

surface; that the particle size of this component may be controlled by calcination at different temperatures, that the iron component is readily reduced to the metallic form which in turn forms an iron carbide that is active for carbon monoxide hydrogenation. Furthermore, the extraction technique does not give rise to ion-exchange at the Bronsted acid sites, thus allowing the acidity of the support in a bifunctional catalyst to remain effective. Further studies concerning the nature of the metal-support interactions and location of the metal component are planned in order to more completely understand the science associated with this new method of catalyst preparation.

Catalytic evaluation of both EX and IW Fe/zeolite, (-15% Fe) catalysts has been conducted. All EX catalysts are effective and long-lived for synthesis gas conversion showing no deactivation over periods of up to 21 days. In contrast, the IW catalysts readily deactivate over the same period under the same evaluation conditions. In situ Mossbauer studies, under Fischer-Tropsch conditions, for the Fe/ZSM-5 catalysts have shown that for the EX catalyst the amount of χ -Fe₅C₂ remains constant during the evaluation, whereas for the IW catalyst, the inactive carbide Fe₃C is formed at the expense of χ -Fe₅C₂, thus leading to deactivation (73).

The effect of calcination, and thereby the effect of iron component particle size, on catalytic activity and product distribution has been studied for as-prepared, AP, calcined at 300°C, H300, and calcined at 500°C, H500 Fe/ZSM-5 catalysts of -15% Fe loading (77). All catalysts are stable and long-lived. As noted previously, the particle size of the iron component increases on calcination at increasing temperatures. These increases are reflected in increasing percentages of CO and H₂ conversion, with the difference between the AP and H300 catalysts being larger

than that between the H300 and H500 catalysts. For hydrocarbon products, the increase in particle size for the AP and H300 catalysts is reflected in an almost two fold decrease in the percentage of methane obtained and an accompanying two fold increase in the percentage of oil (C_{5+} hydrocarbons). The distribution of aromatic (AR), olefin (OL) and saturate (SAT) products within the oil is also dependent upon the particle size changes. The AP catalyst, with the smallest particle size, gives rise to the highest AR content (~10%), the lowest OL content (~60%) and the highest SAT content (~30%). The H300 and H500 catalysts give rise to similar product distributions, viz. AR ~4%, OL ~80% and SAT ~15%. There is obviously a close relationship between iron component particle size and product distribution. This relationship will be studied further in more detail in future research.

The role of the metal has been further studied with a series of Ru/ZSM-5 catalysts of ~1, ~3 and ~7% Ru loading, prepared by the extraction technique from $Ru_3(CO)_{12}$ (78). XPS and ISS have indicated that all as-prepared (AP) catalysts contain RuO_2 which is highly dispersed on the ZSM-5. XRPD was unable to detect the RuO_2 component indicating particles sizes < 50 Å. This conclusion was confirmed by hydrogen chemisorption studies (79); estimates of 34, 38 and 47 Å were obtained for the 1, 3 and 7% Ru catalysts respectively. Calcination in air of the AP catalysts results in an increase in particle size of the RuO_2 component; XRPD is able to detect the RuO_2 , but at this time no accurate determination of the particle sizes has been made. For the used AP catalysts, XRPD is not able to detect the metal component, but XPS has identified Ru metal. It is interesting to note that a significant increase in particle size does not occur during reduction (400°C) or under

evaluation conditions although this does occur on calcination in air at 300° and 500°C. All AP catalysts are efficient and long-lived for carbon monoxide hydrogenation over the temperature range evaluated, viz. 260° to 320°C. Each catalyst was evaluated for 4 days at each temperature (260°, 280°, 300°, 320°C). Percentages of CO and H₂ conversion increase with metal loading, as does the weight percentage of liquid hydrocarbons obtained. The component distribution within the liquid hydrocarbons is dependent upon % Ru loading and the temperature of evaluation. For a particular catalyst, the highest percentages of aromatics (up to 85%) are obtained at the higher temperatures (> 280°C); these aromatics are formed at the expense of the olefins. The highest yield of aromatics is obtained with the lowest % Ru; it is concluded that as the % Ru loading is increased, blockage of the pores occurs, thus restricting access of intermediates to the acid sites. For these Ru/ZSM-5 catalysts, the unsaturate to saturate ratio for C₂ and C₃ hydrocarbons is low. We thus conclude that in these bifunctional catalysts, the Bronsted acidity of the support has been protected by the preparative procedure for ruthenium impregnation allowing the aromatization of unsaturated intermediates produced by the metal component to take place. It should be noted that the percentage of aromatics produced by these catalysts is considerably higher than that reported by other workers who used Ru/ZSM-5 catalysts prepared by conventional methods (59).

The acidity and pore structure of the zeolite support are important factors that influence the distribution of products obtained during synthesis gas conversion. The catalysts Fe/ZSM-5 and Fe/mordenite contain Bronsted acid sites and medium-sized pores and result in the conversion of synthesis gas to gaseous and liquid hydrocarbons containing a high

percentage of unsaturates. Approximately 90% of the liquid (oil) products obtained by using these catalysts are in the gasoline boiling range. The catalyst Fe/13X, which consists of a non-acidic, larger-sized pore zeolite leads to the conversion of synthesis gas to a higher molecular weight distribution, including some waxes, of largely saturated hydrocarbons. For this catalyst, approximately 70% of the liquid (oil) product obtained is in the gasoline boiling range.

The effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in a series of ~15% Fe/mordenite catalysts with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 11, 17 and 62, prepared by the extraction techniques from $\text{Fe}_3(\text{CO})_{12}$ has been evaluated (80). It has been suggested (81) that for a series of mordenites with relatively low ratios, maximum acidity is reached for $\text{SiO}_2/\text{Al}_2\text{O}_3 = 17$. Catalytic evaluation of the AP catalysts has demonstrated that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio affects the product distribution. At a reaction temperature of 280° , after the catalyst was on stream for four days, the percentage of aromatics in the liquid hydrocarbon product was 3, 17 and 6 for the catalysts with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 11, 17$ and 60 respectively. This trend in aromatic percentage correlates well with the Bronsted acidity of the support; furthermore, the support acidity is retained by using the extraction technique for metal impregnation. Thus, by careful choice of the zeolite support in the preparation of a bifunctional catalyst for synthesis gas conversion, the product distribution, particularly for hydrocarbons, may be controlled.

Metal-support interactions are dependent upon the metal, the support, the method of preparation and any pretreatment process. Previous sections have discussed most of these factors and the discussion will not be repeated here. One study, specifically designed to investigate the effect of the method of preparation on metal-zeolite interactions has

recently been completed (72). The acidity of Fe/ZSM-5, EX and IW catalysts has been investigated by infrared characterization of chemisorbed pyridine (72,82). It was found that for the as-prepared EX catalyst, redistribution of Bronsted and Lewis acidity (compared with unloaded ZSM-5) does not occur whereas for the as-prepared IW catalyst, Bronsted acidity is significantly decreased. These data suggest that the IW technique results in incorporation of the iron by ion-exchange whereas the EX technique does not lead to ion-exchange. Thus the type of metal-support interaction in the Fe/ZSM-5 catalysts may be controlled by the method of preparation. Further evidence to support this conclusion has been obtained from the study of Fe/13X, EX and IW catalysts (83). For the former, elemental analysis indicates that the Na/Al ratio does not decrease on iron loading, whereas it is decreased almost to zero for the iron-loaded IW catalysts.

Conclusions

From the work completed to date, the following conclusions may be drawn:

1. The extraction technique, using organometallic compounds, developed in our laboratory, produces supported metal catalysts that contain small particle-sized, highly-dispersed metal oxides.
2. The metal component particle size may be controlled by the application of specific pre-treatment conditions; the ability to control the particle size results in the ability to control product distribution during synthesis gas conversion.
3. Interaction between the metal and the support in a zeolite-supported metal catalyst is such that the Bronsted acidity of the support may be protected; the ability to protect the acid sites of the zeolite affords the opportunity for the production of liquid hydrocarbons containing high percentages of olefins and aromatics during synthesis gas conversion.

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