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Surface Chemistry

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

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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 CH_2(ads) are proposed as the starting intermediates, and their insertion into the metal–carbon bonds of alkyl adsorbates, starting with methyl species CH_3(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 $CH_2{=}CH$(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 CH(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 production after coadsorption of diiodomethane with either ethene (Figure 1 a, second trace) or iodoethane (Figure 1 a, 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 1 a, bottom trace). In contrast, coadsorption of diiodomethane with bromoethene (Figure 1 b, second-from-top trace), iodoethene (Figure 1 b, third-from-top trace), or ethyne (Figure 1 b, bottom trace) all lead to considerable production of propene, pointing to the feasibility of direct insertion of CH_2(ads) groups into metal–vinyl surface bonds. This step, which presumably yields an allyl intermediate $CH_2{=}CH{-}CH_2$(ads), was confirmed by isotopic labeling experiments with CD_2I_2 (Figure 1 c).

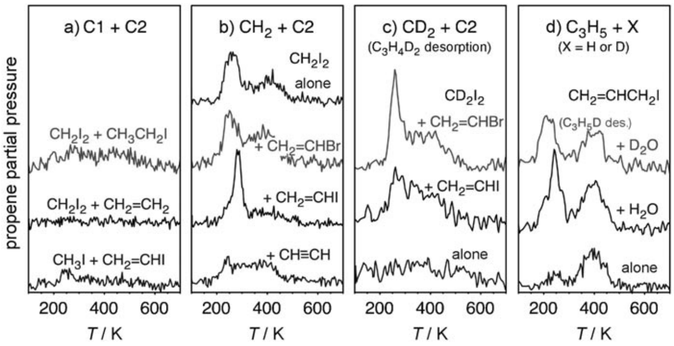

Figure 1. Propene TPD profiles acquired after dosing different combinations of hydrocarbon precursors on V(100) surfaces. a) Ruling out of several possible chain-growth intermediates, including C_2H_5(ads) and C_2H_4(ads). b) Production of C_3H_6 via a C_2H_3(ads) intermediate, prepared by using bromoethene, iodoethene, or ethyne precursors. c) Corroboration of vinyl as an intermediate by coadsorption experiments with [D_2]diiodomethane (and by detecting [D_2]propene, $C_3H_4D_2$). 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.

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

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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 1 a, 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 1 d, 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 1 d shows the desorption traces for C_3H_6 (middle trace) and C_3H_5D (top trace) acquired after adsorption of C_3H_5I on V(100) surfaces predosed with H_2O or D_2O 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 C_3H_6 (C_3H_5D) desorption in these experiments exhibits similar kinetics to that seen with methylene moieties (compare the shapes of the propene traces in Figure 1 b, d), which suggests that the hydrogenation step is fast and occurs immediately following allyl formation if sufficient hydrogen atoms are available on the surface.

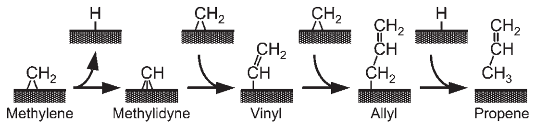

Figure 2. The proposed four-step mechanism for the conversion of surface methylene species to propene.

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 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 homogenous[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 CH_2(ads) + CH_3(ads) observed (data not shown), but also no propyl groups can be formed from CH_2(ads) + C_2H_5(ads) (Figure 1 a, top), and no C–C coupling between two adsorbed methyl species (data not shown) or between adsorbed methyl and vinyl groups (Figure 1 a, 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 (CH_2I_2, 99+ %), [D_2]diiodomethane (CD_2I_2 ,99% atom D), iodomethane (CH_3I, 99%), iodoethane (CH_3CH_2I, 99%), 3-iodopropene (CH_2=$CHCH_2I$, 98%), and deuterated water (D_2O, 99.5% atom D) were purchased from Aldrich, and iodoethene (CH_2=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 (O_2, 99.99%), ethyne ($CH\equiv CH$, 99.6%), and ethene (CH_2=CH_2, 99.999%) were purchased from Matheson, and bromoethene (CH_2=CHBr, 98%) was obtained from Aldrich; all gases were used as supplied.

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