

## Addition of 2% Ethene, Propene and Acetylene in the CO- hydrogenation Experiment for the Determination of Chain Growth Intermediate in the Fisher Tropsch Synthesis on Ru/Alumina Supported Catalyst

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**Summary:** The alumina supported ruthenium catalyst was prepared by co-impregnation method and characterised using B.E.T. surface area measurement and Atomic Absorption Spectroscopy. The prepared catalyst was subjected to Fischer Tropsch Synthesis with simultaneous addition of 2% ethene, propene and acetylene in the feed stream to investigate the possible intermediate in the CO/H<sub>2</sub> reaction. From the experimental data it could be concluded that the formation of >CH<sub>2</sub> group on the surface of the catalyst is the possible intermediate which initiate the chain propagation for the formation of higher hydrocarbons in the Fischer Tropsch Reaction.

### Introduction

The objective of this study was to investigate the influence of ethene, propene and acetylene on the CO/hydrogenation reaction and to extend information on the possible intermediates for the chain growth mechanism. Data on the interaction of low molecular weight olefins in CO/hydrogenation reaction (i.e. ethylene, propene and butene) is available in the literature [2-20].

#### *Catalyst preparation*

Alumina supported ruthenium catalyst was prepared by co-impregnation method as described in reference [1]. To ensure high metallic dispersion loading of only 1% w/w of ruthenium was used. The variable for the preparation procedures and the characterisation result of the prepared sample using Atomic Absorption Spectroscopy are summarised in Table 1.

### Results and Discussion

Table (2) present the selectivity data obtained for the addition of 2% ethene, propene and acetylene in the CO-hydrogenation reaction.

The addition of ethene to the feed mixture increases the production of methane, propene and propane. The increase in methane production is the result of disproportionation/self hydrogenation of ethene [22], the addition of -CH<sub>2</sub> monomer into

Table 1: Measured characteristics of the catalysts

Catalyst sample	Weight of support (g)	Weight of Ru (g)	Surface area m <sup>2</sup> g <sup>-1</sup>	Ru 100 loadings % (w/w)	Ru (Ru)*
Ru/Al <sub>2</sub> O <sub>3</sub>	2.5	0.025	84	0.96	100

a = Atomic absorption

Table 2: Rate enhancement and yields of hydrocarbons product observed when 5% ethene and different percentage of propene was added to the feed mixture for CO-hydrogenation study (reproduced from reference 21)

Catalyst	Additive	Rate enhancement factor					
		C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>
2.6 % Ru/silica	Ethene	1.2	13	24	22	30	
1.5 % Ru/13 x -zeolite	Ethene	1.8	7.2	8	4.4	4.5	
17% Ru/titania	Ethene	0.2	1.6	1.9	1.7	1.6	
5% Ru/magnesia	Ethene	0.6	1.5	1.4	1.3	1.2	
2.6 % Ru/silica	0.00 %	88.5	4.2	3.9	2.9	0.5	
	0.45 %	48.4	16.7	20.8	9.5	4.6	
	12.0 %	32.5	17.1	28.4	14.3	7.7	

C<sub>2</sub> products increases the production of C<sub>3</sub> products. It has been reported in the literature that the addition of ethene in CO-hydrogenation reaction modified product compositions [21]. For comparison, the literature values of the rate enhancement when ethene is added in CO-hydrogenation is presented in Table 3. A similar trend is observed in our case up to C<sub>3</sub> carbon, but no rate enhancement in C<sub>4</sub> products were observed. The discrepancy between our results and

Table 3: Yield of higher hydrocarbons data collected before/after 2% ethene, propene and acetylene addition in the CO/H<sub>2</sub> feed mixture.

Additive	Yields of hydrocarbons (%)							
	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>4</sub>	C <sub>4</sub>
2% ethene	60/70	-	18	21/12	5/10	0.05/1.1	0.07/0.04	
2% propene	55/22	6/27	20/30	-	-	5/6	7/8	
2% acetylene	56/15	5/15	17/35	2/6	3/8	4/6	5/6.2	

\*Normal CO/H<sub>2</sub> with additives.

those reported in the literature could be attributed to the percentage of ethene used in the feed stream.

Our results are consistent with the results of Bell *et al.* [23] who noted an increase in the rate of CH<sub>4</sub> formation for Ru/SiO<sub>2</sub> catalyst upon addition of ethene, but no affect in C<sub>4</sub> production was observed on addition of 2% ethene in the CO/H<sub>2</sub> reaction.

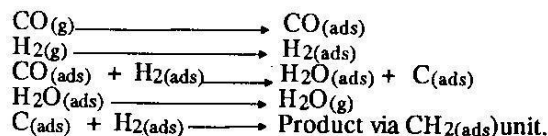
Table (2) presents the selectivity data for 2% addition of propene in the CO-hydrogenation. It is observed that the formation of CH<sub>4</sub> is suppressed, whereas the formation of C<sub>2</sub> and C<sub>4</sub> product increases. This is in agreement with the results of Bell *et al.*, [24] Kobori *et al.*, [20] and Kibly *et al.*, [17]. They reported the suppression of CH<sub>4</sub> and an increase in C<sub>2</sub> and C<sub>4</sub> products. It is proposed that hydrogenation of propene gives C<sub>1</sub> and C<sub>2</sub> products and the addition of -CH, -CH<sub>2</sub> monomers to propene yields C<sub>4</sub> products. For comparison the results of addition of propene from the literature [21] is presented in Table 3. The discrepancy in our results and the results from literature on the production of C<sub>4</sub> products is possibly due to the concentration of propene in the feed mixture.

Addition of 2% acetylene in CO-hydrogenation gives methane and higher hydrocarbons. The methane product is suppressed but the production of higher hydrocarbons increases.

This study with the addition of 2% ethene, propene and acetylene in CO-hydrogenation reaction shows clearly that ethene is involved in the chain growth to a considerable extent and higher

hydrocarbon production increases by at least one order of magnitude by the addition of ethene either as an intermediate or as a reactant.

All the data of this study led us to postulate the following possible reaction scheme for Fischer Tropsch Synthesis reaction.



### Experimental

The equipment used for the study is shown schematically in Fig. 1. It consists of a 1 cm i.d. silica tube reactor for continuous flow reaction with the catalyst held on a sintered disc. The catalyst was surrounded by a furnace controlled by a modified Pye 104 chromatograph oven controller. This not only gave temperature control but also a temperature ramping facility. The reactor was fitted with an internal finger which projected into the catalyst bed in order to provide temperature monitoring by a chrome-alumel thermocouple.

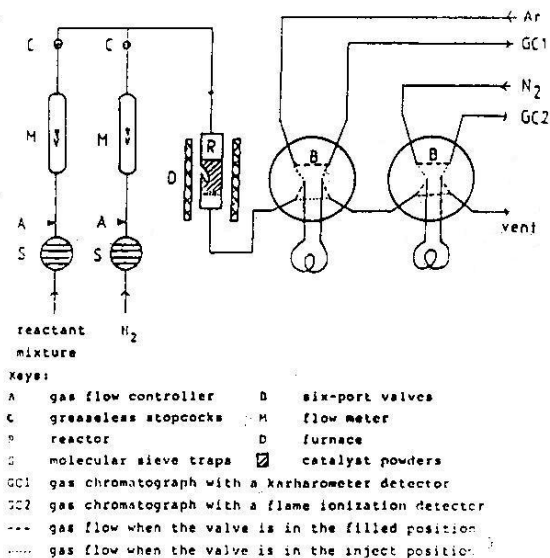


Fig.1: Experimental lay out for the CO-hydrogenation reaction.

The gas supply to the reactor came from the confluence of two lines. The first supplied hydrogen. The second line carried the feed stock which contains 10.45% CO, 47.40% H<sub>2</sub> and 42.15% Ar. 2% ethene, propene and acetylene is simultaneously mixed in the feed stream.

The reactor exhaust was connected to two gas sampling valves connected in series. The first allowed gas samples to be passed into a Pye 104 gas chromatograph equipped with a 2m Poropak-Q column and a Flame Ionisation Detector for examination of product hydrocarbons. The second gas sampling valve allowed samples to be passed into a Pye 104 chromatograph fitted with a Poropak-N pre-column and a 5A molecular sieve main column. This chromatograph was fitted with a Katharometer for analysis of unreacted hydrogen and carbon monoxide.

The G.L.C. gas analysis was performed by using standard calibration gases provided by Phase Separation Ltd. (U.K.).

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