NEW CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL

Third Quarterly Technical ReportGrant No: DE-FG22-80PC30228**MASTER**

Period Covered: February 1, 1982 - April 30, 1982

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Abstract

The evaluation of some iron/mordenite catalysts for synthesis gas conversion has been conducted. Mordenites with $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratios of 11.4, 17.4 and 61.8:1 have been used. The effect of $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio on the product distribution has been determined.

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New Catalysts for the Indirect Liquefaction of Coal

During the third quarter of the second year of support under grant No. DE-FG22-80PC30228, evaluation of the catalytic ability of some mordenite-supported iron catalysts for synthesis gas conversion was conducted. The catalysts were prepared from $\text{Fe}_3(\text{CO})_{12}$ and mordenites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 11.4/1; 17.4/1 and 61.8/1 by the extraction technique previously reported; the weight percent iron loadings were approximately 15%. All catalysts contain $\gamma\text{-Fe}_2\text{O}_3$ on the zeolite surface. Chemisorption experiments have been conducted on Fe/Mordenite catalysts prepared by using tetrahydrofuran (THF) and cyclohexane (CHX) as solvents in the preparation; the results are presented in Table 1. The Fe/mordenite catalysts prepared in cyclohexane have been evaluated for their ability to catalyze synthesis gas conversion by using a mixture of H_2 : CO, 1:1 at 300 psig and at 280°C and 300°C as previously described. Prior to catalytic evaluation, each catalyst was first reduced in H_2 at 450°C, and then carbided at 250°C in 1:1 synthesis gas. The catalytic data obtained are presented in the accompanying figures; in each figure the first three points (corresponding to 2, 4 and 6 days under evaluation conditions) are data obtained at 280°C, the second three points (8, 10 and 12 days) are data obtained at 300°C.

NOTE: ● $\text{SiO}_2/\text{Al}_2\text{O}_3 = 11.4$; ▲ $\text{SiO}_2/\text{Al}_2\text{O}_3 = 17.4$; ■ $\text{SiO}_2/\text{Al}_2\text{O}_3 = 61.8$.

From the data presented, the following conclusions may be drawn

1. All catalysts are effective for synthesis gas conversion. % CO and % H_2 conversions (Figure 1) increase with time at 280°C and remain fairly constant at 300°C. Incomplete formation of the active carbide (Fe_5C_2) before run conditions would account for this behavior.

2. Increase in particle size of the iron component is reflected in an increase in % CO and % H_2 conversion (Table 1 and Figure 1).

3. All catalysts are effective for the water gas shift reaction; the equilibrium

is moved further to the right at 300°C compared with 280°C (Figure 2). An increased production of CO_2 reflects an increase in particle size of the iron component, and % CO conversion.

4. The % hydrocarbons obtained in the reactor effluent increases at the higher temperature (Figure 2). The increased percentage yield may be correlated with an increase in particle size of the iron component (Figure 2 and Table 1).

5. Significant quantities of low molecular weight ($\text{C}_1\text{-C}_4$) hydrocarbons are obtained (Figures 3 and 4). In general, the catalyst with the smallest particle sized iron component produces the highest yield of $\text{C}_1\text{-C}_4$ hydrocarbons.

6. All catalysts produce significant quantities of liquid hydrocarbons, C_{5+} (oil) (Figure 4). The catalyst with the smallest particle-sized iron component produces the lowest yield of oil.

7. The Fe/mordenite catalyst with the strongest acidity ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 17.4) produces no wax; those with lower acidity produce significant quantities of wax (Figure 4). Cracking of high molecular weight hydrocarbons is effective for the catalyst with the strongest acidity, less effective for catalysts with lower acidity.

8. The Fe/mordenite catalyst with the strongest acidity ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 17.4) produces the highest % aromatics in the liquid hydrocarbon product (Figure 5). The highest yield of olefins is obtained with the Fe/mordenite catalyst with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 11.4 suggesting the acid sites in this catalyst are effective for oligomerization of low molecular weight olefins but not so effective for production of aromatics.

9. The Fe/mordenite catalyst with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 11.4 produces

high yields of olefinic products, both gaseous and liquid (Figures 6 and 7).

10. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio affects the % liquid hydrocarbon product boiling in the gasoline range (Table 2).

Further study of Fe/mordenite catalysts is in progress in order to determine factors which control the formation of liquid hydrocarbons from synthesis gas.

Table 1. Chemisorption Data for Fe/Mordenite Catalysts (1)

SiO ₂ /Al ₂ O ₃ Ratio	BET S.A. (m ² ·g ⁻¹)	Est. Fe Particle size (2) ..(Å)	
		THF	CHX
11.4	440	130	90
17.4	350	110	35
61.8	460	350	150

(1) J. A. Goodwin and K. Irwin, University of Pittsburgh

(2) Assume CO/Fe = 1/2

Table 2. % Liquid Hydrocarbon Product boiling
in the Gasoline Range (<204°C)

Days on stream (°C)	SiO ₂ /Al ₂ O ₃ Ratio		
	11.4	17.4	61.8
2 (280)	88	+	83
4 (280)	89	+	83
6 (280)	90	+	81
8 (300)	92	87	84
10 (300)	91	87	85
12 (300)	90	87	85

+Insufficient sample for analysis

Papers Presented

"Evaluation of Some New Zeolite-Supported Metal Catalysts for Synthesis Gas Conversion", G. A. Melson, J. E. Crawford, J. W. Crites, K. J. Mbadcam, J. M. Stencel and V. U. S. Rao. Symposium on Advances in Zeolite Chemistry, 183rd National American Chemical Society Meeting, Las Vegas, Nevada, March 1982. (see Preprints, Division of Petroleum Chemistry, Inc., American Chemical Society, 27, 576 (1982)).

"Comparison of Nitrate and Carbonyl Impregnated Metals on Oxide Supports", J. M. Stencel, J. R. Diehl, C. A. Spitler, K. J. Mbadcam and G. A. Melson, 183rd National American Chemical Society Meeting, Las Vegas, Nevada, March 1982.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7