

Preparation and olefin-metathesis activity of cyclopentylidene-oxo initiator sites on a molybdenum carbide surface

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Abstract

A low surface area planar sample of bulk β - Mo_2C can be activated for olefin-metathesis reactions through the dissociative chemisorption of cyclopentanone to yield surface alkylidene-oxo species. This methodology allows the formation of a sufficiently high coverage of active sites to permit investigation of heterogeneous metathesis by surface science techniques. Reflectance absorbance infrared spectroscopy measurements were used to isolate η^1 and η^2 -adsorbed cyclopentanone. The η^2 -state was found to be the direct precursor for alkylidene-oxo formation. Olefin-metathesis reactions were carried out using propene and cyclopentene. The surface chemistry of cyclopentanone and cyclopentylidene on β - Mo_2C is compared to analogous organometallic systems.

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1. Introduction

Surface science studies have proven extremely successful in revealing fundamental details on several catalytic reactions. However, there is, to our knowledge, no report of the isolation and spectroscopic analysis of terminal alkylidenes on pure metal surfaces, although there are many examples of bridge-bonded surface alkylidenes [1–4]. This is consistent with the fact that metal surfaces present an array of contiguous atoms and, as in multinuclear organometallic complexes, μ -alkylidene bonding is energetically preferred [5,6]. The absence of data for terminal alkylidenes on metals is in line with the fact that there are very few reports of olefin-metathesis using unsupported metals. Tysoe and co-workers [7] demonstrated that a high-temperature (>650 K) olefin metathesis process may be effected using molybdenum, and that oxide layers grown on Mo are active

for olefin-metathesis at temperatures below 650 K. Nuckolls and co-workers [8] observed olefin-metathesis reactions at room temperature on 4-bromophenyldiazomethane and trimethylsilyldiazomethane exposed Ru films. We have shown that molybdenum can be rendered active for low-temperature olefin-metathesis reactions by forming a carbide, Mo_2C , phase and using ketone or aldehyde chemisorption to create alkylidene-oxo initiator sites [9,10]. Surface spectroscopy studies show that terminal alkylidenes, serving as metathesis initiators and propagators, may be isolated on the carbide surface [10].

Metal carbides display significant structural and electronic changes relative to the pure metals. For example, α - Mo_2C and β - Mo_2C are orthorhombic and hexagonal phases, respectively. Formation of interstitial carbides leads to lattice expansion and adds ionic and covalent contributions to the metallic bonding. Results of computational studies by several groups may be used to illustrate the modifications brought about by carbide formation. Liu and Rodriguez reported DFT calculations on the α - $\text{Mo}_2\text{C}(001)$ surface [11]. They calculated that the

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Mo–Mo distance at hcp sites, overlying interstitial carbon, is 3.14 Å, showing considerable expansion of the lattice by comparison to the Mo–Mo distance of 2.75 Å for the Mo(110) surface. They also found that surface Mo atoms with one and two carbon neighbours were approximately 0.19 e and 0.33 e more positive, respectively, than Mo atoms on the Mo(110) surface. Calculated densities of states for β -Mo₂C and for early transition metal carbides show C_{sp} –Mo_{4d} hybridization [12,13] in agreement with experimental measurements [14]. This metal to non-metal directional bonding is consistent with the hardness of carbide materials [13]. Furthermore, as pointed out by Grossman et al. [13], the metal-carbon directional bonding results in substantial variations in charge density, relative to that for the pure metal, over the unit cell.

The greater Mo–Mo distances, relative to pure Mo, combined with Mo–C directional bonding should lead to increased corrugation of the charge density across the surface. Indeed, a comparison of scanning tunneling microscopy (STM) data for Mo₂C(0001) [15], Mo(112) and Mo(111) [16] clearly show more featured atomically resolved images for the carbide. The STM technique is sensitive to the local density of states and hence to the electronic corrugation along the surface. We propose that the increased corrugation enhances the probability of forming adsorption states involving single metal atoms. In contrast, terraces on metal single crystals present low-corrugation, jellium, electron density profiles. As a consequence, several different adsorption sites are often energetically accessible. Alloy and metal compound formation may provide methods to better isolate surface sites. For example, work by Goodman and co-workers [17] on the acetoxylation of ethylene to vinyl acetate on gold-palladium shows that alloy formation is an effective method to isolate single Pd sites. Similarly, the selective formation of terminal alkylidenes on β -Mo₂C shows that interstitial carbide formation leads to single Mo site surface chemistry [10,18,19]. The latter observation is especially interesting in that formation of carbide phases from molybdenum nanoparticles can occur in the presence of hydrocarbons at relatively low temperatures [20]. Work by Chen and co-workers on molybdenum carbide surface films clearly shows that subsurface carbon is required to obtain chemisorption properties characteristic of bulk carbides [21–23].

This paper describes the spectroscopic study of the formation of cyclopentylidene initiating sites for olefin-metathesis on β -Mo₂C. The bulk carbide sample was prepared by carburizing a pure molybdenum foil as described in Section 2. The alkylidene groups were formed through the dissociative adsorption of cyclopentanone on the clean carbide surface. Cyclopentanone and cyclopentylidene groups have been used in many organometallic studies. Bryan and Mayer [24,25] reported the reaction of cyclopentanone with the single-metal atom complex $WCl_2(PMePh_2)_4$ to yield an isolable $O=W=cyclopentylidene$ product. As shown below, the interaction of cyclopentanone with the β -Mo₂C surface displays many similarities

with the homogeneous reaction. Chisholm et al. reported detailed studies of the formation of $O=W_2-\mu$ -alkylidene complexes through the reductive cleavage of the carbonyl bond of ketones, including cyclopentanone [26]. Osborn and co-workers used tungsten-cyclopentylidene complexes as Wittig reagents [27] and as olefin-metathesis catalysts [28]. Cyclopentanone η^2 -W ligands have been isolated [24,25,29].

2. Experimental

The experiments were carried out under ultrahigh vacuum (uhv) conditions. The sample was prepared by Ramannathan and co-workers [30] by carburizing a Mo foil ($12 \times 8 \times 1.5 \text{ mm}^3$) in a flowing 20% CH₄/H₂ mixture. The reaction was performed by raising the temperature of the quartz reactor to 1373 K at a rate of 8 K/s. and then maintaining the temperature constant until carburization was complete. XRD measurements determined the structure to be bulk β -Mo₂C. The freshly prepared carbide was passivated at room temperature using a flowing 0.5% O₂/He mixture. The sample was mounted on a variable temperature (100–1400 K) stage in the uhv chamber and cleaned using ion bombardment to remove sulfur contamination. Exposure to propene was used to remove oxygen as CO. X-ray photoelectron spectroscopy (XPS) measurements were used to determine the cleanliness of the surface and to verify that the stoichiometry of the surface region was Mo₂C. XPS was also used to monitor the surface coverage of adsorbates and to search for carbon and oxygen deposition through adsorbate bond breaking. Reflectance absorbance infrared spectroscopy (RAIRS) was used to measure the vibrational spectrum of the adsorbate exposed surface. Spectra were acquired by referencing 800 sample scans to 800 scans of the clean surface. Unless otherwise indicated all of the RAIRS spectra were measured with the sample held at 100 K. The maximum surface coverage in a chemisorbed layer is approximately 10^{15} adsorbates cm^{-2} . As a result, it is often difficult to measure vibrational spectra of hydrocarbon sub-monolayers. Narrow band MCT and InSb detectors are used to obtain the best signal to noise ratio possible. Hence, data for the CH stretching region and for the 2200–800 cm^{-1} region are presented separately. Desorption spectra were measured by placing the sample face close to the entrance of a shrouded quadrupole mass spectrometer while ramping the sample temperature at a rate of 1 K/s. Gases were introduced into the uhv chamber using leak valves and exposures are expressed as Langmuirs ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr s}$).

3. Results and discussion

RAIRS spectra for cyclopentanone on β -Mo₂C are displayed in Figs. 1–5. Data for the carbonyl stretching bands, the CH₂ deformation and ring modes are shown in Figs. 1 and 4, and CH stretching region data are shown in Figs. 2, 3 and 5. Figs. 1 and 2 display spectra recorded for increasing

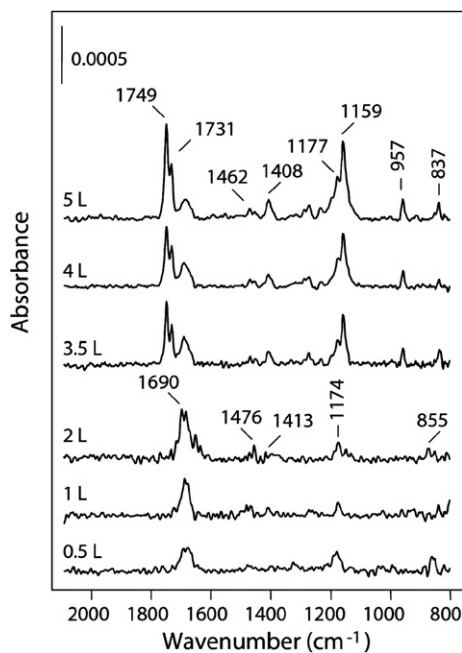


Fig. 1. Reflectance infrared (RAIRS) spectra recorded as a function of the exposure of clean β - Mo_2C at 100 K to cyclopentanone. Exposure is expressed in Langmuirs. 1 L = 1×10^{-6} Torr s.

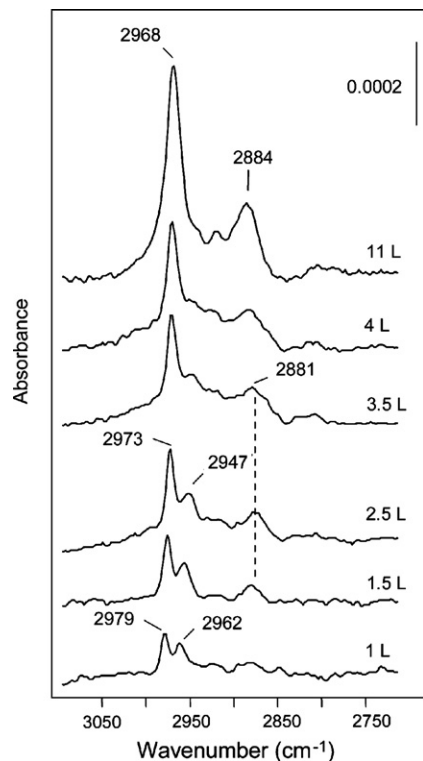


Fig. 2. CH_2 stretching region RAIRS spectra recorded as a function of the exposure of clean β - Mo_2C at 100 K to cyclopentanone.

exposures with the sample held at 100 K and Fig. 3 displays spectra recorded during exposure at 200 K. Figs. 4 and 5 display spectra recorded at 100 K following brief anneals to the indicated temperatures. The combined RAIRS data pro-

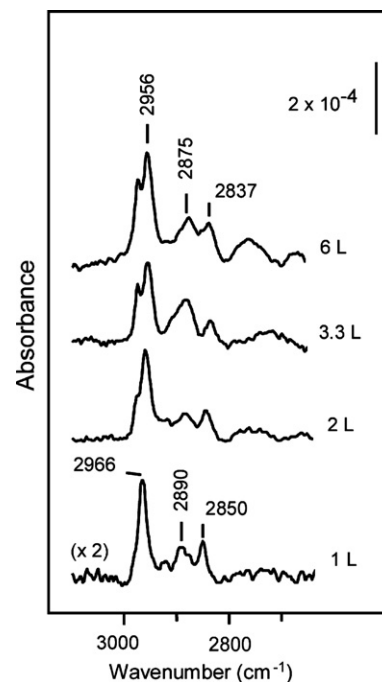


Fig. 3. CH_2 stretching region RAIRS spectra recorded at 200 K during exposure of β - Mo_2C to cyclopentanone.

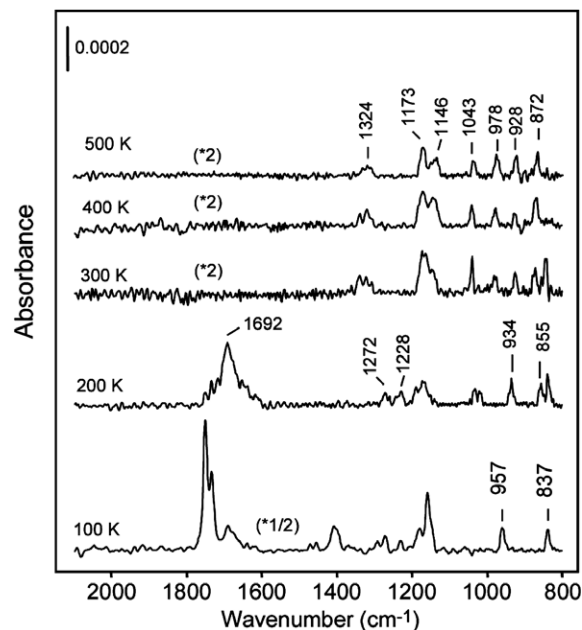


Fig. 4. RAIRS spectra recorded at 100 K following anneals of cyclopentanone exposed β - Mo_2C to the indicated temperatures.

vides information on the adsorption states formed as a function of surface coverage and, interdependently, as a function of the sample temperature.

Fig. 1 shows that an exposure of 3.5 L at 100 K yields features at 1750, 1735, 1159 and 957 cm^{-1} characteristic of free cyclopentanone [31]. This marks the saturation of the chemisorption layer and the formation of a condensed, multilayer, phase. The carbonyl band at 1690 cm^{-1} ,

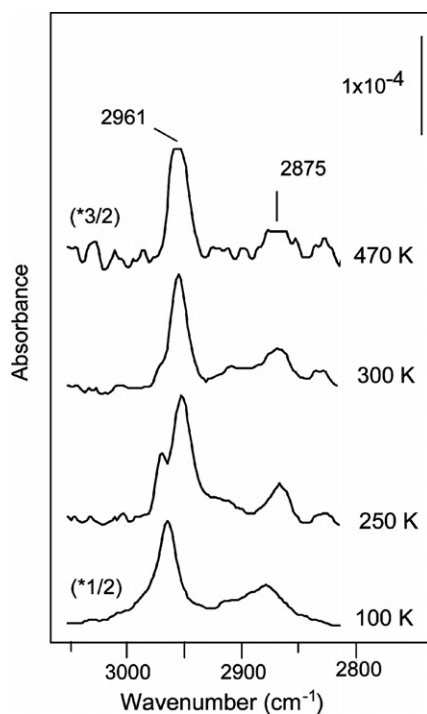


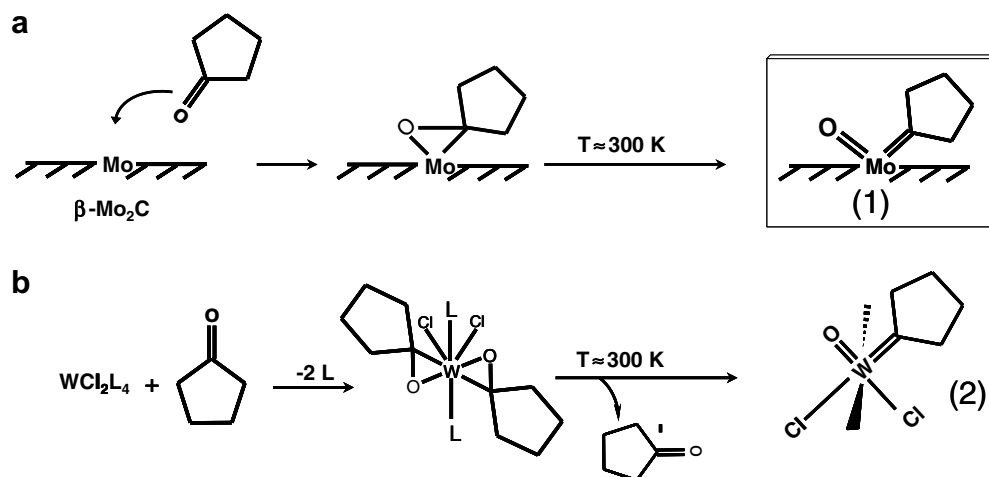
Fig. 5. CH_2 stretching region RAIRS spectra recorded at 100 K following anneals of cyclopentanone exposed $\beta\text{-Mo}_2\text{C}$ to the indicated temperatures.

observed at lower exposures is characteristic of an $\eta^1(\text{O})$ chemisorption state [18,19]. This attribution is made on the basis of the $\sim 50\text{ cm}^{-1}$ redshift of the $\nu(\text{CO})$ frequency, coupled with the strong intensity of the band. The metal surface selection rule [32] states that the intensity of a RAIRS band varies as $\cos^2\theta$ as a function of the angle between the normal to the surface and the transition dipole. Hence, the strong intensity of the band is consistent with a $\eta^1(\text{O})$ -type geometry, with the CO bond tilted well away from the plane of the surface. The $\nu(\text{CH}_2)$ data in Fig. 2 show that the multilayer displays strong bands at 2968 and 2884 cm^{-1} as for free cyclopentanone. In contrast, the chemisorbed layer displays two bands in the $\nu_{\text{as}}(\text{CH}_2)$ stretching region, at ~ 2979 and 2962 cm^{-1} . The extra band in the chemisorbed layer could arise for two very different reasons. It could be a consequence of the lowering of the symmetry of the molecule on chemisorption, leading to new RAIRS active modes, or it could be due to the existence of a second adsorption state. The latter interpretation is supported by data shown in Fig. 3 for exposures carried out with the sample held at 200 K. In particular, a band at 2966 cm^{-1} is first observed followed by the growth of a high-frequency shoulder as the coverage of the chemisorbed layer is increased.

The RAIRS spectra displayed in Figs. 4 and 5 confirm that there are two different states of cyclopentanone in the chemisorbed layer. Heating to 200 K removes the condensed layer, leaving a strong $\nu(\text{CO})$ signal due to the η^1 -state, which in turn is removed on heating to 300 K (Fig. 4). The $\nu(\text{CH}_2)$ stretching spectra (Fig. 5) show the high-frequency ν_{as} shoulder at 250 K. This band is selec-

tively removed on heating to 300 K indicating that it is also due to the η^1 -state. The obvious candidate for a second molecular adsorption state is $\eta^2\text{-(C,O)}$ -cyclopentanone. Due to the metal surface selection rule, RAIRS is expected to be insensitive to the characteristic $\nu(\text{C-O})$ vibration of an η^2 -state. However, evidence for the existence of a η^2 -state can be gained from a comparison of the 300, 400 and 500 K spectra shown in Fig. 4. Fig. 4 shows that the removal of the η^1 -state coincides with the development of new bands at 1324, 1043 and 978 cm^{-1} . The latter band is characteristic of a surface oxo group [9,18,19,33] indicating that carbonyl bond scission has taken place. In contrast, the absence of a new band in the 1600–2200 cm^{-1} region shows that decarbonylation leading to the formation of CO_{ads} does not occur. (This, however, does not rule out a decarbonylation channel in which the CO product immediately desorbs from the surface.) Heating from 300 K to 400–500 K leads to more clearly resolved peaks at 1146 and 872 cm^{-1} . Heating to 500 K and above (data not shown) shifts the low frequency $\nu(\text{CH}_2)$ peak from 2875 to 2896 cm^{-1} . Apart from the oxo band, all of the clearly resolved bands observed at 300–500 K are characteristic, by comparison to vibrational data for cyclopentanone, of a C_5H_8 ring. Hence, the subtle changes detected between 300 and 500 K are attributed to the conversion of one cyclic- C_5H_8 species into another. That is, the results are consistent with the transformation of the η^2 -state into surface cyclopentylidene-oxo. The band at 2837 cm^{-1} , in Fig. 3, is attributed to a ring-opened decomposition product of cyclopentanone. Thermal desorption measurements show that molecular desorption of cyclopentanone does not occur in the 200–300 K range. This observation implies that conversion from the η^1 -state to the η^2 -state takes place.

Some additional information on the various adsorption states can be obtained from XPS measurements (data not shown). Cyclopentanone exposure at 100 K gives rise to a C(1s) peak at 284.8 eV at low surface coverages. Higher exposures leads to an additional peak at 288.1 eV, due to the carbonyl carbon. The sub-monolayer O(1s) spectrum at 100 K displays peaks at 530.0, 530.9 and 532.5 eV. The peaks at 288.1 and 532.5 eV are partially removed on heating to 200 K and completely removed on heating to 300 K, indicating that they are characteristic of both the η^1 -state and the multilayer. Annealing to the 300–400 K range leads to a peak at 531.9 eV which we attribute to the oxo species. The peak at 530.9 eV is selectively removed on heating to 600 K indicating that it is due to the η^2 -state identified by RAIRS measurements. The C(1s) spectra recorded on annealing to the 500–900 K range can be deconvoluted into four components located at 285.8, 284.7, 283.4 and 282.8 eV, where the $I[\text{C}(1\text{s})\ 284.7]/I[\text{C}(1\text{s})\ 285.8]$ intensity ratio is close to 4:1. The 282.8 and 283.4 eV peaks are due to bulk and surface carbide carbon, respectively. The 284.7 and 285.8 eV peaks are attributed to the C_4H_8 alkyl carbons and, tentatively, to the alkylidene carbon of the cyclopentylidene ring, respectively.



Scheme 1. (a) Illustration of carbonyl bond scission to form a surface oxo-alkylidene complex on $\beta\text{-Mo}_2\text{C}$ (1). (b) Illustration of carbonyl bond scission to form a tungsten oxo-alkylidene complex (2) as reported by Bryan and Mayer [25].

The dissociative adsorption of cyclopentanone on $\beta\text{-Mo}_2\text{C}$ to form surface oxo and cyclopentylidene (Scheme 1a) is an interesting system for comparing heterogeneous and homogeneous chemistry. In particular, Bryan and Mayer [25] reported the oxidative addition of cyclopentanone to $\text{WCl}_2(\text{PMePh}_2)_4$ to give a W(VI) oxo-alkylidene complex (Scheme 1b). They reported that two equivalents of cyclopentanone yields a bis(η^2 -cyclopentanone) complex which rearranges, at room temperature, to form one equivalent each of the oxo-cyclopentylidene complex and free cyclopentanone. The bis(η^2 -cyclopentanone) complex was found to be stable at room temperature in the presence of five equivalents of cyclopentanone. In contrast, the preparation of an oxo-isopropylidene complex required that only one equivalent of acetone be used. The half-equivalent of the bis(η^2 -acetone) complex thereby formed rearranged to yield the oxo-alkylidene product. Reaction of the latter complex with acetone lead to the complete removal of the alkylidene and the formation of products including tetramethylethylene and $\text{W}(\text{O})\text{Cl}_2(\text{PMePh}_2)_3$. The same set of products were produced by reacting two equivalents of acetone with $\text{WCl}_2(\text{PMePh}_2)_4$. Rapid ketone ligand exchange was observed for the bis-ketone complexes, and the barrier to rotation of alkylidene groups was found to be significant.

There are both significant similarities and differences between the interaction of aldehydes and ketones with $\text{WCl}_2(\text{PMePh}_2)_4$ and with the $\beta\text{-Mo}_2\text{C}$ surface. First we note the similarities. The RAIRS spectrum measured on annealing cyclopentanone/ $\beta\text{-Mo}_2\text{C}$ to 500 K displays bands at 1043, 978 and 872 cm^{-1} and the cyclopentylidene-W-oxo complex display infrared bands at 1098, 952 and 889 cm^{-1} [25]. X-ray crystallography measurements by Bryan and Mayer [25] show that distances and angles within the cyclopentylidene ring are the same as those for gas-phase cyclopentanone. Hence, the bands at 872 and 889 cm^{-1} are assigned to the ring breathing mode of cyclopentylidene by reference to data for cyclopentanone

[31]. As mentioned above, the bands at 978 and 952 cm^{-1} are readily assigned to the Mo-oxo vibration [19,25,33]. It is more problematic to assign the 1098 and 1043 cm^{-1} modes. The liquid-phase spectrum displays infrared and Raman bands at ~ 1021 and $\sim 1148\text{ cm}^{-1}$, while a mode predicted to occur at 1066 cm^{-1} is not observed [31]. Modes in this region involve strong coupling between CC and CH_2 vibrations. We tentatively assign the RAIRS band at 1043 cm^{-1} to a mixed Mo=C, ring vibration and CH_2 mode. It is well known that alkylidene, alkylidyne and imido metal-carbon (nitrogen) stretching modes couple strongly with CC stretching and CH deformation modes [34–36]. The latter assignment may be compared with those reported for $\text{Mo}=\text{C}_4\text{H}_6$ (1131 cm^{-1}) [9,19] and Mo-ethylidene ($1132/1120\text{ cm}^{-1}$) [18] formed through cyclobutanone and acetaldehyde dissociation on $\beta\text{-Mo}_2\text{C}$, and for Ti-neopentylidene (1121 cm^{-1}) formed during the chemical vapour deposition of TiC films [37].

The tungsten bis- η^2 -ketone complexes display facile ligand exchange reactions. For example, Bryan and Mayer [25] reported that the bis- η^2 -acetone complex undergoes complete exchange with acetone- d_6 within 10 min of mixing at room temperature. They also give the example of η^2 -acetone displacement to form a bis- η^2 -cyclopentanone complex. A similar, but not identical, phenomenon is observed for ketones on $\beta\text{-Mo}_2\text{C}$. Results are shown in Fig. 6 for an experiment performed by depositing ~ 5 layers of cyclopentanone on the surface at 100 K followed by the addition of a roughly equivalent amount of cyclohexanone to form a duplex layer. RAIRS spectra recorded on heating the duplex to 300 K show the presence of both cyclohexanone and cyclopentanone derived bands on the surface. Displacement reactions on metal surfaces under ultrahigh vacuum conditions have been studied by a number of groups [38,39]. Here, both displacement and an overall increase in the surface coverage of ketones takes place. Extensive measurements show that the amount of alkylidene formed depends on total exposure to the parent ketone

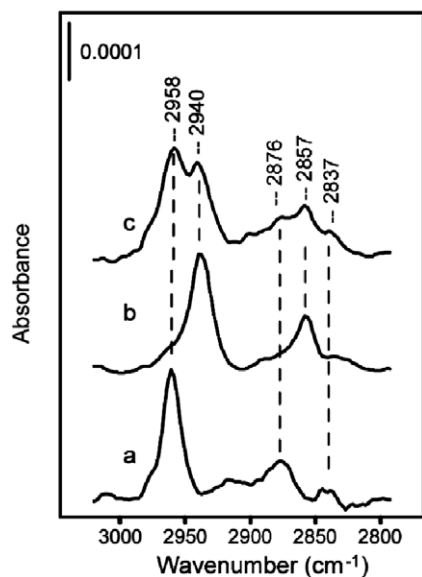


Fig. 6. CH₂ stretching region RAIRS spectra recorded following an anneal of (a) approximately five layers of cyclopentanone on β -Mo₂C from 100 to 300 K, (b) following an anneal of approximately five layers of cyclohexanone to 300 K, and (c) following an anneal of approximately five layers of cyclohexanone on five layers of cyclopentanone to 300 K.

at 100 K, and not just on the exposure required to form a monolayer. That is, the multilayer serves as a precursor [40] state for alkylidene formation. On heating the sample, competition between desorption from the multilayer and chemisorption from the multilayer occurs [40], and some of the condensed phase partitions into the chemisorbed phase.

The most striking difference between the reactivity of the β -Mo₂C surface and the WCl₂(PMePh₂)₄ complex towards ketones and aldehydes is that Wittig-type reactions, leading to the removal of alkylidene groups through olefin formation, are less favored on the carbide surface [19]. Alkylidenes may be isolated on the carbide surface using cyclobutanone [9,19], cyclopentanone [10], cyclohexanone [9] and acetaldehyde [18] as adsorbates. Additional experiments indicate that a number of other ketones, including acetone, may be used. In contrast, clean formation of alkylidene-W-oxo complexes was observed [25] for cyclopentanone, 3-methylcyclopentanone, 2-cyclopentene-1-one and indenone, but not for acetone, 2-butanone, acetaldehyde, pivaldehyde, cyclobutanone and cyclohexanone. Bryan and Mayer [25] concluded that the cyclopentyl ring offered sufficient steric hindrance to inhibit Wittig-type reactions, but was not so bulky as to prevent formation of the η^2 -cyclopentanone complex. Clearly the carbide surface provides a less sterically hindered environment, for alkylidene formation, than the metal atom surrounded by ligands in the organometallic complex. Furthermore, the existence of a weakly bound precursor state [40–42], in which the adsorbate is trapped at the surface for a very long period relative to time required to form a chemisorption bond at a suitable surface site, makes the surface a sterically less demanding environment. The adsorbate can undergo rota-

tional motion as it moves across the surface [43]. Further work is required to determine the extent to which Wittig-type reactions occur at the carbide surface, and to understand why they appear to be less favored than alkylidene formation and olefin-metathesis reactions.

Cyclopentylidene groups on β -Mo₂C function as initiation sites for cross-metathesis reactions. For example, as shown in Fig. 7, propene interacts with cyclopentylidene to generate gas-phase methylidenecyclopentane ($m/e = 82, 67, 54$) and ethylidenecyclopentane ($m/e = 96, 67, 54$). The corresponding adsorbed ethylidene and methylidene propagator species were detected using RAIRS [10], and the formation of butene [44] shows that catalytic turnover occurs. Maximum desorption signal for methylidenecyclopentane and ethylidenecyclopentane is observed in the 400–500 K region. These are typical reaction temperatures for olefin-metathesis using molybdena catalysts [45]. Fig. 8 displays evidence for the initiation of a ring opening polymerization (ROMP) reaction between cyclopentene and the cyclopentylidene functionalized surface. Exposure of the surface at 100 K to cyclopentene yields sharp bands at 3060 and 2851 cm⁻¹ characteristic of the condensed molecule [46]. The cyclopentene signal is removed on heating to 200 K. Exposure to background cyclopentene (2×10^{-8} Torr) while heating to 470 K leads to new bands at 2820–2830 cm⁻¹, 2946, 2926 cm⁻¹ and a broad peak at ~ 3050 cm⁻¹. The low frequency band shows that cyclopentene is captured by the surface, presumably by a ring-opening metathesis reaction. Polycyclopentene displays vibrational bands at 3005, 2923, 2852 and 2840 cm⁻¹ [47]. The match between the polymer spectrum [47] and the surface spectrum following reaction with cyclopentene is only good, indicating that long chains are not formed under the present reaction conditions. It is reasonable to assume that olefin-metathesis on the extended β -Mo₂C surface

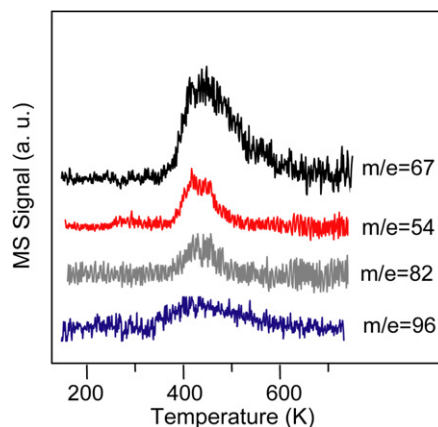


Fig. 7. Thermal desorption mass spectrometry data for the interaction of propene with cyclopentylidene functionalized β -Mo₂C. The experiments were performed by exposing the alkylidene functionalized surface to 2×10^{-8} Torr propene while heating the sample at 1 K/s. The $m/e = 82$ and 96 traces are due to the parent peaks for methylidenecyclopentane and ethylidenecyclopentane, respectively. The $m/e = 67$ and 54 peaks are common to both products.

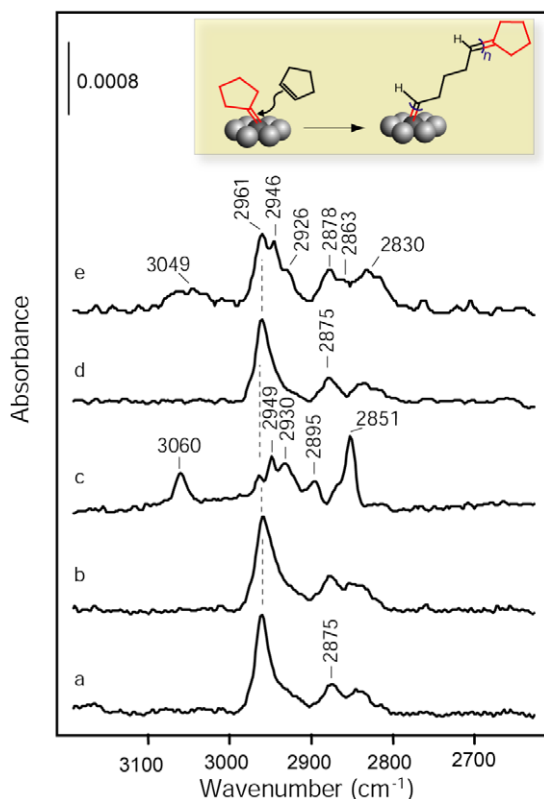


Fig. 8. RAIRS data for the interaction of cyclopentene with cyclopentylidene functionalized β - Mo_2C . (a) 10 L cyclopentanone annealed from 100 to 300 K. (b) 1.5 L cyclopentene at 100 K on the surface treated as in (a). (c) 9 L cyclopentene at 100 K on the surface treated as in (a). (d) Spectrum recorded on annealing the cyclopentene exposed surface (c) to 200 K. (e) Spectrum recorded on exposing the surface (d) to 2×10^{-8} Torr cyclopentene while raising the temperature by 1 K/s to 470 K.

occurs via the Langmuir–Hinshelwood mechanism for heterogeneous catalysis. That is, the olefin adsorbs on the carbide surface and then diffuses to an alkylidene site, where metathesis takes place following the Chauvin mechanism [48,49]. The formation of a trapped precursor state facilitates this process by allowing the olefin to hop to many sites before it can desorb from the surface. This residence time, in which the trapped adsorbate can sample many sites, is a major difference between a reaction on a surface and in an organometallic complex. Gao et al. [50] have recently reported that di- σ -bonded ethylene reacts with CH_2 on a MoAl alloy surface to form a C_3 metallacyclobutane.

The determination of the structure and composition of the active site for olefin metathesis on β - Mo_2C is a very difficult task as XRD and NMR cannot be used. It is assumed that alkylidene-oxo formation on the surface occurs on a single metal site, leading to two multiple bonds to the same molybdenum atom. This conclusion is supported by the observation of surface oxo species (Fig. 4) following cyclopentanone dissociation. Migration of an oxygen atom from the dissociation site to a neighbouring metal atom to form an isolated oxo group is not expected, as the oxygen atom is likely to get trapped in a high-coordination adsorption

site between metal atoms. It is also consistent with the metathesis activity of alkylidene-W-oxo complexes as reported by Schrock and co-workers [51,52]. Very little is known about the active sites in high surface area supported olefin-metathesis catalysts, due to the inherent difficulties of studying heterogeneous catalysts and to the very low concentration of active sites. For example, Handzlik and Ogonowski [53] determined the number of active sites in a $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalyst as less than $\sim 0.4\%$ of the total number of Mo atoms. In contrast, very high coverages (>0.3 of a monolayer) of alkylidenes can be formed on the β - Mo_2C through the dissociative chemisorption of aldehydes or ketones. The resulting systems are not truly single-site [54] catalysts for the following two reasons. First, surfaces are intrinsically heterogeneous systems presenting edge, terrace and defect sites, for example. However, the extraordinarily high quality of the vibrational spectra of alkylidenes on β - Mo_2C [10,18] is consistent with a single site description. The second problem begins once the reaction is initiated. As mentioned above, the olefin reactant can sample many alkylidene sites during its residence time on the surface. Hence, once propagator species are formed it is possible that the consumption of the initiator, for example, may be relatively slow compared to that of the other alkylidenes, effectively making it into a spectator species [44]. However, when one considers that the latter two phenomena are intrinsic to surface chemistry on metals, it is appropriate to describe the alkylidene functionalized β - Mo_2C catalyst as a well-defined surface system.

In summary, molybdenum carbide formation is assumed to play a number of roles in inducing metathesis activity. First, it ensures the formation of terminal alkylidenes [9,10,18]. Second, carburization or reduction of molybdenum oxides may play a role in the formation of alkylidenes from olefin precursors. As we have pointed out elsewhere [18], the formation of trace quantities of ketones or aldehydes during the catalyst induction period could lead to alkylidene formation. Third, directional Mo–C bonding, and oxo formation, increases the oxidation state of molybdenum atoms at the carbide surface [11,13]. Fourth, carbide formation tames the reactivity of molybdenum [21,22]. Metallic molybdenum is so reactive that it would lead to dissociative chemisorption of olefins rather than to the synthesis steps required for metathesis. Finally, the carbide may be readily passivated by adding a small quantity of extra carbon to the surface. This happens intrinsically through decomposition of olefin reactants on the surface. The carbide then presents the ideal case of reactive metathesis sites isolated on an otherwise poorly reactive surface. As a result, incoming olefin reactants can diffuse to alkylidene sites with little chance of undergoing molecular decomposition or strong chemisorption. The latter five points are all related to the ‘materials gap’ concept sometimes invoked in discussions of the challenges facing the application of single crystal surface science to an understanding of heterogeneous catalysis. The ‘gap’ describes the differences between the substrate under study and the

active phase for the reaction being investigated. In the case of $\beta\text{-Mo}_2\text{C}$, as an olefin metathesis catalyst, there is effectively little or no 'materials gap'. Hence, it is a highly suitable system for further surface science studies of heterogeneous catalysis. In terms of applications, the ability to perform well-defined olefin-metathesis at carbide surfaces opens many opportunities in the use of heterogeneous catalysis to prepare of new hybrid organic-inorganic materials where the inorganic component is a metallic electrical conductor [8,10,55–59]. Such materials science work will always benefit from the fascinating continuing developments in the area of well-defined homogeneous olefin-metathesis catalysts [60,61].

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