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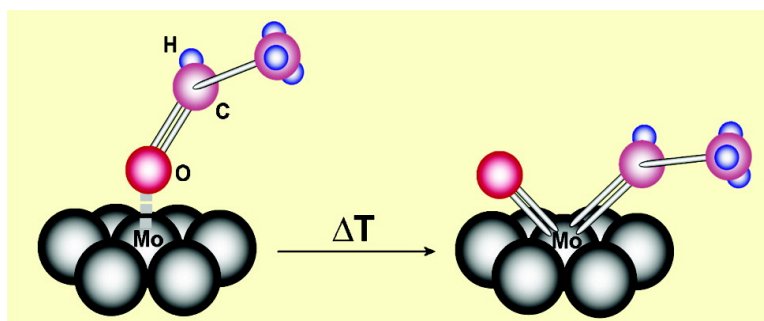
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Dissociation of Acetaldehyde on β-Mo₂C To Yield Ethylidene and Oxo Surface Groups: A Possible Pathway for Active Site Formation in Heterogeneous Olefin Metathesis

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The initiating and propagating intermediates in homogeneous olefin metathesis are metal alkylidenes, as described by the Hérisson−Chauvin mechanism.[1] It is generally assumed that the same mechanism holds for heterogeneously catalyzed olefin metathesis. However, it is not clearly known how the initiating site forms at the surface,[2] although several mechanisms have been proposed over the past three decades.[3] Vibrational spectroscopy investigations related to this question are extremely challenging due to the small number of active sites. For example, dynamic counting experiments revealed that <1% of Mo atoms in a highly dispersed Mo/Al₂O₃ catalyst are active for propene metathesis.[4] We show that acetaldehyde undergoes carbonyl bond-specific dissociation on β-Mo₂C to yield surface ethylidene−oxo species. This novel surface reaction permits the first measurement of the complete infrared spectrum of one of the Hérisson−Chauvin intermediates in propene metathesis. Since alkylidene-functionalized molybdenum carbide is active for olefin metathesis,[5] our results also suggest a possible route for initiator formation in heterogeneous olefin metathesis.

The experiments were performed on clean molybdenum carbide under ultra-high-vacuum conditions. A temperature-programmed carburization method was used to transform molybdenum foil into bulk β-Mo₂C.[6] The reflection absorption infrared (RAIRS) spectrum for acetaldehyde on β-Mo₂C at 130 K (Figure 1) is characteristic of an η¹-adsorption state. The intense downshifted ν(CO) band at 1669 cm⁻¹, typical of chemisorption via the carbonyl oxygen, is eliminated by annealing to 300 K. Despite the disappearance of the ν(CO) band, all of the deformation mode bands characteristic of the CHCH₃ moiety are observed in the 300 K spectrum. Similarly, as shown in the inset to Figure 1, all of the ν(CH) stretching bands characteristic of the η¹-state remain on annealing to 300−400 K. A relatively intense new band at 968 cm⁻¹ is observed at 300 K. This band is also observed in experiments performed using deuterated acetaldehyde and is characteristic of a terminal oxo (Mo=O) surface species.[7] The observation of surface oxo suggests that CO bond scission occurs as the sample is annealed to 300 K. All other literature data[8] for the dissociation of aldehydes on metal surfaces show that either CH or CC bonds, rather than the carbonyl bond, are cleaved.

Table 1 enables a comparison of spectra observed at 300 K (Figure 1) with the assigned spectrum of gas-phase acetaldehyde,[9] DFT-calculated frequencies for an oxo=MoCl₂=CHCH₃ model complex,[10] and IR frequencies for ethylidene formed by the interaction of methylcyclopropane with photoreduced Mo⁶⁺/SiO₂.[11] In agreement with calculations by Handzlik[12] for a
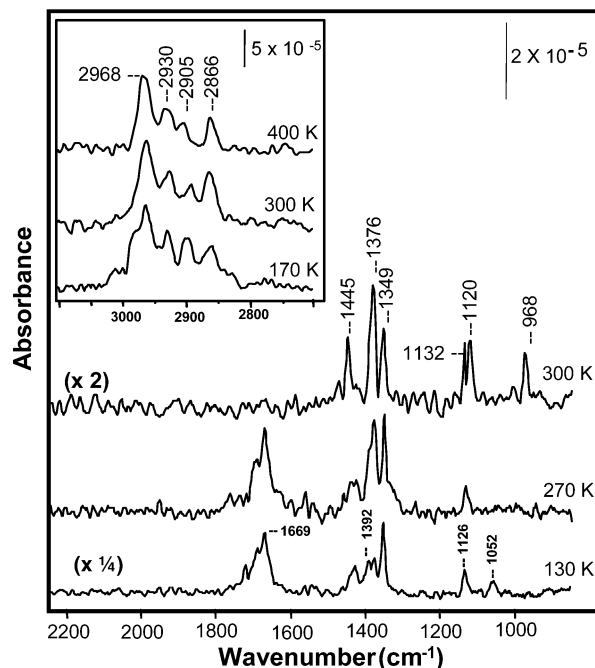
Figure 1. RAIRS spectra for 5 L (1 L = 1 × 10⁻⁶ Torr·s) acetaldehyde on β-Mo₂C at 100 K, followed by annealing to the indicated temperatures.

Table 1. Measured and Calculated Frequencies (cm⁻¹) for O=Mo=CHCH₃ Referenced to Data for Acetaldehyde

	acetaldehyde	ethylidene		
mode	gas phase[a]	Mo/SiO₂[b]	OMoCl₂	β-Mo₂C
ν_as(CH₃)	3014	2985	3004 (2218)	2968 (2220)
ν_as(CH₃)	2964	2910	2990 (2207)	2930 (2189)
ν_s(CH₃)	2923	2890	2948 (2179)	2905 (2143)
ν(CH)	2715	2850	2876 (2066)	2866 (2103)
ν(CO)	1766			
δ_as(CH₃)	1436		1426 (1007)	1445 (1044)
δ_as(CH₃)	1434	1423		
δ_s(CH₃)	1395		1353 (1027)	1376 (1027)
δ(CH)	1352			1349
ρ(CH₃)	1113		952 (899)	
δ(CH)	1098		921 (777)	
ν(Mo=C) + δ(CH)			1219 (1037)	
ν(Mo=C) + ν(CC) + δ(CH₃)₃			1038 (1122)	1120 (1135)
ν(Mo=C)			977 (977)	968 (985)

[a] Reference 9. [b] Reference 11. Data for CDCD₃ are included in parentheses. ν(CH₃/CH) and δ(CH₃/CH) modes of ethylidene are not assigned in this table.

CH₃CH=Mo=O/Al₂(OH)₆ model complex, four distinct ν(CH) bands are present in the 3005−2850 cm⁻¹ region in each case. The

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observed ν(CH) frequencies (Figure 1) are close to those for ethylidene on Mo/SiO$_2$,[11] providing compelling evidence for a surface oxo−Mo−ethylidene complex on β-Mo$_2$C. As shown by DFT simulations, both the CH deformation and CC stretching modes are coupled to the Mo=C stretching vibration. This is in keeping with the acknowledged difficulty in assigning modes as pure metal−carbon or metal−nitrogen stretching vibrations in alkylidene or imido complexes.[13] The intense doublet observed at 1132/1120 cm^{-1} at 300 K is very close in frequency to bands detected for cyclobutylidene[4] (1130 cm^{-1}) on β-Mo$_2$C and for surface Ti−neopentylidene[14] (1121 cm^{-1}) formed during the chemical vapor deposition of TiC using tetraneopentyltitanium. These observations provide the first database for the attribution of alkylidene vibrational modes containing metal−carbon stretching character.

Spectroscopic detection of tilted or flat-lying, highly activated states of adsorbed carbon monoxide has been reported for Cr, W, and Mo surfaces.[15] Hence, it is not entirely surprising that the carbonyl bond scission of acetaldehyde takes place on β-Mo$_2$C. What is surprising is that carbonyl bond-specific dissociation occurs, and that the surface product is a terminal alkylidene. A metal surface typically presents a multitude of adsorption sites, and one might anticipate the formation of a bridging alkylidene rather than a terminal alkylidene. This is borne out by the fact that, to the best of our knowledge, spectroscopic data for terminal alkylidenes have only been reported for TiC films and β-Mo$_2$C surfaces. This suggests a special role for metal carbides in stabilizing terminal alkylidenes. We propose that the unique chemistry observed in this study is related to the fact that acetaldehyde forms a strongly chemisorbed η^1-state, as evidenced by the observation of the characteristic ν(CO) band up to at least 280 K. The strong chemisorption bond keeps the η^1-state intact on β-Mo$_2$C until it can undergo carbonyl bond dissociation, presumably via an η^2-intermediate. While there is no precedent in the surface science literature for the carbonyl bond-specific dissociation of an aldehyde on a metal surface to yield an alkylidene species, Chisholm et al.[16] have reported the formation of μ-alkylidenes through the reaction of aldehydes with ditungsten hexaalkoxides. The oxidative addition of aldehydes and ketones to WCl$_2$(PMePh$_2$)$_4$ has been reported by Bryan and Mayer.[17] An η^2-acetaldehyde complex was observed to lead to a small amount of W−oxo, thereby implying the formation of a nonisolated ethylidene−W−oxo product.[17b]

The observation of the formation of ethylidene from chemisorbed acetaldehyde leads us to suggest a new pathway for alkylidene formation on Mo- and W-based heterogeneous olefin metathesis catalysts. In this pathway, surface alkylidenes are formed from aldehydes and ketones produced during the catalyst induction period. A number of observations from the catalysis literature support this proposal. First, in the context of olefin oxidation, the oxidation of propylene on supported molybdenum oxide catalysts leads to the formation of C$_2$ and C$_3$ aldehydes and ketones.[18] More specifically, in the context of olefin metathesis, Basrur et al.[19] have reported that trace amounts of acetone and acetaldehyde are formed during the induction period for propylene metathesis over supported WO$_3$. They concluded that acetaldehyde and surface alkylidene are simultaneously formed by metathetical exchange between the olefin and oxo groups. The exchange reaction has, however, no precedent

in the organometallic literature. Our proposal differs in that we assume a two-step mechanism in which the carbonyl-bond-containing oxygenate is first formed by olefin oxidation, and then this species generates the metathesis active site through the oxidative addition reaction reported herein. We note that the interaction of acetaldehyde with Mo(IV) dimers on SiO$_2$ results in a ν(CH) spectrum consistent with the formation of Mo−ethylidene species,[20] thereby suggesting that the surface reaction reported herein is not specific to β-Mo$_2$C. If the latter assignment of the spectrum in ref 20 is correct, then the observation supports arguments for a role for alkylidene as well as pinacolate intermediates in some carbonyl reductive coupling reactions.[21]

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