Carbon Monoxide Hydrogenation Over Ru-Mn-K/Al$_2$O$_3$ Catalysts

S. Tajammul HUSSAIN & M. Ashraf ATTA
A.Q. Khan Research Laboratories,
Rawalpindi-PAKİSTAN

The catalytic behavior of a series Ru/Al$_2$O$_3$ catalysts promoted with various levels of Mn and K prepared by coimpregnation were investigated in the CO-hydrogenation reaction. Catalytic studies showed that the addition of Mn enhances the production of Fischer Tropsch products and K promotion in particular enhances the production of unsaturated hydrocarbons while inhibiting the methanation reaction. The influence of K and Mn on the Fischer Tropsch product selectivity in CO-hydrogenation studies is discussed in terms of ensemble and electronic effects, and the production of a new surface site Ru:Mn:K.

Introduction

Metal-supported catalysts have been widely used in research for investigate the CO-hydrogenation reaction. Depending on the metal used and the reaction conditions, a variety of products may be formed, including methane, olefins, paraffins and oxygenated products such as alcohol. The importance of unsaturated hydrocarbons as starting materials in the chemical industry increases interest in searching ways for enhancing the product selectivity towards olefinic products in CO-hydrogenation.

Many studies have been dedicated to investigate the effect of additives on the FTS reaction[1-5]. Alkali is one of the interesting additive for this reaction, and it is known that the addition of alkali additives results, in most cases, in a decrease in catalytic activity and in selective formation of olefins and higher hydrocarbons.

Potassium and manganese as promoters have been employed in catalysis to enhance the selectivity and/or the reactivity of metal catalysts for reactions such as the Fischer-Tropsch Synthesis of hydrocarbons and ammonia synthesis[6-10]. The influence of alkali and manganese metals on the Fischer Tropsch Synthesis reaction as reported in the literature can be summarised as follows:

1. The change in catalytic behavior is due to the ensemble (geometric) and electronic (ligand) effect[11-12].

2. The CO binding energy of the metal increases[13], indicating possible electronic interaction between the metal and K.

3. The CO stretch frequency is reduced[14], indicating surface modification due to presence of metal-K bimetallic[15].

4. The CO dissociation rate over many transition metals' catalysts increases[16-17]. Hence the formation of the respective oxides of the metal is expected.

5. The methanation rate decreases and the yield of higher hydrocarbons increases[18].

The present studies were undertaken to investigate the catalytic behavior a series of Ru:Mn/Al$_2$O$_3$ catalysts promoted with different levels of potassium in the CO-hydrogenation reaction and to study the combined effect of potassium and manganese on catalytic activity and selectivity.

Experimental Work

Catalyst Preparation

Ru/alumine catalysts were prepared by impregnating a high surface area alumina support with Ru$_3$(CO)$_{12}$ and MnCl$_2$ (Aldrich Chemicals U.K.) in an n-hexane solution to give a Ru (ruthenium) loading of 1% w/w. Two sets of samples were prepared, one without Mn and the other with 20 % w/w Mn. 0.09, 0.18 and 0.27 M solutions of K$_2$CO$_3$ (supplied by Alpha Products Ltd. U.K.) were dissolved in water and added to the prepared catalyst samples with constant stirring. Three sets of samples for each catalyst (without Mn and with 20% Mn) were prepared with 1.65, 2.8 and 4.0 % "K" w/w. The solvent from the prepared samples was removed in a stream of hydrogen at 423 K. The temperature of the powder was raised from room temperature to 423 K at a heating rate of I K/min. The temperature was kept at this level onernight, after which it was raised to 723 K at the same heating rate and kept at that temperature for 16 hours. The procedure was necessary to allow for the gradual decomposition of the ruthenium, manganese and potassium precursor and to prevent their desublimation. The catalyst samples were designated as 100:00 (without Mn and with different K concentraitons) and 100:20 with 20% Mn loading and with different K concentraitons).

Catalytic Experiments

The catalytic experiments were carried out using a conventional flow system at atmospheric pressure. The reactor was constructed from pyrex glass tubing of 12 mm internal diameter. The catalyst was held in place by means of quartz wool. The reactor was externally heated by a furnace connected to a temperature controller. For a typical experiment, the reactor contained 1 g of catalyst.

Before each experiment, the catalyst was pretreated in situ with hydrogen flow at 673 K for 16 hours, and then cooled to the reaction temperature before switching pure hydrogen to the reactant feed. The reactant feed was a premixed hydrogen-carbon monoxide-argon mixture, with a volumetric composition of 42:10:48 supplied by B.O.C. Specialist Gases Ltd. U.K. The total gas flow rate over the catalyst was close to 50 ml/min. Constant activity was obtained after nearly 25-30 minutes on stream. The reaction was performed in the temperature range of 468-578 K.

Exit gases were analysed with a Pye Unicam 4500 programmable gas chromatography equipped with a flame ionization detector. A poropak Q column of 1.5 m length and 80-100 mesh size was used to separate the hydrocarbons formed. The main products, including CH$_4$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_8$, C$_4$H$_8$, and C$_4$H$_{10}$, were adequately analysed by the gas chromatograph in a temperature-programmed mode between 40 and 160 °C. Calibration of the detector response was carried out by injecting gas mixtures of known composition supplied by Phase Separation Ltd, U.K.

The calculations in the study were carried out following the procedures described in the reference[33].

Results and Discussion

Catalytic activity

Arrhenius plots of CO consumption, methane and C$_2$– C$_4$ hydrocarbon production as well as total hydrocarbon production were consistent for all the samples investigated, using data for CO conversion of less than 10%. Representative data on total conversion as a function of temperature, and on product distribution as a function of K loading, are presented in Figures 1 and 2, respectively. Table 1 summarizes the apparent activation energies for the production of methane and higher hydrocarbons, and for total hydrocarbon production, calculated for a CO conversion of less than 10%. When compared with the parent catalyst (100:00) reported in reference 4, the activity of the catalyst for total hydrocarbon production is found to decrease with the addition of K. The decrease in activity with the addition of K is attributed to the presence of a higher level of carbon on the surface of the system. It has been reported in the literature that the presence of K enhances CO dissociation[12−22]. However, one could argue that the addition of potassium suppresses both the methanation rate as well as the rate of formation of Firscher Tropsch products.
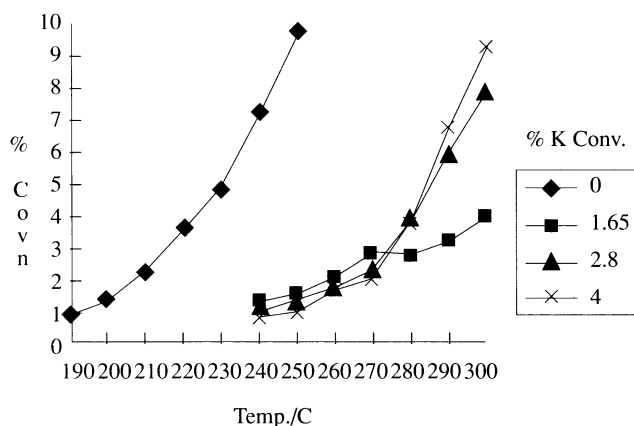

Figure 1. Total conversion as a function of temperature in CO-hydrogenation over Ru-Mn-K/Al$_2$O$_3$ with different K loadings
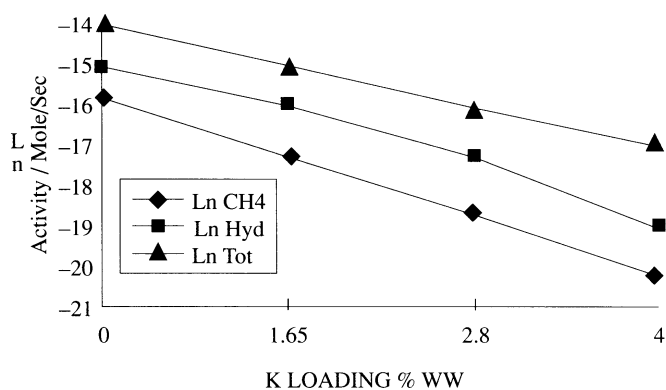
Figure 2. Methane, C$_2$– C$_4$ hydrocarbon and total hydrocarbon production at 553 K in CO-hydrogenation reaction on Ru-Mn-K/Alumina, system.

However, because the Fischer-Tropsch reaction is inhibited to a lesser extent than the methanation reaction, it is apparent that the role of potassium as a catalytic modifier is to limit methane formation in preference to hydrocarbon chain growth. The decline in activity with potassium addition may be understood if one considers that at least some of the added potassium would simply physically cover or block part of the Ru active sites, which in itself would lead to a decline in catalytic activity. This decline is much more pronounced on the Mn doped samples, supporting the argument of Ru surface coverage by K and Mn: K. Studies on bimetallic systems have revealed that a large ensemble consisting of 4 to 6 adjacent Ru metal atoms is required for hydrogen adsorption[23]. The methanation reaction is more hydrogen demanding than the Fischer Tropsch reaction. Delmon et al.[24] have suggested that an ensemble size of 12 Ni atoms is needed for the methanation reaction. It does seem that the ensemble effect produced by the addition of potassium and Mn plays a part in reducing the availability of hydrogen on the surface, inhibiting its dissociative adsorption and hence bringing about the observed decline in the activity of the catalyst.

Table 1. Activation energies for the products in CO-hydrogenation reactions.

Catalyst Ru-K (% K)	Methane E$_a$ KJ/mol	Hydrocarbons E$_a$ KJ/mol	Total Hydrocarbons E$_a$ KJ/mol
0.00	129 ± 4	133 ± 3	136 ± 2
1.65	137 ± 3	141 ± 4	130 ± 3
2.8	123 ± 2	124 ± 2	120 ± 3
4.0	113 ± 5	117 ± 3	110 ± 4

Catalyst Ru-Mn-K (% K)	Methane E$_a$ KJ/mol	Hydrocarbons E$_a$ KJ/mol	Total Hydrocarbons E$_a$ KJ/mol
0.00	110 ± 4	118 ± 3	107 ± 4
1.65	114 ± 3	120 ± 4	110 ± 5
2.8	116 ± 3	125 ± 3	108 ± 4
4.0	93 ± 6	100 ± 4	90 ± 4

The possibility that an electronic effect may play a role in depressing hydrogen chemisorption can also be considered. Many authors have argued that the combined effect of Ru:Mn:K and Ru:K produces a new surface site which brings about an increase in the electron density at the transition metal size[25-26]. Taking this hypothesis into consideration and the fact that upon its chemisorption hydrogen donates electron density to the metal adsorption site, it would not be surprising to suggest that the addition of potassium and the combined effect of K:Mn should decrease the surface coverage of hydrogen through a geometric effect covering the Ru active sites of hydrogen adsorption. Instead, this combined effect seems to generate a new surface site (Ru:Mn:K). If this is so, then in both cases, the ensemble effect and the electronic effect would tend to reduce the ability of the catalyst for hydrogenation or dissociative adsorption of hydrogen. If so, it is reasonable that the formation of methane by hydrogenation of methyl groups on the surface is suppressed, something which has been observed in the present investigation.

Selectivity changes by additives

As has been mentioned earlier, the role of potassium and manganese as a catalytic modifier is not confined in limiting methane formation but also includes producing new surface site Ru:Mn:K which contributes in shifting of product selectivity towards higher hydrocarbons in the case of Ru:K doped catalysts, and towards olefinic products in the case of the Ru:Mn:K doped system. The preferential formation of higher hydrocarbons and shifting of product selectivity towards olefinic products in case of Mn doped samples may be attributed to the depression of the hydrogenation of the surface intermediate by potassium and mangenese addition, which in turns enhances chain propagation by altering the mechanistic pathyways of the F-T synthesis. The creation of new surface sites responsible for selectivity changes in the catalysts investigated could also be the reason for the observed enhancement in hydrocarbon and olefin formation[27-29].

Figures 3 and 4 show that changes in product selectivities as a function of K doping for the sample investigated. For comparison purposes, the selectivity changes for the parent catalyst are also plotted. The addition of K and Mn to the system has a marked effect on the selectivity, in this case the product selectivities being shifted towards olefinic products.

The observed behavior in the system can be explained on the basis of changes in the strength of CO adsorption. When the surface coverage of carbon is increased by the addition of K, the ability of the catalyst to hydrogenate decreases and the readsorption of olefins becomes less likely to occur. If this is so, then it is quite reasonable to assume that the formation of methane by the hydrogenation of CH$_x$ species on the surface is suppressed and the olefin/paraffin ratio in the primary products increases. The addition of K on the Mn doped samples enhances this effect, resulting in an increase in olefinic product selectivity. It is essentially the competition between dissociative CO chemisorption and hydrogen adsorption through the ensemble effect and ligand effect on the active catalyst sites that leads to change in product distribution.
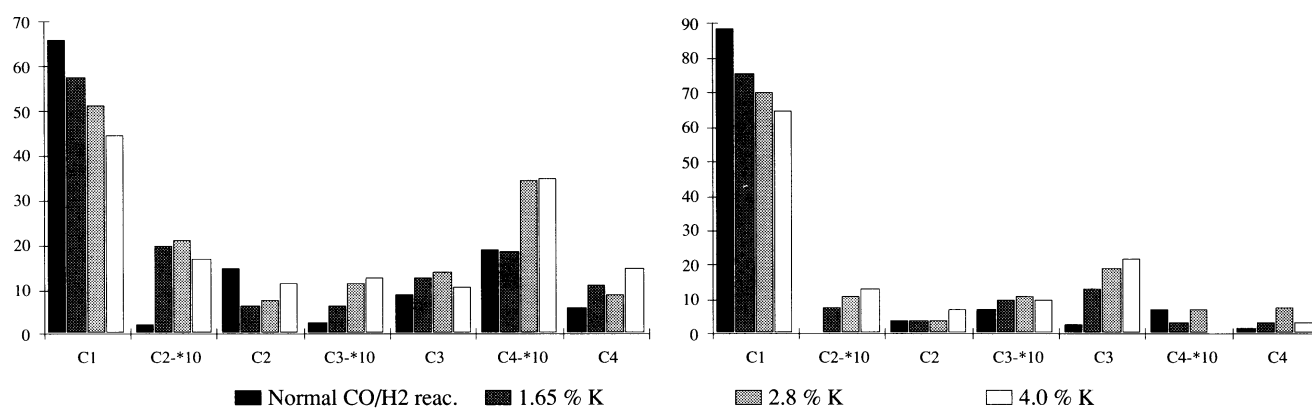

Figure 3. The effect of K addition on product selectivities of 100:00 and 100:20 Ru/Mn catalysts in CO-hydrogenation with different K loadings.
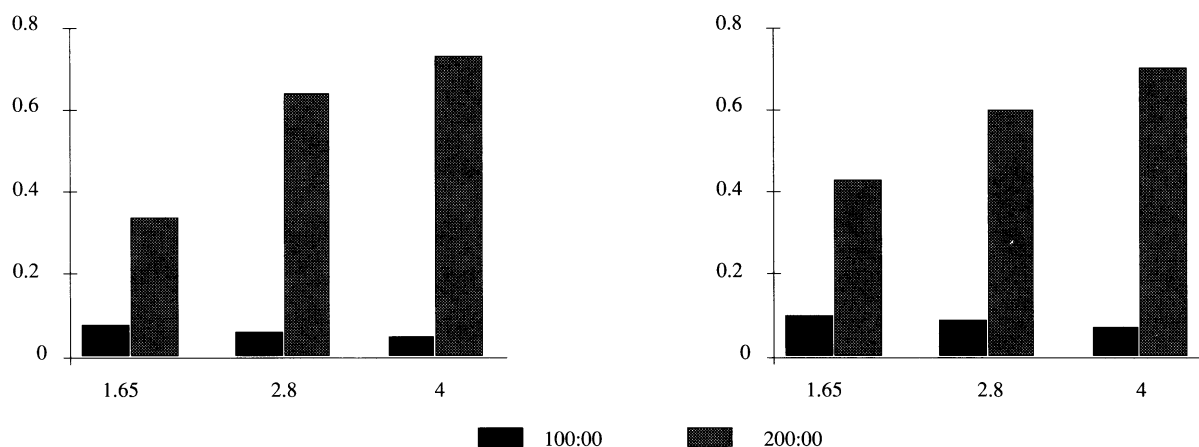

Figure 4. The effect of K addition on alkanes/alkenes selectivity for 100:00 and 100:20 Ru/Mn catalysts in CO-hydrogenation.

After studying Figures 3 and 4, it may be observed that the ethylene/ethane ratio in CO-hydrogenation is significantly lower than the propene/propane ratio, and that this effect is more pronounced in Ru:K:Mn supported samples. This suggest that ethylene is more significantly consumed than higher olefins by species in the reaction mixture. It is generally accepted that olefins are formed by β-elimination from appropriate alkyl fragments[30]. This is a clear indication that higher olefins are less reactive than ethylene with the species in the Syngas mixture, which is consistent with the generalization that the higher olefins, ethylene has the greatest ability to coordinate with the transition metals[31]. Figure 3 & 4 clearly indicate the effect of K and K:Mn addition on the selectivity pattern of the catalysts studied. If enhancement of olefin selectivity is partly due to the reduced ability of the modified catalyst to adsorb hydrogen, than the results obtained

are not surprising. The other reason for this increase in olefins and higher hydrocarbon selectivity may be an acceleration in the abstraction of β-hydrogen atoms from the adsorbed alkyl species[32].

Conclusions

The following points emerges from the study.

1. Methanation activity decreases by the addition of K on the samples with or without Mn.

2. The addition of K to the catalysts shifts product selectivity from methane towards higher hydrocarbons on the sample without Mn.

3. On the Mn doped samples, the addition of K shifts the product selectivity towards olefinic products.

4. It is likely that a new surface site Ru:Mn:K, which is mainly responsible for the increase in olefinic selectivity, is generated.

References

1. R.B. Anderson, in **"Catalysis"** ed. P.H. Emmett, vol.4, Reinhold, New York, (1956).

2. P.J. Denny and D.A. Whan, **"Catalysis"** vol. **2**, p. 49-51, The Chemical Society London, (1981).

3. G.L. King, J.A. Cusumano and R.L. Garten, **Catal. Rev. Sci. Eng., 23,** 233-236 (1981).

4. S.T. Hussain, B.H. Sakakini and J.C. Vickerman, **"Catalysis and Surf. Charact."**, eds. T.J. Dines, C.H. Rochester and J. Thomson, The Royal Society of Chemistry, p. 234-241 (1992).

5. N.I. Dunhill, B.H. Sakakini and J.C. Vickerman, **Proc. 9th Int. Congr. on Catal. Calagary, 3,** 1166-1170 (1988).

6. E.C. Kruissink, H.L. Pelt, J.R.H. Ross and L.L. Van Reijen, **Appl. Catal. 1,** 23-27 (1981).

7. S. Kagfami, S. Natio, Y. Kikuzona and K. Tamaru, **J. Chem. Soc. Commun.,** 256-258 (1983).

8. M.M. McClory and R.D. Gonzalez, **J. Catal., 89,** 392-395 (1984).

9. S.C. Chung, J.G. Goodwin and I. Wender., **J. Catal., 95,** 435-439 (1985).

10. K. Aika, H. Hori and A. Ozaki, **J. Catal., 27,** 424-427 (1972).

11. **"Physics and Chemistry of Alkali Metal Adsorption"**, eds. H.P. Bonzel, A.M. Bradshaw and G. Ertl, Elsevier Sc. Publishers, Amesterdam, 1989.

12. L. Ng. K. Uram, Z. Xu, P.L. Jones and T.J. Yates, **J. Chem. Phys., 86,** 6523-6525 (1987).

13. M.P. Ki. Skimova, **Surf. Sci., 111,** 592-597 (1981).

14. W. Eberhardt, F.M. Hoffman, R. Depaola, D. Heskett, I. Strathy, W. Plummer and H.R. Masen, **Phys. Rev. Lettr., 54,** 1856-1858 (1985).

15. J. Lee, C.P. Hanrahn, J. Arias, R.M. Martin and H. Metiu, **Phys. Rev. Lettr. 51,** 1803-1807 (1983).

16. J.W. Erickson and P.J. Estrup, and G.A. Somoraji, **Surf. Sci., 167,** 519-522 (1986).

17. C.T. Campbell and D.W., Goodman, **J. Phys. Chem., 92,** 2569-2572 (1989).

18. H. Kolbet, K.D. Tilmitz and R. Ralek, **13th Intl. Sci. Eng. Conv. Soc. Aut. Eng.,** 482-486 (1982).

19. C.S. Kellner and A.T. Bell, **J. Catal., 71,** 297-301 (1981).

20. N.D. Lung and A.R. Williams, **Phys. Rev. Lett., 37,** 212-214 (1976).

21. E.E. Garfunkel, J.E. Crowell, **Surf. Sci., 121,** 303-307 (1982).

22. G. Borden, G. Gaffner and H.P. Bonzel, **Surf. Sci., 84,** 295-298 (1979).

23. J.C. Vickerman and K. Christman, **Surf. Sci., 120,** 1-5 (1982).

24. J.A. Dalmon and G.A. Martin, **Proc. 7th Intl. Congr. Catal.,** Tokoyo, p. 402-405 (1980), Kodansha, Elsevier, Tokoyo/Amesterdam.

25. M.E. Dry, "**Catalysis Science & Technology**", eds. J.R. Anderson and M Boudart, vol. **1,** p. 27-30 51981), Springer-Verlag, New York.

26. M.E. Dry, T. Shingles, L.J. Boshoff and G.J. Oosthuizen, **J. Catal., 15,** 190-193 (1969).

27. S.J. Madon and W.F. Taylor, **J. Catal., 69,** 32-36 (1981).

28. L. Konig and J. Gaube, **Chem. Eng. Tech., 55,** 14-18 (1983).

29. S.R. Morris, R.B. Moyes, P.B. Wells and R. Whyman, in "**Metal Support and Metal Additive Effects in Catal**", ed. B. Imelik, Elsevier, Amesterdam, (1982).

30. A.T. Bell, **Catal. Rev. Sci. Eng., 23,** 203 (1981).

31. G. Henric-Olive and S. Olive, **Angew Chem.,** Int. Ed. Engl., **15,** 136-139 (1976).

32. T. Okuhara, K. Kobayashi, T. Kimura, M. Misono and Y. Yoneda, **J. Chem. Soc. Chem. Comm.,** p. 1114-1116 (1981).

33. B.H. Sakakni, **Turkish J. Chem., 18(3),** 197 (1994)