

Hydrocarbon Chain Growth on V(100) Single-Crystal Surfaces via Vinyl Intermediates**

Min Shen and Francisco Zaera*

Hydrogenation of CO to hydrocarbon fuels is typically carried out by Fischer–Tropsch catalysis.^[1–4] The reaction mechanism of this process has been widely studied in the past, but still remains controversial.^[5–10] In the most popular reaction scheme, methylene surface groups $\text{CH}_2(\text{ads})$ are proposed as the starting intermediates, and their insertion into the metal–carbon bonds of alkyl adsorbates, starting with methyl species $\text{CH}_3(\text{ads})$, as the way chain growth proceeds.^[11,12] However, this well-accepted mechanism has been recently questioned from both theoretical^[13–15] and experimental^[9,10] points of view. A particularly curious (and controversial)^[16,17] alternative has been provided by Maitlis and co-workers, who, based on studies using organometallic compounds^[10,18] and isotope labeling in heterogeneous catalysis,^[19] have argued for vinyl moieties $\text{CH}_2=\text{CH}(\text{ads})$ as more plausible chain-propagation intermediates. Density functional theory has been used to show the viability of methylene surface species coupling with methylidyne moieties $\text{CH}(\text{ads})$ to produce adsorbed vinyl intermediates,^[20] but, to the best of our knowledge, no direct experimental evidence has been advanced to support such a route. Here we present what we think is the first piece of surface-science evidence for chain propagation via vinyl intermediates in Fischer–Tropsch type reactions.

Methylene surface moieties were generated on a V(100) single-crystal surface by thermal activation of adsorbed CH_2I_2 ,^[21–24] and their thermal chemistry characterized by temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). Several products were identified by the TPD data, including hydrogen (295 K), methane (315 K), ethene (295 K), and propene (300 K); see Figure S1, Supporting Information. Propene desorption in particular exhibits a complex behavior as a function of surface coverage, with one single peak seen around 260 K at low coverages, a second feature developing around 410 K for intermediate CH_2I_2 exposures, and a decrease in yield for both peaks and their merging into one broad feature centered at 305 K near saturation (Figure S2, Supporting Information).

The mechanism by which propene is formed was surveyed by comparing propene TPD data acquired for a number of relevant coadsorption systems, again relying on the use of halohydrocarbons as precursors for key surface intermediates^[24,25] (Figure 1). The lack of any significant propene

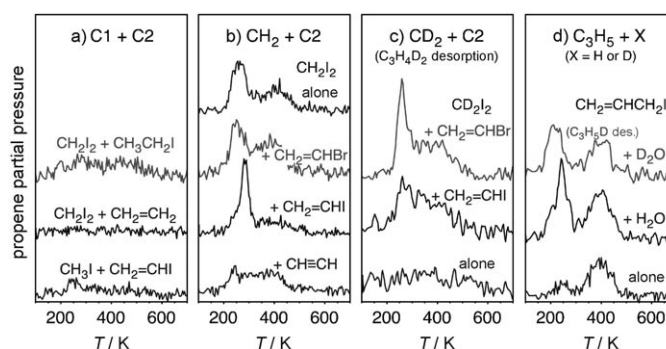


Figure 1. Propene TPD profiles acquired after dosing different combinations of hydrocarbon precursors on V(100) surfaces. a) Ruling out of several possible chain-growth intermediates, including $\text{C}_2\text{H}_5(\text{ads})$ and $\text{C}_2\text{H}_4(\text{ads})$. b) Production of C_3H_6 via a $\text{C}_2\text{H}_3(\text{ads})$ intermediate, prepared by using bromoethene, iodoethene, or ethyne precursors. c) Corroboration of vinyl as an intermediate by coadsorption experiments with $[\text{D}_2]$ diiodomethane (and by detecting $[\text{D}_2]$ propene, $\text{C}_3\text{H}_4\text{D}_2$). d) Test of the last step of the mechanism, the hydrogenation of allyl surface groups, by coadsorption of allyl iodide with hydrogen or deuterium predosed by surface activation of H_2O or D_2O at 180 K. All data are plotted on the same (arbitrary) scale to allow direct comparison of yields.

production after coadsorption of diiodomethane with either ethene (Figure 1a, second trace) or iodoethane (Figure 1a, top trace) excludes both ethene and ethyl surface species as major chain-propagation intermediates. Thus, the mechanism involving methylene insertion into metal–alkyl bonds on the surface, as proposed on other metal surfaces, can be ruled out on V(100). Thermal activation of vinyl surface species in the presence of methyl moieties does not produce any propene on the surface either (Figure 1a, bottom trace). In contrast, coadsorption of diiodomethane with bromoethene (Figure 1b, second-from-top trace), iodoethene (Figure 1b, third-from-top trace), or ethyne (Figure 1b, bottom trace) all lead to considerable production of propene, pointing to the feasibility of direct insertion of $\text{CH}_2(\text{ads})$ groups into metal–vinyl surface bonds. This step, which presumably yields an allyl intermediate $\text{CH}_2=\text{CH}-\text{CH}_2(\text{ads})$, was confirmed by isotopic labeling experiments with CD_2I_2 (Figure 1c).

The origin of the vinyl moiety involved in propene production in this system is more difficult to assess. The two

[*] Dr. M. Shen, Prof. F. Zaera
Department of Chemistry
University of California
Riverside, CA 92521 (USA)
Fax: (+1) 951-827-3962
E-mail: zaera@ucr.edu
Homepage: <http://www.zaera.chem.ucr.edu/>

[**] Funding for this work was provided by the U.S. National Science Foundation.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.200802338>.

most intuitive routes for vinyl formation starting from methylene are dehydrogenation of the ethene produced by self-coupling of two methylene(ads) species, and coupling of one methylene(ads) with one methylidyne(ads) produced by partial dehydrogenation of some of the surface methylene groups. The former reaction sequence is less likely, because thermal activation of ethene coadsorbed with diiodomethane does not produce any detectable propene (Figure 1a, second trace), and because the interaction of ethene with V(100) is quite weak and does not lead to any appreciable dehydrogenation (Figure S3, Supporting Information). Therefore, the initial dehydrogenation of some of the methylene(ads) to methylidyne(ads) appears to be the most probable first step during the chain-propagation reaction reported here. This idea is supported by C 1s XPS data for diiodomethane on V(100) obtained as a function of annealing temperature, which display a peak shift from 282.5 to 281.6 eV around 300 K consistent with methylene dehydrogenation (Figure S4, Supporting Information), and by additional isotope labeling experiments (Figure S5, Supporting Information), which also suggest that this dehydrogenation takes place below 300 K and may be the rate-limiting step for the formation of both the vinyl(ads) intermediate and the methane also observed in the TPD experiments. The need for an initial dehydrogenation step from methylene to methylidyne before chain growth is consistent with the maxima in propylene desorption yield seen at intermediate diiodomethane exposure (Figure S2, Supporting Information), because high coverages may block the extra surface sites required for the C–H scission step. Numerous theoretical studies indicate that methylidyne(ads) is the most stable surface species under Fischer–Tropsch reaction conditions.^[13–15]

In our proposed mechanism, the allyl groups that form by addition of methylene to vinyl surface species must then react with adsorbed hydrogen to yield the final propene product. Certainly, allyl surface species themselves, which can be produced by thermal activation of 3-iodopropene,^[26] are easily hydrogenated to propene (Figure 1d, bottom trace). That process can be promoted further by providing additional hydrogen (or deuterium) to the surface, which in this case can be accomplished by using water^[27] (since dissociative adsorption of molecular hydrogen displays a low adsorption coefficient on V(100) surfaces, and can therefore not be easily used for this purpose).^[28] Figure 1d shows the desorption traces for C₃H₆ (middle trace) and C₃H₅D (top trace) acquired after adsorption of C₃H₅I on V(100) surfaces predosed with H₂O or D₂O at 180 K, a temperature at which about half of the water molecules dissociate to generate H (D) and OH (OD) surface species.^[27] The C₃H₆ (C₃H₅D) desorption in these experiments exhibits similar kinetics to that seen with methylene moieties (compare the shapes of the propene traces in Figure 1b,d), which suggests that the hydrogenation step is fast and occurs immediately following allyl formation if sufficient hydrogen atoms are available on the surface.

In summary, the data reported here point to a four-step mechanism for the conversion of surface methylene species to propene, as indicated in Figure 2: 1) dehydrogenation of some methylene surface moieties to methylidyne, the rate-limiting

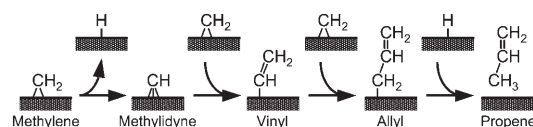


Figure 2. The proposed four-step mechanism for the conversion of surface methylene species to propene.

step; 2) coupling of these methylidyne species with other methylene groups to produce vinyl intermediates; 3) reaction of the vinyl intermediate with a third methylene group to form an allyl species; and 4) rapid hydrogenation of the allyl group to give propene. This is the first direct identification of vinyl groups as intermediates during Fischer–Tropsch-type reactions, in support of the Maitlis mechanism. It may, however, be chemistry uniquely associated with vanadium. Certainly, vanadium has been previously shown to catalyze carbon–carbon coupling steps in both homogeneous^[29] and heterogeneous^[30] catalysis, even though, according to our data, methylene insertion into metal–alkyl bonds seems to be particularly unfavorable on V(100). Not only was no ethyl formation from CH₂(ads) + CH₃(ads) observed (data not shown), but also no propyl groups can be formed from CH₂(ads) + C₂H₅(ads) (Figure 1a, top), and no C–C coupling between two adsorbed methyl species (data not shown) or between adsorbed methyl and vinyl groups (Figure 1a, bottom) is seen either. On the other hand, self-coupling of methylene (Figure S1, Supporting Information) or vinyl (data not shown) surface species are easily observed on V(100). A delicate balance exists between dehydrogenation and carbon–carbon bond-formation steps in these surface hydrocarbon species that defines selectivity on different metal surfaces. On vanadium, alkyl groups may be dehydrogenated easily, and may not survive long enough to participate in chain-growth mechanisms.

Experimental Section

All experiments reported here were carried out in an ultrahigh-vacuum (UHV) chamber equipped with instrumentation for TPD and XPS, as reported elsewhere.^[31,32] A V(100) single crystal (99.99% purity, Goodfellow Cambridge Limited, ca. 12 mm in diameter and ca. 2 mm thick) was used as the solid substrate after cleaning by a procedure described in detail before.^[33,34] Diiodomethane (CH₂I₂, 99+%), [D₂]diiodomethane (CD₂I₂, 99% atom D), iodoethane (CH₃I, 99%), iodoethane (CH₃CH₂I, 99%), 3-iodopropene (CH₂=CHCH₂I, 98%), and deuterated water (D₂O, 99.5% atom D) were purchased from Aldrich, and iodoethene (CH₂=CHI, 90+%) was provided by Oakwood Products, Inc. All these chemicals were purified by repeated freeze–pump–thaw cycles prior to use, and frequently checked in situ by mass spectrometry. Oxygen (O₂, 99.99%), ethyne (CH≡CH, 99.6%), and ethene (CH₂=CH₂, 99.999%) were purchased from Matheson, and bromoethene (CH₂=CHBr, 98%) was obtained from Aldrich; all gases were used as supplied.

Received: May 19, 2008

Published online: July 23, 2008

Keywords: C–C coupling · heterogeneous catalysis · hydrocarbons · surface chemistry · vanadium

- [1] F. Fischer, H. Tropsch, *Ber. Dtsch. Chem. Ges. A* **1926**, 59, 830.
- [2] M. A. Vannice, *Catal. Rev. Sci. Eng.* **1976**, 14, 153.
- [3] P. Biloen, W. M. H. Sachtler, *Adv. Catal.* **1981**, 30, 165.
- [4] A. A. Adesina, *Appl. Catal. A* **1996**, 138, 345.
- [5] L. R. Beanan, J. B. Keister, *Organometallics* **1985**, 4, 1713.
- [6] C. A. Mims, L. E. McCandlish, M. T. Melchior, *Catal. Lett.* **1988**, 1, 121.
- [7] K. R. Krishna, A. T. Bell, *Catal. Lett.* **1992**, 14, 305.
- [8] H. Schulz, *Appl. Catal. A* **1999**, 186, 3.
- [9] M. J. Overrett, R. O. Hill, J. R. Moss, *Coord. Chem. Rev.* **2000**, 206, 581.
- [10] P. M. Maitlis, *J. Organomet. Chem.* **2004**, 689, 4366.
- [11] R. C. Brady, R. Pettit, *J. Am. Chem. Soc.* **1981**, 103, 1287.
- [12] M. E. Dry, *Stud. Surf. Sci. Catal.* **2004**, 152, 533.
- [13] Z. P. Liu, P. Hu, *J. Am. Chem. Soc.* **2002**, 124, 11568.
- [14] I. M. Ciobica, G. J. Kramer, Q. Ge, M. Neurock, R. A. van Santen, *J. Catal.* **2002**, 212, 136.
- [15] J. Cheng, X.-Q. Gong, P. Hu, M. Lok, P. Ellis, S. French, *J. Catal.* **2008**, 254, 285.
- [16] B. Shi, B. H. Davis, *Catal. Today* **2000**, 58, 255.
- [17] S. B. Ndlovu, N. S. Phala, M. Hearshaw-Timme, P. Beagly, J. R. Moss, M. Claeys, E. Van Steen, *Catal. Today* **2002**, 71, 343.
- [18] P. M. Maitlis, V. Zanolli, *Catal. Lett.* **2008**, 122, 80.
- [19] M. L. Turner, N. Marsih, B. E. Mann, R. Quyoum, H. C. Long, P. M. Maitlis, *J. Am. Chem. Soc.* **2002**, 124, 10456.
- [20] Q. Ge, M. Neurock, H. A. Wright, N. Srinivasan, *J. Phys. Chem. B* **2002**, 106, 2826.
- [21] F. Zaera, *Chem. Rev.* **1995**, 95, 2651.
- [22] B. E. Bent, *Chem. Rev.* **1996**, 96, 1361.
- [23] H. S. Guo, F. Zaera, *Surf. Sci.* **2003**, 547, 284.
- [24] Z. Ma, F. Zaera, *Surf. Sci. Rep.* **2006**, 61, 229.
- [25] F. Zaera, *Acc. Chem. Res.* **1992**, 25, 260.
- [26] D. Chrysostomou, F. Zaera, *J. Phys. Chem. B* **2001**, 105, 1003.
- [27] M. Shen, F. Zaera, *J. Phys. Chem. C* **2007**, 111, 13570.
- [28] H. Schiechl, D. Gleispach, A. Winkler, *J. Phys. Chem. B* **2001**, 105, 3849.
- [29] T. Hirao, *Chem. Rev.* **1997**, 97, 2707.
- [30] A. Gervasini, G. Fornasari, G. Bellussi, *Appl. Catal. A* **1992**, 83, 235.
- [31] S. Tjandra, F. Zaera, *Surf. Sci.* **1993**, 289, 255.
- [32] M. Shen, F. Zaera, *J. Phys. Chem. C* **2008**, 112, 1636.
- [33] V. Jensen, J. N. Anderson, H. B. Nielsen, D. L. Adams, *Surf. Sci.* **1982**, 116, 66.
- [34] M. Shen, Q. Ma, I. Lee, F. Zaera, *J. Phys. Chem. C* **2007**, 111, 6033.