

Item 1

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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

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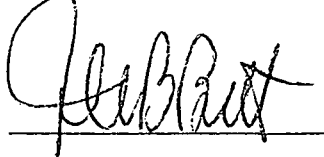
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Name: John B. Butt

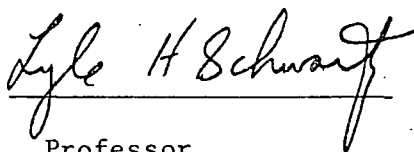


Title: Professor

Telephone: (312) 492-7620

Date: 2/26/81

Lyle H. Schwartz



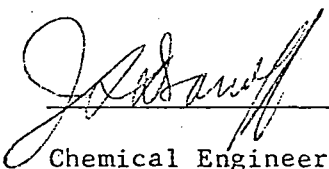
Professor

(312) 492-3606

3/2/81

Endorsements: Department Heads

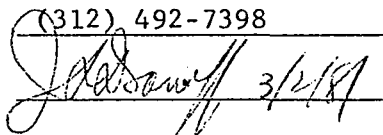
Name: J. S. Dranoff



Department: Chemical Engineering

Telephone: (312) 492-7398

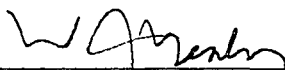
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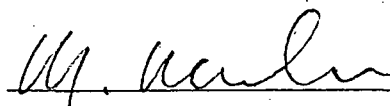
William J. Gealy, Director
Office of Research & Sponsored
Programs

Telephone: 312/492-3003

Date:

March 11, 1981

M. Meshii



Materials Science & Engineering

(312) 492-3213

The past year has seen completion of two major tasks in the research program:

1) A detailed study of the characterization of particle size in supported $\alpha\text{-Fe}_2\text{O}_3$ and related characterizations of the reduced metal with silica gel support.

2) A reaction study of a series of silica supported Fe-Ni, Fe-Co, Fe-Cu, Fe-K and the corresponding pure metals. Synthesis activity and selectivity were particular objectives of this work, and a particular correlation of the conversion dependence of selectivity and water-gas shift activity was observed. We feel this to be an important finding: the catalysts which are good water-gas shift catalysts are the ones which are inhibited during the synthesis. A mechanism of product inhibition by water formation has been proposed to explain the conversion dependence of selectivity.

In the following is given a summary report of these two studies. Full papers reporting these results have been prepared. Item 1) above has been accepted by the Journal of Physical Chemistry and 2) is under review by the Journal of Catalysis. Copies of the full papers are included as Appendices to this report.

1. Particle Size Determination in $\alpha\text{-Fe}_2\text{O}_3$

The determination of the effective surface area of a supported catalyst is a critical step in quantitative activity evaluation, and well established methods involving chemisorption or titration -- normally with hydrogen and oxygen -- have been worked out for supported noble metals. Iron containing catalysts have not been so extensively studied by these means, but are susceptible to characterization by transmission electron microscopy (TEM), x-ray diffraction (XRD) and, less commonly, Mössbauer effect spectroscopy (MES).

In the course of studies of the catalytic activity of 5%-Fe/SiO₂ , Unmuth et al. (1) examined the precursor $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ via XRD and MES, the former yielding a value of 180Å for the average oxide particle size and the latter also, in agreement with earlier measurements of Kündig et al (2) on similar dimension materials. However, subsequent more refined XRD analysis in this laboratory, using the line shape analysis of Warren and Averbach, gave average particle size values of 100Å, considerably smaller. These discrepancies are important, since the size of the oxide precursor determines the size of the reduced metal crystallite and there is a large difference in percentage metal exposed for crystallites ca. 100Å vs. those ca. 200Å.

To examine the XRD results more closely, a series of TEM experiments has been carried out. These reveal that, in fact, the $\alpha\text{-Fe}_2\text{O}_3$ was agglomerated into larger cluster particles with diameters $\approx 800\text{Å}$, composed of tightly packed subgrains of diameter $\approx 100\text{Å}$. It is thus clear that TEM is a critical adjunct to XRD in the characterization of these iron-based catalysts.

The agreement between XRD and MES particle sizes indicates that interparticle effects in the agglomerated particles are not important in determining the magnetic behavior of the small subgrains. Consequently the same caution must be invoked in the use of MES data alone to estimate exposed surface area as in the use of XRD alone.

2. Iron Alloy Synthesis Catalysts: Conversion Dependence of Selectivity and Water-Gas Shift

The performance of several silica-supported systems, Fe-Ni, Fe-Co, Fe-Cu, Fe-K and the pure metals Fe, Ni and Co, were studied for the conversion of CO to hydrocarbons. Alloy formation and catalyst carburization were characterized using MES, as described previously (3). Specific reaction rates were measured in a differential flow reactor at atmospheric pressure, 250-300°C, and turnover frequencies based on the surface area measurement determined via flow-desorption from a catalyst cooled in H₂.

The flow-desorption method for measurement of area is a new technique developed in this laboratory. In this procedure, the catalyst is reduced in H₂ at 425°C for 24 hr, then cooled in H₂ to 0°C. After purging the sample in argon, it is isolated from the flow system and heated to 425°C for 15 minutes. A valve is then switched which allows the H₂ desorption pulse to pass through a calibrated thermal conductivity detector. Results are presented in Table 1 for the catalysts of this study. These are in general agreement with XRD and TEM measurements, but the most convincing justification is the agreement of specific activity for catalysts in this study with that in the literature for similar catalysts. A comparison was made with the data of Vannice (4) for turnover frequency for methane

formation in which area was based on static H_2 uptake. The results agree within 30% for Ni and 35% for Co in those cases where comparisons could be made.

When used as synthesis catalysts (3:1; H_2 :CO, ca. 250°C) the Fe, Fe-K and Fe-Cu catalysts carburized completely. Alloying Co with Fe completely suppressed carburization; the MES indicates an inhomogeneous Fe-Co BCC alloy is formed. The Fe-Ni catalysts carburize rapidly but incompletely, with preferential carburization of the BCC phase. Hence, there is a wide variety of behavior of these materials with respect to carburization, and direct comparison of activity/selectivity is accordingly difficult.

Our evaluation of the activity of these catalysts, using methane turnover frequency N_t as a base, has included a careful study of the conversion (to C_5) dependence of this quantity. Many prior workers have ignored any conversion dependence of activity or selectivity, but there are significant differences among the series here. Over the 1-6% conversion studied, Ni, Co and Fe-Ni showed no N_t sensitivity, while Fe, Fe-K, Fe-Cu and Fe-Co were strongly inhibited with N_t decreasing by a factor of two or more with increasing conversion.

The ratio of CO_2/H_2O was taken as a measure of water-gas shift activity, and this quantity was also determined as a function of conversion. Higher values of the ratio indicate higher shift activity, and in all cases where there was an increase observed with conversion, plots of CO_2/H_2O vs conversion could be extrapolated to the origin, indicating that water is the initial oxygen-containing product. While numerous detailed differences were noted for the various materials, a striking general pattern was observed: Catalysts Ni, Co and Fe-Ni showed a negligible or very small CO_2/H_2O ratio over the range of conversion, while Fe, Fe-K, Fe-Cu and Fe-Co demonstrated generally increasing CO_2/H_2O with

conversion. This is the same ordering as for N_c inhibition with conversion. The Fe-Co catalysts demonstrated the highest shift activity, even though shift activity of Co is very small. The synergistic effect of alloying Co with Fe is attributed to the inhibition of carbide formation in the alloy. Shift activity and conversion inhibition are summarized in Table 2.

The olefin/paraffin ratio is yet another measure of selectivity of importance in synthesis catalysis. In general, the ratios $C_2=C_2/C_2$ and $C_3=C_3/C_3$ decreased with increasing conversion for all catalysts, consistent with the belief that the initial products are olefins. Those catalysts which are incompletely carburized possess lower hydrogenation activity (higher olefin/paraffin), as indicated in Table 3. Two catalysts of particular interest here are Fe-K and Fe-Co. On the basis of hydrocarbon formation, Fe-K has the highest apparent activity, however its ability to incorporate initial products into growing chains is not as good as that of Fe-Co. The Fe-Co produced the highest olefin content, has highest water-gas shift activity, and excellent ability to incorporate olefins into growing chains. At high conversions its selectivity to high hydrocarbons may exceed that of Fe-K.

On the basis of these data we feel that high water-gas shift activity is a desirable feature of a Fischer-Tropsch catalyst because of the lower consumption of hydrogen. However, it would also appear that the rate of hydrocarbon formation over high shift activity catalysts is inhibited by water formation. For production of higher hydrocarbons, there are also

two factors to consider, 1) the intrinsic ability of the catalyst to form higher hydrocarbons and, 2) the incorporation of olefins into hydrocarbons of longer chain length. Promoting iron with electron donors may be responsible for increasing chain length via the former, however limiting the hydrogenation activity of iron appears to be the key to forming longer chains via the latter.

Unpredictable shifts in activity and selectivity occur when iron is alloyed with metals that suppress carbide formation. Cobalt is the prime example in the present work, with definite synergistic effects obtained with the bimetallic. This offers hope that alloying agents chosen independently of electronic considerations can be found to produce active and selective Fisher-Tropsch Catalysts.

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TABLE 1

CATALYST CODE, METAL LOADING, AND H₂ UPTAKE
FROM FLOW CHEMISORPTION

Code	Metal Loading (wgt %)	Mole Ratio Fe:M	H ₂ Uptake (μ mole/gm)
Fe-1	4.94		17.8 ± 0.9
Fe-2	9.33		24.7 ± 1.7
Ni-1	4.58		22.6 ± 1.3
Co-1	4.61		23.1 ± 0.5
Fe-Ni-1*	3.41 (Fe) 0.83 (Ni)	4.32	13.7 ± 1.7
Fe-Ni-2*	2.25 (Fe) 2.37 (Ni)	1.00	17.5 ± 0.7
Fe-Co-1*	3.85 (Fe) 1.02 (Co)	3.98	22.7 ± 0.9
Fe-K-1†	4.94 (Fe) .065 (K)	54	13.7 ± 1.7
Fe-K-2*	9.96 (Fe) .121 (K)	57	17.5 ± 0.7
Fe-Cu-1*	3.6 (Fe) 1.1 (Cu)	3.41	10.6 ± 0.7

* Co-impregnation

† Sequential impregnation of calcined Fe-1

TABLE 2

MOSSBAUER PARAMETERS FOR Fe-Ni AND Fe-Co ALLOYS

Sample	Compound	I.S.* (mm/sec)	Q.S.† (mm/sec)	H (kOe)	Area Fraction
Fe-Co-1 (Fig. 1a)	1) BCC Fe-Co Alloy	.02 ± .03	-.03 ± .03	354 ± 3	.56
	2) Fe ⁺³ "oxide"	.36	1.02		.44
Fe-Ni-1 (Fig. 1b)	1) BCC Fe-Ni alloy	.02‡	0‡	338	.22
	2) Fe _I carbide	.22	.05	162	Fe _I /Fe _{II} = 3.44
	3) Fe _{II} carbide	.19	-.29‡	227	

* Isomer shift with respect to iron metal

† $(V_2 - V_1) + (V_5 - V_6)$ or the distance between a quadrupole doublet

‡ Constrained to this value

TABLE 3

RATING THE CATALYSTS IN ORDER OF THEIR TENDENCY
TO HYDROGENATE OLEFINS

For C ₂ :		For C ₃ :
Ni-1	Decreasing Tendency to Hydrogenate Increasing olefin/paraffin ratio ↓	Ni-1
Fe-Ni-2		Fe-Ni-2
Fe-Ni-1		Fe-Ni-1
Fe-Cu-1		Fe-Cu-1
Co-1		(Fe-1
(Fe-1		Fe-2
Fe-2		Co-1
Fe-K-1		Fe-K-1
Fe-K-2		Fe-K-2
Fe-Co-1		Fe-Co-1

