

Communications to the Editor

Demonstration by ^{13}C NMR Spectroscopy of Regiospecific Carbon–Carbon Coupling during Fischer–Tropsch Probe Reactions

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The hydrogenation of CO over heterogeneous metal catalysts (≥ 200 °C); the Fischer–Tropsch, FT, reaction) leads to alkenes, alkanes, and oxygenates.¹ As secondary processes (involving the reabsorption and further reaction of primary products) occur, extremely complex product mixtures can be obtained. This complexity of products has allowed only partial success to attempts to rationalize these reactions.

We have now carried out FT reactions under largely kinetic control, at low temperature, giving primary products substantially free of those from secondary reactions. These investigations have involved the addition of $^{13}\text{C}_2\text{H}_4$ probes to a hydrogenation of ^{12}CO over supported Ru or Rh catalysts. The products, analyzed by ^{13}C NMR spectroscopy (a hitherto rarely used technique for such investigations), show the *regiospecific* formation of the 1-alkene isotopomers, $^{12}\text{CH}_2=^{13}\text{CH}^{13}\text{CH}_3$, $^{12}\text{CH}_2=^{12}\text{CH}^{13}\text{CH}_2$, $^{13}\text{CH}_3$, and $^{12}\text{CH}_2=^{12}\text{CH}^{13}\text{CH}_2$, $^{13}\text{CH}_2^{13}\text{CH}_3$. This demonstrates clearly, for the first time, the sequential nature of the FT polymerization.

Probe molecule studies, widely used to provide information about heterogeneously catalyzed reactions,² are based on the premise that, if the added probe resembles an intermediate of the reaction being investigated, incorporation of the probe will occur. We previously showed, using GC-MS, that, when $^{13}\text{C}_2\text{H}_4$ is added as a probe molecule to FT reactions over Rh or Ru catalysts, the hydrocarbon products contain two ^{13}C atoms.³ The amount of $^{13}\text{C}_2$ incorporation was mathematically modeled by a methylene polymerization involving surface alkenyl species as the chain carriers.⁴ However, establishing a detailed mechanism requires knowing the exact positions of the ^{13}C 's within each hydrocarbon. Since GC-MS cannot provide it, we have now obtained this information using $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy.⁵

(1) Fischer, F.; Tropsch, H. *Brennst.-Chem.* **1926**, 7, 97; *Chem. Ber.* **1926**, 59, 830. Anderson, R. B. *The Fischer–Tropsch Reaction*; Academic Press: London, U.K., 1984. Roeper, M. in *Catalysis in C₁ Chemistry*; Keim, W., Ed.; D. Reidel: Dordrecht, The Netherlands, 1983. Sheldon, R. A. *Chemicals from Synthesis Gas*, D. Reidel: Dordrecht, The Netherlands, 1983. Wender, I.; Sternberg, H. W. *Adv. Catal.* **1957**, 9, 594. Pichler, H.; Schulz, H. *Chem. Ing. Tech.*, **1970**, 42, 1162. Iglesias, E.; Reyes, S. C.; Madon, R. J.; Soled, S. L. *Adv. Catal.* **1993**, 39, 221.

(2) Eidus, Ya. T. *Russ. Chem. Rev.* **1967**, 36, 338; Baker, J. A.; Bell, A. T. *J. Catal.* **1982**, 78, 165. Jordan, D. S.; Bell, A. T. *J. Phys. Chem.* **1986**, 90, 4797.

(3) Turner, M. L.; Long, H. C.; Shenton, A.; Byers, P. K.; Maitlis, P. M. *Chem.–Eur. J.* **1995**, 1, 549. Long, H. C.; Turner, M. L.; Fornasiero, P.; Kašpar, J.; Graziani, M.; Maitlis, P. M. *J. Catal.* **1997**, 167, 172.

(4) Maitlis, P. M.; Long, H. C.; Quyoum, R.; Turner, M. L.; Wang, Z.-Q. *J. Chem. Soc., Chem. Commun.* **1996**, 1. Turner, M. L.; Byers, P. K.; Long, H. C.; Maitlis, P. M. *J. Am. Chem. Soc.* **1993**, 115, 4417. Addition of vinyl bromide or tetravinylsilane also resulted in incorporation of vinyl, but ethyl from $\text{C}_2\text{H}_5\text{X}$ was not incorporated.

(5) The use of ^1H NMR for analysis has been reported: Mims, C. A.; McCandlish, L. E. *J. Phys. Chem.* **1987**, 91, 929; Mims, C. A.; McCandlish, L. E.; Melchior, M. T. *Catal. Lett.* **1988**, 1, 121.

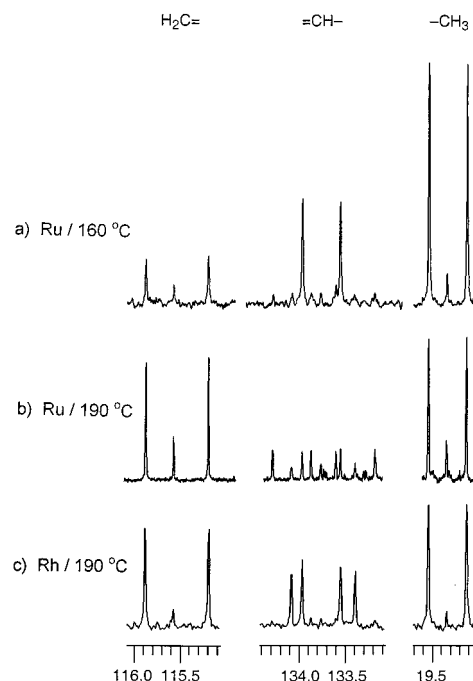


Figure 1. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (δ) of propene- $^{13}\text{C}_2$ showing the $\text{H}_2\text{C}=\text{CH}$, and CH_3 regions; conditions $^{13}\text{CO}/\text{H}_2 + ^{13}\text{CH}_2=^{13}\text{CH}_2$, (a) Ru/SiO₂, 160 °C, (b) Ru/SiO₂/190 °C, and (c) Rh/CeO_x/SiO₂/190 °C.

CO hydrogenation over a Ru/SiO₂ catalyst ($^{12}\text{CO}/\text{H}_2 = 1:2$; 1 atm, 160 °C) gives mainly 1-alkenes as primary products. Addition of ethene ($^{13}\text{C}_2\text{H}_4$) to this reaction and analysis of the products by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy showed that the labeled propene formed is largely the single isotopomer $^{13}\text{CH}_3^{13}\text{CH}=\text{CH}_2$.⁶ Thus the $^{13}\text{CH}=\text{CH}$ resonance (a doublet centered at $\delta 133.76$; Figure 1a) has the coupling expected between an sp^2 and an sp^3 carbon, $^1J(^{13}\text{C}-^{13}\text{C})$ 42 Hz.⁷ Small amounts of three further isotopomers were detected: the signal for the terminal $^{13}\text{CH}_2=$ (made up of $^{12}\text{CH}_3^{13}\text{CH}=\text{CH}_2$ and $^{13}\text{CH}_3^{13}\text{CH}=\text{CH}_2$) is a low-intensity doublet centered at $\delta 115.54$ with $^1J(^{13}\text{C}-^{13}\text{C})$ 70 Hz, the coupling expected between two sp^2 carbons; there is also a spike at 115.54, indicating a trace of a propene isotopomer containing only one olefinic ^{13}C .⁸

These conclusions are confirmed by the doublet ($^1J(^{13}\text{C}-^{13}\text{C})$ 42 Hz) centered at $\delta 19.35$ due to the methyl of $^{13}\text{CH}_3-^{13}\text{CH}=\text{CH}_2$. This also showed a small spike at 19.35, confirming the presence of some $^{13}\text{CH}_3^{12}\text{CH}=\text{CH}_2$ isotopomer. The low abundance of $^{13}\text{C}_1$ and $^{13}\text{C}_3$ isotopomers shows that only a very small amount of ethene cleavage has occurred, consistent with the GC-MS results.⁹

Significantly, 1-butene- $^{13}\text{C}_2$ is also clearly seen (Figure 2): the doublets at $\delta 13.05$ and at 26.66 both show $^1J(^{13}\text{C}-^{13}\text{C})$ of 35

(6) See Supporting Information. The spectra were assigned by comparison with those of authentic samples accurately measured in CDCl_3 under the same conditions. Identification was also based on the amounts, and the isotopic abundances, of the products analyzed by GC-MS.

(7) Marshall, J. L. *Carbon–carbon and Carbon–proton NMR Couplings*; Verlag Chemie International: Deerfield Beach, Florida, 1983.

(8) It is unlikely that the two small spikes at $\delta 115.54$ and 19.35 belong to $^{13}\text{CH}_3^{12}\text{CH}=\text{CH}_2$, formed by rearrangement; no splitting due to $^2J(^{13}\text{C}-^{13}\text{C})$ was detected.

(9) By contrast, a ^{13}C NMR study of propene from a $^{13}\text{C}_2\text{H}_4$ -probe FT reaction (over Co/Al; 240 °C; 1 atm) by Percy, L. T.; Walter, R. I. *J. Catal.* **1990**, 121, 228) showed it to contain $^{12}\text{C}_3\text{H}_6$ plus seven isotopomers arising from incorporation of ^{13}C 's.

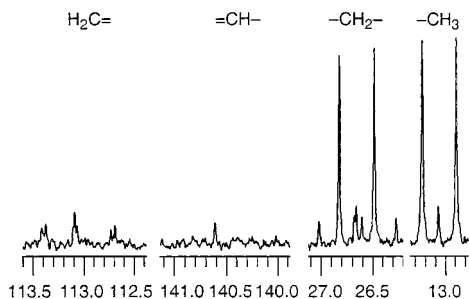


Figure 2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (δ) of 1-butene- $^{13}\text{C}_2$ showing the $\text{H}_2\text{C}=\text{}$, $=\text{CH}-$, CH_2- , and CH_3 regions; conditions $^{13}\text{CO}/\text{H}_2 + ^{13}\text{CH}_2=^{13}\text{CH}_2$, Ru/SiO₂, 160 °C.

Hz and hence are due to the terminal $^{13}\text{CH}_3$ and the adjacent allylic $^{13}\text{CH}_2$, respectively. On the latter resonance there is no sign of any coupling ($J \sim 43$ Hz) to the vinylic ^{13}CH ,¹⁰ and therefore, one may conclude that the main labeling (>95%) arises from $^{13}\text{CH}_3^{13}\text{CH}_2^{12}\text{CH}=\text{CH}_2$. This is confirmed by the very low intensity of signals due to $\text{CH}=\text{}$ and to $=\text{CH}_2$ at δ 140.6 and 113.1, respectively. Resonances due to 1-pentene- $^{13}\text{C}_2$ ($^{13}\text{CH}_2-^{13}\text{CH}_2^{12}\text{CH}_2^{12}\text{CH}=\text{CH}_2$; Me, δ 13.59, adjacent CH_2 , 22.05, $^1J(^{13}\text{C}-^{13}\text{C})$ 35 Hz) are also seen and again here no coupling is evident to the allylic carbon (δ 35.93), nor to a sp^2 carbon, indicating that also the 1-pentene is composed primarily of the one isotopomer. Although the resonances of the individual higher 1-alkenes ($\text{CH}_3\text{CH}_2(\text{CH}_2)_n\text{CH}=\text{CH}_2$, $n = 2, 3, 4$) are close together, again peaks in the regions associated with ^{13}C 's in $\text{CH}_2-\text{CH}=\text{CH}_2$ are very weak, while those associated with CH_3CH_2 occur as strong doublets $J \sim 35$ Hz in the regions $\delta \sim 13.9-14.3$ and $22.5-22.9$. That indicates that there, too, the labels are at the ethyl ends ($^{13}\text{CH}_3^{13}\text{CH}_2$) of the 1-alkenes.

n -Alkanes are also formed, and both the GC-MS and the ^{13}C NMR data agree in showing that only two ^{13}C atoms are incorporated in each molecule. They are adjacent and are invariably in the end ethyl ($^{13}\text{CH}_3^{13}\text{CH}_2(^{12}\text{CH}_2)_n^{12}\text{CH}_3$). The selectivity for 1-alkenes was enhanced at higher flow rates,⁶ whereas alkane selectivity decreased, indicating that alkanes are secondary products arising by hydrogenation of the 1-alkenes.

Analysis of the propene $\text{CH}=\text{NMR}$ resonances of a FT probe reaction at 190 °C over Ru/SiO₂ showed the presence of propene- $^{13}\text{C}_3$ and $^{-13}\text{C}_1$ as well as of $^{13}\text{CH}_2=^{13}\text{CH}^{12}\text{CH}_3$ and $^{13}\text{CH}_3-^{13}\text{CH}=\text{CH}_2$ (Figure 1b). Thus substantial secondary C-C cleavage and isomerization reactions occur at 190 °C, confirmed by the significant levels of $^{13}\text{C}_3$ and $^{13}\text{C}_1$ incorporation detected by GC-MS.

CO hydrogenation over Rh/CeO_x/SiO₂ (190 °C) gave results similar to those for the 160 °C reaction over Ru except that both

(10) Some internal alkenes (especially *cis*- and *trans*-2-butenes) are also seen. We and others (Rodríguez, E.; Leconte, M.; Basset, J. M.; Tanaka, K. *J. Catal.* **1989**, *119*, 230.) have shown they come from ethene dimerizations. In confirmation, appreciable amounts are $^{13}\text{C}_4$ -labeled; other $^{13}\text{C}_4$ -labeled alkenes must also arise similarly.

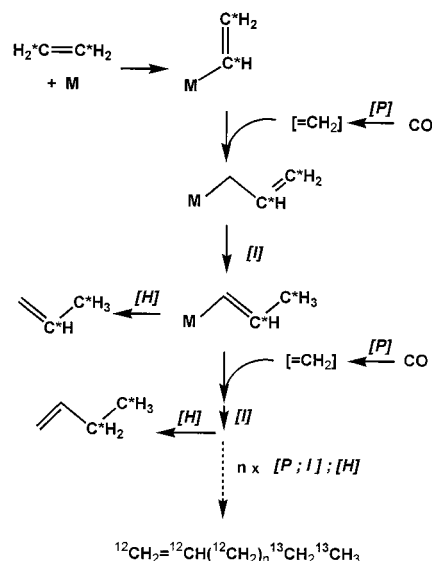


Figure 3. Schematic representation of the proposed route to the regiospecific formation of $^{13}\text{CH}_3^{13}\text{CH}=\text{CH}_2$; $^{13}\text{CH}_3^{13}\text{CH}_2^{13}\text{CH}=\text{CH}_2$; and $^{13}\text{CH}_3^{13}\text{CH}_2(^{13}\text{CH}_2)_n^{13}\text{CH}=\text{CH}_2$ ($n \geq 1$) from surface methylene, $^{13}\text{CH}_2$ (from ^{13}CO), and surface vinyl ($^{13}\text{CH}=\text{CH}_2$), derived from the probe, $^{13}\text{CH}_2=^{13}\text{CH}_2$. $\text{C}^* = ^{13}\text{C}$; [P], propagation, [I], isomerization, [H], hydrogenolysis steps.

propene isotopomers, $^{13}\text{CH}_2=^{13}\text{CH}^{12}\text{CH}_3$ and $^{13}\text{CH}_3^{13}\text{CH}=\text{CH}_2$, were clearly seen (Figure 1c).^{11,12}

Thus we can say that the 1-olefins formed from reaction of a $^{13}\text{C}_2\text{H}_4$ probe with $^{12}\text{CH}_2$ derived from ^{12}CO and H_2 over Ru at 160 °C are chiefly the following: $^{13}\text{CH}_2=^{13}\text{CH}_2$; $^{13}\text{CH}_3-^{13}\text{CH}=\text{CH}_2$; $^{13}\text{CH}_3^{13}\text{CH}_2^{12}\text{CH}=\text{CH}_2$; and $^{13}\text{CH}_3^{13}\text{CH}_2(^{12}\text{CH}_2)_n-^{12}\text{CH}=\text{CH}_2$.

This is a clear and unambiguous demonstration of a stepwise polymerization of methylene. The pattern of labeling found, with the two ^{13}C 's adjacent and furthest from the vinylic $=\text{CH}_2$, together with our earlier results,⁴ is completely consistent with the alkenyl cycle we proposed earlier,⁴ where the 1-alkenes liberated arise from surface alkenyls by hydrogenolysis (Figure 3).

Acknowledgment. We thank the EPSRC, the Royal Society, ORS, and the Institut Teknologi Bandung, Indonesia, for support.

Supporting Information Available: Full experimental details of the catalyst preparations and of the CO hydrogenation reactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(11) The observation of both propene- $^{13}\text{C}_2$ isotopomers from reactions at 190 °C over Ru and Rh indicates that secondary processes (1,3-H shifts) become important under these conditions. This also supports the postulated intermediacy of surface alkenyl and surface allylic species in the Fischer-Tropsch reaction (see Figure 3).

(12) Only small amounts of $^{13}\text{C}_1$ and $^{13}\text{C}_3$ products could be detected in the Rh reaction, showing that C-C cleavage reactions were again minimal. The clean doublet centered at δ 13.05 (J 35 Hz) shows that the 1-butene product here too is $^{13}\text{CH}_3^{13}\text{CH}_2^{12}\text{CH}=\text{CH}_2$.