

Vinyl Initiation of Fischer–Tropsch Polymerization over Rhodium

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Recent interest in rhodium-catalyzed Fischer–Tropsch reactions has built upon the observation that the activity of such catalysts for alkene formation is substantially promoted by reducible oxides, especially those of Ti, Zr, and the lanthanides, and that under some conditions the selectivity of the reaction toward oxygenates (in particular, ethanol) is also enhanced.¹ We here report evidence that, in such rhodium-catalyzed reactions, (i) separate processes are responsible for hydrocarbon and for oxygenate formation, (ii) the generation of a surface vinyl is rate-limiting in the production of hydrocarbons, and (iii) a mechanism for vinyl-initiated hydrocarbon formation can be mathematically modeled and gives good agreement with experimental data.

We have developed organorhodium models for methylene polymerization which directly explore the relationship between reactions in metal complexes and in heterogeneous Fischer–Tropsch catalysis. They show that C–C couplings between two methyls, two μ -methyls, or one methyl and one μ -methylene do not occur easily in dirhodium complexes.² By contrast, coupling between a vinyl and a μ -methylene takes place readily, especially in the presence of one-electron oxidizers.³ These results have led us to propose a mechanism for chain propagation in rhodium-catalyzed Fischer–Tropsch reactions which involves reaction of surface methylenes with intermediate surface vinyl and surface alkenyl species rather than with surface alkyls.⁴ Chain termination and release of the alkene then occurs by reaction of a surface alkenyl with a surface hydride. The mechanism also readily accounts for the formation of 1-alkenes as primary products of reaction and for the anomaly in the Anderson–Schulz–Flory (ASF) distribution of hydrocarbons at C₂.

Using pure Si(¹³CH=¹³CH₂)₄ as probe, we have now confirmed initial tests of this mechanism⁵ over rhodium–ceria–silica cat-

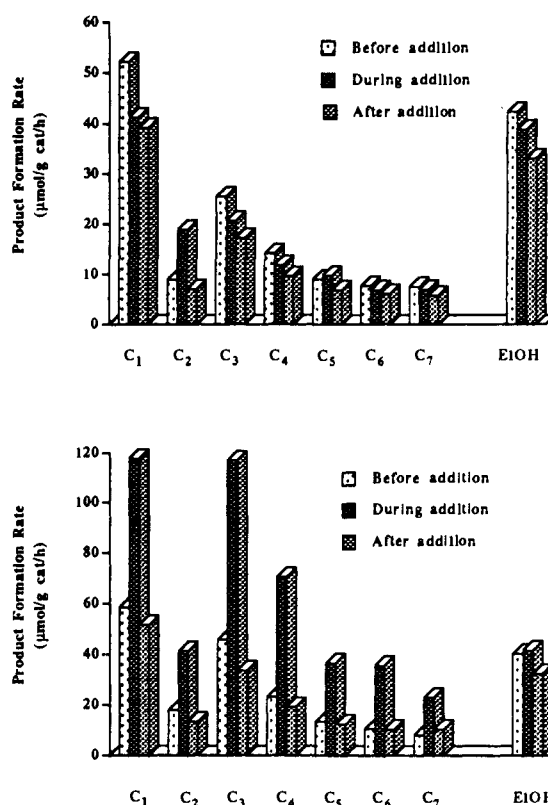


Figure 1. Effect of (a) tetravinylsilane and (b) vinyl bromide addition on product formation in Fischer–Tropsch synthesis over rhodium–ceria–silica catalysts. For each group of C_n products three values are given: before, during, and after addition of the probe molecule. Estimated errors in the figures are <5%.

alysts⁶ and have also shown that vinylic halides, in particular vinyl bromide and Br¹³CH=¹³CH₂, are even more effective as initiators (Figure 1).⁷ GC-MS analysis of the products (Table I, top) from cofeeding labeled ¹³C₂H₃Br (Matheson of Canada, 99% ¹³C₂) to the ¹²CO + H₂ showed that there was very significant incorporation of ¹³C₂ (10²–10⁴ above natural abundance) into alkenes and alkanes up to C₇, while the abundances of ¹³C₁ or ¹³C₃ are strictly at the expected natural level. This confirms that vinyl units are indeed incorporated into Fischer–Tropsch hydrocarbon products.⁸ The data show essentially no incorporation of ¹³C into the oxygenates produced, indicating that the oxygenates are not formed from the vinyls and that they arise by a completely different path.

An ASF plot of the C₁–C₇ hydrocarbon formation established that the chain growth probability α was not affected by the addition of vinyl halide or tetravinylsilane and remained at 0.4. This shows that the rate of propagation was unaltered on addition of the probe. However, while the overall activity showed only a small decrease⁹ when tetravinylsilane was the probe, it increased 2–3-fold when vinyl bromide was used (Figure 1).¹⁰

In all cases the effect of the probe molecule was lost after the pulse had been transmitted through the catalyst and the activity returned to normal again. These observations imply that vinylic

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(6) Rhodium (4%)-ceria (9%)-silica, prepared by the incipient wetness method, CO:H₂ = 1:2, 1 atm/498 K. Similar data are obtained over rhodium–silica catalysts, without ceria, but their activity is much lower.

(7) The probe molecules (1.4 × 10⁻⁴ mol) were added to the synthesis gas (10⁻² mol of carbon), of which ca. 4% was converted, giving an effective ratio of probe to converted CO ca. 1:3.

(8) Indirect experiments (using ¹²C₂H₄ and ¹³CO/H₂) over ruthenium (and cobalt) catalysts have indicated that C₂ incorporation also occurs with these catalysts: Krishna, K. R.; Bell, A. T. *Catal. Lett.* **1992**, *14*, 305. Mims, C. A.; McCandlish, L. E.; Melchior, M. T. *Catal. Lett.* **1981**, *1*, 121. Mims, C. A.; Krajewski, J. J.; Rose, K. D.; Melchior, M. T. *Catal. Lett.* **1990**, *7*, 119. Adesina, A. A.; Hudgins, A. A.; Silveston, P. L. *Appl. Catal.* **1990**, *62*, 295.

Table I. Comparison of Experimental (GC-MS Data) and Calculated Incorporation of $^{13}\text{C}_x$ Derived from $\text{Br}^{13}\text{CH}=\text{CH}_2$ and $\text{Si}(^{13}\text{CH}=\text{CH}_2)_4$ into Selected Products (1-Alkenes) of Fischer-Tropsch Synthesis over Rhodium-Ceria-Silica Catalysts^a

	Experimental Normalized Mass Spectrometric Intensities													
	$^{13}\text{C}_x$ from $^{13}\text{CH}_2=\text{CHBr}$ (%)						$^{13}\text{C}_x$ from $\text{Si}(^{13}\text{CH}=\text{CH}_2)_4$ (%)							
	$x^b = 0$	1	2	3	4	5	6	$x^b = 0$	1	2	3	4	5	6
propene	63	3	31	3			70	5	23	1				
1-butene	51	4	7	3	35		71	4	6	1	18			
1-pentene	85	4	6	1	3	1	78	5	3	1	14			
1-hexene	81	5	5	1	4	1	76	5	3	1	14	1		
1-heptene	84	8	4	1	2	1	82	9	2	1	5	1		
1-octene	81	9					81	9						
MeCHO	97	2					97	3						
EtOH	97	2					97	2						

Calculated Percentage $^{13}\text{C}_2$ -Labeled					
surface vinyl (γ)	100	80	60	40	20
propene	40	32	24	16	8
1-butene	16	13	10	6	3
1-pentene	6	5	4	3	1
1-hexene	3	2	2	1	1
1-heptene	1	1			

^a Experimental data are derived from mass spectroscopic peak intensities, while the calculated values list the percentage of $^{13}\text{C}_2$ label in each 1-alkene that would be expected if $\gamma\%$ of surface vinyls are $^{-13}\text{C}_2\text{H}_3$.
^b No values for $x = 7$ and 8.

(or closely similar¹¹) species, which initiate the Fischer-Tropsch polymerization, are formed on the metal surface from these probe molecules.¹² White et al.¹³ and Zaera¹⁴ have recently demonstrated that vinyls can be at least transient species on a metal surface, which offers support to our hypothesis.

We propose that the reaction is built up as indicated in Scheme I, with the main body of the polymerization being the (irreversible) linear homologue of each surface alkenyl species ($^*\text{CH}=\text{CH}-\text{R} = \text{A}_n$) with methylene ($^*\text{CH}_2^* = \text{M}$). If the rate constants for each step (k_p) are similar, then the rate of appearance of a given species A_n will be given by the rate of reaction to form it, $k_p[\text{A}_{n-1}][\text{M}]$. Under steady-state conditions, the rate of formation must equal the rate of disappearance by (i) homologue, $k_p[\text{A}_n][\text{M}]$ plus (ii) chain termination by hydrogen transfer, $k_t[\text{A}_n][\text{H}]$ and (iii) coupling with an A_2 (surface vinyl) species, $k_c[\text{A}_n][\text{A}_2]$. Hence

(9) However, large amounts of ethane were coproduced in both reactions; labeling showed it to arise by hydrogenation/hydrogenolysis of the vinylic probe.

(10) Ethyl bromide does not initiate Fischer-Tropsch reactions; further, when vinyl bromide is added as probe molecule, ethyl bromide, but no vinyl bromide, can be detected among the exit gases.

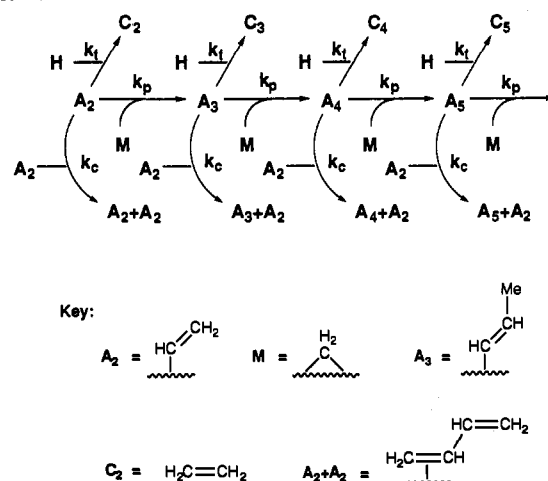
(11) The catalytic experiments are an extension of our detailed studies on characterized organorhodium complexes, which indicate a preference for coupling involving Rh- σ -alkenyls.^{3,4} However, it is conceivable that C_2 species other than vinyl are involved in the catalyses; experiments to test this possibility are now planned.

(12) It is likely that transfer of vinyl to rhodium from tetravinylsilane occurs with greater difficulty than from vinyl bromide. More significantly, our data suggest that one vinyl is transferred per molecule of tetravinylsilane; thus residual Vi_3Si - may remain on the surface for a time, shielding some rhodiums toward further reaction. This could account for the effect of initiation by vinyl here being the same as that which obtains in its absence.

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Scheme I^a



^a k_p = rate constant for propagation; k_c = rate constant for alkenyl coupling; k_t = rate constant for termination by reaction with surface hydride.

$$d[\text{A}_n]/dt =$$

$$k_p[\text{A}_{n-1}][\text{M}] - k_p[\text{A}_n][\text{M}] - k_t[\text{A}_n][\text{H}] - k_c[\text{A}_n][\text{A}_2] = 0$$

from which $[\text{A}_n]/[\text{A}_{n-1}]$ is given by

$$[\text{A}_n]/[\text{A}_{n-1}] = k_p[\text{M}]/\{k_p[\text{M}] + k_t[\text{H}] + k_c[\text{A}_2]\} = \alpha$$

where α is defined as the chain growth probability. From this equation one can calculate the expected level of $^{13}\text{C}_2$ incorporation for different assumed labeled fractions of A_2 in the surface (Table 1, bottom). This shows that, even with 100% $^{13}\text{C}_2$ in A_2 , the label is detectable only up to C_7 hydrocarbons; it also allows the amount of $^{13}\text{C}_2$ present in the surface vinyls, A_2 , to be estimated from a knowledge of the labeling found in the C_3 and C_4 hydrocarbons. Thus there is some 30% incorporation of $^{13}\text{C}_2$ into the C_3 and ca. 9% incorporation of $^{13}\text{C}_2$ into the C_4 hydrocarbons. These values are consistent with a level of initiation of around 70% by added $^{13}\text{C}_2\text{H}_3$. Thus vinyl is an extremely effective promoter of Fischer-Tropsch polymerization.

In summary, vinyl $^{13}\text{C}_2$ (both from vinyl bromide and tetravinylsilane) is incorporated into products in a manner consistent with a rhodium-vinyl-initiating Fischer-Tropsch polymerization of surface methylenes.¹⁵ The addition of vinyl bromide (as a source of vinyl) to a Fischer-Tropsch reaction over rhodium-ceria-silica markedly promotes the reaction but has no effect on the distribution of products.

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Supplementary Material Available: Details of experimental procedures (3 pages). Ordering information is given on any current masthead.

(15) The C_4 and C_5 hydrocarbons also contained substantial amounts of $^{13}\text{C}_4$ -labeled products. The first must arise by a metal-promoted coupling of $^{13}\text{C}_2\text{H}_3$ in the surface¹⁶ and hydrogenation. The branched C_5 hydrocarbons also contain high levels of $^{13}\text{C}_4$ ¹² C_1 hydrocarbons, which probably arise by coupling ($\text{A}_3 + \text{A}_2$) of an isoallyl and a vinyl rather than by homologue of the C_4 -coupled product, since the level of $^{13}\text{C}_4$ incorporation in the C_5 -branched hydrocarbons is higher than it is for the C_4 -coupled product.