

A MECHANISTIC STUDY OF THE CHAIN PROPAGATION STEP IN THE FISCHER-TROPSCH SYNTHESIS

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KEY WORDS: Fischer-Tropsch synthesis, methylene, labelling studies

INTRODUCTION

The reductive polymerization of carbon monoxide to hydrocarbon mixtures (the Fischer-Tropsch synthesis) is a reaction that has attracted considerable interest ever since it was first discovered.^{1,2} Typically, syn gas (CO/H_2) is passed over a heated, supported metal catalyst at atmospheric pressure or above which leads to the formation of a complex product mixture composed mainly of linear alkenes and alkanes.

The mechanism of the polymerization has long been the subject of debate. Early proposals by Fischer and Tropsch were that surface methylene, formed by the hydrogenation of dissociated CO, polymerized on the surface. Experiments by Brady and Pettit³ confirmed the importance of methylene in hydrocarbon formation. They, and others⁴ proposed that chain growth was initiated by surface alkyl/hydride groups thus giving surface alkyls as the chain carriers. This mechanism, however, is not without limitations; for example, low levels of C_2 hydrocarbons are formed which are not accounted for by this mechanism. Consequently, there has been renewed interest in the mechanism of C-C bond formation in the Fischer-Tropsch synthesis. One approach, used by us and others⁵ involved studies of the reactions of well-defined metal complexes as model systems.

Early studies in this field were initiated by the decomposition reactions of organometallic complexes such as $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CH}_2)]_2(\text{Me})(\text{MeCN})]^+$ which modelled a portion of a rhodium catalyst during carbon monoxide hydrogenation.⁶ ^{13}C and D labelling studies indicated that C-C coupling proceeded by an unexpected route where vinyl ($-\text{CH}=\text{CH}_2$), rather than alkyl, was implicated as the key intermediate which coupled further with surface methylene to give the products.⁷ Such alkenyl + methylene couplings may well represent lower energy processes than the couplings of the corresponding of alkyl + methylene groups.⁸ These findings prompted further interest in the mechanism of C-C bond formation, and the nature of the intermediate species in the heterogeneously metal catalyzed hydrogenation of CO.

Our studies have further investigated the mechanism of the Fischer-Tropsch reaction, and in particular, evaluated the roles played by vinyl and methylene groups in hydrocarbon formation. This approach utilizes probe reactions which other workers,⁹ have been found to be successful in providing mechanistic information during CO hydrogenation and extends earlier work involving the co-reaction of model reactants, including vinyl and methylene precursors, with CO and H_2 under Fischer-Tropsch reaction conditions.¹⁰ For this study, ^{13}C probe molecules were used since unambiguous mechanistic information could be gained if they were incorporated into the products. Furthermore, other reactions of the probes could be investigated.

EXPERIMENTAL

Equipment

Quantitative analysis of the reaction products was carried out by gas chromatography on a Supelco SPB-1 (60 m x 0.53 mm x 5 mm) capillary column. The level of ^{13}C incorporation was analysed by GC-MS (HP 5890 - 5171 A).

Catalyst preparation

The catalysts were prepared by impregnation of the support (Davisil grade 645 silica gel) to incipient wetness to give metal loadings of 4%. $\text{Rh}(\text{NO}_3)_3$, $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added to the support and slowly heated to 373 K with frequent stirring at which temperature the catalysts were fully dried. A solution of $\text{Ce}(\text{NO}_3)_3$ was added to the rhodium catalyst in order to increase the activity.

Reaction conditions and catalyst activation

The catalyst was reduced under a steady stream of hydrogen (1 atm, 700 cm³ h⁻¹), with programmed heating (4 K min⁻¹) from room temperature to 673 K. The catalyst was then cooled to the reaction temperature under hydrogen and the gas flow was switched to syn gas (1 atm, flow rate 500 cm³ h⁻¹). The products of the reaction were either sampled directly from the gas stream and analyzed by gas chromatography or collected in a liquid nitrogen trap and analyzed by GC-MS. For the runs with probes, the products were analyzed by GC and GC-MS before, during and after probe additions. A background GC was initially obtained to show the distribution of the products. After a period of 1.5 h, the probe molecule was added to the syn gas feed stream. Nitromethane and ethene were directly injected into the gas mixture through a septum and diazomethane gas was introduced by diverting the syn gas flow through the vessel which contained the diazomethane gas, prepared in situ. A GC analysis was performed after the probe had been added. After a further 1.5 h period, a final GC was carried out to determine the activity of the catalyst after addition of probe. Products were identified by comparison of their mass spectra with Wiley library spectra, stored in the HP ChemStation software.

RESULTS

Vinyl and methylene probes were individually reacted with CO-H₂ over Co/SiO₂, Ru/SiO₂, Rh/Ce/SiO₂ catalysts under Fischer-Tropsch reaction conditions (CO:H₂ = 1:2, 1 atm over 1 g catalyst). Diazomethane and nitromethane were used as sources of methylene (C₁) and vinyl species (C₂) were derived from ethene. Prior to any probe addition, the products of CO hydrogenation were typical for those obtained for the polymerization, containing mainly linear alkenes and alkanes together with some oxygenates. The product distribution followed modified Anderson-Schulz-Flory kinetics, with high C₁ and low C₂ fractions and a stepwise linear decrease beyond C₃.¹¹

Vinyl probe addition

The effect of adding ethene as a source of vinyl to the CO hydrogenation was to increase the formation rate of the C₂ to C₇ hydrocarbons. During addition of the probe, the probability of chain growth, α , decreased for the various catalysts studied. Selected data of ¹³C_x incorporation into the C_n hydrocarbons when ¹³C₂-ethene was used as a probe over cobalt for example, (= 0, 1, 2,...n) are given in Table 1.

Methylene probe addition

Diazomethane and nitromethane were used as sources of methylene since it was expected that under the experimental conditions those probes would decompose to give methylene intermediates, as previously reported.^{12,3} Probe addition to the syn gas feed caused significant changes to the product distributions; in particular, there was an increase in the formation rate of C₃ to higher products and an increase in the probability of chain growth. The results of ¹³C_x incorporation into the hydrocarbon products when ¹³CH₂N₂ or ¹³CH₃NO₂ was added to the CO hydrogenation over cobalt are summarized in Table 2.

DISCUSSION

Effect of probe molecule addition

The addition of the methylene (C₁) and vinyl (C₂) probe molecules to each of the experiments increased the amounts of higher hydrocarbons produced. Ethene addition caused an increase in C₂ to C₇ products; the effect was largest, as might be expected, for the formation of ethane by hydrogenation/hydrogenolysis. Addition of nitromethane and diazomethane probes to the CO hydrogenation increased the formation rate of C₃ to higher products. The changes in the hydrocarbon production during probe addition are marked by changes in the chain growth probabilities for each of the experiments; addition of ethene had the effect of decreasing α while methylene probe addition caused an increase in α . The latter is consistent with an increase in the rate of propagation during methylene probe addition.

¹³C labelling studies

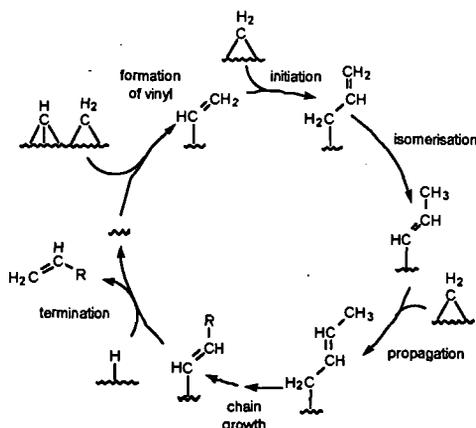
Addition of ¹³C₂-ethene to the ¹²CO/H₂ stream over all the catalysts studied clearly showed incorporation of ¹³C₂ units into the hydrocarbon products (Table 1). The levels of ¹³C₂ obtained are highly significant since they are many orders of magnitude greater than natural abundance. Incorporation of ¹³C₁ and ¹³C₃ units into the products are slightly higher than expected over cobalt. Thus, it is apparent that ethene undergoes some hydrogenolysis leading to the incorporation of ¹³C₁ units into the reaction products. Furthermore, there is little incorporation

of ^{13}C above natural abundance into the oxygenates indicating that they are not formed from vinyl groups. Similar patterns of ^{13}C labelling in the reaction products are obtained for the various catalysts studied.

The effect of adding $^{13}\text{CH}_2\text{N}_2$ or $^{13}\text{CH}_3\text{NO}_2$ to the ^{12}CO hydrogenation over cobalt gave results consistent with the incorporation of $^{13}\text{C}_1$ units into the hydrocarbon products (see Table 2). For both probes, the levels of $^{13}\text{C}_1$ incorporation are significant since they exceed those expected on the basis of natural abundance. In fact, the extent of ^{13}C incorporation in the products of the reaction is consistent with the mixing of methylene groups derived from the syn gas reaction ($^{12}\text{CH}_2$) with those derived from the probe ($^{13}\text{CH}_2$). It is clear from Table 2 that the arrangement of $^{13}\text{C}_x$ atoms in the products is close to that expected on the basis of random mixing of the methylene groups for the ratio of ^{12}C to ^{13}C used in these experiments. Furthermore, similar ^{13}C levels are obtained irrespective of whether $^{13}\text{CH}_2\text{N}_2$ or $^{13}\text{CH}_3\text{NO}_2$ is used as the methylene source suggesting that both probes react on the surface to yield a common intermediate. By contrast, identical experiments over rhodium catalysts showed quite different behaviour giving two parallel chain growth pathways each of which forms hydrocarbons. One is the hydrogenation of CO and the other is an oligomerization of the probe derived intermediates. Thus, over rhodium, there is very little crossover between the two routes and the hydrocarbon products effectively contain either only ^{12}C atoms with ^{13}C at natural abundance only, or fully ^{13}C -labelled hydrocarbons which contain little or no ^{12}C .

The alkenyl mechanism for Fischer-Tropsch homologation

The results show that there is most incorporation of $^{13}\text{C}_2$ units when $^{13}\text{C}_2$ -ethene is added to the $^{12}\text{CO}/\text{H}_2$ mixture. The degree of $^{13}\text{C}_2$ incorporation decreases with increasing number of carbons in the hydrocarbon products which is consistent with the C_2 species being involved in chain initiation. Addition of other probes such as ethyl bromide, vinyl bromide and tetra vinylsilane indicate that the initiating species is the unsaturated vinyl group. The addition of methylene probes to the ^{12}CO hydrogenation result in the incorporation of $^{13}\text{C}_1$ units in the reaction products according to the alkenyl mechanism. The pattern of $^{13}\text{C}_1$ distribution in the products is determined by the nature of the metal. Thus, over cobalt, the degree of $^{13}\text{C}_1$ incorporation is consistent with a distribution based on random mixing of the methylenes derived from the probe and those from the syn gas. By contrast, similar reactions over rhodium lead to parallel chain growth pathways. One is CO hydrogenation, which forms products derived exclusively from ^{12}C , the other is a homopolymerization of methylene intermediates derived from the probe giving fully ^{13}C labelled products and there is very little crossover between the two routes. It is proposed that over rhodium, alternative methylene intermediates, possibly CH_2N , may form which lead to independent polymerization pathways.



The alkenyl mechanism for Fischer-Tropsch homologation. Hydrocarbon formation is initiated by vinyl and propagated by methylene groups.

Table 1. Incorporation of $^{13}\text{C}_x$ from $^{13}\text{C}_2\text{H}_4$ over Co/SiO_2

x	0	1	2	3	4	5	6
1-butene	50	8 (2)	32	7	3		
1-pentene	55	9 (3)	27	8	2	1	
1-hexene	62	9 (4)	19	6	3	1	0

Figures in parentheses correspond to the expected % $^{13}\text{C}_1$ at natural abundance.

Table 2. Incorporation of $^{13}\text{C}_x$ from $^{13}\text{CH}_3\text{NO}_2$ and $^{13}\text{CH}_2\text{N}_2$ over Co/SiO_2

x	$^{13}\text{CH}_2\text{N}_2$						$^{13}\text{CH}_3\text{NO}_2$							
	0	1	2	3	4	5	6	0	1	2	3	4	5	6
1-butene	66	18	10	2	4			70	17	6	3	5		
1-pentene	75	15	7	2	1	0		73	15	7	2	1	0	
1-hexene	76	18	4	1	0	0	0	76	18	4	1	0	0	0

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