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Carbon−Carbon Coupling and Linear Alkene Formation on Oxygen-Modified Mo(100) Surfaces

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Alkyl fragments bound to metal surfaces have been studied extensively under ultrahigh vacuum (UHV) conditions because of their importance as intermediates in the heterogeneous catalytic conversion of hydrocarbons.[1] In many of these studies the adsorbed alkyl groups have been produced by the dissociation of alkyl halides on metal surfaces.[2] However, the retention of halogen atoms on the surface is inevitable in this procedure and may interfere with the surface chemistry of interest. In this communication, we report the observation of remarkably facile carbon−carbon coupling reactions to form linear C_{2+} alkyl groups on Mo(100) surfaces, with submonolayer oxygen coverages, that have been dosed with gas phase methyl radicals to form adsorbed methyl groups in UHV. During temperature programmed desorption, the adsorbed alkyl groups selectively undergo β-hydrogen elimination to produce linear 1-alkenes up to C_5H_{10}. Formation of C_{2+} alkanes and partial oxidation products (alcohols, ethers, or aldehydes) is not observed. The chemistry of adsorbed methyl groups on the Mo surfaces is very sensitive to the surface structure and composition.

The experiments were performed in an UHV system equipped with instrumentation for low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), temperature-programmed desorption (TPD), and high-resolution electron energy loss spectroscopy (HREELS).[3] Two oxygen modified Mo(100) surfaces with coverages of ~0.9 monolayer (ML) and ~1.4 ML were prepared.[4] After exposing Mo(100) to O_2 at room temperature, a coverage of 0.9 ML-O was produced by annealing at 1350 K in UHV until LEED showed a (2×2) + weak(4×2) pattern, and the 1.4 ML-O coverage was produced by annealing at 950 K until LEED showed a diffuse(1×1) pattern.[8,9] CH_3 radicals were dosed onto the O/Mo(100) surface at 325 K, without coadsorption of side products, by pyrolysis of azomethane in a quartz tube directed toward the sample.[10] More details about the generation of gas-phase methyl radicals in UHV can be found in refs 11 and 12. Note that the translational energy of CH_3 radicals is thermalized to the quartz tube temperature which is ~1200 K.[12] Figure 1 shows TPD results after dosing CH_3 to saturation coverage on 0.9 ML O/Mo(100) and 1.4 ML O/Mo(100). For both surfaces, the main hydrocarbon species in TPD is CH_4 (16 amu) which desorbs over a broad temperature range from 370 to 620 K. Because H_2 does not adsorb on these surfaces at 320 K, formation of CH_4 indicates that methyl groups dehydrogenate to form CH_x ($x \leq 2$) and either adsorbed hydrogen or hydroxyl groups.[3,13] Surface hydrogen then reacts either with intact CH_3 to produce CH_4, with adsorbed hydrogen to produce H_2, or with hydroxyl to produce H_2O at 380 = 650 K on the 0.9 ML-O surface and at 380 = 550 K on the 1.4 ML-O surface.[14] Desorption of CO occurs at 380−650 K (α-CO) from both surfaces and at 750−960 K (β-CO) only from the 0.9 ML-O surface. Desorption at 31 amu (CH_3O^+) and 29 amu (CHO^+) was undetectable, indicating that partial oxidation of adsorbed methyl to methanol or formaldehyde does not occur.[15] No surface carbon was detectable by Auger following TPD.

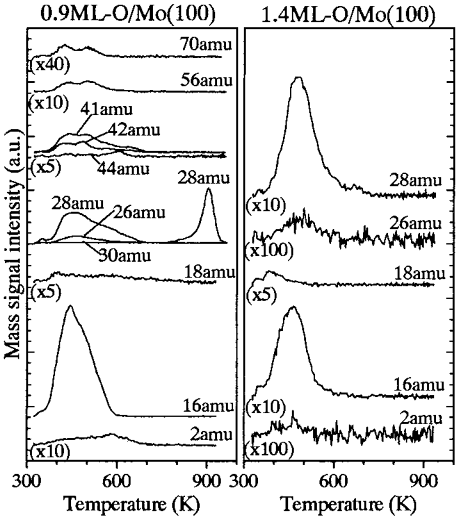

Figure 1. TPD after dosing CH_3, from the pyrolysis of azomethane, to near saturation coverage on 0.9 ML-O and 1.4 ML-O surfaces at 325 K. The heating rate was ~3 K/s.

The desorption peaks detected at 26, 41, 42, 56, and 70 amu were identified as alkenes by least-squares fitting the TPD spectra from 23 masses to the measured fragmentation patterns of C_1−C_5 alkanes, alkenes, and oxygenates. The yield of C_2−C_5 alkenes was strongly dependent on the oxygen coverage. C_2−C_5 alkenes accounted for 16% of the carbon adsorbed on the 0.9 ML-O surface. On the 1.4 ML-O surface, only 1% of the carbon appeared as C_2H_4 (26 amu), and no higher alkenes were detectable. Desorption of C_{2+} alkanes (for example, C_2H_6 at 30 amu and C_3H_8 at 44 amu) was not detectable. The small 44 amu peak at 600 K corresponds to a trace of CO_2.

The hydrocarbon product yields, in units of the clean Mo(100) surface atom density, are displayed on a log scale in Figure 2. The distribution of C_{2+} alkenes follows a Schulz-Flory distribution, the log(yield) decreases linearly with the carbon number, consistent with a growth mechanism involving sequential addition of C_1 units. The yield for sequential alkenes from the 0.9 ML-O surface decreases by about 70%, indicating a chain growth probability of ~0.3. By analogy to the Fischer−Tropsch synthesis

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[1] Bent, B. E. *Chem. Rev.* **1996**, *96*, 1361.

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[4] HREELS indicates that only 4-fold hollow oxygen is present on the 0.9 ML-O surface, but both 4-fold hollow and terminal oxygen (Mo═O) are present on the 1.4 ML-O surface.[3,5,6] Previous studies of these surfaces showed that the 0.9 ML-O surface has metallic properties and the 1.4 ML-O surface has the oxide properties of MoO_2.[7]

[5] Meyer, J. A., Ph.D. Thesis, Brown University, 1990.

[6] Kim, S. H.; Stair, P. C., unpublished results.

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[10] The exposure reported here is calculated from the background pressure rise. It is not corrected for the amount of CH_3 produced in the pyrolysis and for the pressure enhancement at the crystal surface due to the dosing geometry.

[11] Peng, X. D.; Viswanathan, R.; Smudde, G. H.; Stair, P. C. *Rev. Sci. Instrum.* **1992**, *63*, 3930.

[12] Fairbrother, D. H.; Briggman, K. A.; Dickens, K. A.; Stair, P. C.; Weitz, E. *Rev. Sci. Instrum.* **1997**, *68*, 2031.

[13] Smudde, G. H.; Yu, M.; Stair, P. C. *J. Am. Chem. Soc.* **1993**, *115*, 1988.

[14] In the desorption profiles for 18 amu, a small peak near 390 K decreased with CH_3 exposure, indicating that it originates from background water adsorption; however, the intensity of the H_2O peak above 450 K increased with CH_3 exposure. The high-temperature H_2O desorption results from reactions of surface OH groups.

[15] In a check experiment, adsorbed methoxy was generated on O/Mo(100) by dosing CH_3OH at a surface temperature of 325 K. The gaseous products in TPD were CO, CH_3OH, HCHO, CH_4, H_2, and a small amount of H_2O, but no C_2H_4. The TPD profiles were different from those after dosing CH_3.

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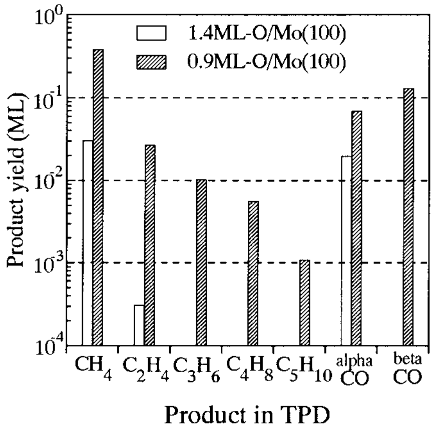
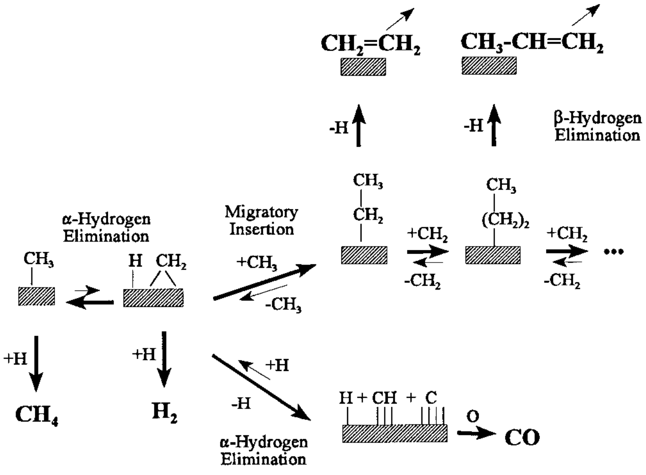


Figure 2. Distribution of desorption products containing carbon. The product yield has been calculated from fitting the integrated areas of TPD for m/e = 15, 16, 26, 28, 39, 41, 42, 54, 55, 56, and 70 amu with fragmentation and ionization probabilities for CH_4, CO, and the linear alkenes from C_2 to C_5 in the mass spectrometer ionizer. C_2-C_5 alkenes accounted for 16% of the carbon adsorbed on the 0.9 ML-O surface.

Scheme 1



process, we surmise that migratory insertion of methylene into the C-surface bond of another adsorbed alkyl group is the most likely mechanism for C−C bond formation.[16] The absence of ethane indicates that direct coupling of adsorbed methyl groups does not occur. Likewise, the formation of ethylene by either the concerted reaction of two methyl groups or the condensation of two methylene groups cannot explain the formation of C_3 to C_5 alkenes since the ethylene would desorb directly from the surface at the reaction temperature, 320 K.[6]

Scheme 1, adapted from ref 1, represents the reactions consistent with the chemistry observed for methyl groups adsorbed on O/Mo(100). Molecules desorbed into the gas phase are indicated in bold. The occurrence of this remarkably complex chemistry starting from a simple alkyl species suggests that all the reactions leading to these products must proceed simultaneously. The evolution of C_2-C_5 alkenes at >380 K is reaction-limited and not desorption-limited.[6] The rate-limiting step in alkene formation is most likely β-hydrogen elimination from adsorbed C_{2+} alkyl groups.[16] Desorption of CH_4 and H_2 is also reaction-limited. Since the onset of CH_4, H_2, and alkene desorption is at the same temperature, their formation proceeds through a common rate-limiting step, i.e. the release of atomic hydrogen on the surface. However, the reaction of adsorbed CH_3 with the surface hydrogen produced by β-hydrogen elimination can account for only a small fraction of the methane yield, particularly on the 1.4 ML-O surface. Therefore, α-hydrogen elimination from adsorbed CH_x and β-hydrogen elimination from adsorbed C_{2+} alkyl groups must proceed simultaneously. The absence of alkanes from hydrogenation of surface alkyl groups is consistent with the chemistry of ethyl groups on Ni(100); without coadsorbed atomic hydrogen, β-hydrogen elimination is the preferred reaction path.[17] Surface hydrogen, produced by dehydrogenation of CH_3 on O/Mo(100), is primarily consumed by hydrogenation of CH_3 to CH_4 because of the much larger coverage of CH_3 compared to that of other alkyl groups.[13]

CH_4 comprises $\sim$60% of the molecules desorbed from both surfaces, indicating that the majority species on the surface before TPD is CH_3. The formation of alkenes vs CO is largely determined by the relative rates of migratory insertion vs dehydrogenation of CH_2. During TPD, the atomic carbon combines with surface oxygen to form CO. Thus, the alkene and CO yields indicate that the methylene insertion/dehydrogenation branching ratio is 0.34 and 0.01 on the 0.9 ML-O and 1.4 ML-O surfaces, respectively. Since the kinetics of methane and CO formation and hence the CH_x dehydrogenation rate are similar on the two surfaces (similar TPD spectra), it appears that the rate of migratory insertion increases by a factor $\sim$30 on the 0.9 ML-O surface relative to the 1.4 ML-O surface. This is the key to the observed C−C bond formation on the 0.9 ML-O surface.

The effect of preadsorbed oxygen on the rate of migratory insertion can be correlated with changes in the physical properties of the O/Mo(100) surface at oxygen coverages near 1 ML.[4] Up to 1 ML coverage, oxygen forms a chemisorbed phase with the oxygen atoms located in 4-fold hollow sites on the Mo(100) surface. The surface polarizability is consistent with a metallic electronic structure and the formal oxidation state of the surface molybdenum atoms is 1.0. Just above 1 ML oxygen coverage, the electronic polarizability of the surface changes to a value consistent with oxide formation; the molybdenum oxidation state increases to 4.0, and the surface structure becomes disordered.[8,9] In view of these substantial changes in surface properties, it is not surprising that there is a strong effect on surface chemistry. For example, the selectivity in catalytic hydrogenolysis of methylcyclopropane over oxygen-modified Mo(111) surfaces has been attributed to the formation of Lewis acid sites when the oxygen coverage exceeds 1 ML.[7] At the present time it is not clear why the rate of migratory insertion is suppressed so strongly above 1 ML oxygen coverage on Mo(100) while the rates of CH_x dehydrogenation and CH_3 hydrogenation are apparently unefected. The effect cannot be explained simply by the bimolecular kinetics resulting from an increase in the CH_3 coverage on the 0.9 ML-O surface. For CH_3 coverages producing almost the same yield of CH_4 (data not shown), the yield of C_2H_4 is $\sim$8 times higher on the 0.9 ML-O surface than on the 1.4 ML-O surface.[6] Similarly, facile C−C bond formation cannot be simply attributed to the metallic properties of molybdenum surfaces. It was not reported for CH_3 adsorption on the Mo(110) surface[18] but has been observed on the clean and oxygen-covered Ni(100) surface.[19] Additional experiments are required to understand this interesting chemistry.

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