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NEW CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL. FINAL TECHNICAL REPORT

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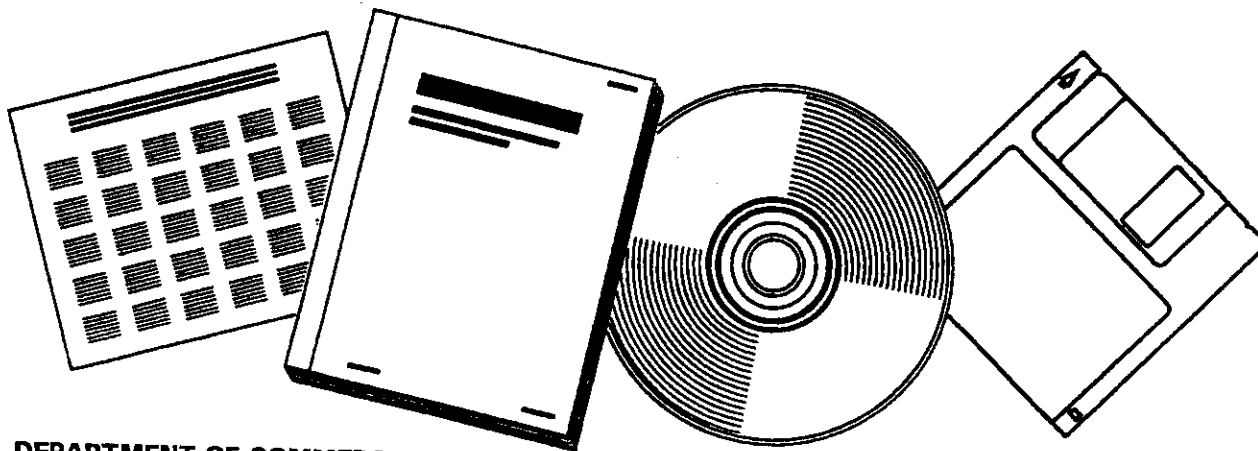
NEW CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL

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INTRODUCTION

The indirect liquefaction of coal is a two-step process. In the first step, coal is gasified and "scrubbed" to give synthesis gas (mixtures of mainly carbon monoxide and hydrogen of various mole ratios); in the second step, the synthesis gas mixture undergoes reaction over a catalyst. Usually, a variety of liquid and gaseous products, that must be separated, are obtained from the second step. The catalysts used in this second step are, like those in the direct liquefaction process, readily poisoned particularly by sulfur compounds; however, the synthesis gas mixtures can be purified after the gasification step if sulfur-containing coals are employed. Low-sulfur coals such as those found in the Appalachian region of western Virginia, southern West Virginia and eastern Kentucky (reserves estimated to be approximately 16% of U.S. coals containing less than 1% sulfur) are ideal raw materials for the indirect liquefaction process since any sulfur-containing impurities would be of low concentration in the synthesis gas mixtures and the liquefaction catalysts should have extended lifetimes. The indirect liquefaction process has several advantages over direct liquefaction processes. First, the technology for the initial gasification step is well proven and understood; second, the synthesis gas obtained is, or can be made into, a "clean" reactant mixture source; and third, the conversion of synthesis gas mixtures to hydrocarbon or oxygenated products has been studied for several years and commercial plants have demonstrated that fuels and chemical feedstocks can be obtained by this approach. Recently, the use of a synthetic shape-selective zeolite, Mobil's ZSM-5, has been shown to convert methanol, which may be obtained from synthesis gas, to high-octane gasoline in good yield.

In order to make the indirect liquefaction of coal a viable process, and the products obtained therefrom competetive with those obtained from crude oil, more research is necessary to increase the efficiency and selectivity of the synthesis gas conversion. This translates to the development of new catalysts and new procedures for the hydrogenation of carbon monoxide. It is anticipated that the development of new, product selective catalysts for the indirect liquefaction of coal will lead to the production of synthetic liquid fuels which in turn will assist the U.S. in significantly reducing imported oil.

SCIENTIFIC DISCUSSION

Background

The catalyzed reaction between carbon monoxide and hydrogen has been studied since the early part of this century. In 1902, Sabatier and Senderens (1) synthesized methane by using a reduced nickel catalyst, and patents for the formation of a liquid containing hydrocarbon and oxygenated organic compounds were taken out in 1913 and 1914 by the Badische Anilin und Soda-Fabrik, A.G. company (2). In 1923, the first paper describing the formation of a synthetic oil (named synthol) produced from carbon monoxide and hydrogen was published by Fischer and Tropsch (3). The conditions for the reaction were 400°, pressures > 100 atmospheres and the presence of an iron-based catalyst. Since that time, a considerable amount of research on the "Fischer-Tropsch reaction" has been carried out. The Fischer-Tropsch reaction is really a collection of reactions since a wide variety of products may be obtained from carbon monoxide and hydrogen:

$$CO+H_2 \rightarrow C_aH_b + C_cH_d(OH)_e + aldehydes + acids, etc.$$
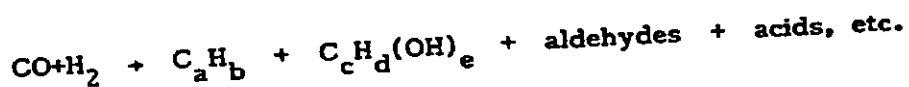
The use of different catalysts and reaction conditions can influence the course of the reaction with the result that products ranging from methane through oxygen-containing compounds to gasoline and high molecular weight waxy paraffins have been produced. The early work on the Fischer-Tropsch reaction will not be reviewed here, however, certain key references covering this work are listed at the end of the text, see refs. 4-7.

Although several plants using the Fischer-Tropsch process were constructed during the World War II years, the only commercial plants currently in operation are run by the South African Coal Oil and Gas Corporation Limited, SASOL, and financed by the South African Government. The SASOL process uses an iron-based catalyst and medium (-25 atmos) pressure for the production of a variety of products including liquefied petroleum gas (C_3-C_4 hydrocarbons), gasoline range hydrocarbons (C_5-C_{11}), diesel fuels and waxes. The liquid fuels which are obtained are produced from inexpensive coal (compared to available U.S. coal supplies) and at prices which are very high by current U.S. standards. In order for the indirect liquefaction of coal to be economically feasible in the U.S., new, more efficient processes must be developed. It has been found that for the majority of "conventional" catalysts, the Fischer-Tropsch reaction follows Schulz-Flory kinetics (8,9). The Schulz-Flory equation predicts limitations in the selectivity of products for the CO/H_2 reaction. For example, the maximum C_2 obtainable is 30%; the maximum gasoline range hydrocarbons (C_5-C_{11}) obtainable is 47% and the maximum C_9-C_{25} diesel fraction is 54%. Agreement between predicted

and found product distributions is good (10). The only product that can be selectively obtained is methane; this restriction in selectivity is the major limitation associated with the use of the conventional catalysts that have been employed in processes for the indirect liquefaction of coal.

Since it has been demonstrated that the Fischer-Tropsch reaction can produce a range of products including fuels and petrochemicals from gasified coal, research should now concentrate on the development of new, long-lived, efficient and product-selective catalysts. It is anticipated that such catalysts will function in a different manner from those that are currently used, i.e., the mechanism of the reaction will be different from that which is operative when using conventional Fischer-Tropsch catalysts. Research into the development of new potentially active catalysts for the hydrogenation of carbon monoxide must involve correlations between catalyst structure and product distribution. We have used this investigative approach to catalyst development in the research described herein.

Heterogeneous catalysts for the CO/H_2 reaction have been investigated in more detail than homogeneous catalysts (11-14); many of these catalysts involve metal atoms on "inert" supports (15). Some of the earliest Fischer-Tropsch catalysts involved metal ions or atoms and oxide supports; for example, it has been known since the 1920's that ZnO either alone or with Cr_2O_3 will selectively catalyze the formation of methanol (16). Copper-zinc oxide catalysts have also been investigated and recently, Klier et al. studied these catalysts in more detail (17). Vannice (7) has reviewed the catalytic synthesis of hydrocarbons from synthesis gas mixtures; both the kinetics of methanation and the nature of adsorbed species on heterogeneous catalysts were discussed. Vannice

also studied the catalytic formation of hydrocarbons from synthesis gas mixtures using supported Group VIII metals as heterogeneous catalysts (18). An ordering of turnover numbers at 275° for methane formation by using Ru, Fe, Ni, Co, Rh, Pd, Pt and Ir on alumina was obtained and the kinetics of methanation with these catalysts was studied. Recently, Rofer-DePoorter proposed a comprehensive mechanism for the Fischer-Tropsch synthesis (19). This mechanism recognizes the existence of a variety of elementary reactions in the overall synthesis.

Zeolites have been used as supports for several transition metals in order to produce bi-functional catalysts for carbon monoxide hydrogenation (20-22). In these bifunctional catalysts, the role of the metal is to activate the reactants and to initiate the reduction and polymerization processes; the zeolite controls the type and molecular weight distribution of the products. Both metal salts and metal carbonyls have been used as the source of the transition metal. For example, the ion-exchange method has been used with metal salts to prepare a variety of zeolite-supported iron (23-26), cobalt (26-28), nickel (26-29), ruthenium (30-35), rhodium (36) and iridium (37) catalysts. In the ion-exchange method, the compensating cation in the zeolite, often Na^+, is exchanged for the transition metal ion. Recently, Scherzer and Fort (38) have reported a new preparation method for zeolite-supported metal catalysts. In this method, a metal-exchanged zeolite is reacted with an anionic, water-soluble metal cyanide complex; both single and polymetallic catalysts may be prepared. Impregnation methods, particularly the wet impregnation technique, have also employed aqueous solutions of metal salts; drying and reduction in hydrogen usually follows the impregnation process (39,40). However, a low dispersion of the metal usually results

from either incomplete or ineffective reduction of the metal due to relatively large particle sizes and/or strong interactions between the oxidized form of the metal and the zeolite. Some of the catalysts described above have been studied for carbon monoxide hydrogenation and have shown selectivity for a specific product or product range. Fraenkel and Gates (27) have shown that Co/A zeolites, when reduced with cadmium vapors and then with hydrogen, produce propylene in 60-100% yield from synthesis gas. Jacobs and coworkers (33,34) showed that, with Ru/Y zeolites, the number of carbon atoms in the product chain can be affected by the size of the ruthenium metal particles present in the zeolite. Nijs and Jacobs (41) have proposed "an extended Schulz-Flory model" that accounts for the product distributions obtained with Ru/Y zeolites (33) and for the product distributions reported by Vanhove and coworkers (42) for Co/Al_2O_3 catalysts. This extended Schulz-Flory model takes into account the range of sizes of the metal particles and shows that the product distribution can be predicted for carbon monoxide hydrogenation if this information is known.

Recently, the use of metal carbonyls for the preparation of supported metal catalysts has been reported by several authors. Decarbonylation of supported carbonyls may be achieved by heating in vacuo or in an inert atmosphere; this decarbonylation may lead to coordinatively unsaturated species on the surface of the support, as noted by Brenner (43), which may be capable of binding carbon monoxide and/or hydrogen in a manner such that a different mechanism for the Fischer-Tropsch reaction will result. Sublimation has been the main method used for the preparation of zeolite-supported metal carbonyls; this is usually carried out under vacuum at ambient or elevated temperatures. Sublimation was

used to prepare Y-zeolite supported iron (44-46), nickel (47), molybdenum (48), ruthenium (48), rhenium (48) and rhodium (49) catalysts and osmium/X zeolite catalysts (50). Dry grinding and wet impregnation have also been used as methods of preparation for iron (51,52), ruthenium (52) and cobalt (52) Y-zeolite catalysts. Ballivet-Tkatchenko and coworkers (46), in preliminary catalytic studies of synthesis gas conversion over an Fe/Y catalyst, have shown that less C_2 and C_3 olefins and more C_{4+} hydrocarbons are produced than with a conventionally prepared Fe/Al_2O_3 catalyst. Later work by the same group (51,52) showed that the conversion of 1:1 synthesis gas over an iron carbonyl/Y zeolite catalyst produced only trace amounts of C_{9+} hydrocarbons, and that the unsaturate to saturate ratio for the C_3 hydrocarbons is significantly higher than that of the C_2 hydrocarbons, viz. 47 versus 7.1. Recently, the use of sublimation of $Ru_3(CO)_{12}$ for the preparation of some zeolite-supported ruthenium catalysts was reported (53). Selectivities for methane and for C_2-C_4 alkenes increased and decreased respectively with increasing temperature between 220° and 320° for all catalysts.

Although the preparation of some supported metal carbonyls has been reported, with the exception of IR studies in the ν(CO) region and the measurement and interpretation of temperature-programmed decomposition spectra by Brenner and coworkers, in depth studies involving the application of physical characterization techniques to investigate the surface science of the catalysts and to determine the nature of the interaction between the metal carbonyl and the support have not been undertaken. A major drawback to the methods used to prepare supported metal catalysts from metal carbonyls is that low metal loadings are often obtained

and the metal-containing species are in the form of crystallites that are unevenly dispersed on the support surface.

In our laboratory, we have developed a new method for the preparation of supported metal catalysts from metal carbonyls, referred to as the extraction technique, that results in materials containing highly-dispersed, small particle-sized metal species on the support. The restriction of low metal loadings has also been overcome by the use of this technique; supported metal catalysts with greater than 20 wt. % metal may routinely be prepared. All prepared catalysts have been characterized by bulk and surface-sensitive techniques and conclusions concerning the metal species and the nature of the interaction between these species and the support have been drawn. Correlations between the structure of the catalyst and its activity for synthesis gas conversion have been made.

Most of the work reported in the literature for synthesis gas conversion using catalysts involving zeolites has employed the shape-selective zeolite ZSM-5, developed by Mobil Oil; several patents for catalysts used to produce hydrocarbons have been issued. These catalysts consist of a metal component, such as zinc, chromium or copper, that favors the production of methanol from synthesis gas which can then be upgraded by the ZSM-5 to produce gasoline-range hydrocarbons (54-56) or contain iron in different forms in conjunction with ZSM-5 (55,57). Chang, Lang and Silvestri (57) report examples of product distributions from four different iron-containing catalysts, evaluated at 370° and 515 psia using synthesis gas of 1:1, H_2:CO ratio; for each catalyst the yield of liquid hydrocarbon product, C_{5+}, is low and the amount of methane produced is high. Three reports have been published in the literature by workers from Mobil Oil on the conversion of synthesis gas over transition metal catalysts

-8-

containing ZSM-5. Chang, Lang and Silvestri (39) reported the production of aromatic hydrocarbons from synthesis gas when Fe/ZSM-5, Zr/ZSM-5 or ZrCr/ZSM-5 catalysts were used. In a parallel paper, Caesar, Brennan, Garwood and Ciric (58) described the production of liquid hydrocarbons in 60% yield from the reaction of synthesis gas over a commercial potassium promoted iron ammonia synthesis catalyst mixed with ZSM-5. Essentially all of the liquid product obtained boiled in the gasoline range, i.e. the boiling point was less than 204°C. Ruthenium/ZSM-5 catalysts have been described by Huang and Haag (59). These authors found that Ru/Al_2O_3 mixed with ZSM-5 is active for the conversion of synthesis gas to gasoline range hydrocarbons that contain significant quantities of aromatics. Parametric studies were performed in order to maximize the yield of aromatics and to minimize the methane yield. Rao and coworkers have reported a comparison of iron catalysts prepared by the wet impregnation technique using $Fe(NO_3)_3$ and the zeolites ZSM-5 and silicalite (40,60). Silicalite is the extreme end of the ZSM-5 aluminosilicate series in which no aluminum is present; thus, silicalite is not technically a zeolite, it can more accurately be described as a molecular sieve form of SiO_2. The liquid hydrocarbon products obtained from the Fe/ZSM-5 and Fe/silicalite catalysts were significantly different when synthesis gas, H_2:CO, 2:1 was used as the reactant; it was concluded that the acid sites present in the ZSM-5 were responsible for the conversion of olefins and oxygenates to aromatics. These authors also studied the effect of the transition metal by comparing an Fe/ZSM-5 catalyst containing 11.1 wt. % Fe with an Fe-Co/ZSM-5 catalyst containing 5.6% Fe and 4.5% Co. For the Fe/ZSM-5 catalyst the liquid product was higher in aromatics and lower in olefins than the liquid product obtained

by using the Fe-Co/ ZSM-5 catalyst. Recently, we have described some Fe/ZSM-5 catalysts prepared from $Fe_3(CO)_{12}$ and the acid form of ZSM-5 by the extraction technique (61). These catalysts contain 1.6 to 21.1 wt. % Fe and were characterized by surface sensitive and bulk experimental techniques. A 16.0% Fe/ZSM-5 catalyst was evaluated for synthesis gas conversion; this catalyst, unlike an Fe/ZSM-5 catalyst of similar iron loading prepared by the wet impregnation method using an aqueous solution of $Fe(NO_3)_3$, did not readily deactivate under evaluation conditions, 300°, 300 psig of 1:1, H_2:CO. Calcination of the prepared catalyst was shown to result in changes in the iron component that increased the percentage of synthesis gas conversion and affected the product distribution. The "as-prepared" catalyst results in a hydrocarbon distribution of 38% aromatics (AR), 36% olefins (OL) and 26% saturates (SAT), whereas the distribution obtained by using the calcined catalyst is 9% AR, 60% OL and 32% SAT. For both catalysts, approximately 90% of the liquid hydrocarbon product boiled in the gasoline range (< 204°C).

In spite of the demonstrated ability of transition metal/zeolite catalysts to selectively catalyze the conversion of synthesis gas to liquid hydrocarbons, very little has been reported on the relationship between the surface science of the catalysts and their selectivity. In order to carry out an effective program of catalyst synthesis and evaluation, correlations between the nature of the catalyst and its activity must be made. Through such correlations, conclusions concerning the mechanism of the catalyzed reaction may be drawn. This approach has been employed during our investigations.

Completed Research

During the past five years, a research program aimed at the development of supported metal catalysts that are both efficient and selective for the production of liquid (gasoline range) hydrocarbons from synthesis gas has been conducted. The work was divided into four tasks, although each task was closely related.

First, a procedure for the synthesis of potential catalysts containing highly dispersed, small particle-sized transition metal compounds on oxide and zeolite supports was developed.

Second, the chemical composition and physical characteristics of the prepared materials were determined by the application of a variety of surface sensitive and bulk characterization techniques, such as X-ray photoelectron spectroscopy (XPS), ion-scattering spectrometry (ISS), X-ray powder diffractometry (XRPD) and, for iron-based catalysts, Mossbauer spectroscopy. These techniques were also applied to pre-treated (calcined) and used (after evaluation in the microreactor) catalysts. In some cases, in situ measurements on catalysts after reduction, carburization and during evaluation were made in order to determine chemical and physical changes taking place during those procedures and to identify active surface species.

The third task was to evaluate the catalytic activity of the materials prepared by the first task and characterized through the second task, making comparisons with supported metal catalysts prepared by conventional procedures.

Finally, the fourth task involved making correlations between the surface science of the catalysts and their ability to function as thermally stable, efficient and product selective catalysts for synthesis gas

conversion. Through these correlations, we have been able to determine important factors that control the behavior of the catalysts. A summary of the completed research and conclusions reached will be presented. It should be emphasized that this research project is ongoing and many questions remain unanswered at this time; research will continue and build upon the completed research, with the ultimate objective of the program being to design, and tailor-make, product-selective catalysts for the indirect liquefaction of coal.

The extraction procedure (developed in our laboratory) has been applied to the synthesis of a variety of oxide and zeolite-supported metal catalysts. The initial work involved alumina as the support and the carbonyls, $Ir_4(CO)_{12}$, $Os_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $Rh_6(CO)_{16}$. Alumina-supported metal carbonyls were prepared, characterized by infrared spectroscopy (IR), X-ray fluorescence spectroscopy (XRFS), scanning electron microscopy (SEM) and X-ray powder diffractometry, (XRPD) and their thermal stability studied (62,63,64). In the prepared materials, the metal component was identified as a carbonyl, derived from the original cluster carbonyl by degradation through interaction with the alumina support. Unlike previously reported procedures for the preparation of supported metal catalysts from carbonyls, the extraction procedure pro-duces highly dispersed, small particle-sized (< 50 A) species on the support. This initial work, aimed primarily at developing synthetic procedures and characterization techniques, was followed by research aimed at the development of supported Fe, Co and Ru catalysts.

Iron/oxide catalysts were prepared by the extraction procedure using $Fe_3(CO)_{12}$ and cyclohexane or THF, designated the EX catalysts and, for comparison purposes, by the incipient wetness technique using

aqueous solutions of $Fe(NO_3)_3$, designated the IW catalysts (65). The oxides employed were MgO, ZnO, TiO_2, Al_2O_3, SiO_2 and ThO_2. The use of the extraction procedure overcomes the solubility and crystallization problems normally encountered with the use of carbonyls for the preparation of supported metal catalysts by impregnation or sublimation and enabled materials with iron loadings from 1% to ~16 wt % Fe to be prepared. For the as-prepared EX catalysts, the iron component was identified by XPS as an iron(III) oxide; depth profiling studies with Ar^+ indicated that most of the iron oxide was located on the surface of the support. XRPD studies with CuK_α radiation were unable to detect the iron component, only support diffraction lines were observed; thus it was concluded that the iron oxide particles were < 50 A. For the IW catalysts, XRPD identifies the iron component as larger (~200 A) particles of α-Fe_2O_3. Calcination at 500°C of the as-prepared EX catalysts was found to increase the particle size of the iron component; XRPD was able to identify this component as larger-sized (~150 A) particles of α-Fe_2O_3. For the Fe/ZnO system, calcination also leads to the formation of some $ZnFe_2O_4$. Fe/(support metal) intensity ratios (Fe/Si, Fe/Al and Fe/Th) were obtained from XPS and ISS studies of both EX and IW Fe/SiO_2, Fe/Al_2O_3 and Fe/ThO_2 catalysts. For the as-prepared EX catalysts studied, the ratios were greater than for the IW catalysts, confirming that the extraction technique produces a higher degree of dispersion and smaller particle sizes for the iron component than are produced by the incipient wetness technique, in agreement with XRPD studies. For calcined EX catalysts, the ratios are lower than for the as-prepared EX catalysts; as the temperature of calcination is increased (300° to 500°) the ratio obtained decreases, but not to the value obtained for the IW

catalysts. Thus, calcination of the EX catalysts may be used to control both dispersion and particle size of the iron component.

From this investigation, it was concluded that by using the extraction technique, adsorption of the iron carbonyl on the support is accompanied by oxidative decomposition of the cluster carbonyl (as found previously for Ir/, Os/, Ru/ and Rh/Al_2O_3 systems) with the formation of highly dispersed, small particle-sized iron oxides on the support surface. Strong metal-support interaction (SMSI) is induced in the formation of supported metal catalysts by the use of the technique. Futhermore, careful pretreatment of the as-prepared catalysts by calcination in air can be used to control the dispersion and particle size of the iron oxide. It should be noted that Fe/oxide catalysts, prepared by the incipient wetness technique for comparison purposes, contain a low degree of dispersion of large particle-sized iron oxides and that control of the particle size range is not achieved by using conventional methods of preparation.

Mossbauer spectroscopic studies have been conducted for further characterization of the as-prepared and calcined Fe/oxide EX catalysts. For Fe/MgO, Fe/ZnO and Fe/TiO_2 as-prepared (AP) catalysts, the iron component is present as small, superparamagnetic particles of α-Fe_2O_3 (66). Strong metal-supported interactions are present which increase on calcination, the formation of $ZnFe_2O_4$ was confirmed. For the Fe/TiO_2 catalysts, metal-support interactions are less strong than in the Fe/MgO and Fe/ZnO catalysts.

Mossbauer spectroscopic characterization studies of Fe/SiO_2 (67), Fe/Al_2O_3 (68) and Fe/ThO_2 (69) catalysts (~15 wt % Fe) have been completed (70). All as-prepared (AP) catalysts contain small particle-

-14-

sized superparamagnetic (SP) α-Fe_2O_3. Calcination (500°C) leads to larger-sized particles of α-Fe_2O_3, a conclusion in agreement with the previously discussed XRPD, XPS and ISS studies. In situ studies of the calcined (H500) catalysts were carried out after reduction in H_2, after carburization in a 2:1 H_2:CO mixture and under Fischer-Tropsch reaction conditions (used); iron containing species were identified.

The Fe/SiO_2 catalyst has a high selectivity for methane, presumably due to the small particle size and SMSI. However, for the Fe/Al_2O_3 catalyst in which a SMSI is also present, higher selectivity for propylene and propane is favored. The Fe/ThO_2 catalyst is unique in the sense that when the particle size is relatively small (calcination for 24 hours), a high selectivity for C_5-C_{10} hydrocarbons is observed. When the particle size is larger (calcination for 48 hours) the selectivity is shifted to C_5 hydrocarbons and oxygenated products. Further, extended time catalytic evaluations of the Fe/SiO_2, Fe/Al_2O_3 and Fe/ThO_2 (AP) catalysts have been conducted in a continuous flow, fixed-bed microreactor system (63). One important conclusion that may be reached from the catalytic data is that the Fe/SiO_2, Fe/Al_2O_3 and Fe/ThO_2 catalysts prepared by the extraction technique are thermally stable and long-lived without significant deactivation occurring over the period of evaluation. It should be noted that catalysts prepared by the incipient wetness technique show significant deactivation when evaluated under similar conditions. These observations have also been noted for Fe/zeolite catalysts to be discussed later. The difference in behavior must be related to the method of preparation of the catalysts and thus to the high degree of dispersion and control of metal particle size that are achieved by using the extraction technique.

Three series of zeolite-supported iron catalysts of weight percent iron loading (% Fe) varying from ~1% to ~17% have been prepared from $Fe_3(CO)_{12}$ and the zeolites ZSM-5, mordenite and 13X by the extraction procedure (71). ZSM-5 (SiO_2/Al_2O_3 ~30) and mordenite SiO_2/Al_2O_3 ~11,17,20,62) were used in the acid form and 13X (SiO_2/Al_2O_3 ~1) was used in the sodium form. All materials were characterized by the surface and bulk techniques described earlier. Infrared spectra of the prepared materials do not show the presence of $\nu(CO)$ bands; thus it is concluded that decomposition of $Fe_3(CO)_{12}$ accompanies adsorption onto the supports during preparation. For catalysts with < 10% Fe loading, only the support is detected by XRPD suggesting that the particle size of the iron-containing species is < 50 A. However, above 10% Fe, a diffraction pattern associated with $\gamma-Fe_2O_3$ and/or Fe_3O_4 is observed in addition to that for the support. XPS data confirm the presence of iron oxides in all the prepared catalysts; a detailed study of the XPS data for the Fe/ZSM-5 catalysts has been reported (61). Ion scattering spectrometry (ISS), with $^4He^+$ sputtering, has been employed to study the surface of the Fe/zeolite catalysts. It is concluded that the iron oxide particles in the catalysts prepared from $Fe_3(CO)_{12}$ are considerably smaller than those obtained by using iron nitrate. Depth profiling studies (XPS and ISS) have demonstrated that some iron (~1%) is incorporated into, and is strongly interacting with, the zeolite support in the EX catalysts; data for the Fe/ZSM-5 catalysts have been reported (61).

Recent studies (72) of the infrared spectra of chemisorbed pyridine on Fe/ZSM-5 (EX) catalysts have suggested that, in the as-prepared form, the iron is not interacting with the support at the Bronsted acid sites whereas for Fe/ZSM-5 (IW) catalysts prepared from aqueous

solutions of iron nitrate, ion-exchange does take place. This is an important conclusion since it indicates that by using the extraction technique, the Bronsted acid sites in a zeolite support may be protected on incorporation of the metal component in the formation of a bifunctional zeolite-supported metal catalyst. This protection is not afforded when similar catalysts are prepared by using aqueous solutions of iron salts.

Mossbauer spectroscopy has identified the surface iron-containing species as small particle-sized γ-Fe_2O_3 in a superparamagnetic form in Fe/ZSM-5 (73) and Fe/13X (74) catalysts. For Fe/ZSM-5 catalysts, with ~15% Fe, magnetic and Mossbauer studies (75) have concluded that the EX catalysts contain γ-Fe_2O_3 particles of diameter 60-66 A, whereas the IW catalysts contain α-Fe_2O_3 particles of > 100 A diameter. Calcination at 500°C of the EX catalysts leads to an increase in particle size of the iron component; data from XRPD, XPS and Mossbauer spectroscopy has identified the iron component as α-Fe_2O_3 of particle size of ~100 A. Characterization of the used EX catalysts (~15% Fe) has shown the presence of χ-Fe_5C_2 and Fe_3O_4 for all materials investigated. For an Fe/ZSM-5 catalyst, it is estimated that ~80% of the iron is in the metallic form after the reduction step (73); following the carbiding step, χ-Fe_5C_2 and Fe_3O_4 are detected. Similar studies on Fe/mordenite catalysts have shown that with increasing number of acid sites in the mordenite framework, a better dispersion of superparamagnetic α-Fe_2O_3 is obtained (74). The highest dispersion is observed with the mordenite having the highest number of acid sites ($SiO_2/Al_2O_3=17$).

Thus, from the characterization studies, it is concluded that the extraction technique, when applied to the preparation of Fe/zeolite catalysts, results in the formation of small particle sized γ-Fe_2O_3 on the