

# Spectroscopic Studies of the Determination of Chain Growth Intermediate in the Fischer Tropsch Synthesis Reaction on the Bimetallic Supported System

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**Summary:** The ruthenium-manganese bimetallic alloy system was prepared by co-impregnation method from the ionic solution of ruthenium chloride and manganese chloride dispersed on the high surface area aluminium oxide support and reduced to metallic form at 450°C under hydrogen flow. The prepared sample was characterised using BET surface area measurement and atomic adsorption spectroscopy.

The prepared sample was then subjected to carbon monoxide hydrogenation reaction in the continuous flow reactor. The sample was then taken out of the reactor and transferred to Secondary ion mass spectrometer, X-ray photo electron spectrometer and Infra red spectrometer for study.

The study indicates the presence of CH<sub>2</sub> group on the surface. On the basis of this intermediate a mechanism for the formation of higher hydrocarbons in the Fischer Tropsch Synthesis has been postulated.

In this manuscript modern spectroscopic techniques have been used in determining the chain growth intermediate for the well known Fischer Tropsch Synthesis used for the production of hydrocarbon products in the Petrochemical Industry.

## Introduction

Ruthenium is well known to be a good Fischer Tropsch catalyst for the production of hydrocarbons [1]. Manganese, when combined with ruthenium increases the product selectivity towards olefinic products in the CO/H<sub>2</sub> study [2-7]. The Fischer Tropsch Synthesis is a well known reaction in the petrochemical industry for the production of hydrocarbon products from CO/hydrogenation on the supported catalyst system. The mechanism of this famous reaction is still a debatable issue. Many research groups have given the chain growth intermediate for the production of higher hydrocarbons using different procedures [8-10]. All these studies are based on conventional methods or mere speculations.

This manuscript describes the use of surface science techniques in elucidating the mechanism of this reaction.

## Results and Discussion

### *Static secondary ion mass spectrometry*

The positive secondary ions generated on bombardment of the surface of the catalyst with an

argon ion beam were analysed using a VG 12-12 quadrupole mass spectrometer. The incident argon ions had an energy of 2 KeV, a current of 1nA/cm<sup>2</sup> was used.

Figure 2 (a,b) shows typical high resolution spectra recorded before and after CO/H<sub>2</sub> experiment. The presence of CH<sub>2</sub> peak at a.m.u. 14 on the catalyst sample after the CO/H<sub>2</sub> reaction indicates the possible intermediate which propagates the formation of higher hydrocarbons. The presence of Ru<sup>+</sup>, Mn<sup>+</sup>, indicates that the procedure applied for the reduction of the catalyst sample, reduces the metal to zero valence state. The presence RuMn<sup>+</sup> peak at amu 155 indicates the presence of bimetallic alloy.

### *X-ray photo electron spectroscopy*

XPS spectra were recorded in an ESCA-III instrument, using MgK $\alpha$  radiation. Targets were sputtered with an argon ion beam with an ion current of 20 $\mu$ A. Ru3d<sub>5/2</sub> signal was used for quantitative analysis. Binding energy of Ru3d<sub>5/2</sub> was referenced to C1s peak at 284 eV [11]. All the binding energies were calculated using a computer program and with reference to C1s binding energy.

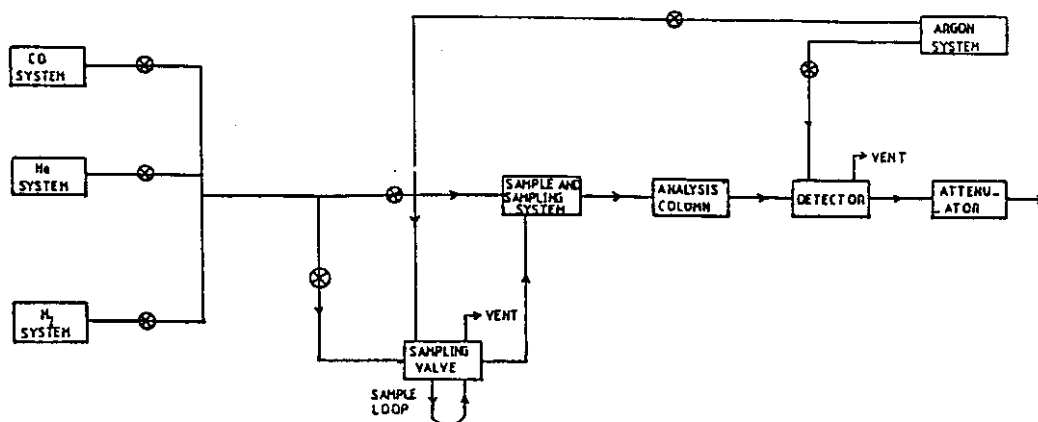


Fig.1: The apparatus for CO/H<sub>2</sub> reaction.

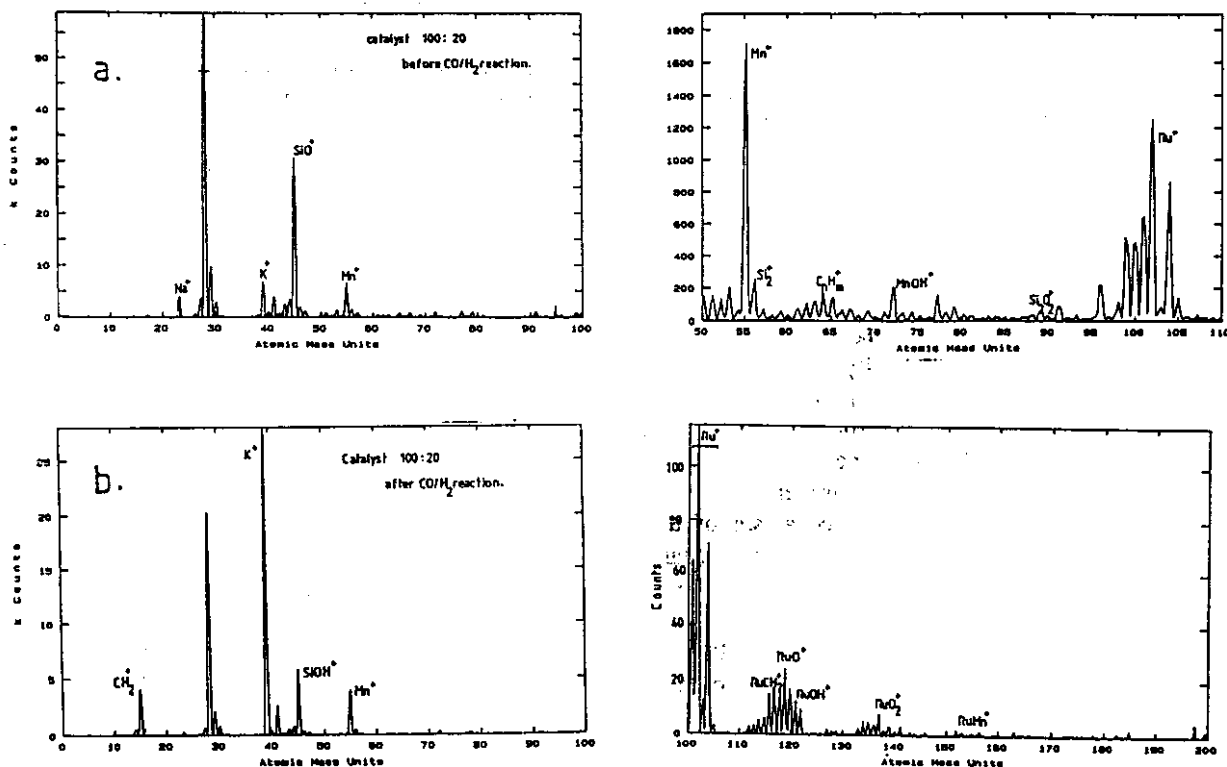


Fig. 2: (a,b) The positive ion SSIMS spectra collected before and after CO/H<sub>2</sub> reaction.

Figure 3 presents the XPS spectra of the catalyst sample before and after CO/H<sub>2</sub> reaction. The appearance of an additional peak at 287eV [12] on the sample after CO/H<sub>2</sub> reaction indicates the presence of CH<sub>2</sub> peak. This supports our SSIMS findings. The shift of Ru3d<sub>5/2</sub> peak from 283.10 to 283.30 reflects

the presence of RuO on the sample after CO/H<sub>2</sub> reaction. This is expected, since water is one of the product of Fischer Tropsch Synthesis, hence Ru react with water to give RuO. Apart from the presence of RuO, the shift in Ru3d<sub>5/2</sub> binding energy is also attributed to the electronic interaction between Ru

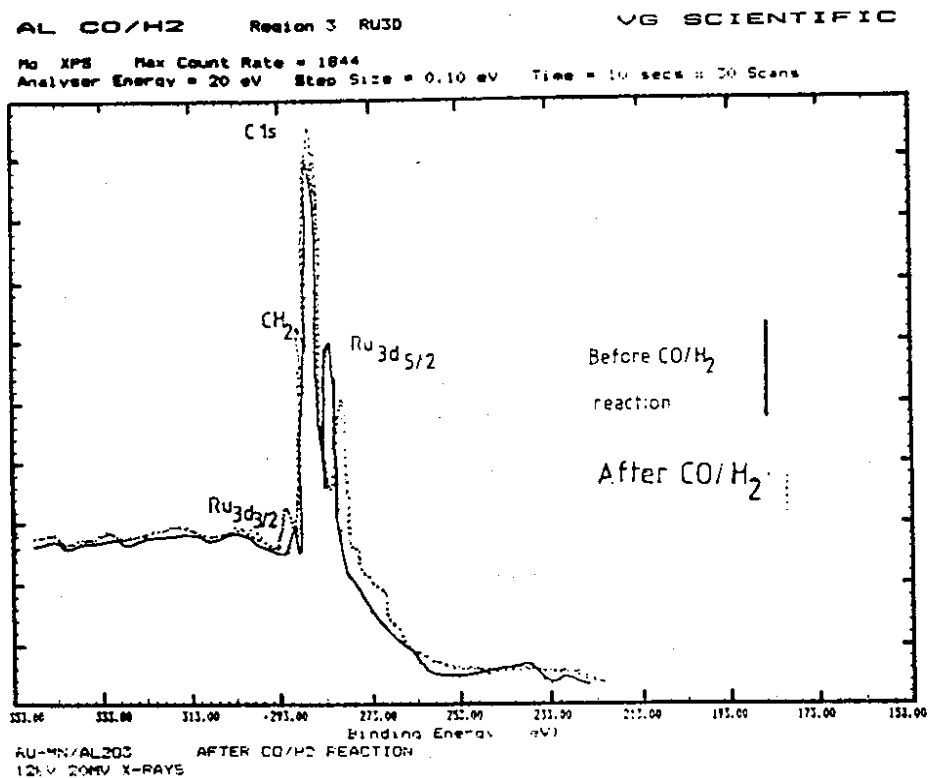


Fig.3: The XPS spectra collected before and after CO/H<sub>2</sub> reaction.

and Mn which form a bimetallic. The SSIMS data and the experimental findings described in reference 2 support this suggestion.

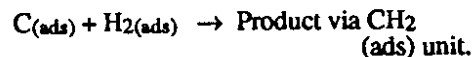
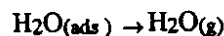
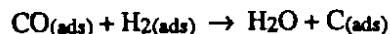
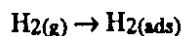
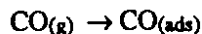
#### IR spectroscopy

The IR spectra before and after CO/H<sub>2</sub> were recorded at room temperature using a research grade FTIR (Digilab FTS 40) instrument. The FTIR is equipped with the computer controlled facilities, like background subtraction, multispectra display base line correction and peak analysis programme.

Figure 4 presents the IR spectrum recorded before and after CO/H<sub>2</sub> reaction. Studying the figure 4, an immediate conclusion could be drawn by the appearance of an additional band on the sample after CO/H<sub>2</sub> reaction at 2310 cm<sup>-1</sup>. This band corresponds to CH<sub>2</sub> group [13]. The bands appearing at 1640 cm<sup>-1</sup> and between 2800-3000 cm<sup>-1</sup> indicate the presence of water vapours and OH group [14].

On the basis of the experimental data collected from the study, the mechanism of the CO/H<sub>2</sub> reaction

is postulated for the production of higher hydrocarbons involving the use of solid bimetallic alloy system.



#### Conclusion

From the study presented the following conclusions could be drawn.

- (i). The spectra adsorbed on the surface of the system after the CO/H<sub>2</sub> reflects the process of adsorption.
- (ii). The evacuation of the prepared sample does not affect the adsorbed species.

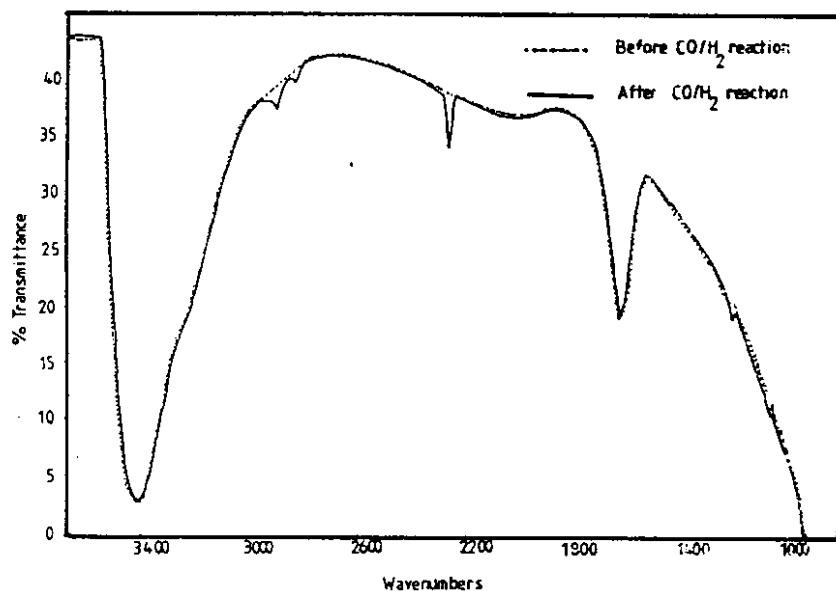


Fig. 4: The IR spectra collected before and after CO/H<sub>2</sub> reaction.

- (iii) The higher hydrocarbons are formed by the presence of group CH<sub>2</sub> on the surface which initiates the chain propagation.

## Experimental

### Catalyst preparation

The catalyst was prepared from RuCl<sub>3</sub> and MnCl<sub>2</sub> by co-impregnation method described previously [2] dispersed on the high surface area alumina oxide support. Catalyst sample was reduced in flowing hydrogen at 723 K for ca. 15 h. Ruthenium loading was 1% (w/w) and manganese loading was in the atomic ratio 0.20. The final composition and the surface area was determined by atomic adsorption and BET surface area measurement. The sample is designated as Rm/x:y where x:y is the ruthenium:manganese ratio in the sample. Measured characteristics of the sample are presented in Table 1.

Table 1: Measured characteristics of the prepared sample.

Catalyst sample	Wt. of support (g)	Wt. of Ru (g) m <sup>2</sup> g <sup>-1</sup>	Surface area	Ru loadings % (w/w)	Mn loadings	100 Ru (Ru) <sup>a</sup>
100:20	2.5	0.025	129	0.98	0.198	100

a = atomic adsorption.

Catalytic hydrogenation of CO was carried out in a single pass flow reactor at atmospheric pressure with the premixed gas of composition 10.45% CO: 47.40% H<sub>2</sub>: 42.15% Ar (v/v/v) supplied by B.O.C. Specialist Gases Ltd. U.K. The experimental layout is presented in figure 1. After the reaction the sample was taken out of the reactor and transferred to SSIMS, XPS and IR instruments for further study. Prior to CO/H<sub>2</sub> experiment SSIMS XPS and IR spectra was collected for comparison.

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