Evidence for Vinylic Intermediates in the Fischer–Tropsch Reaction to give Alkenes and Alkanes

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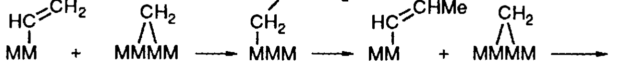
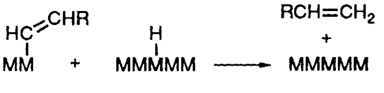
Labelling experiments showing that $^{13}C_2$ [from $Si(^{13}C_2H_3)_4$] can be incorporated into the C_3 and C_4 products from $CO–H_2$ over $Rh–CeO_2–SiO_2$ are consistent with the intermediacy of surface vinyls, as had been suggested by the analysis of decomposition reactions of model dirhodium complexes.

Detailed analysis of the decomposition paths followed by a variety of dinuclear rhodium complexes (such as $[\{C_5Me_5Rh(\mu\text{-}CH_2)Me\}_2]$ or $[\{C_5Me_5Rh(\mu\text{-}CH_2)(CH{=}CH_2)\}_2]$) has led us to propose a new mechanism for the polymerisation step of the Fischer–Tropsch (F–T) reaction giving alk-1-enes.[1] Chain propagation is now postulated to occur *via* reaction of surface methylenes with vinyl or alkenyl surface species, for example, Scheme 1. The surface alkenyls combine with surface–H to release the alkene product, Scheme 2.

These features differentiate it significantly from older mechanisms where surface alkyls have been postulated as the chain carriers.[2] Although surface vinyls have not yet been detected,[3] this would not be surprising if such species were highly reactive; however, surface vinylidene has been found on Ru.[4]



Scheme 1



Scheme 2

We have also suggested that this type of alkenyl–methylene polymerisation may be facilitated by the presence of certain oxidants. We describe the first results from direct tests of our proposal, in which $CO–H_2$ mixtures were passed over promoted rhodium, and which are consistent with it.

Two rhodium catalysts were used: (A) Rh (4%)/CeO_2 (9%)/SiO_2 (made by the incipient wetness technique on Davisil 645, 60—100 mesh, and pre-reduced at 400 °C in hydrogen) and (B), Rh(5%)/SiO_2 (prepared by Rochester and McQuire, Dundee University). Rhodium itself is a good methanation catalyst but, when combined with certain oxide promoters (*e.g.* of Ce, La, Mo, Th, Ti, V), the activity and, at lower temperatures, the selectivity (towards oxygenates, especially ethanol) are improved.[5]

Tetravinylsilane, $Si(CH{=}CH_2)_4$, was chosen as a source of vinyl to test the hypothesis since silicon-containing by-products should have little effect on the reaction; this was the case (Table 1). To avoid ambiguity, doubly labelled $Si(^{13}C_2H_3)_4$ was used to determine incorporation.

Table 1. Products from Fischer–Tropsch reactions [$CO + H_2$/catalyst, with and without added $Si(C_2H_3)_4$].[a]

	CH_4	C_2H_6	C_3	C_4	C_5	MeCHO
Percentage yields						
Catalyst:						
(A) Rh (4%)/CeO_2(9%)/SiO_2	71	12	10	5	2	tr
(A) Rh (4%)/CeO_2(9%)/SiO_2 + $Si(C_2H_3)_4$	48	31	10	9	2	tr
(B) Rh (5%)/SiO_2	70	6	12	8	5	tr
(B) Rh (5%)/SiO_2 + $Si(C_2H_3)_4$	60	16	12	9	3	tr

[a] Conditions: $H_2:CO = 2$, 1 atm, flow rate 300 cm^3 h^{-1}; 250 °C; catalyst (1 g) in a fixed bed microreactor (6 × 350 mm). The exit gases were collected in a sample tube (25 cm^3) and were analysed by GC–MS (Poropak Q; Carlo Erba chromatograph; Kratos MS-25).

Table 2. Labelling found in gases from $CO + H_2 + Si(^{13}C_2H_3)_n$-$(^{12}C_2H_3)_{4-n}$.[a]

	Percentages			
	$^{12}C_n$	$^{12}C_{n-1}{}^{13}C_1$	$^{12}C_{n-2}{}^{13}C_2$	$^{12}C_{n-3}{}^{13}C_3$
Catalyst:				
(A) Rh/CeO_2/SiO_2				
ethane	55	5	40	
propane	80	4	15	
propene	85	5	8	
butene	70	7	20	5
(B) Rh/SiO_2				
ethane	50	10	40	
propane	95	3	2	
propene	97	3	tr	
butene	95	3	tr	

[a] Conditions as for Table 1.

To make the required material, $^{13}C_2H_3MgBr$ (from $^{13}C_2H_3Br$, 99%, Matheson of Canada), diluted with an equal amount of normal $^{12}C_2H_3MgBr$, was reacted with $SiCl_4$, giving a labelled $Si(^*C_2H_3)_4$ which contained a statistical mixture of $Si(^{13}C_2H_3)_n(^{12}C_2H_3)_{4-n}$ (n = 0—4), with 44% $^{13}C_2H_3$. The isotopic content of the $Si(^*C_2H_3)_4$ was analysed by ^1H and ^{13}C NMR spectroscopy and by GC–MS. A pulse (0.5 µl) of the $Si(^*C_2H_3)_4$ was passed over the catalyst in hydrogen (1 atm/250 °C) and the products were collected and analysed. Catalyst (A) gave ethane (89%; $^{12}C_2H_6:{}^{13}C_2H_6 = 1$; negligible $^{12}C^{13}CH_6$), some methane (9%), and traces of C_3—C_5 hydrocarbons, while catalyst (B) efficiently reduced and cleaved the vinyl giving largely methane (98%) and only 1% ethane.

To obtain sufficient amounts of products for analysis, the F–T reactions were carried out by passing the CO–H_2 mixture over the catalyst in a microreactor at 250 °C (Table 1); catalyst (B) had *ca.* 60% of the activity of catalyst (A). A pulse (0.5 µl) of $Si(^*C_2H_3)_4$ was then introduced into the syn-gas stream passing through the catalyst (1 atm/250 °C) and the gases were again collected and analysed by GC–MS for isotopic content (Table 2). The values for ethane for both catalysts reflect the hydrogenation of $Si(^*C_2H_3)_4$, and show the expected high proportion of doubly labelled $^{13}C_2H_6$. The labels in the propene, propane, and butene from the reaction over catalyst (B) are not significantly different from natural abundance, indicating only low incorporation of vinyl into these products over that catalyst. This is consistent with our observation that cleavage of vinyl occurs over this catalyst with great facility.

A dramatic difference is shown by the results from the catalyst (A) experiments; the amounts of one ^{13}C present in the C_3 and the C_4 products are close to those expected for natural abundance. However, the amounts of $^{13}C_2$ for propene, propane, and butene are very much higher (by *ca.* four orders of magnitude) than would be expected for natural abundance. That indicates that labelled vinyl has been incorporated directly into these products.

Since vinyl can be efficiently incorporated, it can, therefore, be a key intermediate in, F–T polymerisation over Rh–CeO_2–SiO_2. This type of oligomerisation is promoted by a mild co-oxidising site, a result which mirrors the model experiments described previously.[1] Vinyl species added externally are cleaved too rapidly over catalyst (B), and, therefore, those experiments give no useful information about the surface polymerisation steps involved.

Data on other organometallic models, both dinuclear and mononuclear,[6] and also from detailed analysis of F–T kinetics,[7] are now providing further support for our proposals. Work is proceeding to define further the role of the co-oxidants used in the F–T reactions.

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