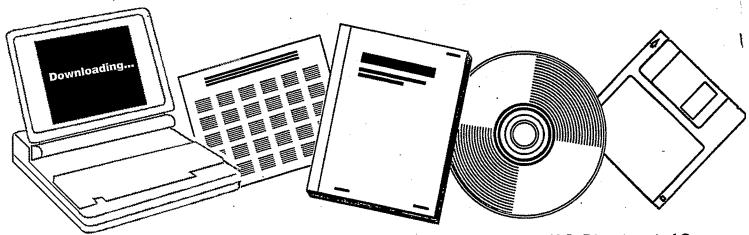# NTiS

SUPPORTED METAL CARBONYLS: NEW CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL. FINAL REPORT FOR PERIOD TO DECEMBER 31, 1980

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SUPPORTED METAL CARBONYLS: NEW CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL

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The synthesis of two series of supported metal catalysts has been achieved during the period of the contract. The first series consisted of iron on the oxide supports, MgO, ZnO, TiO_2, Al_2O_3, SiO_2 and ThO_2; the second comprised iron, cobalt and iron/cobalt mixtures on the zeolite supports ZSM-5, NU-1, mordenite and 13X. All potentially active catalytic materials were prepared by techniques developed in our laboratory during the previous contract period (Contract No. DE-AC 22-79PC10318) using metal carbonyls as the source of the metal component; metal loadings ranged between 1 and 20%. Characterization of some of the materials was achieved by using the techniques of X-ray powder diffraction (XRPD), ion-scattering spectrometry (ISS), secondary ion mass spectroscopy (SIMS), electron spectroscopy for chemical analysis (ESCA), scanning electron microscopy (SEM) Mossbauer spectroscopy (MS) and thermogravimatric analysis (TGA). Evaluation of the catalytic ability of some of the materials for the hydrogenation of carbon monoxide was conducted.

Oxide - Supported Metallic Catalysts

It is concluded from the characterization studies that the "as - prepared" materials consist of highly dispersed, small particle-sized (<50 Å) iron oxides containing both Fe^{2+} and Fe^{3+} on the support surface (XRPD, ESCA). For the Fe/MgO and Fe/ZnO systems, the Fe:Mg and Fe:Zn ratios decrease on sputtering with Ne gas, (ISS, SIMS). Calcination of the materials in air at 500°C results in the formation of a layer of larger particle sized iron oxides, e.g. Fe_3O_4 and/or compound formation between the iron and the support e.g. $MgFe_2O_4$, $ZnFe_2O_4$ for the Fe/MgO and Fe/ZnO systems respectively (XRPD, ESCA). TGA studies demonstrate that reduction of both the as - prepared and calcined materials occurs in flowing H_2 in the temperature range 350-450°C. The catalytic ability of the iron on oxide support materials was evaluated by using a continuous-flow micro reactor system. Typical conditions were 2:1 H_2: CO synthesis gas mixture at 300 psi,

flow rate - 20 ml/min., temperature 300-325°C. Prior to evaluation, all mate-rials were reduced at 400°C for two hours in H_2 and then carbided for 1 hour at 250°C with the 2:1 synthesis gas mixture. Reduction of CO was not observed for the MgO and ZnO supported iron materials. Samples recovered from the reaction system and characterized by XRPD and MS consist of both the unstable carbide Fe_5C_2 (Hägg) and the very stable carbide Fe_3C (cementite). For the iron on alu-mina and silica materials, evaluation of catalytic activity under similar condi-tions to those described above showed that they are active for the synthesis of gaseous hydrocarbons, both paraffins and olefins. The product distribution of mainly light gases (C_1 and C_2) and LPG (C_3 and C_4) hydrocarbons does follow an Anderson-Schultz-Flory plot. The yields of gaseous hydrocarbons from catalysts prepared by our developed synthetic procedure are significantly higher than for those materials prepared by conventional procedures (incipient wetness or precip-itation). It was further noted that for the Fe/SiO_2 system, selectivity for higher hydrocarbons and percent CO conversion both increase with an increase in particle size. Used materials recovered from the micro reactor showed the pre-sence of Fe_5C_2 with the Fe/Al_2O_3 catalysts and both Fe_5C_2 and Fe_3C for the Fe/SiO_2 catalysts (XRPD, MS).

Zeolite - Supported Metallic Catalysts

Characterization studies indicate that the "as - prepared" materials comprise small particle-sized highly dispersed metal oxides (<50 Å) on the support surface (XRPD, ESCA); the metals Co and Fe are present in both +2 and +3 oxidation states. For the as - prepared Fe/ZSM-5 material, the Fe/Si ratio increases on sputtering with a noble gas (ISS, SIMS). In the supported bimetallic Fe/Co samples, the metals are both present in the +2 oxidation state (ESCA), suggesting the deposi-tion of cobalt results in reduction of the previously deposited iron. Heating the prepared catalysts in air at 500°C produces the oxides $\alpha-Fe_2O_3$, Co_3O_4 and the mixed oxide $Fe_2O_3 \cdot CoO$ (XRPD). The behavior of the mixed oxide materials is simi-

lar to the Fe/MgO and Fe/ZnO systems discussed earlier. Catalytic evaluation of the Fe/ZSM-5 materials (as - prepared, calcined at 500°C) showed that the product distribution from the as - prepared sample differed considerably from that obtained with catalysts prepared by conventional impregnation techniques, i.e. a much lower percentage of CO_2 was produced (~ 27% vs 50-60%) and the aromatic , fraction of the oil product, as analyzed by FIA, was more than double that obtained by using a "conventional" catalyst. For the material heated at 500°C, the product distribution was similar to that obtained by using a conventional catalyst. It is proposed that this difference in catalytic behavior is due to differences in the chemical and physical nature of the iron on the support and to differences in the distribution and interaction of the iron with the support. Preliminary data from the Fe/NU-1 materials indicate similar behavior to that found for the Fe/ZSM-5 system. Characterization of the used catalysts indicates the presence of Fe_5C_2 for the as - prepared materials whereas the used catalysts from the heated samples showed th. presence of Fe_5C_2, Fe_2C, Fe_3C and some unreduced iron oxides (XRPD). The Co/ZSM-5 and Co/NU-1 materials produce oil at rates which are comparable with those prepared by conventional techniques and the product distributions were similar. XRPD analysis of the used catalysts showed the presence of both high and low temperature forms of Co metal and the carbide Co_2C.

In conclusion, work completed during the period of the contract has lead to the development of two series of metal-supported materials which have been charactized by a variety of spectroscopic techniques and evaluated for their ability to catalyse the hydrogenation of carbon monoxide. Some of the newly-developed materials have been shown to produce distributions of products which are significantly different from those which are obtained by using conventionally - prepared catalytic materials. Preliminary attempts to correlate catalytic activity with the nature of the catalyst have been made. Further studies are needed to more fully characterize these new materials and to determine those factors which are important

in producing catalysts which give rise to "non Fischer-Tropsch" product distributions.

Papers presented during period of contract

Melson, G. A., Crawford, J. E., Mbadcam, K. J., Brown, F. R. and Makovsky, L. E., "Alumina-Supported Metal Carbonyls: Synthesis and Characterization," 19th Symposium of the Pittsburgh Catalysis Society. Monroeville, PA, May 1980.

Melson, G. A., Crawford, J. E., Mbadcam, K. J., Stencel, J. M. and Brown, F. R., "Characterization of Some Supported Iron and Cobalt Catalysts," SE-SW ACS Regional Meeting, New Orleans, LA, December 1980.