Probing the Role of Oxygen Coordination in Hydrocarbon Oxidation: Methyl Radical Addition to Oxygen on Mo(110)

K. T. Queeney, D. A. Chen, and C. M. Friend*
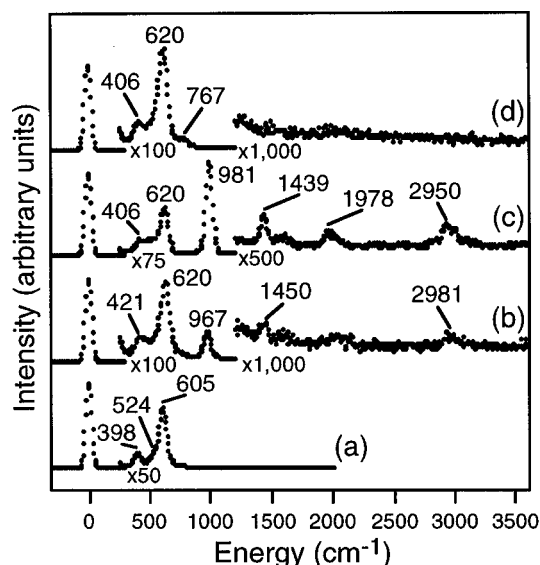
*Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138*

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Oxidation of alkanes, especially methane, to form essential chemical starting materials comprises a central problem in heterogeneous catalysis. Oxides of molybdenum are specifically known to oxidize methane to formaldehyde;[1–5] however, there is considerable debate[3,4,6,7] over whether terminal (Mo=O) or bridging oxygen atoms are the active species. Herein we report studies on the addition of gas-phase methyl radicals[8] to oxygen on Mo(110) and the microscopic reverse, methyl radical evolution from methoxy derived from methanol.[9,10] Analysis of both these pathways indicates that methoxy formation on oxidized Mo(110) does *not* directly involve terminal Mo=O sites.

All experiments were performed in a stainless steel ultrahigh vacuum chamber, described previously.[11] The protocols for temperature programmed reaction experiments and crystal cleaning have also been reported.[12–14] Electron energy loss spectra were acquired with an LK-2000 spectrometer, using a primary beam energy of 3 eV and specular detection. Azomethane was synthesized according to the protocol of Renaud and Leitch[15] and subsequently pyrolyzed to •CH₃ and N₂.[16,17]

Three distinct oxygen overlayers were prepared under different conditions.[18] The quasi-threefold site on Mo(110) is selectively populated by atomic oxygen when the surface is exposed to O_2 (~1×10^{-9} Torr)[19] at ~100 K and subsequently heated to 500 K. Alternatively, O_2 exposure (~1×10^{-9} Torr) at 1200 K for 5 min followed by cooling to 350 K in the oxygen atmosphere populates quasi-threefold and terminal surface sites (Mo=O) and deposits subsurface oxygen. If the crystal is

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(19) Directed dosing through a stainless steel tube of ~1 cm diameter is used for all oxygen exposures. The pressure rise reported is due to background pressure rise in the chamber during dosing and does not account for enhanced exposure at the crystal face.

Figure 1. Electron energy loss spectra, recorded at a crystal temperature of ~100 K, of (a) the quasi-threefold oxygen overlayer; (b) the overlayer in (a) after exposure to methyl radicals and subsequent annealing to 500 K; (c) the overlayer in (a) after exposure to methanol and subsequent annealing to 500 K; (d) the overlayer in (a) after exposure to methyl radicals and subsequent annealing to 700 K. Typical resolution was ~60 cm⁻¹.

cooled *without* O_2 present after the 1200 K exposure, there is quasi-threefold and subsurface oxygen but *no* terminal oxygen. Terminal and subsurface oxygen are readily identified by their electron energy loss signatures near 1000 and 735 cm⁻¹, respectively.[18]

Gas-phase methyl radicals react readily with oxygen bound in the quasi-threefold sites, based on electron energy loss data (Figure 1a,b). The oxygen overlayer exhibits characteristic losses for ν(Mo–O) and δ(Mo–O) at 605 and 398 cm⁻¹, respectively (Figure 1a). The small shoulder at 524 cm⁻¹ is attributed to ν(Mo–O) of oxygen in long-bridge sites, which are populated at lower coverages.[18] The spectrum obtained after exposing this surface to gaseous methyl radicals and subsequently heating to 500 K clearly corresponds to adsorbed methoxy, based on its correspondence to the reference spectrum obtained following methanol adsorption and heating to 500 K (Figure 1c). The loss at 967 cm⁻¹ in Figure 1b is attributed to ν(CO) of methoxy, as confirmed by the shift to 937 cm⁻¹ when •CH₃ reacts with an ¹⁸O overlayer (data not shown); the ν(C¹⁸O) energy predicted using the harmonic oscillator approximation is 941 cm⁻¹.[20] The features at 1450 and 2981 cm⁻¹ are assigned to δ(CH₃) and ν(CH) modes of methoxy.[21] Minor peak shifts for methoxy formed from •CH₃ addition versus methanol dissociation are attributed to a lower surface coverage of methoxy from •CH₃ addition. As expected, the ν(CO) frequency increases as a function of methoxy coverage due to enhanced dipole–dipole interactions. The feature at 1978 cm⁻¹ in the methanol spectrum (Figure 1c) is attributed to the overtone of ν(CO) from methoxy.[22]
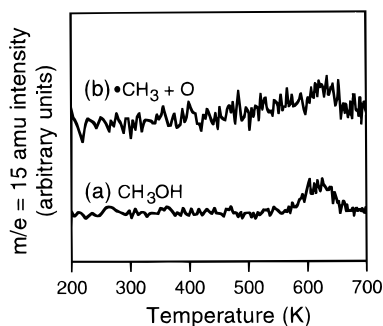
Spectroscopic identification of methoxy formation from methyl radical addition to quasi-threefold oxygen is confirmed

(20) The feature at 967 cm⁻¹ cannot be assigned to ν(Mo=O), because it disappears after annealing to 700 K (Figure 1d), whereas terminal oxygen on oxidized Mo(110) is stable to ~1200 K.[29] Furthermore, labeling Mo=O species with ¹⁸O results in a 50-cm⁻¹ red-shift of ν(Mo=O),[30] in contrast with the 30-cm⁻¹ shift seen here for ν(CO); both of these shifts agree well with their respective harmonic oscillator predictions.
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Figure 2. Temperature programmed reaction data for $m/e = 15$ (•CH₃) evolved from (a) methanol adsorbed on the quasi-threefold oxygen overlayer and (b) methyl radicals added to the quasi-threefold oxygen overlayer.[35] The adsorption temperature was 100−120 K; however, the surface exposed to methyl radicals was heated to 500 K prior to temperature programmed reaction to minimize background from methane evolved below 600 K in (b). The heating rate was 5−7 K s⁻¹.

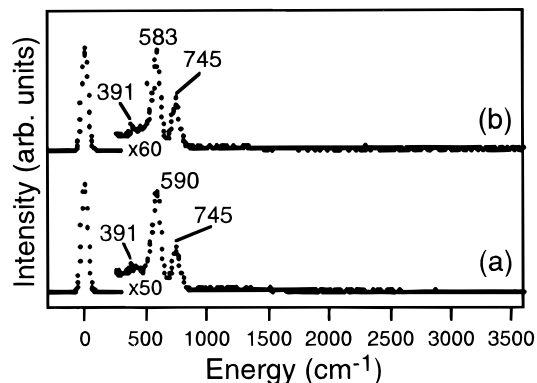by temperature programmed reaction experiments (Figure 2b). Specifically, gaseous methyl radicals are evolved at ∼625 K, which is characteristic of methanol decomposition via a methoxy intermediate on more highly-oxidized Mo(110),[9,10,23] and is shown in this work to occur as well for methanol reaction on the quasi-threefold oxygen overlayer (Figure 2a).

Addition of methyl radicals to oxygen in the quasi-threefold sites indicates that terminal oxygen is *not* required for this process. To further probe for a special role of Mo=O species in methyl oxidation chemistry, vibrational characteristics of the microscopic reverse—methoxy decomposition to methyl and adsorbed oxygen—were studied. Importantly, when methoxy is formed via methyl addition to the quasi-threefold overlayer, no Mo=O species are detected in electron energy loss spectra obtained after methyl radical evolution at 625 K (Figure 1d). The same result is obtained after decomposition of methoxy formed via methanol adsorption.

Further evidence that terminal oxygen is not essential for either methyl radical evolution from methoxy or methyl radical addition to oxidized Mo(110) comes from comparison of methyl radical and methanol reactivity on highly-oxidized Mo(110) with and without Mo=O. Methoxy is formed by methyl radical addition to oxygen in either case, based on the appearance of characteristic methoxy vibrational losses and the observation of methyl radical evolution at ∼625 K (data not shown). Importantly, there is no evidence that C−O bond scission in methoxy deposits Mo=O species. Specifically, when the highly-oxidized overlayer without terminal oxygen is exposed to either methanol or methyl radicals to form methoxy, and subsequently heated to 700 K (past the temperature of methyl radical evolution), no Mo=O species are left behind, as illustrated by the lack of any ν(Mo=O) peaks after reaction of methanol on this overlayer (Figure 3).

The facile addition of methyl radicals to oxygen bound in quasi-threefold sites on Mo(110) is consistent with the tendency of methoxy to bind in high coordination sites on other metal surfaces[24−26] and supports a semiempirical (ASED-MO) calculation which predicts a quasi-threefold binding site for

Figure 3. Electron energy loss data of (a) the highly-oxidized Mo-(110) surface *without* Mo=O species and (b) the surface in (a) after exposure to methanol and subsequent annealing to 700 K, i.e., after methyl radical evolution. In both cases, the oxygen overlayer was prepared with ¹⁸O₂, to increase the energy difference between ν-(Moₓ¹⁸Oᵧ) (arising from subsurface oxygen)[18] at 745 cm⁻¹ and ν(Mo=¹⁶O) at ∼980−1000 cm⁻¹. Resolution was 59−60 cm⁻¹.

methoxy on clean and oxygen-covered Mo(110).[27] Therefore, addition to Mo=O would most likely require migration of the methoxy or would lead to unstable binding.

Although methoxy forms readily on Mo(110), methyl does not add to oxygen in fourfold sites on Mo(100); instead, metal−alkyl bonds are formed, leading to eventual hydrocarbon production.[28] These results indicate a strong structural sensitivity of this reaction. Electronic structure calculations are planned to evaluate structural effects on these two surfaces. Further studies are also underway to determine the possible role of Mo=O species in the stabilization of methoxy species formed by methyl radical addition.

(23) Methyl radical evolution seems to be sensitive to the overall degree of Mo oxidation, since no •CH₃ is observed to evolve from methoxy on MoO₃.[34] Since larger amounts of subsurface oxygen may be generated on Mo(110) by greater exposures of O₂ at 1200 K, it is possible that eventually increased oxidation of Mo(110) will shut down this pathway as well. Studies are underway to address this point.

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