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C−O Bond Formation by Direct Addition of Methyl Radicals to Surface Oxygen on Rh(111)

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Alkane oxidation is an industrial process of the utmost importance. Recently, high selectivities for production of CO and H_2 from alkane oxidation have been achieved using rhodium monolith catalysts.[1−3] In an effort to develop a fundamental understanding of the operative reaction mechanisms, we have been studying the oxidation of alkyls on oxygen-covered Rh(111)[4,5] and have proposed that alkoxides are formed by the addition of alkyls to surface oxygen on oxygen-covered Rh(111). Herein, we report that methoxy is formed by the direct addition of methyl radicals to surface oxygen at 100 K.

Azomethane, synthesized using a literature preparation,[6] is pyrolyzed in a heated quartz tube to produce $\cdot CH_3$ and N_2.[7] The yield of methyl is estimated to be 30%; methane and small amounts of ethane are also formed. No intact azomethane is detected. All experiments are performed in an ultrahigh-vacuum chamber, with a base pressure below 1×10^{-10} Torr, described in detail previously.[8] The preparation of the crystal[9] and oxygen overlayer[10] and the procedures used in data collection[11] are also described elsewhere.

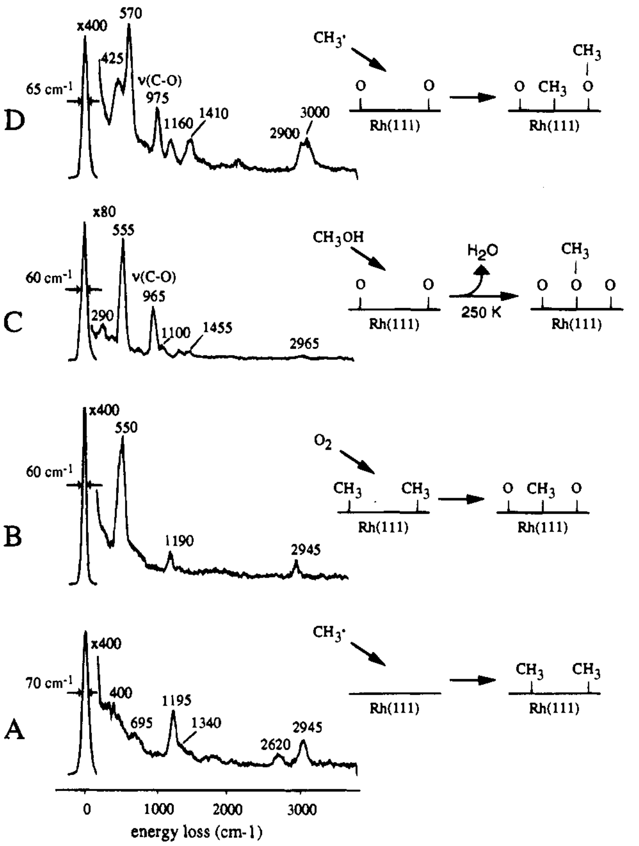

Figure 1. High-resolution electron energy loss spectra following (A) exposure of clean Rh(111) to methyl radicals at 100 K; (B) exposure of clean Rh(111) to methyl radicals, followed by exposure to dioxygen at 100 K; (C) multilayer exposure of CH_3OH on Rh(111)-p(2×1)-O annealed to 250 K; and (D) exposure of Rh(111)-p(2×1)-O to methyl radicals at 100 K. All oxygen is ^{16}O.

Adsorbed methoxy and methyl are detected following exposure of oxygen-covered Rh(111) to methyl radicals for all combinations of methyl (0.1−0.25 monolayers) and oxygen (0.2−0.5 monolayers) coverages studied (Figure 1D). Modes due to methoxy are assigned by comparison to spectra obtained for CH_3O produced from CH_3OH dissociation on Rh(111)-p(2×1)-O (Figure 1C, Table 1).[12,13] The mode at 975 cm^{-1} is unequivocally assigned to the C−O stretch in methoxy on the basis of the shift to 940 cm^{-1} when methyl reacts with ^{18}O-labeled overlayers. The strong loss at 570 cm^{-1}, due to the Rh−O stretch, also shifts to 530 cm^{-1} on ^{18}O-covered Rh(111). The peak near 2100 cm^{-1} is attributed to dinitrogen and disappears by 200 K, as N_2 desorbs.[14] Peaks are assigned to adsorbed methyl by comparing the data obtained following exposure of Rh(111)-p(2×1)-O to $\cdot CH_3$ to analogous experiments for clean Rh(111) (Figure 1A, Table 1).[15−17] The peaks associated with CH_3O persist above 250 K. Adsorbed CO is subsequently formed from CH_3O dehydrogenation.[18]

Temperature-programmed reaction data confirm that carbon−oxygen bonds are formed in the direct reaction of methyl radicals with surface oxygen on Rh(111)-p(2×1)-O at 100 K. Carbon monoxide evolves around 440 K, the measured desorption temperature for CO,[19] and CO_2 around 400 K during temperature-programmed reaction following exposure of Rh(111)-p(2×1)-O to $\cdot CH_3$. Oxidation of surface carbon yields carbon dioxide above 500 K, whereas CO oxidation occurs near 400 K on Rh(111)-p(2×1)-O. Small amounts of formaldehyde also evolve around 290 K in temperature-programmed reaction following exposure of Rh(111)-p(2×1)-O to methyl radicals, consistent with our observation of formaldehyde formation from methoxy on Rh(111)-p(2×1)-O at this temperature.[20] Surface methyl, also produced during the exposure of Rh(111)-p(2×1)-O to gaseous $\cdot CH_3$, undergoes competing hydrogenation to methane at 300 K, and dehydrogenation to atomic carbon.[21] No other products, in particular, no C_2 products, are formed.[22]

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(14) Dinitrogen desorbs from Rh(111)-p(2×1)-O at ~135 K and from clean Rh(111) at ~175 K.[19]

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(17) The weakened ν(CH) coordinate at 2620 cm^{-1} on clean Rh(111) is absent in the methyl adsorbed on oxygen-covered Rh(111), independent of the order of adsorption (Figure 1A,B,D). The observed methyl stretching frequencies of 2900 and 3000 cm^{-1} are in good agreement with those observed for unperturbed methyl ligands in transition metal complexes.[24]

(18) The ν(C≡O) mode at 2060 cm^{-1} appears upon heating to 300 K. Similar results were obtained for thermal treatment of CH_3O formed from CH_3OH on Rh(111)-(2×1)-O.

(19) Bol, C. W. J.; Friend, C. M. Unpublished data.

(20) Contrary to the observations of Solymosi etal.[23] we observe small amounts of formaldehyde evolution around 290 K in the reaction of methanol on oxygen-covered Rh(111) at the highest oxygen coverages.

(21) At least part of the methane is formed via reaction of surface methyl with hydrogen derived from methoxy dehydrogenation. When methyl reacts on oxygen-covered Rh(111) preexposed to d_3-methanol, both d_0- and d_1-methane are formed. Molecular desorption of methane does not contribute to the evolution at 300 K, given that it desorbs from Rh(111)-p(2×1)-O around 140 K.

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Table 1. Vibrational Assignments of High-Resolution Electron Energy Loss Spectra, Corresponding to Figure 1A−D[a]

CH_3 on Rh(111), 100 K	CH_3 adsorbed on O-covered Rh(111), 100 K[b]	CH_3O from CH_3OH on Rh(111)-p(2×1)-O, 250 K	reaction of CH_3 on Rh(111)-p(2×1)-O, 100 K[c]		assignment
			CH_3	CH_3O	
		290			$\nu(Rh{-}OCH_3)$
400			425 (nr)[d]		$\nu(Rh{-}CH_3)$
	550	555		570 (530)	$\nu(Rh{-}O)$
695					$\varrho(CH_3)_{methyl}$
		965		975 (940)	$\nu(C{-}O)_{methoxy}$
		1100			$\varrho(CH_3)_{methoxy}$
1195	1190		1160 (1160)		$\delta_s(CH_3)_{methyl}$
1340			nr		$\delta_a(CH_3)_{methyl}$
		1455		1410 (1410)	$\delta_a(CH_3)_{methoxy}$
2620					$\nu_s(CH_3)_{methyl}$
2945	2945	2965	2900/3000	(2910/3000)	$\nu_a(CH_3)$

[a] All oxygen is ^{16}O, unless otherwise noted. [b] Data corresponds to Figure 1B; CH_3 was adsorbed first, followed by oxygen ($\theta_{methyl} \approx 0.10$, $\theta_O \approx 0.20$). [c] Numbers in parentheses indicate frequencies for reaction on ^{18}O-labeled surface. [d] Not resolved.

Methoxy is *not* formed when methyl is adsorbed on clean Rh(111) first, followed by oxygen adsorption (Figure 1B). All observed losses can be assigned to adsorbed methyl and atomic oxygen. No losses indicative of methoxy are observed at 100 K, nor after annealing up to 300 K, in 50 K intervals, at any combination of oxygen (0.1−0.3 monolayers) and methyl (0.1−0.3 monolayers) coverages studied. Instead, methyl coadsorbed with surface oxygen dehydrogenates to surface carbon. The adsorbed carbon subsequently reacts with oxygen to form CO and CO_2, during temperature-programmed reaction following exposure of clean Rh(111) to gaseous $^{\bullet}CH_3$ and subsequent adsorption of oxygen at 100 K. Importantly, no CO or CO_2 evolves below 440 K, confirming that CH_3O is not formed from the insertion of oxygen into the $Rh{-}CH_3$ bond. Recombination with surface hydrogen is a competing pathway, leading to methane evolution at 215 K.

Both temperature-programmed reaction and high-resolution electron energy loss data indicate methoxy formation by the direct reaction of methyl radicals with surface oxygen at low temperature. A mechanism in which a "hot" methyl precursor adds to surface oxygen cannot be excluded on the basis of our data. However, methoxy is *not* formed through the reaction of equilibrated adsorbed methyl and oxygen. These observations indicate that a high steady-state oxygen coverage will favor methoxy formation from methyl radicals produced from methane activation, whereas low coverages will favor the formation of surface-bound methyl, which dehydrogenates to yield mainly CO.

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(22) For high $^{\bullet}CH_3$ exposures, evolution of ethane is observed around 140 K, attributed to the molecular desorption of ethane, present as impurity in the radical source, although the recombination of $^{\bullet}CH_3$ on the surface at 100 K at high coverage cannot be excluded on the basis of our data.

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