NEW CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL. FIRST ANNUAL TECHNICAL REPORT, AUGUST 1, 1981-JULY 31, 1981

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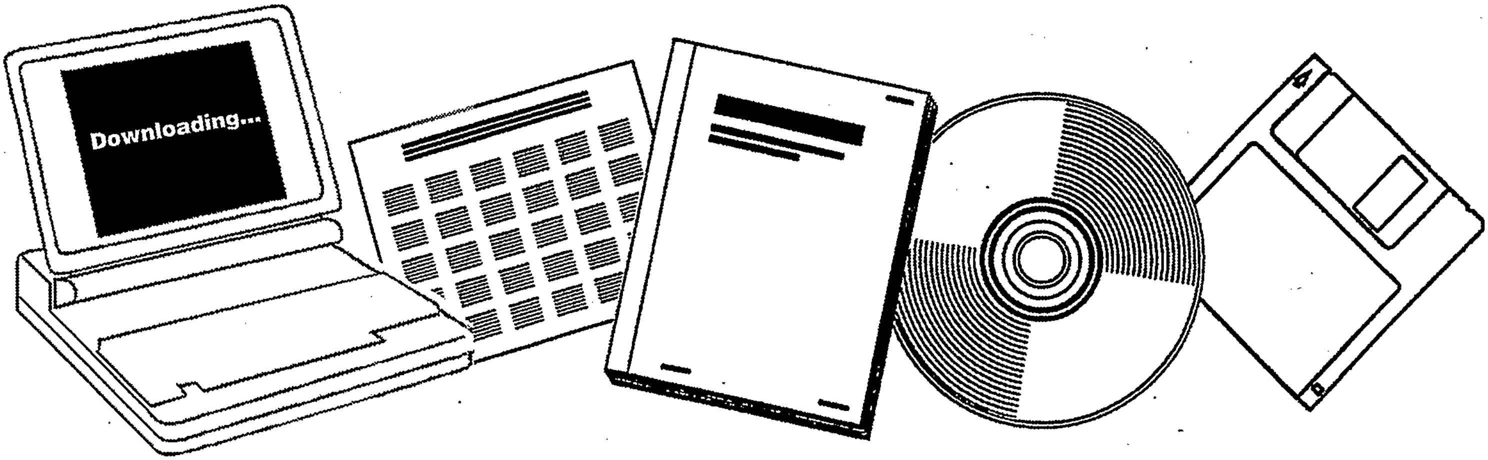

NEW CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL

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Abstract

The synthesis, characterization and evaluation of catalytic activity for synthesis gas conversion of some supported metal catalysts has been achieved during the period of grant support. These catalysts are significantly different from those obtained by conventional synthetic procedures and result in different product distributions when used for synthesis gas conversion.

New Catalysts for the Indirect Liquefaction of Coal

During the second six months of the first year of support under grant No. DE-FG22-80PC30228 work has continued to develop new catalysts for synthesis gas conversion. The results obtained during this six month period will be discussed in three separate areas, viz:1. Synthesis, 2. Characterization, 3. Catalytic Activity.

1. Synthesis

The synthetic procedures developed in our laboratory have been applied to the synthesis of some new zeolite-supported metal catalysts. Specifically during the past six months series of supported iron materials on the zeolites 13X and mordenite ($SiO_2/Al_2O_3 = 62$) have been prepared with weight percent iron (% Fe) varying from ~2 - ~20%. Iron/mordenite catalysts with mordenites of varying SiO_2/Al_2O_3 ratios (~11, 17, 20 and 62) and % Fe loadings of ~16% have also been prepared. A new area of work involving zeolite-supported ruthenium catalysts has been initiated. These potentially catalytic materials have been prepared from $Ru_3(CO)_{12}$ and the zeolite ZSM-5 by procedures similar to those used for the preparation of the above catalysts. Weight percent ruthenium (% Ru) has been varied from ~1 - 10%. Thermal decomposition of these materials has been studied.

2. Characterization

Continued use of both surface and bulk characterization techniques has been made for materials prepared both before and during the period of the report. These include infrared spectrometry (IR), electron spectroscopy for chemical analysis (ESCA), X-ray powder diffractometry (XRPD), ion scattering spectroscopy (ISS), secondary ion mass spectrometry (SIMS) and BET surface area measurements. For iron/oxide materials, these techniques have demonstrated that strong metal-support interactions are present. Although the data has been obtained for these materials, at this time a complete interpretation has not been completed and further discussion will be delayed until a following report. For the iron/mordenite materials, BET data (N_2 adsorption) indicate a significant decrease in the surface area on loading (Table 1) suggesting a high degree of dispersion for the iron oxide on the surface. As the SiO_2/Al_2O_3 ratio increases the BET surface area increases suggesting a lower degree of dispersion as the ratio increases. Calcination of the materials results in an increase in the determined surface area which may be associated with an increase in particle size of the iron oxide component. ESCA data indicate the presence of both Fe^{3+} and Fe^{2+} in the as-prepared (AR) samples (Table 2), data obtained for calcined and used samples also indicate the presence of both oxidation states for the iron oxides. XRPD data did not detect the iron oxide component in the AR samples indicating a particle size < 60 Å. However, calcination of the AR materials results in a growth in particle size; XRPD detects both α-Fe_2O_3 and the support in these calcined materials. ISS data has been obtained both for the Fe/13X series and the Fe/mordenite materials. For all samples studied the Fe/Si ratio is very much larger than that obtained for conventionally prepared materials indicating a high degree of dispersion for the iron oxide component. Plots of Fe/Si versus % Fe loading for the series of materials show an increase in Fe/Si as % Fe increases but around 8% Fe the slope of the plots decrease. This is similar to the behavior for Fe/ZSM-5 materials and it is suggested that above 8% Fe an increase in particle size of the iron oxide occurs; further loading results in buildup of iron oxide crystallites on the support surface. For both plots, intercepts on the % Fe axis (~1.2% for mordenite-supported and ~1.6% for 13X supported materials) suggest some incorporation of iron into the cavities of the zeolite. It should be noted that these intercepts are greater than that found for Fe/ZSM-5 materials which contains smaller cavities than either

13X or mordenite zeolites. For the Ru/ZSM-5 materials, IR indicates deposition of the carbonyl on the support surface; calcination results in decarbonylation and possible oxidation of the ruthenium to RuO_2.

3. Catalytic Activity

The Chemical Data Systems Series 804 CF-HP microreactor is now operational. Modifications to the GC system were made and an integrator for analysis of gaseous products up to and including C_4 hydrocarbons has been incorporated. An FIA system for analysis of liquid hydrocarbon products has been built, tested and is being used as samples are made available from the microreactor. Catalytic activity data for Fe/ZSM-5 and Fe/13X catalysts has been obtained. Effects of % Fe loading, support, temperature and time on stream have been evaluated (Tables 3, 4 and 5). Comparison of % synthesis gas conversion and product distribution with conventionally-prepared Fe/ZSM-5 catalysts have been made (Tables 5 and 6). It is concluded that the Fe/ZSM-5 as prepared samples have significantly different activities for synthesis gas conversion than those prepared by conventional procedures. Complete parametric studies of catalytic activity for the Fe/13X and Fe/ZSM-5 catalysts are in progress; results will be presented in subsequent reports.

Paper accepted for publication:

"$Fe_3(CO)_{12}$ Impregnated ZSM-5: Characterization and Liquefaction Activity". J. M. Stencel, J. R. Diehl, L. J. Douglas, C. A. Spitler, J. E. Crawford and G. A. Melson. Colloids and Surfaces (1981).

Papers presented:

"Correlation of Structural Characteristics and Catalytic Activities for Some Oxide-Supported Iron Catalysts", K. J. Mbadcam, G. A. Melson, J. M. Stencel and R. A. Diffenbach. ACS National Meeting, Atlanta, GA, April 1981.

"Characterization and Evaluation of Some ZSM-5 and NU-1 Supported Iron and Cobalt Catalysts for the Fischer-Tropsch Reaction". J. E. Crawford, G. A. Melson, J. M. Stencel, D. J. Fauth and V. U. S. Rao. ACS National Meeting, Atlanta, GA, April 1981.

"Supported Metal Catalysts: Identification of Surface Species by ESCA". G. A. Melson, J. E. Crawford, J. W. Crites, K. J. Mbadcam, J. M. Stencel and L. J. Douglas. Central and Great Lakes ACS Regional Meeting, Dayton, OH, May 1981.

"Iron Carbonyl-Impregnated ZSM-5: Characterization and Liquefaction Activity". J. M. Stencel, J. R. Diehl, L. J. Douglas, J. E. Crawford and G. A. Melson. ACS 55th Colloid and Surface Science Symposium, Cleveland, OH, June 1981.

TABLE 1. B.E.T. Surface Area (Sq. M/G) by N_2 Adsorption

Catalyst	Ratio SiO_2/Al_2O_3 11.40	17.40	20.40	61.82
Unsupported H-Mordenite 200°C/3 hrs.	443.5	354.1	416.9	462.7
As Received (AR)*	53.5	61.9	146.4	323.3
AR Calcined 500°C/24 hrs.	279.6	287.8	314.1	365.7

*Iron supported H-Mordenite with ~16-17% Fe loading.

TABLE 2. Iron Oxidation States From ESCA/XPS.

Fe/H-Mordenite SiO_2/Al_2O_3 Ratio	Ratio SiO_2/Al_2O_3 11.40	17.40	20.40	61.82
AR	Fe^{2+}/Fe^{3+}	Fe^{2+}/Fe^{3+}	Fe^{2+}/Fe^{3+}	Fe^{2+}/Fe^{3+}
AR SP	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{3+}
500°C	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{3+}
500°C SP	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{3+}
AR Used	Fe^{2+}/Fe^{3+}	-----	-----	Fe^{2+}/Fe^{3+}
AR Used SP	Fe^{2+}/Fe^{3+}	-----	-----	Fe^{2+}/Fe^{3+}
500°C Used	Fe^{2+}/Fe^{3+}	-----	-----	-----
500°C Used SP	Fe^{2+}/Fe^{3+}	-----	-----	-----

TABLE 3. EFFECT OF % LOADING ON CATALYTIC ACTIVITY FOR SYNTHESIS GAS CONVERSION

Fe/ZSM-5

	7% Fe		16% Fe	
Temp °C	280	300	280	300
CO conv %	10	25	38	74
H_2 conv %	31	51	66	81
Reactor Effluent Wt %				
CO	78	65	56	23
H_2	5	3	2	1
CO_2	3	12	16	48
H_2O	8	9	12	7
HC	6	10	13	21
CH_4	31	35	32	39
Liquid HC	25	23	21	23
AR	11	13	8	9
OL	50	42	60	64
SAT	39	45	33	27

TABLE 4. EFFECT OF SUPPORT ON CATALYTIC ACTIVITY FOR SYNTHESIS GAS CONVERSION

	13X (15.4% Fe)		ZSM-5 (16% Fe)	
Temp °C	280	300	280	300
CO conv %	75	83	38	74
H_2 conv %	74	80	66	81
Reactor Effluent Wt %				
CO	23	16	56	23
H_2	2	1	3	2
CO_2	49	57	16	48
H_2O	8	6	12	7
HC	18	20	13	21
CH_4	18	28	32	39
Liq. HC	32	23	21	23
AR	4	4	8	9
OL	52	38	60	64
SAT	44	57	33	27
WAX	12	6	2	1
$C_2^=/C_2$	.21	.04	.25	.12
$C_3^=/C_3$	1.3	.40	.91	.44
$C_4^=/C_4$	.60	.23	1.5	.80

TABLE 5. CONVERSION AND SELECTIVITY TO LIQUID HYDROCARBONS FOR FE/ZSM-5 CATALYSTS PREPARED BY DIFFERENT METHODS

Time Interval (Hrs)		0-48	48-96	96-168
16% Fe ($Fe_2(CO)_{12}$)	CO conv %	55	54	55
	H_2 conv %	65	64	65
	Liquid HC %	49	47	47
14.5% Fe (Impreg)	CO conv %	76	70	72
	H_2 conv %	66	71	73
	Liquid HC %	31	18	14

TABLE 6. EFFECT OF PREPARATIVE TECHNIQUE ON CATALYTIC ACTIVITY FOR SYNTHESIS GAS CONVERSION

Fe/ZSM-5

	14.5% Fe (Impreg)		16% Fe $(Fe_3(CO)_{12})$	
Temp	280	300	280	300
CO conv %	70	84	51	79
H_2 conv %	71	78	62	72
Reactor Effluent Wt %				
CO	28	15	47	22
H_2	2	1	3	2
CO_2	42	55	23	48
H_2O	12	7	13	9
HC	17	22	14	19
CH_4	41	45	14	18
Liquid HC	18	16	49	44
AR			4	4
OL			79	81
SAT			17	16
$C_2^=/C_2$	.12	.06	.66	.51
$C_3^=/C_3$	.79	.74	3.8	2.4
$C_4^=/C_4$	.44	.21	.59	.60