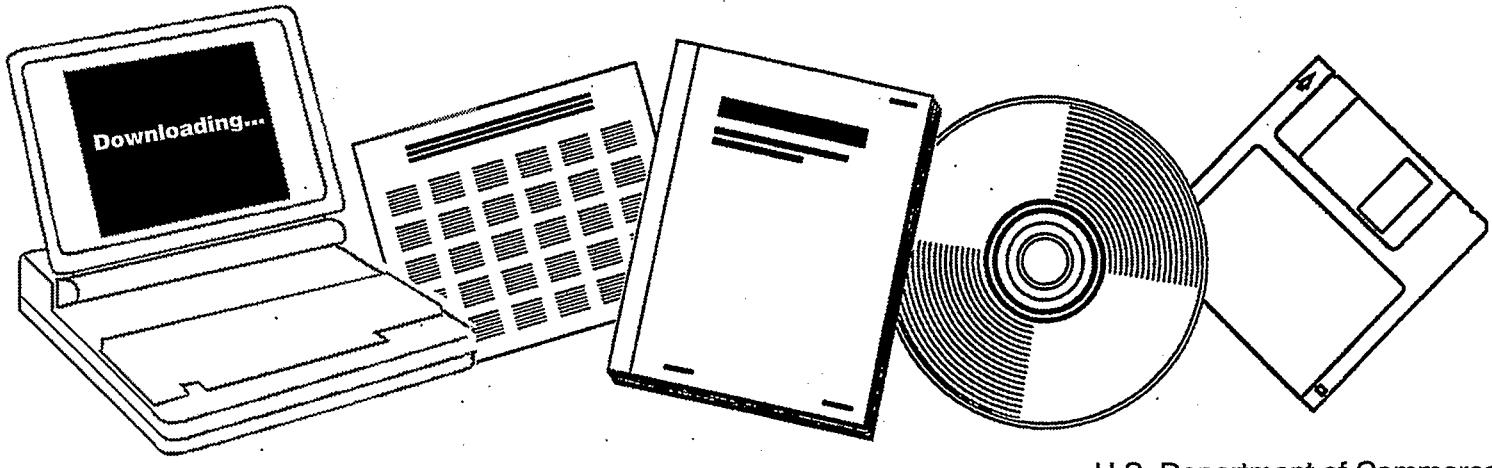
NEW CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL. SECOND QUARTERLY TECHNICAL REPORT, NOVEMBER 1, 1981-JANUARY 31, 1982

VIRGINIA COMMONWEALTH UNIV., RICHMOND.
DEPT. OF CHEMISTRY

1982



DOE/PC/30228--T4

NEW CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL

DOE/PC/30228--T4

DE82 017190

Second Quarterly Technical Report
Grant No: DE-FG22-80PC30228

Period Covered: November 1, 1982 - January 31, 1982

Principal Investigator: Gordon A. Melson
Department of Chemistry
Virginia Commonwealth University
Richmond, Virginia 23284

Abstract

The evaluation of some iron/zeolite catalysts for synthesis gas conversion has been conducted. Effects of % iron loading, pre-treatment and support have been determined.

New Catalysts for the Indirect Liquefaction of Coal

During the second three months of the second year of support under grant No. DE-FG22-80PC30228, evaluation of the catalytic ability of some zeolite supported iron catalysts for synthesis gas conversion has been conducted. The catalysts were prepared from $Fe_3(CO)_{12}$ and the zeolite support ZSM-5 by the extraction technique previously reported. The weight percent iron loadings were approximately 7 and 15% Fe; these catalysts are designated "as-received" or "AR". The AR catalysts were calcined in air at 500°C to produce the "H, 500" catalysts. Previous studies have demonstrated that calcination leads to an increase in the particle size of the supported iron oxide. These materials allowed the effect of percent iron loading and increase in particle size of the iron component to be evaluated. Data obtained previously and reported in the First Quarterly Technical Report for some Fe/13X catalysts has been used for comparison in order to determine the effect of the support for similar zeolite-supported iron catalysts. All catalysts have been evaluated by using a synthesis gas mixture of H_2:CO, 1:1 at 300 psig and at 280° and 300°C with a Chemical Data Systems Series 804 CF-HP microreactor. Effluent gases were analysed by gas chromatography; liquid products by FIA chromatography as described in previous reports. Each catalyst was evaluated for a period of approximately three weeks.

The catalytic data obtained are present in the attached tables. The effects of % Fe loading, calcination and support will be discussed separately.

1. % Fe Loading

Table 1 presents a summary of the data for 7.0% Fe/ZSM-5 and 15.0% Fe/ZSM-5, as-received catalysts. It can readily be seen that an increase in % Fe loading leads to an increase in % CO and H_2 conversion and to approximately twice the yield of hydrocarbons in the reactor effluent. However, within the overall hydrocarbon product, the distribution does not vary significantly. For the liquid hy-

drocarbons, an increase in % Fe loading increases the % olefins, accompanied by a decrease in % aromatics and % saturates. It should also be noted that the increase in hydrocarbons in the effluent is accompanied by a significant increase in the % CO_2 produced.

2. Calcination

Table 2 presents a summary of the data for 15.0% Fe/ZSM-5, as received and 15.0% Fe/ZSM-5, calcined at 500°C. The differences in product distribution may be associated with differences in particle size of the iron oxide component. For the as-received catalyst, the high % CH_4 obtained, compared with the yield for the H, 500 catalyst, is consistent with the presence of small particle sized species. It should also be noted that the yield of liquid hydrocarbon product is significantly greater in the H, 500 catalyst compared with the AR catalyst. The composition of the liquid hydrocarbon product is also affected by the change in particle size of the iron oxide; for the H, 500 catalyst the yield of olefins is increased and the aromatics and saturates are decreased. The increase in particle size leads to an increase in the % CO and H_2 conversion although the % CO_2 is increased by the calcination pre-treatment. Further studies are in progress concerning the relation between particle size and product distribution.

3. Support

In Table 3 is presented some data for Fe/ZSM-5 and Fe/13X catalysts of similar weight % Fe loading in order to determine the affect of the support on catalytic activity and product distribution. Both catalysts are in the as-received form. It should be noted that the Fe/13X catalyst results in a heavier hydrocarbon product distribution compared with the Fe/ZSM-5 catalyst. The hydrocarbon product distribution is also different for the two catalysts, the Fe/13X producing lower yields of aromatics and olefins and higher saturates. This result may be associated with the larger pore size of the 13X support compared with the

ZSM-5 support and the lack of available acid sites in the 13X support. Further studies are in progress to determine the role of the support in zeolite-supported metal catalysts.

Work will continue to determine the factors which are important to maximize the yield of liquid hydrocarbon product and to correlate catalyst structure with product distribution.

Table 1: COMPARISON OF % Fe LOADING FOR Fe/ZSM-5 CATALYSTS

CATALYST TEMP (°C)	CONVERSION (%) CO	H_2	REACTOR EFFLUENT DISTRIBUTION (wt. %) CO	H_2	CO_2	H_2O	HC	HYDROCARBON PRODUCT DISTRIBUTION (wt. %) CH_4	C_2	C_3	C_4	C_{5+}	WAX	LIQUID PRODUCT DISTRIBUTION (%) AR	OL	SAT
7.0% Fe/ZSM-5 AR																
280	10	31	78	5	3	8	6	31	16	14	14	25	0	11	50	39
300	25	51	65	3	12	9	10	35	17	13	11	23	0	13	42	45
15.0% Fe/ZSM-5 AR																
280	38	66	56	2	16	12	13	32	17	17	10	24	0	8	60	33
300	74	81	23	1	48	7	21	39	17	11	7	25	0	9	65	26

Table 2: EFFECT OF CALCINATION (500°C) FOR Fe/ZSM-5 CATALYSTS

CATALYST TEMP (°C)	CONVERSION (%) CO	H_2	REACTOR EFFLUENT DISTRIBUTION (wt. %) CO	H_2	CO_2	H_2O	HC	HYDROCARBON PRODUCT DISTRIBUTION (wt. %) CH_4	C_2	C_3	C_4	C_{5+}	WAX	LIQUID PRODUCT DISTRIBUTION (%) AR	OL	SAT
15.0% Fe/ZSM-5 AR																
280	38	66	56	2	16	12	13	32	17	17	10	21	0	8	60	33
300	73	80	24	1	48	6	20	39	16	14	9	20	0	9	65	26
15.0% Fe/ZSM-5 H,500																
280	58	65	39	2	33	10	16	18	12	15	12	46	0	3	78	18
300	87	79	11	1	60	6	22	22	11	13	8	41	0	3	84	13

Table 3: EFFECT OF SUPPORT FOR Fe/ZEOLITE (AR) CATALYSTS

CATALYST TEMP (°C)	CONVERSION (%) CO	H_2	REACTOR EFFLUENT DISTRIBUTION (wt. %) CO	H_2	CO_2	H_2O	HC	HYDROCARBON PRODUCT DISTRIBUTION (wt. %) CH_4	C_2	C_3	C_4	C_{5+}	WAX	LIQUID PRODUCT DISTRIBUTION (%) AR	OL	SAT
15.0% Fe/ZSM-5																
280	38	66	56	2	16	12	13	32	17	17	10	21	0	8	60	33
300	73	80	24	1	48	6	20	39	16	14	9	20	0	9	65	26
14.3% Fe/13X																
280	49	57	49	3	27	9	12	14	10	17	14	38	8	2	48	50
300	77	76	21	2	49	9	19	12	7	13	9	40	19	3	59	38