

# Bond Forming Reactions Involving C<sub>1</sub> Moieties: Late Versus Early Transition Metal Surfaces

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**Abstract** A brief survey is provided on the contrast in the surface chemistry of C<sub>1</sub> adsorbed species on vanadium versus nickel and platinum single crystals. Mechanistic insights from modern surface-studies under ultrahigh vacuum are offered to explain reaction selectivities in terms of relative rates for different types of surface elementary steps, namely, hydrogenation, dehydrogenation, coupling, and methylene and oxygen insertions. It is clear from the surface chemistry reviewed here that early transition metals such as vanadium are quite reactive, but also that they are still able to promote interesting bond-forming reactions, and could possibly be used to prepare novel catalysis.

**Keywords** Selectivity · Methyl · Methylene · Formaldehyde · Methanol · Vanadium · Nickel · Single crystal · Temperature programmed desorption · Surface chemistry · Ultrahigh vacuum

## 1 Introduction

The chemistry of C<sub>1</sub> fragments on metal surfaces is central to many catalytic processes, including methanation [1], Fisher–Tropsch synthesis [2, 3], methane partial oxidation [4], water–gas shift [5, 6], and combustion [7]. That chemistry often involves several reaction pathways, and its selectivity is typically defined by small differences in activation energies among those [8]. Therefore, tuning a catalyst to promote a specific reaction requires a detailed knowledge of the mechanisms involved [9]. Modern

surface-science studies using model systems, often single crystals, and controlled conditions (ultrahigh vacuum, UHV) have helped in this endeavor [10, 11]. For instance, it has been established that hydrocarbon reforming requires a careful balance among dehydrogenation steps from different positions within the hydrocarbon chain of early adsorbed intermediates such as alkyl moieties [12]. Most transition metals are efficient dehydrogenation catalysts, but differences among them are clear. Nickel, for instance, shows a particular preference for hydrogen removal at the  $\alpha$  position and therefore helps undesirable hydrogenolysis steps, whereas platinum promotes hydride abstractions from position farther along the carbon chain and with that more desirable isomerization and cyclization processes.

Many surface elementary steps have already been identified, and their relative rates evaluated, on a variety of metal surfaces [13–15]. However, the majority of that work has focused on late transition metals; early transition metals are usually very reactive and therefore considered of limited use for subtle catalytic processes designed to yield thermodynamically unstable products. They are also difficult to maintain in their metallic state, and seen more often in catalysis in the form of oxides, nitrides, or other oxidized forms. Nevertheless, complexes of early transition metals do perform a variety of interesting catalytic reaction in homogeneous phases [16]. Also, some reactions require the use of reducible metals, to more easily carry out redox processes. The surface reactivity of early transition metals is certainly worth exploring in some details. Unfortunately, there are very limited studies on this chemistry to date.

Here we discussed some aspects of the chemistry of C<sub>1</sub> hydrocarbon fragments on vanadium versus nickel and platinum surfaces. The conversion of methyl and methylene moieties is addressed first, with particular emphasis on reactions involving the formation of new C–C or C–O

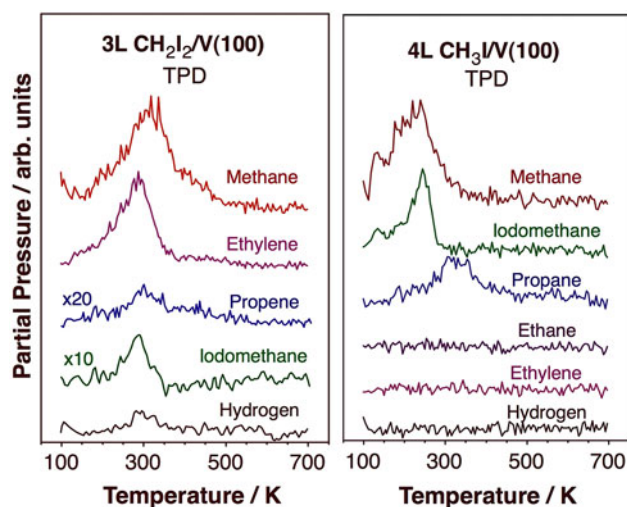
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bonds. The reactivity of adsorbed oxygenated species, specifically methanol and formaldehyde, is described next. The surface chemistry observed with those reactants is described in terms of relative rates for different surface elementary steps, including hydrogenation, dehydrogenation, coupling, and insertion reactions. Interesting reactions leading to the production of associative products are identified, and discussed in terms of relative rates for key competing surface steps.

## 2 Surface Chemistry of Methylene and Methyl Groups

Typically, modern surface-science studies on the reactivity of adsorbates on model surfaces (single crystals) and under controlled environments (ultrahigh vacuum, UHV) are initiated by carrying out survey temperature programmed desorption (TPD) experiments [10, 17, 18]. If unstable intermediates are involved, such as is the case here, appropriate precursors may be used: alkylidene and alkyl intermediates, for instance, may be produced in situ on the surface via the thermal activation of the corresponding adsorbed halohydrocarbons [13, 15, 19, 20]. Figure 1 displays the results from TPD experiments with diiodomethane (left) and iodomethane (right) to illustrate the thermal chemistry of methylene and methyl moieties, respectively, adsorbed on V(100) single-crystal surfaces. Methane production is seen in both cases, a clear indication of the potential for vanadium surfaces to promote certain hydrogenation reactions. Similar chemistry has been documented on the surfaces of single-crystals of other transition metals, both for methylene groups on Cu(100) [21], Cu(110) [22], Ag(111) [23], Ni(100) [24], Ni(110) [25], Pd(100) [26], Pt(111) [27–29], Rh(111) [30, 31], Ru(001) [32, 33], Mo(100) [34, 35], and Mo(110) [36], and for methyl moieties on Cu(100) [37], Cu(111) [37, 38], Cu(110) [22, 37], Ni(100) [24, 39], Ni(111) [40, 41], Ni(110) [42], Pd(100) [43, 44], Pt(111) [27, 28, 45, 46], Rh(111) [47, 48], Ru(001) [49], Mo(100) [35, 50], and Mo(110) [51]. Ethylene production via coupling of methylene is also seen in Fig. 1, which is somewhat surprising since this is a reaction more common on coinage metals [23, 52]. When starting from diiodomethane, iodomethane is produced as well on this V(100) surface, an indication that hydrogenation reactions compete kinetically with carbon–halogen dissociation steps. But perhaps the most interesting observation from the experiments reported here on the vanadium single-crystal surface is the formation of C<sub>3</sub> products (propene from CH<sub>2</sub>I<sub>2</sub>, propane from CH<sub>3</sub>I).

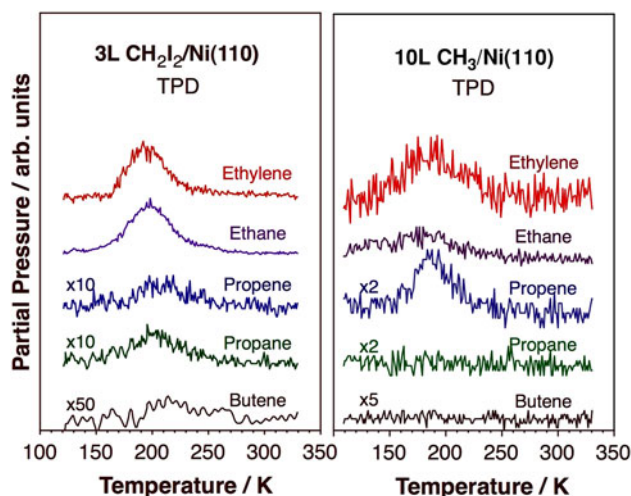
Chain growth such as that seen in Fig. 1 is typical of Fischer–Tropsch catalysts [2, 3], and is most often accomplished by methylene insertion steps into metal–alkyl bonds. The growing alkyl chains can, at each stage of



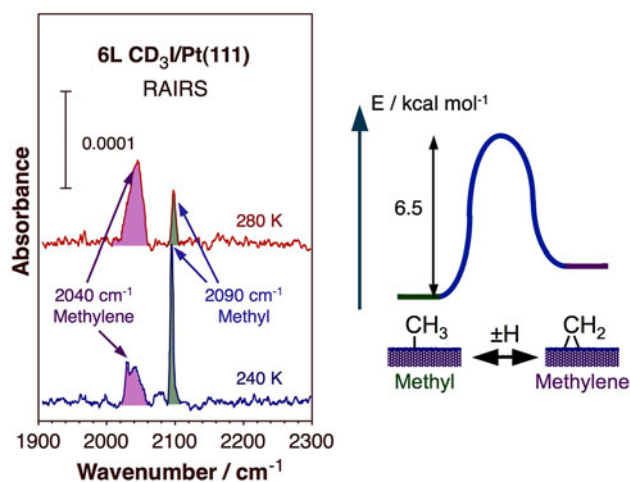
**Fig. 1** Survey temperature programmed desorption (TPD) traces for 3.0 L of diiodomethane (*left panel*) and 4.0 L of iodomethane (*right panel*) adsorbed on a V(100) single-crystal surface at 100 K. The desorption of all main products, which include methane and iodomethane (and, in the case of diiodomethane, ethylene), is shown. Of particular interest to the discussion in this report is the production of propylene from CH<sub>2</sub>I<sub>2</sub> and of propane from CH<sub>3</sub>I

their growth, undergo disproportionation via  $\beta$ -hydride elimination to produce the corresponding alkene, and also reductive elimination with surface hydrogen to yield the appropriate alkane. In the UHV surface-science community this type of chain-growth reaction was first observed in experiments with coadsorbed methyl and methylene groups on copper surfaces [20, 52]. In fact, we have reported that such carbon–carbon forming reactions are possible on Ni(110) even when starting with either diiodomethane [25] or iodomethane [42] alone: chain growth to up to C<sub>4</sub> products was observed on that surface (Fig. 2). This indicates that a pseudo-equilibrium between methyl and methylene surface groups can be achieved on the Ni(110) surface at rates comparable to those of methylene insertion steps. All three rates need to be competitive, though: the coexistence of methyl and methylene species is also possible on Pt(111), as indicated by the reflection–absorption infrared spectroscopy (RAIRS) data in Fig. 3 [27, 28], but there methylene insertions are comparatively too slow to promote any significant chain growth (ethylidyne formation has been reported on Pt(111) covered with high coverages of methyl groups, but the mechanism for that reaction has not been established [53]). It is also worth mentioning that similar chain growth is observed only when starting with large (multilayer) coverages of methyl moieties on Ni(100) surfaces [39, 54, 55], and has not yet been seen on Ni(111) [40, 41, 56–58]. This suggests that the insertion steps may be structure sensitive.

On V(100), however, hydrocarbon chain growth reactions do not follow the well-established mechanism based



**Fig. 2** TPD of the chain-growth products detected upon thermal activation of 3.0 L of diiodomethane (*left panel*) or 10.0 L of iodomethane (*right panel*) adsorbed on a Ni(110) surface. The production of hydrocarbon chains with up to four carbons is seen here, in traces with similar shapes for each alkane–alkene pair. The hydrocarbons in this system are made via methylene insertion steps into metal–alkyl bonds, as in Fischer–Tropsch catalytic processes



**Fig. 3** Reflection-absorption infrared spectra (RAIRS) indicating the coexistence of perdeuteromethyl and perdeuteromethylene species on a Pt(111) single-crystal surface, as obtained via the thermal activation of 6.0 L of  $\text{CD}_3\text{I}$  initially adsorbed at 100 K and subsequently annealed to either 240 (*bottom trace*) or 280 (*top*) K. The temperature dependence of the relative populations of both species, together with isotope-exchange kinetic experiments, was used to estimate the relative energetics of the two surface groups and their activation energy of interconversion. Although methyl and methylene coexist on Pt(111) over a reasonable range of temperatures, no chain growth is seen on this surface

on methylene insertions into metal–alkyl bonds. The key evidence for ruling such step sequence is provided in the left panel of Fig. 4: no significant propene is made either by insertion of methylene moieties into vanadium–ethyl bonds (followed by  $\beta$ -hydride elimination of the resulting

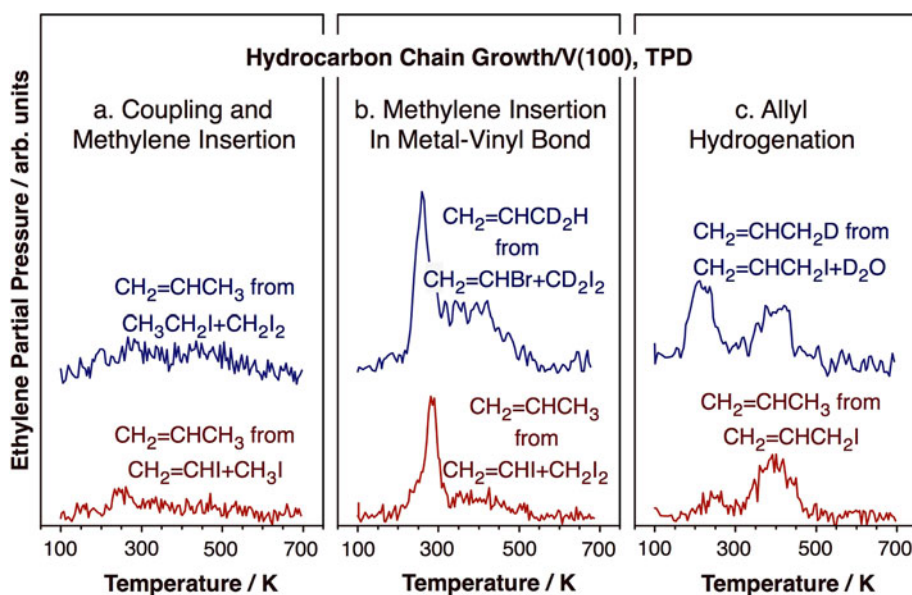
propyl intermediate; top trace) or by coupling of vinyl and methyl surface species (bottom trace) [59]. Instead, propene appears to be made via the insertion of methylene moieties into a vanadium–vinyl bond (Fig. 4, center panel) followed by hydrogenation of the resulting allylic intermediate (Fig. 4, right panel) [59]. Central to this mechanism is the early formation of a vinyl surface intermediate, presumably via the insertion of a methylene species into a vanadium–methylidyne bond. It appears that in this case the pool of  $\text{C}_1$  surface species is shifted towards more dehydrogenated moieties, a combination of methylidyne and methylene instead of the methylene and methyl mixture seen in most late transition metals. Nevertheless, hydrogenation reactions are still possible (witness the need to hydrogenate the surface allylic intermediate to propene), and so are methylene insertion steps (albeit on vanadium–methylidyne and vanadium–vinyl instead of vanadium–methyl bonds).

### 3 Oxygen Insertion Steps

Given the prominence that oxygen has in catalysis based on early transition metals, the possibility of the promotion of atomic oxygen insertion steps into metal–carbon bonds has also been explored on the V(100) single-crystal surface. Figure 5 displays TPD data obtained for the production of methane (left), ethylene (center) and propene (right) from diiodomethane adsorbed on V(100) surfaces predosed with increasing amounts of oxygen. The  $\text{O}_2$  was predosed at 350 K in order to assure dissociative adsorption and the formation of layers of atomic oxygen on the surface [60, 61]. For reference, monolayer formation requires approximately 1.0 L  $\text{O}_2$  exposures, and a thin oxide layer forms on the surface after doses above  $\sim 2.0$  L [60]. As indicated by the data in Fig. 5, the main effect of coadsorbed oxygen in the chemistry of methylene moieties on V(100) is to inhibit all conversion. This is manifested by both a steady shift in all reaction temperatures toward higher values and an eventual decrease in their yields.

No oxygen-containing products were ever detected in these experiments, evidence of the difficulty to promote oxygen insertion steps on the vanadium surface. This is in contrast to what has been seen on other surfaces, on Cu(100) [21], Ag(111) [62], Ni(110) [63, 64], Pd(100) [43], Rh(111) [47, 65], and Ru(001) [66] in particular. Figure 6 reports TPD data for formaldehyde formation from both methylene (top traces) [63] and methyl (bottom traces) [64] species coadsorbed with both normal ( $^{16}\text{O}$ ) and heavy ( $^{18}\text{O}$ ) oxygen on Ni(110) surfaces. In the case of methylene moieties, formaldehyde is produced via a straightforward oxygen insertion step into the nickel–methylene bond [63]. With methyl groups, on the other

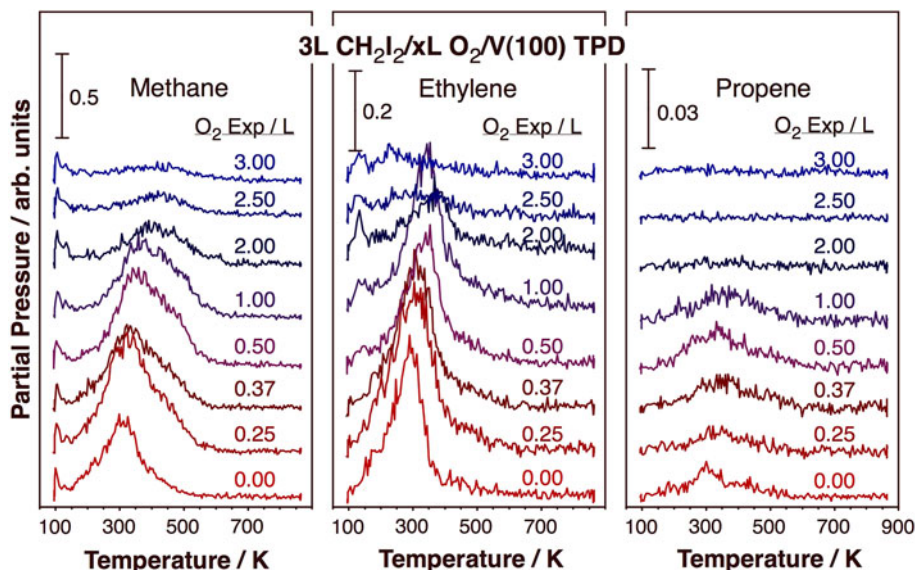




**Fig. 4** Selected propene TPD traces to support the mechanism proposed in the text for hydrocarbon chain growth on V(100). *Left a* traces from coadsorption of ethyl iodide and diiodomethane (*top*) or vinyl iodide and iodomethane (*bottom*), used to rule out methylene insertion into vanadium–ethyl and coupling steps, respectively. *Center b* propene desorption from reactions with either perdeuteriodiomethane and vinyl bromide (*top*) or diiodomethane and vinyl

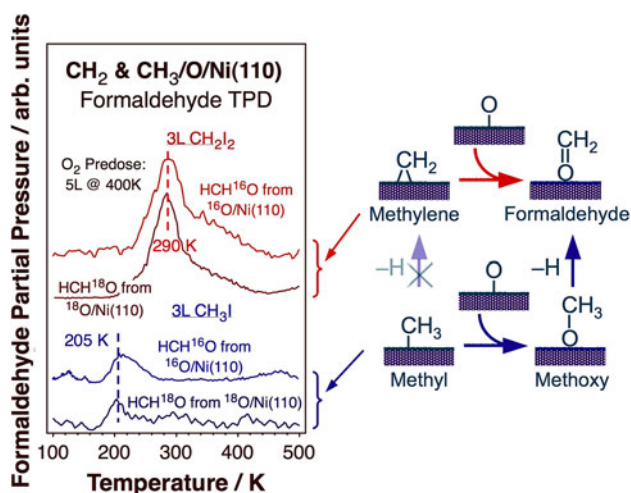
iodide (*bottom*), used to highlight the likelihood of vinyl intermediates being involved in the chain growth. *Right c* propene production from allyl iodide, adsorbed alone (*bottom*) or together with deuterated water (used as an extra source of hydrogen–deuterium in this case), provided to show the feasibility of the corresponding hydrogenation step

**Fig. 5** TPD for the production of methane (*left*), ethylene (*center*) and propene (*right*) from 3.0 L of diiodomethane adsorbed on V(100) predosed with various amounts of oxygen. The main effect of the coadsorbed oxygen is to inhibit all conversions



hand, formaldehyde formation is significantly more facile, and must therefore involve an initial oxygen insertion into the nickel–methyl bond (followed by  $\beta$ -hydride elimination) rather than the reverse sequence, methyl dehydrogenation to methylene followed by oxygen insertion into the nickel–methylene bond [63]. The ease with which the oxygen insertion step takes place, as implied here, has also been documented by us on Ni(100) [67–71], in that case by using branched alkyl groups to produce ketones (which are

more stable and do not rapidly decompose further upon their formation). It should also be pointed out that an alternative alkyl–oxygen bond formation mechanism via an Eley–Rideal step involving gas-phase methyl radicals has been reported on Mo(110) [51, 72]. Nevertheless, because of the great affinity of early transition metals toward oxygen, the reverse C–O bond scission reaction is still more favorable on the surfaces of early transition metals, as we discuss next.

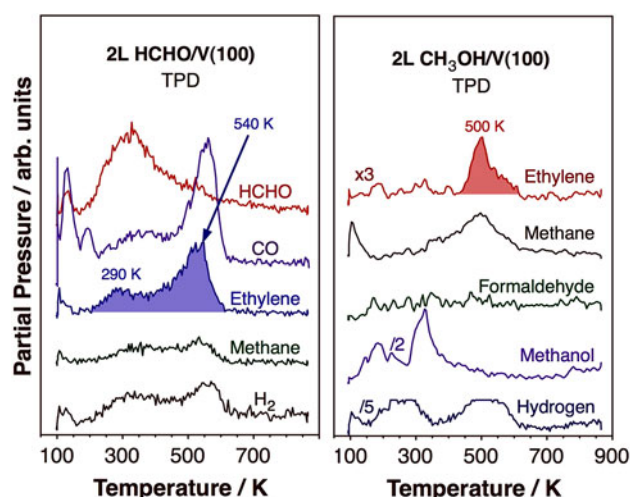


**Fig. 6** Formaldehyde TPD for either 3.0 L of diiodomethane (*top*) or 3.0 L of iodomethane (*bottom*) coadsorbed with either regular ( $^{16}\text{O}$ ) or heavy ( $^{18}\text{O}$ ) oxygen on Ni(110). Formaldehyde is produced in all cases, by the mechanism sketched on the *right*. To notice in particular is the ease with which formaldehyde is made from methyl groups, an observation that indicates that oxygen insertion into nickel–methyl bonds precedes any dehydrogenation reactions from methyl surface moieties

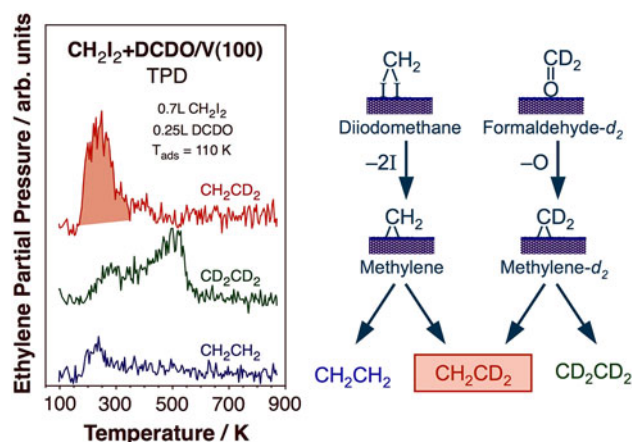
#### 4 Surface Chemistry of Formaldehyde and Methanol

Survey TPD data for both formaldehyde and methanol on V(100) are reported in Fig. 7 (left and right panels, respectively). Methane production is seen in both cases, indicating the occurrence of facile C–O bond-scission steps. The fact that no formaldehyde is produced from methanol points to a slower  $\beta$ -hydride elimination step. All these trends are opposite to those seen on late transition metals [73–75]. Nevertheless, significant amounts of carbon monoxide are produced here, as on many other metals, and that may still involve the formation of an intermediate formaldehyde species [76–83].

Perhaps the most interesting result from these experiments is the observation of ethylene production from thermal activation of either formaldehyde or methanol on V(100). In the case of formaldehyde in particular, this occurs in two very distinct temperature regimes, around 290 and 540 K respectively, and by two different mechanisms. Additional isotope-labeling experiments were carried out to get some insight into those. As an example of the result from that work, Fig. 8 reports the TPD traces obtained from experiments with mixed layer of coadsorbed diiodomethane and perdeuteroformaldehyde [84]. Diiodomethane was used as a source of surface methylene groups, to test the possibility of cross coupling with methylene groups produced by the activation of the perdeuteroformaldehyde. This is clearly indicated for the low-temperature state by the large TPD signal for  $\text{CH}_2\text{CD}_2$ . It is quite likely that some of the formaldehyde adsorbed on the V(100)



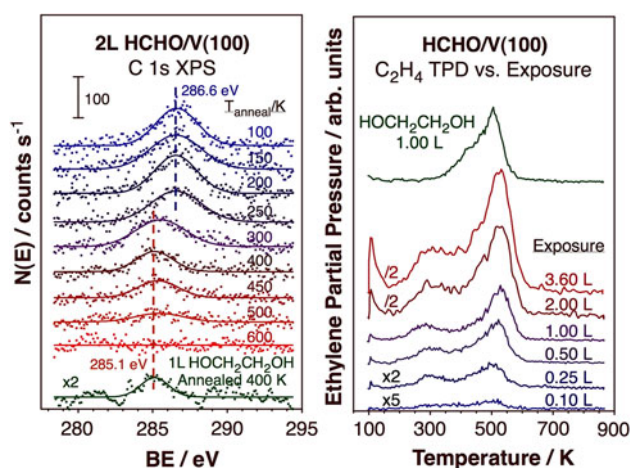
**Fig. 7** Survey TPD traces for 2.0 L of formaldehyde (*left panel*) and 2.0 L of methanol (*right panel*) adsorbed at 100 K on a V(100) single-crystal surface. Desorption signals are seen in both cases for both methane and ethylene. Moreover, ethylene production from formaldehyde occurs in two distinct temperature regimes, by two different reaction mechanisms



**Fig. 8** Mixed-isotope TPD experiments used to probe the mechanism of ethylene formation from formaldehyde adsorbed on V(100). 0.25 L of perdeuteroformaldehyde was dosed on a surface previously exposed to 0.7 L of normal diiodomethane, a good precursor for the formation of surface methylene groups. The detection of large quantities of mixed-isotope ethylene at low temperatures, below 300 K, strongly suggest the formation of surface perdeuteromethylene via C–O bond scission in some of the adsorbed DCDO (followed by coupling with the regular methylene from  $\text{CH}_2\text{I}_2$ ). On the other hand, no cross coupling is seen at high ( $\sim 500$  K) temperatures, indicative of the early formation of a dimeric intermediate

surface undergoes C–O bond scission to produce surface methylene species below  $\sim 250$  K.

On the other hand, no isotope scrambling is seen in Fig. 8 during the production of ethylene in the high-temperature state. There, formaldehyde is produced via a dimeric intermediate produced by an early C–C bond-forming reaction, a conclusion supported by additional



**Fig. 9** *Left* C 1s X-ray photoelectron spectra (XPS) for 2.0 L of formaldehyde dosed on V(100) as a function of annealing temperature. The shift in binding energy seen around 300 K, from 286.6 to 285.1 eV, is consistent with the formation of a new dimeric intermediate on the surface. The similarity of the peak obtained with HCHO above 300 K with that recorded for 1.0 L of ethylene glycol (bottom trace) suggest a common intermediate to both system, a  $-\text{OCH}_2\text{CH}_2\text{O}-$  diolate. *Right* Ethylene TPD for formaldehyde on V(100) as a function of initial exposure. The trace obtained for 1.0 L of ethylene glycol is provided at the top for comparison. Again, the favorable comparison between the two systems supports the idea of the diolate intermediate

isotope labeling and spectroscopic studies described in detail elsewhere [84]. That intermediate is likely to be a diolate, as suggested by the data in Fig. 9, which highlights the similarities in the C 1s XPS spectra (left panel) and ethylene TPD traces (right panel) obtained with formaldehyde and ethylene glycol (a precursor for the formation of the  $-\text{OCH}_2\text{CH}_2\text{O}-$  surface species). The conclusion is that coupling of formaldehyde adsorbates through their carbon ends takes precedent over any C–O bond-scission or dehydrogenation steps on the vanadium surface. The most common thermal chemistry seen for formaldehyde on transition metal surfaces has been its decomposition to carbon monoxide and hydrogen [15, 72, 75, 85–91], but diolate formation as reported here is known in homogeneous catalysis with titanium [92] and vanadium [93, 94] low-valent compounds, and has also been reported on the surfaces of titanium [95] and uranium [96] oxides. The only other precedent for diolate formation on a metal is that reported on Mo(110) [86], another early transition metal.

A central issue in the mechanism of diolate formation from aldehydes in these metal-based systems is the oxidation state required at the metal center to promote the reaction. In homogeneous phase, this so-called McMurry reaction was first proposed to involve zero-valent titanium [92] but  $\text{V}^{2+}$  ions [93, 97]. On surfaces, Barteau and co-workers claim that the reaction does not occur on metallic  $\text{Ti}^0$  centers but rather on low-oxidation titanium

ion sites [98]. In the case of V(100), the surface always remains in its metallic state, as indicated by XPS. On the other hand, it may be argued that it only occurs once some of the initial formaldehyde has decomposed into methylene and atomic oxygen on the surface. Certainly, oxygen preadsorption on V(100) inhibits most of the thermal chemistry of the adsorbed formaldehyde, but significantly shifts the selectivity of ethylene production from the low- to the high-temperature state, that is, from straight coupling of methylene moieties after C–O bond-scission to diolate formation [84]. It appears that some coadsorbed oxygen is required to partially modify the electronic nature of the neighboring vanadium surface atoms and to promote the dimerization pathway. One final point: the formation of ethylene from methanol most likely follows a mechanism involving sequential dehydrogenations to methoxide and formaldehyde intermediates followed by the same diolate formation reported above when starting with formaldehyde.

## 5 Concluding Remarks

In this brief review we have contrasted the surface chemistry of  $\text{C}_1$  moieties on early (vanadium) versus late (nickel) transition metal surfaces. The differences in reactivity seen between those two groups of metals were interpreted in terms of the relative rates for the different surface elementary steps available to the reactants, which is what defines selectivity in these and, more generally, all catalytic reactions. Some of the results reported here were to be expected. In particular, early transition metals are well known to be more active toward dehydrogenation reactions. Hence, nickel and platinum surfaces tend to favor the formation of highly hydrogenated intermediates such as methyl and methylene groups, whereas vanadium shifts that pool toward more dehydrogenated species, in particular methylene and methylidyne. Nevertheless, methylene insertion steps are still possible on V(100), albeit into metal-alkylidene and metal-vinyl rather than metal-alkyl bonds. This means that, at least in principle, vanadium (and perhaps other early transition metals) is still good at promoting chain growth with hydrocarbons.

Early transition metals also display much higher affinity for oxygen, and therefore discourage oxygen-insertion steps. As discussed above, the reaction of methylene or methyl species with coadsorbed oxygen may lead to the formation of formaldehyde on nickel, but that reaction is not viable on vanadium. On the other hand, when starting from oxygenated reactants, carbon-carbon coupling may be induced on vanadium before the scission of the C–O bond, and dehydrogenation steps may in general be delayed. Again, this provides a new avenue for the



synthesis of interesting new products. Overall, early transition metals may be quite active toward hydrocarbon conversions, but may still favor specific steps of interest for bond-forming processes, different than those typical of late transition metals.

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