 100B electron microscope at 100 KeV. Both bright field and dark field modes have been employed.

Examination of the Fe-1 oxide revealed the existence of large aggregates, roughly spherical in shape and of approximate dimension 80 nm. Most of the aggregate is illuminated in dark field, indicating that the oxide exists in large but imperfect single crystals on the SiO_2 surface. Similar structures have been observed in the oxide forms of all the catalysts examined to date, with sizes in the general range of 40-80 nm, although particles as large as 200 nm have been observed for Ni-1 oxide.

These results are in sharp contrast to particle sizes determined via Mössbauer or x-ray diffraction, which are almost an order of magnitude smaller. As stated before, we believe this is due to the granular structure of these aggregates; individual granules are thought to be separated by low-angle grain boundaries that cause them to appear as discrete particles in the x-ray analysis. Recent work has been done in characterization of the high temperature calcined materials mentioned earlier. Upon calcination at 500°, 1 h., the granular-aggregates are replaced by individual crystallites approxmately 8-10 nm in diameter.

TEM has also been used to follow the changes that occur during reduction, reoxidation and rereduction. The oxide crystallites in Fe-1 often broke up into smaller particles (ca. 10 nm) upon reduction, though in many cases the large aggregate maintained its original dimension. In both cases, however, the individual subgrains attained unique crystallographic identities; no large single crystals could be found in dark field after reduction had occured. The reoxidized Fe-1 could not be viewed in the dark-field mode, presumably because the incorporation of oxygen into the (individual) small crystallites reduced their diffracting power to an unobservable low level. Subsequent rereduction of this material yielded an iron particle morphology that was not greatly different from that observed in the original reduced material. These TEM results are in reasonable agreement with the reduction-reoxidation-reduction model we have previously proposed (Unmuth, et al., J. Catal. 61, 242 (1980)).

While observations of the Fe-1 showed that many of the oxide crystallites broke up during reduction, other catalysts did not necessarily show this behavior. In Ni-i and Fe-Cu-1, for instance, the reduced samples exhibited the same large crystallite morphology found in their respective oxides. Dark field microscopy revealed that the subgrains did indeed establish separate identities upon reduction; however, the aggregates themselves did not break up.

While dark-field microscopy has yielded the most structural information so far, high-resolution bright field microscopy has permitted the examination of the fine structure of the catalyst particles. Observations of Fe-1-oxide at 1.5 nm resolution show what appears to be a cage-like structure for the oxide crystallite, with the base of the cage imbedded in the porous silica gel.

Iron Nitride Catalysts

Fused iron nitrides were employed as Fischer-Tropsch catalysts in early work on the topic, and demonstrated rather different patterns of activity and selectivity from the carbides. Nitrides were more active, with product distribution shifted to lower molecular weight compounds containing higher yields of oxygenates; further, the nitrides were resistant to oxidation and to the deposition of elemental carbon.

We have prepared nitrides which are the analog of Fe-1. These materials are formed upon exposure of Fe-1 to NH_3, 500°, 2 h. Phase identification via Mössbauer spectroscopy reveals a complex mixture of χ'-, ϵ-, and ξ-nitrides, although in one case apparently only the ξ-nitride (Fe_2N) was formed.

The decomposition of unsupported ξ-Fe_2N was investigated in a He atmosphere in the thermo-balance; two decomposition regimes were found, corresponding to temperatures of 620° and 780°C. However, the decomposition of silica supported ξ-Fe_2N in flowing H_2 was characterized by only a single broad peak at much lower temperature, 430°C.

B. Work Projected for 1 April to 31 July, 1980

Currently we are continuing the TEM characterization of the various catalyst samples. In the next few months we plan to extend the scope of these studies to additional alloy materials at various stages of oxidation and reduction, to the Fe-K system, and to the iron nitride catalysts.

We are also planning additional effort in making catalysts of smaller particle size, and will be running activity/selectivity experiments on these for comparison with the Fe-1 and Fe-2 systems. We shall attempt to use the high temperature calcination procedure to make more highly dispersed Fe-K, Fe-Ni, and Fe-Cu catalysts in addition to those containing only Fe.

Additional x-ray characterization of the Fe_2N/SiO_2 catalysts will be carried out, and we will try to develop procedures for making these that result in more reproducible samples. We also hope to initiate experiments on the activity/selectivity of these catalysts during this period.

A final task in the coming months will be the design of a "high pressure" (ca. 20 atm) reactor system for catalytic activity studies. (See Proposed Technical Program.)

C. Effort Devoted to this Project

During the funded period of this contract to date each co-principal investigator has spent 15% of his academic year time on this project. Continuation of this effort is anticipated during the remainder of the year. Summer effort (1980) will be one month for JBB and 1/2 month for LHS. Three full time research assistants have been associated with this project; Mr. Kym Arcuri, Mr. E. Yeh and Mr. R. Matyi. Mr. J. Amelse has been partially supported by funds from this grant supplemented with internal fellowship support. Dr. A. Shapiro has also been working on this project supported by internal fellowship.

D. Publications and Other Activities

Two papers on the iron-nickel catalysts have been accepted by J. Catalysis:

1) "Iron Alloy Fischer-Tropsch Catalysts. I. Oxidation Reduction Studies of the Fe-Ni System." J. Catl. 61, 242 (1980). JBB, LHS, and E. E. Unmuth.
2) "Iron Alloy Fischer-Tropsch Catalysts. II. Carburization Studies of the Fe-Ni System." J. Catal. in press. JBB, LHS and E. E. Unmuth.

A report is in preparation putting together our observations on the particle size determinations in the Fe/SiO_2 system using x-ray diffraction, TEM, Mössbauer spectroscopy and hydrogen chemisorption.

Presentations (JBB)

1) Dept. of Chemical Engineering, Univ. of Calif., Berkeley, CA, April 16, 1979.
2) Materials Research Division, Lawrence Berkeley Laboratory, Berkeley, CA, April 25, 1979.
3) Dept. of Chemical Engineering, Calif. Inst. of Technology, Pasadena, CA, May 4, 1979.
4) Gordon Research Conference on Catalysis, New London, N.H., June 27, 1979 (short presentation).
5) Pittsburgh Catalysis Society, Pittsburgh, PA, Sept. 28, 1979.

Presentations (LHS)

1) Materials Research Society, Boston, MA, Nov. 29, 1979.