

ZSM-5 SUPPORTED Fe AND Ru FROM  $Fe_3(CO)_{12}$  AND  $Ru_3(CO)_{12}$ : STRUCTURE-ACTIVITY CORRELATIONS FOR SYNTHESIS GAS CONVERSION

Ellis B. Zuckerman and Gordon A. Melson

Department of Chemistry, Virginia Commonwealth University, Richmond, VA 23284.

INTRODUCTION

The goal of improving the efficiency and product selectivity in the conversion of synthesis gas ( $CO + H_2$ ) to liquid hydrocarbons has resulted in efforts to develop bifunctional catalysts which combine a transition metal Fischer-Tropsch component with a zeolite support. This combination utilizes the carbon monoxide reduction and carbon chain propagation functions of the metal as well as the shape selectivity and dispersive effects of the zeolite. During the 1970's, workers at Mobil introduced the new synthetic zeolite ZSM-5 which possesses a unique channel structure. In its acid form H<sup>+</sup>-ZSM-5 is capable of isomerizing hydrocarbons and converting reactive species to alkylbenzenes in the gasoline range. The combination of metal oxides with ZSM-5 and the impregnation of metal salts into ZSM-5 have resulted in catalysts which produce gasoline range hydrocarbons containing a high percentage of aromatics from synthesis gas (1-4). Metal particle size and metal-support interaction also affect product selectivity. It has been argued (5) that the former, in particular, is an important factor in controlling the molecular weight distribution of hydrocarbon products from synthesis gas conversion.

During the past decade, there has been considerable interest in the development of supported metal catalysts by the incorporation of metal carbonyls (6,7). It has been demonstrated that this approach, depending on the method of preparation, is a means of rendering the metal component in the form of highly dispersed, small particles on oxide and zeolite supports (8). It thus provides an alternative to conventional aqueous impregnation of metal salts which usually results in the formation of large metal particles and low dispersion. Furthermore, the method of preparation of zeolite-supported metal catalysts affects the interaction of the metal with the Brønsted acid sites of the zeolite. It has been demonstrated (9,10) that the introduction of transition metals by aqueous methods leads to ion-exchange between metal ions and protons and results in a partial depletion of the catalytically active Brønsted acid sites. It also seems reasonable to suspect that physical blockage of the zeolite channels causes an apparent loss of acidity after calcination or reduction if the metal species initially penetrates the zeolite channels.

The present goal of the research effort is to develop supported metal catalysts which are both efficient for synthesis gas conversion and selective for the production of aromatic and branched aliphatic hydrocarbons in the gasoline range. If the metal component can be introduced onto the zeolite particle without extensive penetration of the channel structure and subsequent ion-exchange at the Brønsted acid sites, an efficient bifunctional catalyst should be produced. Such a catalyst would convert reactive intermediates and high molecular weight hydrocarbons produced by the metal component directly on the particle. This would eliminate the necessity for physical transfer of the organic products from the metal site to the zeolite site that is necessary in a mixed metal-zeolite system. Additionally, the products of synthesis gas conversion may be different by using a bifunctional catalyst from those obtained with the mixed system. In order to achieve this goal, we have

prepared bifunctional ZSM-5 supported Fe and Ru in which the catalytic functions of the metal and the support are retained. This was accomplished by using an extraction method reported earlier (8) with  $\text{Fe}_3(\text{CO})_{12}$  and  $\text{Ru}_3(\text{CO})_{12}$  as the source of the metals. It was anticipated that this method would lead initially to a high degree of dispersion of the metal and that the metal would be restricted to the external surface of the zeolite. It was also anticipated that changes in the metal particle size could be induced by subsequent pre-treatment, e.g. calcination. We report here evaluation of some Fe/ZSM-5 and Ru/ZSM-5 catalysts for their activity and product selectivity in the conversion of synthesis gas, and draw conclusions concerning catalyst structure-activity relationships.

### EXPERIMENTAL

ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 32$ ) was received in the  $\text{NH}_4^+$  form and was calcined under vacuum at  $400^\circ\text{C}$  for 3 h to obtain the acid form. Ru/ZSM-5 and Fe/ZSM-5 materials were prepared by an extraction technique (8) using  $\text{Ru}_3(\text{CO})_{12}$  (Strem Chemical) and  $\text{Fe}_3(\text{CO})_{12}$  (Alfa, Ventron Division) with cyclohexane as the solvent. All of the catalysts discussed in this report have metal loadings of approximately 3% by weight. Portions of the as-prepared (AP) catalysts were calcined in air at  $400^\circ\text{C}$  (H-400) in order to induce an increase in the particle size of the metal component.

The materials have been characterized by infrared spectroscopy (IR), X-ray powder diffractometry (XRPD), X-ray photoelectron spectroscopy (XPS), ion scattering spectrometry (ISS), Mossbauer spectroscopy (for Fe), and pyridine chemisorption studies.

For catalytic evaluation, the catalysts were dispersed in silica (200-300 mesh), and reduced under flowing  $\text{H}_2$  at 20.4 atm. Fe catalysts were reduced at  $450^\circ\text{C}$  for 20 h whereas Ru catalysts were reduced at  $400^\circ\text{C}$  for 12-15 h. Following reduction, Fe catalysts underwent a carbiding step in flowing synthesis gas ( $\text{H}_2/\text{CO} = 1$ ) at 6.8 atm and  $250^\circ\text{C}$  for 20 h. Evaluation was carried out by using a fixed-bed, continuous flow microreactor. The reaction conditions consisted of a pressure of 20.4 atm of synthesis gas ( $\text{H}_2/\text{CO} = 1$ ) and reactor temperatures of  $280^\circ\text{C}$  and  $300^\circ\text{C}$ . For studies designed to determine the effects of space velocity, the flow rate was adjusted so that the WHSV was established at 990, 2085, and 3135 cc/g.h. In studies which did not involve space velocity comparisons, the WHSV was set to 2090 cc/g.h. Each evaluation at a given set of conditions was allowed to proceed for a period of 48 h during which the liquid products were collected in an ice-cooled trap which followed a heated trap ( $180^\circ\text{C}$ ) for the collection of high molecular weight products. The gaseous effluent was analyzed by using a gas chromatograph which is an integral part of the reactor system. The liquid product was separated into oil and aqueous fractions; the analysis of the oil was accomplished primarily by a quantitative infrared method described earlier (11). Additional supporting information such as the carbon number distribution and the degree of paraffin branching were obtained by capillary GC and  $^1\text{H}$  NMR spectroscopy respectively.

### RESULTS AND DISCUSSION

#### Characterization

The results of characterization studies have been reported earlier (12); however, because our objective is to enable correlations between the nature of the

catalysts and the results of catalytic evaluation to be drawn, some conclusions are presented here.

In XRPD studies of both Fe/ZSM-5/AP and Ru/ZSM-5/AP, no evidence for the presence of the metal component was detected. This suggests that the metals are highly dispersed with a particle size of  $<50 \text{ \AA}$  and/or that the metal species are non-crystalline. Calcination of the AP materials induces the formation of bulk  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{RuO}_2$ , which have been detected by XRPD. Depth profile studies of both Fe/ZSM-5/AP and Ru/ZSM-5/AP, by ISS, reveal a rather large initial M/Si ratio which rapidly decreases with sputtering. We have interpreted this observation to indicate that the metal component is restricted to the external surface of the zeolite particles (by virtue of the relative sizes of the metal clusters and the diameter of the ZSM-5 channels) and is highly dispersed, perhaps monodispersed at low loadings, on that surface. The ISS depth profiles of calcined materials consist of small initial M/Si ratios which increase slightly with sputtering time and suggest the formation of large metal oxide particles. XPS studies of Fe/ZSM-5/AP and Ru/ZSM-5/AP reveal the presence of metal oxides, but are inconclusive regarding the exact nature of the species. Calcined materials clearly contain the metals in the form of  $\text{Fe}_2\text{O}_3$  and  $\text{RuO}_2$ , and the trends observed with sputtering of AP and calcined samples parallel those observed in ISS studies. Infrared studies of chemisorbed pyridine were conducted as a probe to determine whether channel blockage and/or chemical interaction between the metal and Brønsted acid sites in the zeolite channels had occurred as a result of metal loading or subsequent calcination or reduction. No indication of such interactions was observed.

We have concluded from the results of characterization of Fe/ZSM-5 and Ru/ZSM-5 materials that both contain the metal component in a highly dispersed state on the external surface of the zeolite particles. Calcination, and to a lesser extent reduction, both induce the formation of large particles of the oxides or metals which remain excluded from the zeolite channels. The restriction of the metal to the external surface of the of the ZSM-5 particles should result in the retention of Bronsted acidity and permit access of reactants to the interior of the zeolite.

### Catalytic Evaluation

Fe/ZSM-5/AP, Ru/ZSM-5/AP and Ru/ZSM-5/H-400 catalysts have been evaluated for their efficiency and selectivity in synthesis gas conversion. The three catalysts discussed here have been compared in order to investigate effects of the choice of transition metal and the effects which result from calcination of the Ru/ZSM-5 catalyst prior to evaluation. Furthermore, the effect of varying the space velocity at different temperatures for Fe/ZSM-5/AP and Ru/ZSM-5/AP was examined.

Comparison of the data in Tables 1 and 2 reveals a number of similarities regarding the effects of space velocity and temperature on the two catalysts. For both as-prepared catalysts, the percentages of  $\text{H}_2$  and CO conversion generally decrease at higher space velocities while increasing at higher temperature. The two catalysts exhibit a decreasing activity for the water gas shift reaction at higher space velocity and an increasing activity for the shift reaction at higher temperature. Analysis of the liquid products by a quantitative IR technique reveals an enhanced selectivity for aromatic hydrocarbons coupled with an apparent consumption of olefins and oxygenated species at higher temperature and lower space velocity. The efficiencies of synthesis gas conversion, the shift reaction, and the conversion of Fischer-Tropsch products and intermediates by the acidic and shape selective

TABLE 1. RESULTS FROM CATALYTIC EVALUATION OF A 3% Ru/ZSM-5/AP CATALYST

WHSV ( $\frac{\text{CC}}{\text{g}\cdot\text{h}}$ )	CATALYST TEMP. (°C)	% CONVERSION		REACTOR EFFLUENT DISTRIBUTION (wt. %)				HYDROCARBON PRODUCT DISTRIBUTION (wt. %)					LIQUID PRODUCT DISTRIBUTION (wt. %)					
		H <sub>2</sub>	CO	H <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	HC	CH <sub>4</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub> <sup>+</sup>	WAX	AR	OL	SAT	OX	
990		92	51	54	1	4	21	20	23	5	7	13	52	0	27	7	63	3
2085	280	70	31	64	2	2	18	14	27	5	10	17	41	0	21	11	64	4
3135		49	23	71	3	2	14	10	33	7	12	13	35	0	18	12	65	5
990		89	55	47	1	15	17	20	49	11	13	10	18	0	30	3	65	2
2085	300	75	37	60	2	6	17	16	40	8	11	17	23	0	26	5	66	3
3135		69	35	62	2	4	17	15	43	8	11	10	28	0	21	6	70	3

TABLE 2. RESULTS FROM CATALYTIC EVALUATION OF A 3% Fe/ZSM-5/AP CATALYST

WHSV ( $\frac{\text{CC}}{\text{g}\cdot\text{h}}$ )	CATALYST TEMP. (°C)	% CONVERSION		REACTOR EFFLUENT DISTRIBUTION (wt. %)				HYDROCARBON PRODUCT DISTRIBUTION (wt. %)					LIQUID PRODUCT DISTRIBUTION (wt. %)					
		H <sub>2</sub>	CO	H <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	HC	CH <sub>4</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub> <sup>+</sup>	WAX	AR	OL	SAT	OX	
990		37	37	64	5	12	12	7	37	19	16	16	12	0	47	<1	51	<1
2085	280	28	17	75	5	6	7	7	33	17	21	12	17	0	26	1	72	1
3135		26	16	75	5	7	7	6	32	17	12	15	24	0	19	3	77	1
990		46	49	51	4	26	6	13	55	20	11	7	7	0	47	0	53	0
2085	300	41	31	64	4	15	6	11	43	17	9	18	13	0	48	<1	51	0
3135		42	32	62	4	16	7	11	35	17	15	12	21	0	33	1	66	0

zeolite are known to be influenced by temperature and the residence time of the reactants and products in the catalyst bed. In this respect, the trends mentioned above are not surprising.

Of greater interest is the effect of the choice of metal on the overall behavior of the catalysts. Inspection of Tables 1 and 2 reveals a number of differences in the efficiencies and product selectivities. These serve to distinguish the two catalysts on the basis of the metal component in spite of the presence of the ZSM-5 which is certainly a factor in controlling the nature of the product distribution and may also exert an influence on the properties of the metals. For example, the Ru/ZSM-5/AP catalyst showed higher activity than Fe/ZSM-5/AP for synthesis gas conversion. This observation is consistent with the results reported by Vannice (13) who demonstrated that Ru has the greatest specific activity among Group VIII metals for the conversion of CO/H<sub>2</sub> mixtures to hydrocarbons. Furthermore, Ru is well known to be the most selective of the Group VIII metals for higher molecular weight hydrocarbons, and this is also evident in the present study when the relative quantities of C<sub>5+</sub> hydrocarbons are compared. This same selectivity, on the part of Ru, for species of higher carbon number may also account for the smaller aromatic content of the oil from Ru/ZSM-5/AP compared to that from Fe/ZSM-5/AP. The higher molecular weight products are more likely to be cracked and isomerized by the zeolite whereas lighter products such as C<sub>3</sub> and C<sub>4</sub> olefins are more favorable for conversion to aromatics. If this is the case, then the greater selectivity of Fe for lighter hydrocarbons could explain the greater aromaticity of the oil product from Fe/ZSM-5/AP. Consistent with this explanation is the fact that the normalized ratio of methyl to methylene hydrogen in the aliphatic fraction, obtained from <sup>1</sup>H NMR spectra, is large and is indicative of a significant degree of branching. This suggestion is not meant to preclude other factors which may influence the liquid product distribution. For example, we have considered the possibility that Fe might be more favorable for the formation of the correct chemical species (olefins and alcohols) for conversion to alkylbenzenes.

It should also be noted that the oil product from Ru/ZSM-5/AP contains a substantially larger fraction of olefins and oxygenates than that from Fe/ZSM-5/AP. At first glance this would appear to refute the statement above concerning correct chemical species for aromatization. However, it must be mentioned that the olefins detected in all of these oils are trans and branched  $\alpha$  olefins which, unlike normal  $\alpha$  olefins, are not considered to be primary products of synthesis gas conversion. The presence of these species may result from the activity of the zeolite. The oxygenated fraction consists of aldehydes and acids but no alcohols. Kellner and Bell (14) have reported that acetaldehyde was the only oxygenate produced over a Ru/SiO<sub>2</sub> catalyst.

Finally, it is apparent that the Fe catalyst is more active for the water gas shift reaction than the Ru catalyst. This is in agreement with the fact that the shift reaction is faster over Fe than over Ru, Co or Ni (15).

Comparison of the results of evaluation of the Ru/ZSM-5/AP and the Ru/ZSM-5/H-400 catalysts reveals some striking differences in activity and product selectivity. It should be mentioned, before further discussion, that while the activity and selectivity of the AP catalyst were stable for the 48 h duration of each evaluation period, the H-400 catalyst exhibited significant deactivation over the first 24 h at 280°C. Consequently it is unreasonable to treat the results of the

H-400 evaluation as if they were representative of a behavior which persisted for 48 h; nevertheless, some general comparisons of the two catalysts can be made.

At 280°C and a space velocity of 2090 cc/g.h the percentage conversion of CO and H<sub>2</sub> was much lower over the H-400 catalyst than over the AP catalyst. Furthermore, the selectivity for higher molecular weight hydrocarbons is greater with the H-400 catalyst. Both of these observations may be related to a metal particle size effect as a result of prior calcination. The liquid hydrocarbon product, like that produced over the AP catalyst, contained substantial aromatic and branched aliphatic fractions.

#### CONCLUSIONS

Bifunctional catalysts consisting of Fe and Ru supported on ZSM-5 have been prepared by an extraction technique using metal cluster carbonyls. As anticipated, these precursors of the supported metal component were excluded from the ZSM-5 channels which have a diameter significantly smaller than that of the metal clusters. Evidence for this restriction was obtained from studies of the catalysts by ISS, XPS and pyridine chemisorption. These studies revealed that the metal was present as highly dispersed metal particles on the external surface of the ZSM-5 particles and that obstruction of the zeolite channels and extensive interaction with Bronsted acid sites did not occur. As a result, these materials were found to be efficient bifunctional catalysts for synthesis gas conversion. The metal component produces hydrocarbon and oxygenated products and intermediates which are further converted by the zeolite to mixtures containing substantial fractions of aromatic and branched hydrocarbons.

Calcination of a Ru/ZSM-5 catalyst prior to evaluation results in an increase in the average metal particle size. When evaluated, this catalyst exhibits less activity, but greater selectivity for higher molecular weight products when compared to the as-prepared catalyst. However, rapid deactivation of the calcined catalyst occurred. Although the reason for this is not clear at the time of writing, this behavior is being investigated.

The product distributions obtained by synthesis gas conversion over the above bifunctional catalysts will be compared with those obtained from catalysts consisting of the metal component dispersed on a conventional oxide support as well as from these catalysts physically mixed with ZSM-5. Correlations concerning the nature of the catalysts and differences observed among the various product distributions will be drawn, and mechanistic considerations will be presented.

#### ACKNOWLEDGEMENTS

The authors wish to thank J.M. Stencel and J.R. Diehl of the U.S. Department of Energy, Pittsburgh Energy Technology Center, for assistance in obtaining some of the characterization data (XPS and ISS) and the Department of Energy for financial support.

#### REFERENCES

1. Chang, C.D., Lang, W.H. and Silvestri, A.J., *J. Catal.*, 56, 268 (1979).
2. Caesar, P.D., Brennan, J.A., Garwood, W.E. Ciric, J., *J. Catal.*, 56, 274 (1979).
3. Rao, V.U.S., Gormley, R.J., *Hydrocarbon Process.*, 59 (11), 139 (1980).
4. Huang, T.J., Haag, W.O., in "Catalytic Activation of Carbon Monoxide", ACS Symposium Series, Vol. 152, Peter C. Ford (ed.), American Chemical Society, Washington, D.C., 1980.
5. Nijs, H.H. and Jacobs, P.A., *J. Catal.*, 65, 328 (1980).
6. Zwart, J. and Snel, R., *J. Mol. Catal.*, 30, 305 (1985), and references therein.
7. Phillips, J. and Dumesic, J.A., *Applied Catal.*, 9, 1 (1984), and references therein.
8. Crawford, J.E., Melson, G.A., Makovsky, L.E., Brown, F.R., *J. Catal.*, 83, 454 (1983).
9. Rhee, K.H., Brown, F.R., Finseth, D.H., Stencel, J.M., *Zeolites*, 3, 344 (1983).
10. Shamsi, A., Rao, V.U.S., Gormley, R.J., Obermeyer, R.T., Schehl, R.R., Stencel, J.M., *Ind. Eng. Chem., Prod. Res. Dev.*, 23, 513 (1984).
11. Zuckerman, E.B., Melson, G.A., Finseth, D.H., 35th Southeastern Regional Meeting of the American Chemical Society, Charlotte, NC (1983).
12. Zuckerman, E.B. and Melson, G.A., Abstracts, 191st Annual Meeting of the American Chemical Society, New York, NY (1986).
13. Vannice, M.A., *J. Catal.*, 37, 449 (1975).
14. Kellner, C.S. and Bell, A.T., *J. Catal.*, 71, 288 (1981).
15. Anderson, R.B., "The Fischer-Tropsch Synthesis," Chapter 5. Academic Press, Orlando, 1984.