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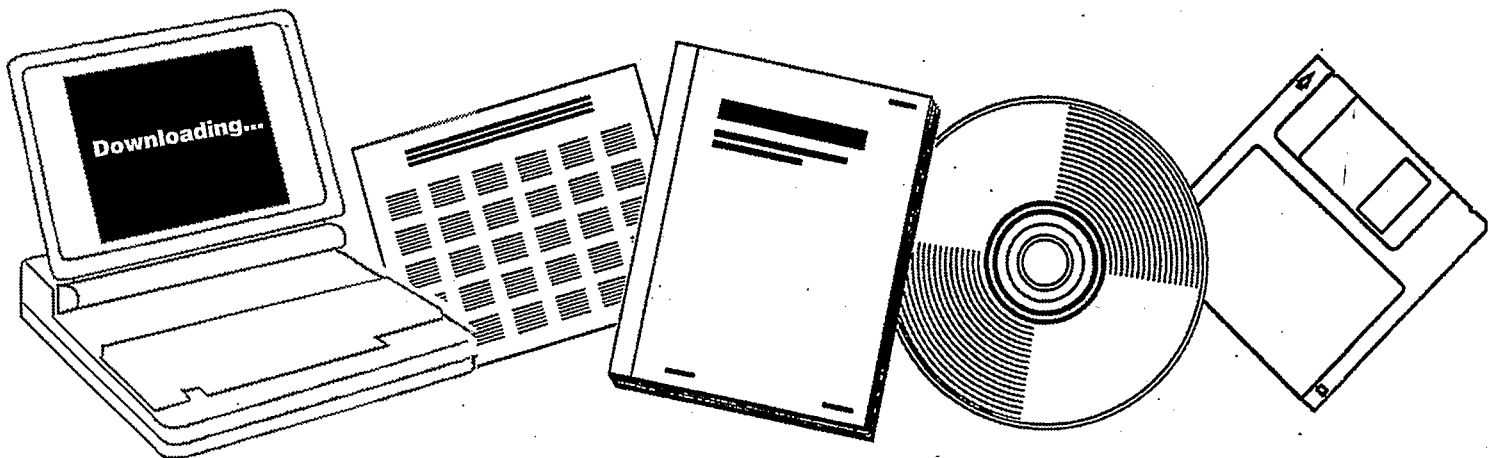
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**SUPPORTED METAL CARBONYLS: NEW CATALYSTS
FOR THE INDIRECT LIQUEFACTION OF COAL.
SEMIANNUAL REPORT FOR PERIOD TO JULY 1,
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SUPPORTED METAL CARBONYLS: NEW CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL

Submitted by: Virginia Commonwealth University
Department of Chemistry
Richmond, VA 23284

Principal Investigator: Dr. Gordon A. Melson
Associate Professor of Chemistry

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Supported Metal Carbonyls: New Catalysts for the Indirect Liquefaction of Coal

Gordon A. Melson

The synthesis, characterization and evaluation of two series of supported metal catalysts has been achieved during the first six months of the contract period. The first series of potentially catalytic materials consisted of iron and cobalt and iron/cobalt mixtures on synthetic zeolite supports; the second series comprised iron and iron/molybdenum, iron/manganese and iron/ruthenium mixtures on oxide supports. The materials were prepared by using procedures recently reported⁽¹⁹⁾. Characterization of the materials was accomplished both in our laboratories at Virginia Commonwealth University and also by using facilities in the Analytical Chemistry (AC) Division at PETC; techniques employed included x-ray diffraction (XRD), ion-scattering spectrometry (ISS), secondary ion mass spectroscopy (SIMS), electron spectroscopy for chemical analysis (ESCA), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The ability of the prepared materials to catalyze the hydrogenation of carbon monoxide was evaluated by using micro-reactors in the Process Sciences (PS) Division at PETC.

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Zeolite-supported Metallic Catalysts

It is concluded from the characterization studies that in the prepared materials, the metals are present on the surface of the supports (zeolites ZSM-5, Nu-1 and mordenite) as small particle-sized ($<50 \text{ \AA}$), highly dispersed metal oxides (XRD and ESCA). Calcination of the materials at 300-500°C in air leads to an increase in the particle size of the metal-containing species and the formation of the oxides Fe_2O_3 and Co_3O_4 for the iron and cobalt containing species respectively (XRD and ESCA). Calcination also leads to changes in appearance of the materials (SEM); however, individual metal-containing particles could not be detected at magnifications up to 30,000X. From ISS and SIMS techniques it is concluded that for both the mono- and bi-metallic species the metal component(s) are present in layers on the surface of the supports (depth profiling studies using ^{20}Ne as the ion source). The catalytic ability of some of the materials was evaluated using 1:1 H_2 :CO gas mixtures at 300 psi in a continuous flow reaction system. The effects of catalyst pre-treatment (calcination) and reaction temperature were evaluated. The results are presented in Table 1. It is apparent that the materials are effective catalysts for the production of both gaseous and liquid hydrocarbons from an artificial synthesis gas mixture. The yield of "oil" is significantly higher than is obtained by using supported iron and cobalt catalysts prepared by conventional procedures (impregnation, precipitation). Analyses of the liquid hydrocarbon products have not yet been received, but are anticipated shortly. Spent supported iron catalysts were recovered after completion of the catalytic runs; XRD and ESCA data are consistent with the presence of the relatively unstable carbides Fe_5C_2 and Fe_2C on the support. Evaluation of catalytic ability for other prepared and characterized materials is currently in progress.

Oxide-supported Metallic Catalysts

Characterization studies indicate that the prepared materials consist of highly dispersed, small particle-sized metal oxides on the support surface (XRD

and ESCA). Calcination in air at 500°C results in the formation of compounds between the metal (iron) and the support, e.g., MgFe_2O_4 for the Fe/MgO system. TGA studies demonstrate that reduction of both the as prepared and calcined materials occurs in flowing H_2 in the temperature range of 350-450°C. The catalytic ability of the iron on oxide support materials was evaluated as previously described (2:1 H_2 :CO mixture); reduction of CO was not observed. Material recovered from the reaction system and characterized by XRD consists of the very stable carbide Fe_3C on the support. Mossbauer data on both as prepared and "spent" catalysts are being obtained to confirm the conclusions concerning the nature of these materials. The effect of pre-treatment conditions on catalytic activity is currently being evaluated.

In conclusion, work completed during the contract period has shown that supported metal species prepared by procedures recently developed in our laboratory are significantly different from those prepared by conventional procedures and that they have significantly different catalytic abilities. Some preliminary conclusions concerning the relationship between catalyst structure and catalyst effectiveness for the hydrogenation of carbon monoxide have been drawn. These studies are continuing.

REFERENCE

1. G. A. Melson, J. E. Crawford, K. J. Mbadcam, F. R. Brown and L. E. Makovsky, 19th Annual Spring Symposium, Pittsburgh Catalysis Society, Monroeville, PA (1980).

Table 1. Evaluation of Catalytic Ability

Sample	Temp. °C	Product Distribution %			Hydrocarbon Product Distribution %			Conversion %		
		H/C	H ₂ O	CO ₂	C ₁	C ₂	C ₃	CO	H ₂	
16% Fe /ZSM-5	280	29.4	36.9	33.7	40.6	21.1	19.9	18.5	23.9	39.6
	300	31.7	41.5	26.9	40.3	18.6	8.8	32.3	21.1	38.5
16% Fe /ZSM-5 Heated at 500°	280	30.9	37.2	31.9	27.4	18.8	14.9	37.3	30.6	49.4
	300	30.4	16.9	52.7	27.8	17.6	10.8	40.1	53.9	62.1
16% Fe/ZSM-5 Heated at 300°	280	41.9	37.4	20.6	38.2	23.8	14.1	23.9	24.0	39.0
	260	35.6	50.2	14.2	35.1	4.6	6.4	51.2	41.2	79.8
20% Co /Nu-1	280	33.7	46.1	20.1	33.0	4.4	6.4	53.4	56.3	94.1
	300	31.3	15.6	53.1	55.5	7.0	6.5	22.3	76.1	95.1