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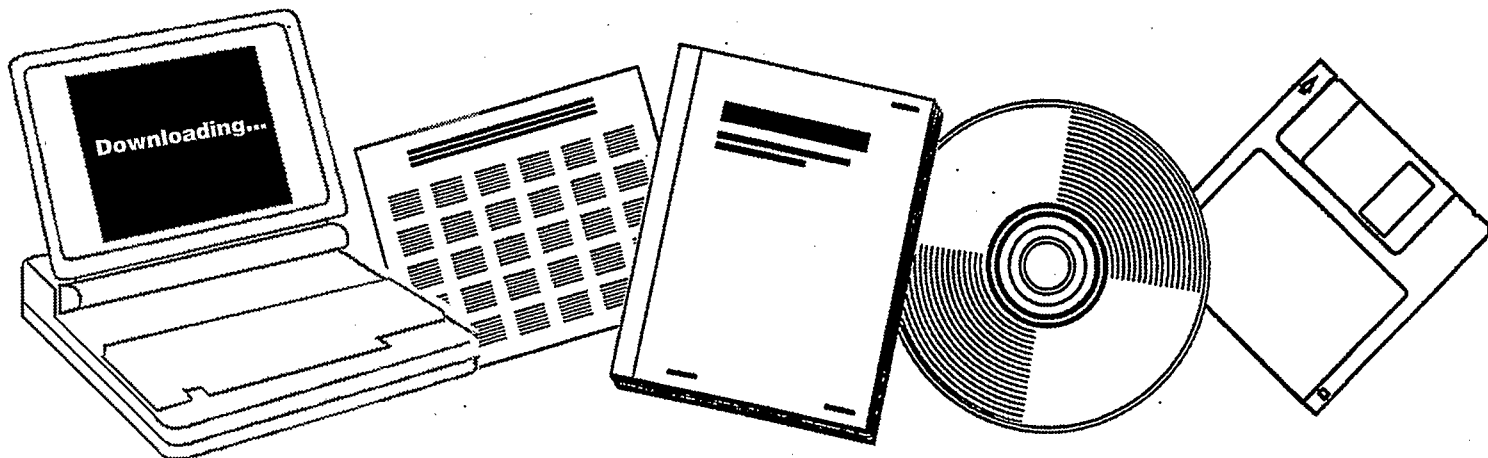
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NEW POTENTIALLY USEFUL CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL

VIRGINIA COMMONWEALTH UNIV., RICHMOND.
DEPT. OF CHEMISTRY

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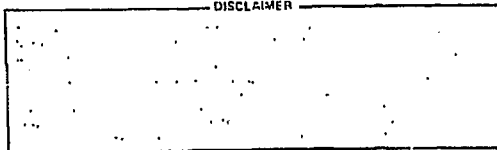
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NEW POTENTIALLY USEFUL CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL

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Abstract

Procedures for the synthesis of some new effective catalysts for the indirect liquefaction of coal via the hydrogenation of carbon monoxide have been developed. These catalysts are synthesized from solutions of transition metal carbonyls and high surface-area aluminas as 1/8" extrudates or pellets by an extraction procedure. The catalysts produced are air-stable but are usually stored in the absence of light; evidence from optical and scanning electron microscope studies indicate that they have an even distribution of a metal carbonyl on the alumina surface and there is no evidence for the presence of crystals or irregular deposits of the carbonyl. The degree of penetration of the metal carbonyl into the extrudate or pellet is dependent on the carbonyl, the alumina, the solvent and the reaction time employed. The alumina-supported carbonyls have been characterized by the application of spectroscopic and thermogravimetric techniques; it is concluded that a strong interaction between the alumina and the carbonyl is present. Decarbonylation may be achieved by heating the supported carbonyls in flowing He, N₂, or H₂. Effective methanation catalysts can be derived from the supported carbonyls after reduction in flowing H₂ at elevated temperatures.

The initial phase of the research has involved the synthesis and characterization of some materials which may serve as catalysts for the indirect liquefaction of coal; more specifically the new catalysts should be capable of the selective production of both new and currently used fuels from synthesis gas (mainly CO and H₂).

Procedures for the synthesis of some new effective catalysts for the CO/H₂ reaction have been developed. These catalysts are synthesized from solutions of the carbonyls Ru₃(CO)₁₂, Ir₄(CO)₁₂, Rh₆(CO)₁₆, and Os₃(CO)₁₂ and high surface area aluminas as 1/8 "extrudates or pellets by an extraction procedure. The developed procedures are similar for the synthesis of each catalyst, however the solvent and reaction times employed vary with the carbonyl and the alumina used. The catalysts produced may be handled in air but are usually stored in the absence of light; evidence from optical and scanning electron microscope studies indicate they have an even distribution of metal carbonyl on the alumina surface and there is no evidence for the presence of crystals or irregular deposits of the carbonyl. (It should be noted that by using previously reported conditions (1-10) for reactions between some of the carbonyls and alumina, uneven distributions of crystals of the original carbonyl on the alumina are produced. The physical properties of these materials are identical to those obtained for samples prepared by dry mixing of the reactants; it is concluded that a physical adsorption takes place and that a high degree of dispersion of the carbonyl does not result by using these previously reported reaction conditions.) The degree of penetration of the metal carbonyl into the extrudate or pellet is dependent on the carbonyl, the alumina, the solvent and the reaction time employed. X-ray fluorescence and scanning electron microscope studies have enabled a distribution profile of the carbonyl through the extrudate or pellet to be determined. Catalysts have been prepared in which the penetration varies from very little (i.e. surface

distribution) to complete distribution through to the center of the support. Adsorption/reaction of the carbonyl is accompanied by significant changes in the carbonyl stretching region of the IR spectra of the materials, however, the degree of penetration of the carbonyl does not affect the frequencies of the observed bands. The alumina-supported carbonyls have been further characterized by a variety of spectroscopic (IR, Raman, ESCA, SEM, X-ray fluorescence, X-ray diffraction) and thermogravimetric techniques. The physical properties of these species are significantly different to those obtained for species prepared by the equivalent of the dry mixing procedures reported by other workers. Thus, we conclude from the characterization studies that a strong interaction between the alumina and the carbonyl is present and that the species we have produced are significantly different from those reported by others. Depending upon the conditions of the preparation, reaction may be accompanied by partial or complete decarbonylation of the metal carbonyl and oxidation of the metal to form metal-surface oxygen bonds. When the alumina-supported carbonyls are heated, both in air and in an inert gas by using thermogravimetric analysis equipment, decarbonylation results which is accompanied by marked changes in both the appearance and spectroscopic properties of the product. By careful choice of the temperature and conditions, partially or completely decarbonylated species can be prepared. These species have been characterized by the techniques mentioned above; it is concluded that decarbonylation achieved by this procedure also gives rise to oxidation of the metal. Decarbonylation achieved by heating the supported carbonyls in flowing H_2 at temperatures up to 450° however produces distributions of the unoxidized metal on the surface. For catalysts derived from $Ru_3(CO)_{12}$ and $Ir_4(CO)_{12}$ by this procedure, chemisorption experiments (H_2 adsorption) indicate a high degree of dispersion of the metal on the alumina support. This dispersion is greater than that produced for catalysts derived from aqueous solutions of the transition metal

halides of the same percent loading. Preliminary experiments for evaluation of the catalytic activity of some of these species have demonstrated that effective methanation catalysts can be derived from the $\text{Ru}_3(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$ and $\text{Ir}_4(\text{CO})_{12}$ supported carbonyls after prior reduction in flowing H_2 at temperatures up to 450° , (reaction conditions 3:1 H_2 :CO at approx. 4 atm. pressure; temperature 400°). Deactivation of the catalysts occurs after several hours, however, reactivation can be achieved by reheating in hydrogen.

Thus, during this initial phase of the research we have developed procedures for the synthesis of some highly dispersed metal carbonyls on alumina supports and demonstrated that these species may be used to form effective catalysts for the hydrogenation of carbon monoxide. The application of a variety of physical techniques has enabled us to make conclusions concerning the chemistry of the dispersed carbonyls and the interaction between the carbonyls and the support.

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