Effect of Oxygen Precoverage on the Reactivity of Methanol on Ru(001) Surfaces

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The thermal decomposition of methanol on oxygen modified Ru(001) surfaces was investigated by reflection−absorption infrared spectroscopy (RAIRS), under UHV conditions. The stability of the different intermediates was interpreted in terms of the oxygen coverage (θ_O ranging from 0.25 to 0.75 ML), as well as of the methanol dose. For a low methanol exposure at 90 K, dissociative adsorption into methoxide (CH_3O-) is favored by increasing oxygen coverage up to 0.6 ML, becoming almost inhibited for $\theta_O = 0.75$ ML. The reactivity of methoxide is also enhanced by increasing θ_O from 0.25 to 0.6 ML, as the oxidation temperature drops from 130 to 100 K. Regardless of the oxygen coverage, the oxidation of methoxide yields the intermediate formaldehyde (H_2CO), whose stability decreases with increasing θ_O. Formate ($HCOO-$) was only identified on surfaces with $\theta_O \geq 0.5$ ML, in the temperature range 100 K $\leq T <$ 130 K, with maximum yield for $\theta_O \approx 0.6$ ML. This was the first spectroscopic observation of the intermediate formate in the decomposition of methoxide on Ru(001) surfaces, proving the participation of preadsorbed oxygen in the reaction. A more stable intermediate, formyl (HCO), which decomposes above 190 K, was only detected on surfaces with $\theta_O = 0.25$ and 0.6 ML, probably being formed on the domain boundaries present on these surfaces, namely Ru(001)−(2×2)-O/clean Ru(001) and Ru(001)−(2×1)-O/Ru(001)−(2×2)-3O, respectively. For a high methanol exposure (methoxide at saturation coverage), methoxide is stabilized by neighboring interactions, and the oxidation process does not occur below 130 K, even for high oxygen coverages ($\theta_O = 0.6$ ML). All of the intermediates other than formate were detected. Either this decomposition channel (the deep oxidation of methanol) is inhibited for high methoxide coverage or any formate produced is not stable on the surface at such high temperatures.

I. Introduction

The control of a reaction path by modification of the catalyst's surface is a key issue in surface science and in heterogeneous catalysis. Hence, all of the effort to clarify the role of modifiers on the reactivity of metal surfaces toward relevant processes is worthy.[1,2] Great interest has been devoted, in recent years, to the effect of preadsorbed oxygen that increases the surface acidity, due to its high electronegativity. Ruthenium surfaces are of particular interest, as they present unique catalytic properties that may be successfully capitalized on at industrial scale, namely in improving the efficiency of direct methanol fuel cells.[3−5] On Ru(001), the oxygen atoms sit on 3-fold hcp sites, forming a (2×2)-O structure for a coverage of 0.25 ML[6,7] and a (2×1)-O overlayer for 0.5 ML,[7,8] at room temperature. Two additional phases were predicted by density functional theory (DFT) calculations: (2×2)-3O and (1×1)-O, corresponding to oxygen coverages of 0.75 and 1 ML, respectively.[9] These phases were later obtained upon heavy dosages of molecular oxygen or NO_2, at high sample temperatures, having been identified by quantitative LEED (low energy electron diffraction),[10] STM (scanning-tunneling microscopy),[11,12] and HREELS (high-resolution electron energy loss spectroscopy).[13] It was shown that the strongly chemisorbed oxygen induces reconstruction in the first two layers of the substrate, which slightly varies depending on the coverage.[6,10]

Methanol is not only a good model molecule for studying the decomposition of oxygenated organic compounds but has

relevant industrial applications.[5,14] This justifies the great interest in investigating its chemistry on various metal surfaces, namely Mo(110),[15] Ru(001),[16−20] Rh(111),[21] Ni(111),[22] Ni(100),[23] Pd(111),[24] Pt(111),[5,25,26] Cu(110),[14] Cu(111),[27,28] and Ag(110),[29] among others. On most surfaces, methanol undergoes O−H bond cleavage, with formation of adsorbed methoxide (H_3CO-). This mechanism is promoted by preadsorbed oxygen, which is essential on Ag, Au, and Cu surfaces at low temperature.[30,31] Whereas on the more reactive metals (groups VIB and VIII), methoxide typically decomposes to adsorbed CO and H, and on group IB metal surfaces only a partial dehydrogenation to formaldehyde (H_2CO-) occurs.[14,31] The mechanism of deep oxidation of methanol, which leads to the formation of CO_2 instead of formaldehyde or CO, has not been fully investigated. It has been reported that, on Pt(111), the production of CO_2 involves an essential process consisting on the reaction of methoxide with molecularly adsorbed oxygen, toward the intermediate formate (HCOO-).[32,33] This species has also been identified on Ag(111)[31] and Cu(100)[34] as the result of a minor methoxide decomposition path, promoted by surface oxygen, and, in the case of Cu(100), only for a very narrow range of oxygen coverages.

On clean Ru(001), the adsorption of methanol has been studied by EELS (electron energy loss spectroscopy),[16,17] RAIRS (reflection−absorption infrared spectroscopy),[18,35] TPD (temperature programmed desorption),[16] LITD (laser induced thermal desorption),[19] and ESDIAD (electron-stimulated desorption ion angular distribution).[20] At low temperature (85−90 K) and for submonolayer coverages, methanol adsorbs only dissociatively,

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as methoxide (CH$_3$O−).[16,18] At saturation coverage, it was proposed that a minor fraction of methanol (20%) follows another reaction channel that involves C−O and C−H bond breaking, producing water (identified by TPD), H$_{(ads)}$, and C$_{(ads)}$.[16] Different bonding sites and geometries, depending on temperature and coverage, were proposed for methoxide on Ru(001) and tentatively correlated with the corresponding C−O stretching wavenumbers.[18] This is not an easy task, since coverage has proved to influence the optimum site and the adsorption geometry and the "isolated molecule" situation is experimentally difficult to detect by vibrational spectroscopy. Recent DFT calculations point to the hcp sites as the most favorable for methoxide on Ru(001), acquiring an almost upright configuration.[36] The decomposition of methoxide on clean Ru(001) has proved to be coverage dependent as well. For low methoxide coverages, the only decomposition channel identified so far has been the complete dehydrogenation into CO and H$_2$.[19] At saturation coverage, this mechanism occurs by annealing in quasi-equilibrium steps, in the range between 110 and 320 K. A second decomposition path, consisting in a partial dehydrogenation into formaldehyde [η^2(C,O)-H$_2$CO], was induced by a one-step thermal activation from 130 K to at least 190 K. Direct adsorption at 190 K may yield formaldehyde in two bonding configurations (bridging [μ_2-η^2(C,O)-H$_2$CO] and chelating [μ_1-η^2(C,O)-H$_2$CO]), but this intermediate only forms on a previously passivated surface, by CO and/or atomic species.[18] Recombination with atomic hydrogen becomes a competing process as methoxide coverage increases, a fraction desorbing as methanol between 220 and 250 K.[19]

The research carried out on the decomposition of methanol on oxygen modified Ru(001) is scarce and concerns only the most common Ru(001)−(2×2)-O[20,37,38] and Ru(001)−(2×1)-O[37] surfaces. In what regards the methoxide yield, it is foreseeable that oxygen preadsorption imparts two kinds of effects: (i) it increases the surface acidity and, therefore, its capacity for adsorbing an electron donor such as methanol; (ii) it acts as a physical site blocker, thus inhibiting the surface capacity for adsorption. The first effect will predominate at low oxygen coverages. Comparing the Ru(001)−(2×2)-O with the clean surface, the major differences pointed out by TPD and EELS for methanol adsorption were, at saturation coverage, the elimination of the minor decomposition channel involving C−O bond cleavage and the fall by ∼20 K of the recombination temperature.[37] Besides, ESDIAD images have shown that such low oxygen coverage induces ordering of the methoxide layer above 120 K.[20] Recent RAIRS work on the decomposition of methoxide on the same modified surface allowed the identification of a different species, formyl [μ_3-η^2(C,O)-HCO], co-adsorbed with methoxide in a precursor configuration (lying down on the surface).[38] Formyl is not stable above 190 K. For higher oxygen precoverages ($\theta_O \approx 0.6$ ML), it has been proposed that methanol adsorbs only nondissociatively, due to the physical site blocking by oxygen atoms at this coverage.[37] In the absence of a systematic analysis of the oxygen and methanol coverage effects, a large number of questions remain to be answered.

It is the aim of the present work to clarify the effect of preadsorbed oxygen on the reactivity of methanol on Ru(001) surfaces. To reduce dipole coupling between neighbor methoxide species and thus highlight the oxygen effect, very low doses of methanol were adsorbed on oxygen phases ranging from 0.25 to 0.75 ML. The possibility of oxygen participation in the surface reactions, yielding relatively unstable intermediates, was investigated by RAIRS. In a second stage, the effect of
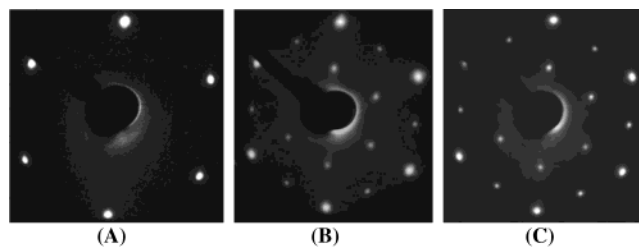
Figure 1. LEED patterns obtained at room temperature: (A) clean Ru(001), 75 V; (B) modified Ru(001)−O layer I (0.5 L of O$_2$), 72 V; (C) modified Ru(001)−O layer III (60 L of O$_2$), 66 V.

methoxide coverage on the stability of the different intermediates was analyzed.

II. Experimental Section

The experiments were performed in a Kratos Analytical bakeable ultrahigh-vacuum (UHV) chamber, operating at a base pressure of 10^{-10} Torr, described in detail elsewhere.[39] The chamber is equipped with a three-grid rear view LEED optics from SPECS and is coupled to a Mattson Research Series 1 FTIR spectrometer, with an external narrow-band MCT detector from EG&G Judson (800−4000 cm^{-1}). The Ru(001) surface was cleaned by sputtering/annealing cycles (2500 eV Ar$^+$ ions, for 30 min, followed by a quick anneal to 1200 K). Before each experiment, the cleanliness of the surface was tested by LEED, as well as by the RAIR spectrum of carbon monoxide at saturation coverage, at 90 K.[40] The gases were introduced through a leak valve, by back-filling the chamber with different dosages. Exposures are quoted in units of Langmuir (1 L = 10^{-6} Torr s), and the corresponding coverages, except those of oxygen, are not calibrated in absolute values. All of the RAIR spectra were obtained by co-addition of 1000 scans at 4 cm^{-1} resolution, keeping the crystal at 90 K, and are presented as the ratio against a RAIR spectrum obtained for the corresponding oxygen modified surface at the same temperature. Methanol (CH$_3$OH 99.8%+, from Fluka) and deuterated methanol-d_4 (CD$_3$OD 99.8%+, from Aldrich) were purified by distillation under vacuum (10^{-7} Torr) before use. Oxygen (O$_2$) N48 and nitric oxide (NO) N30 from Alpha Gaz were used.

Preparation of the Oxygen Modified Surfaces. The clean Ru(001) surface was exposed to various oxygen doses under different conditions, to obtain effective oxygen coverages in the range 0.25−0.75 ML. Layers I and II were prepared by adsorbing 0.5 L[38,41] and 20 L[42] of O$_2$, respectively, at 300 K, followed by flashing to 450 K, for ordering. The lower exposure promotes the formation of domains with a Ru−(2×2)-O superstructure,[41] not exceeding an oxygen total coverage of 0.25 ML, whereas the higher one is expected to produce an oxygen coverage of ∼0.5 ML. Layers III and IV were prepared by dosing 60 and ∼10^3 L of O$_2$, respectively, keeping the crystal at 600 K, and subsequently flashing it to ∼900 K.[11] The calibration of the effective oxygen coverages was made by LEED and by the RAIR spectra of probe molecules, as described in the next paragraph.

III. Results and Discussion

Characterization of the Ru(001)−O Surfaces. The (1×1) LEED pattern obtained for clean Ru(001) at room temperature, shown in Figure 1A, is characteristic of a long range ordered surface with hexagonal symmetry.[43,44]
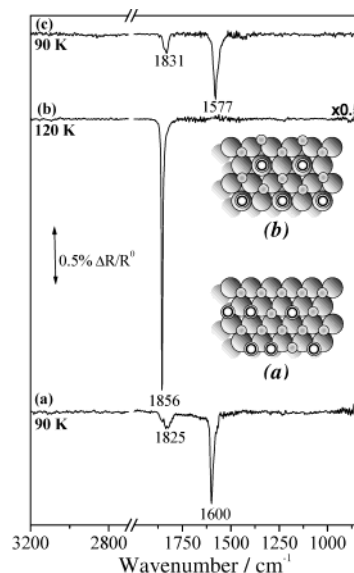
The LEED patterns of all the oxygen precovered surfaces were similar, with apparent (2×2) periodicity. Those referring to layers I and III are shown in Figure 1, parts B and C,

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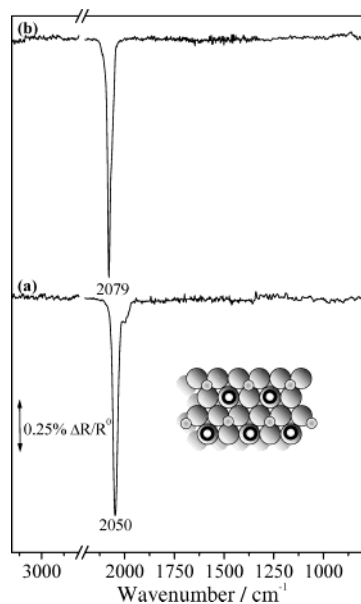
Figure 2. RAIR spectra of CO obtained for saturation coverage, at 90 K: (a) on layer I; (b) on layer II. *Inset*: top-view of the Ru(001)$-$(2×2)$-$(CO+O) surface structure: Large gray spheres, Ru atoms; small gray spheres, O atoms; Black ringed spheres, CO molecules.


Figure 3. RAIR spectra of NO obtained for saturation coverage: (a) on layer III, at 90 K; (b) after annealing to 120 K; (c) on layer IV, at 90 K. Insets: (a) top view of a possible Ru(001)$-$(NO+O) mixed structure for layer III (NO on hcp sites); (b) honeycomb Ru(001)$-$(2×2)$-$(NO+2O) structure: Large gray spheres, Ru atoms; small gray spheres, O atoms; White ringed spheres, NO molecules.

respectively. Such a pattern could be generated by three types of superstructures: (i) a hexagonally symmetric (2×2), labeled as Ru(001)$-$(2×2)-O; (ii) three degenerate domains of 2-fold symmetry, each having a (2×1) structure and rotated by 120° with respect to each other,[7,43] labeled as Ru(001)$-$(2×1)-O; (iii) a (1×1) structure with an additional (2×2) hole layer,[11] labeled as Ru(001)$-$(2×2)-3O. Given the very low oxygen exposure used to prepare layer I, Figure 1B is only consistent with a long range ordered Ru(001)$-$(2×2)-O phase. The patterns obtained for the remaining layers, however, are not conclusive on whether they correspond to a Ru(001)$-$(2×1)-O (more probable in the case of layer II), to a Ru(001)$-$(2×2)-3O structure, or even to large, ordered, domains of both (layers III and IV). To assess the effective oxygen coverage, in the absence of quantitative LEED, the RAIR spectra of adsorbed probe molecules (CO and NO), at saturation coverage, were used. A thorough analysis of CO on the Ru(001)$-$(2×2)-O layer has shown that the band assigned to on-top CO molecules grows and shifts from 2025 to 2051 cm^{-1} with increasing coverage.[42,45] This shift is ascribed essentially to dynamic dipole coupling, although a small contribution may arise from a chemical effect.[45] By exposing layer I to CO at saturation coverage, at 90 K, spectrum a in Figure 2 was obtained, where the νCO mode appears at 2050 cm^{-1}.

This shows that an ordered Ru(001)$-$(2×2)$-$(CO+O) surface (schematized in the inset) was obtained, confirming the Ru-(001)$-$(2×2)-O structure, which corresponds to $\theta_O = 0.25$ ML. The presence of minor clean Ru(001) regions cannot be excluded, since the νCO band is broader than expected.[45] In the CO spectrum shown in Figure 2b, obtained for layer II, the νCO mode appears at 2079 cm^{-1}, which is characteristic of CO adsorbed on a Ru(001)$-$(2×1)-O phase that implies an oxygen effective coverage of 0.5 ML.[42] The characterization of the denser oxygen layers III and IV by adsorption of CO was not conclusive, yielding nonreproducible results: the electronic repulsion between coadsorbed O and CO allows only the adsorption of a very small amount of CO, probably at domain boundaries.[10] In contrast, nitric oxide adsorbs on strongly localized sites on oxygen dense layers, rendering the RAIR

spectra of adsorbed NO a reliable tool for quantification of the oxygen coverage attained.[46] It has been proved by HREELS that the νNO mode for saturation on Ru(001) surfaces, at 90 K, depends on the oxygen precoverage:[13] for $\theta_O = 0.5$ ML, an ordered (2×1)$-$(NO+O) layer is formed,[46] originating a strong band at 1614 cm^{-1}; for $\theta_O = 0.75$ ML, the (2×2)$-$(NO+3O) layer forms,[13] and that mode shifts to 1580 cm^{-1}. The RAIR spectrum obtained for adsorbed NO at saturation coverage on layer III, at 90 K, is shown in Figure 3a. The spectrum corresponding to a subsequent anneal to 120 K is shown as well (Figure 3b).

In the spectrum at 90 K, there is a dominant band with maximum at ~1600 cm^{-1}, and a small one at ~1825 cm^{-1}. The strong band is assigned to the stretching mode of NO adsorbed on hcp 3-fold hollow sites, and the weaker one gives evidence of a small fraction of on-top molecules.[47] The excellent agreement with the HREELS results obtained for $\theta_O = 0.6$ ML and the LEED pattern point to layer III being formed by ordered domains of Ru(001)$-$(2×1)-O and Ru(001)$-$(2×2)-3O superstructures. Besides, the νNO band presents a low frequency shoulder (at ~1570 cm^{-1}), assigned to molecules adsorbed on 3-fold hcp hollow sites localized on (2×2)-3O domains, with six neighbor oxygen atoms. A schematic representation of a possible structure with two oxygen domains is made in inset a of Figure 3. Annealing the previous layer to 120 K results in a remarkable spectral change: a single, very intense (~5%), and narrow (fwhm ~ 7.5 cm^{-1}) band appears at 1856 cm^{-1}, assigned to the stretching mode of on-top NO molecules adsorbed as a very ordered layer. This behavior has been observed before by thermal activation of a (2×1)$-$(NO+O) layer.[46] It corresponds to a rearrangement of the 90 K layer, resulting in a well ordered honeycomb structure, as schematized in inset b of Figure 3: half of the O atoms migrate to fcc sites, which is not possible on a complete (2×2)-3O layer.[13] Thus, the RAIRS data at 120 K confirm the presence of (2×1)-O domains in layer III. Spectrum c in Figure 3 was obtained for NO at saturation coverage on layer IV, at 90 K. The main νNO band, at 1577 cm^{-1}, is characteristic of an ordered Ru(001)$-$(2×2)$-$(NO+3O)
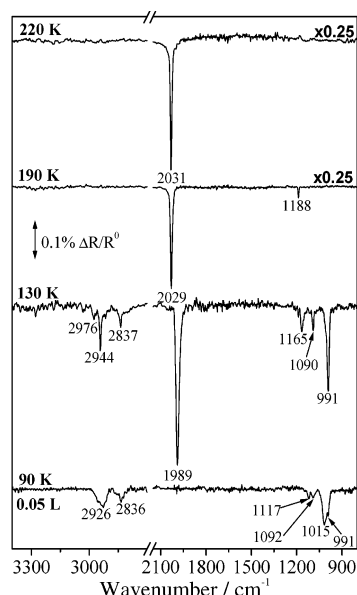
Figure 4. RAIR spectra obtained after exposing layer I ($\theta_O = 0.25$ ML) to 0.05 L of methanol at 90 K, and subsequently annealing up to 220 K. The spectra were scanned at 90 K.

structure, which corresponds to $\theta_O = 0.75$ ML. A small fraction of on-top NO is also observed (band at 1831 cm^{-1}).

In summary, the four modified Ru(001)−O surfaces prepared in this work correspond to $\theta_O = 0.25$, 0.5, 0.6, and 0.75 ML, with ordered Ru(001)−(2×2)-O/clean Ru(001), Ru(001)−(2×1)-O, Ru(001)−(2×1)-O/Ru(001)−(2×2)-3O and Ru(001)−(2×2)-3O structures, respectively.

Influence of the Oxygen Pre-Coverage on the Surface Intermediates. Adsorbing a very low dose of methanol (0.05 L) on layer I ($\theta_O = 0.25$ ML), at 90 K, led to the first RAIR spectrum shown in Figure 4.

Since there is no evidence of the νOH mode and taking into account previous results on Ru(001) surfaces,[16,18,35,37,38] dissociative adsorption is bound to have occurred with O−H bond cleavage, yielding methoxide (CH$_3$O−). The spectrum is weak, but there are unequivocal features: the νCO mode, broad and containing at least two components (at 991 and 1015 cm^{-1}), suggests that methoxide adsorbs as a nonhomogeneous layer, on different neighborhoods and/or sites. For a sufficiently low coverage, methoxide would tend to adsorb on the preferential sites (those of higher adsorption energy), originating a νCO narrow band. Although the exact nature of these sites has been clarified by DFT calculations for clean Ru(001),[36] so far it is not known for the Ru(001)−(2×2)-O surface. The exposure of methanol used here is very low, but it does not correspond to the methoxide "isolated molecule" limit, and therefore, other sites may be occupied as well. The C−H stretching region is not very informative on the bonding and geometry of methoxide, given the strong Fermi resonance between the overtones of the δCH$_3$ modes and the ν_sCH$_3$ that modifies the relative band intensities in this region.[27,35] The bands at 2926 and 2836 cm^{-1} are broad and not resolved, confirming the heterogeneity of the methoxide layer. A strong indication that a fraction of molecules is in a tilted configuration is provided by the small features at 1117 and 1092 cm^{-1}, which are assigned to ρCH$_3$ modes, only allowed under C_s or C_1 local symmetry. This RAIR spectrum indicates that there is no short range order. The absence of a methoxide LEED pattern, in addition to that of oxygen, indicates that neither is there a long range order or it is compatible with a (2×2) symmetry.

The decomposition of this methoxide layer was induced by heating the surface from 90 to 220 K, in 10 K steps. The spectra presented in Figure 4 correspond to the temperatures where relevant changes were observed. At 130 K, the νCO mode of methoxide appears as a single and narrow band at 991 cm^{-1}, the ν_sCH$_3$ becomes narrower at 2837 cm^{-1}, whereas the higher wavenumber region is resolved in two bands, at 2944 and 2976 cm^{-1}, with the latter being very weak. These assignments are not straightforward due to the above-mentioned coupling and possibility of different adsorption geometries. This matter was addressed by adsorbing, on the same surface, a partially deuterated probe, CHD$_2$OH, in which the CH stretching region is free of coupling. For a low coverage at 90 K, the corresponding RAIRS data showed that a significant fraction of methoxide-d_2 is adsorbed in a tilted geometry, presenting a broad and composed νCH band; by thermal activation, the RAIR spectrum of the unreacted methoxide-d_2 presents a single and narrow νCH band, characteristic of three C−H equivalent coordinates, evidencing that the C−O bond is perpendicular to the surface.[48] For CH$_3$O−, a similar behavior to CHD$_2$O− would be expected, and such upright geometry corresponds to a C_{3v} local symmetry. Accordingly, the narrow band at 2944 cm^{-1} and the feature at 2976 cm^{-1} in the spectrum at 130 K (Figure 4) are assigned to methoxide adsorbed in a C_{3v} local symmetry, specifically to the $2\times\delta_s$CH$_3$ (A$_1$) and $2\times\delta_{as}$CH$_3$ (A$_1$+E) modes, respectively, with borrowed intensity from the allowed ν_sCH$_3$ (also A$_1$), at 2837 cm^{-1}. The alternative assignment of one of these bands to the fundamental ν_{as}CH$_3$ (E) may be ruled out, since this mode is forbidden under C_{3v} symmetry. The band at 1090 cm^{-1} cannot be assigned to residual C_s methoxide, since it increases upon annealing. Neither could it be related to the forbidden rocking mode of C_{3v} methoxide. Therefore, it must be correlated to the νCO mode of another intermediate, namely formaldehyde (μ_2-η^2(C,O)-H$_2$CO).[49] Complementary identification of this species would be desirable. However, the ωCH$_2$ mode is expected to yield a very weak band on RAIRS: it was observed by HREELS, mostly due to an impact mechanism, between 1160 and 1280 cm^{-1} (depending on coverage).[49,50] This excludes the assignment of the rather strong band at 1165 cm^{-1} to formaldehyde. The complete analysis of the spectrum at 130 K must take into account the bands at 1989 and 1165 cm^{-1}. They are assignable, respectively, to the νCO mode of on-top carbon monoxide and to the same mode in a less oxidized intermediate, formyl (μ_3-η^2(C,O)-HCO).[38] We may conclude that, at 130 K, some methoxide undergoes dehydrogenation and the remaining rearranges to a notably homogeneous layer, oriented with the CO bond perpendicular to the surface. This ordering concurs with that proposed by other authors using ESDIAD.[20] The geometry acquired by this low-coverage methoxide layer is similar to that predicted for isolated molecules on clean Ru(001), by DFT calculations,[36] and has been observed on other metal surfaces, exclusively for very low methoxide coverages.[15,23]

The thermal decomposition into formyl and carbon monoxide proceeds until 190 K, as shown by the bands at 1188 and 2029 cm^{-1} that increase and shift due to more pronounced dipole coupling. At 220 K, only adsorbed CO is stable on the Ru(001)−(2×2)-O surface.

The influence of increasing oxygen coverage on the adsorption and decomposition of methoxide is shown in the spectra of Figures 5A and B, recorded from layers II ($\theta_O = 0.5$ ML) and III ($\theta_O = 0.6$ ML) dosed with 0.05 L of methanol, at 90 K.

At the adsorption temperature, the C−H stretching bands are shifted to higher wavenumbers in comparison with the corresponding spectrum in Figure 4, evidencing the expected
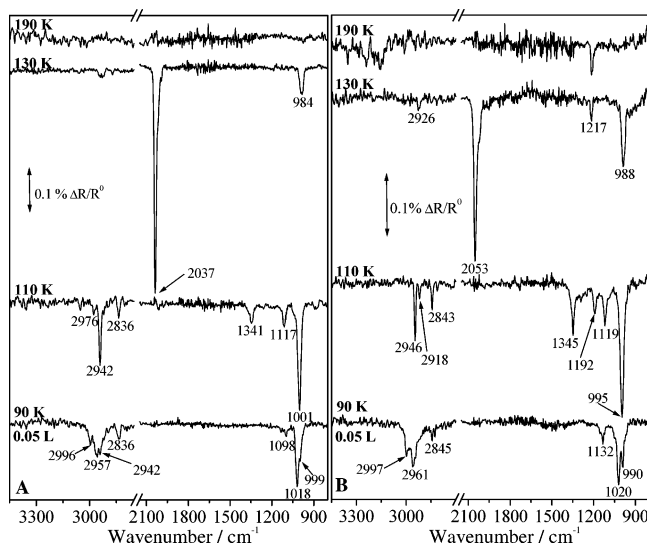
Figure 5. RAIR spectra recorded from (A) layer II (θ_O = 0.5 ML) and (B) layer III (θ_O = 0.6 ML), after being exposed to 0.05 L of methanol at 90 K, and subsequently annealed up to 190 K. The spectra were scanned at 90 K.

strengthening of the C—H bonds by coadsorbed oxygen.[37] However, there are similarities between the low coverage-low-temperature spectra on layers I, II, and III, namely the splitting of the νCO band (1018/999 and 1020/990 cm^{-1} in Figure 5, parts A and B, respectively) and the observation of the ρCH$_3$ mode (at 1098 and 1132 cm^{-1}, respectively). These reveal that the three layers are equivalent in what concerns the adsorption of methoxide on different domains and in local C_s or C_1 symmetry.

An oxygen coverage increase from 0.25 to 0.5 ML rises the methoxide reactivity, as on layer II, at 110 K, there is strong evidence of surface processes that only occur on layer I at 130 K: the formation of decomposition intermediates and the structural rearrangement of the remaining methoxide species. The presence of η^2-formaldehyde is revealed by the band at 1117 cm^{-1}, assigned to the νCO mode.[49,50] The methoxide νCO becomes a single narrow band (its fwhm decreases from 37 to 26 cm^{-1}) at a low wavenumber (1001 cm^{-1}) and increases (the corresponding integrated intensity increases from 0.027 to 0.037). These changes are consistent with a low local coverage, without significant dynamic dipole coupling, and a methoxide homogeneous distribution, probably on the most stable sites. The reorganization toward a C_{3v} local symmetry on layer II has been confirmed by adsorbing the partially deuterated molecule CHD$_2$OH.[48] Accordingly, in the spectrum at 110 K (Figure 5A), the band at 2836 cm^{-1} is assigned to the ν_sCH$_3$ mode, and those at 2942 and 2976 cm^{-1} are assigned to the $2\times\delta_s$CH$_3$ and the $2\times\delta_{as}$CH$_3$ modes in Fermi resonance with ν_sCH$_3$, respectively. On layer III (Figure 5B), the same type of reorganization is suggested by the RAIR spectrum at 110 K. The intermediate formyl is not detected on layer II, but, remarkably, it forms on layer III (the νCO band at 1192 cm^{-1}). A satisfactory explanation is that it forms preferentially on domain boundaries, where discontinuities in the oxygen overlayer and in the substrate reconstruction occur.[6] These boundaries exist on layer I (where clean Ru(001) domains were not excluded) and on layer III (where Ru(001)−(2×1)-O and Ru(001)−(2×2)-3O domains coexist) but are not present on layer II, since it was characterized as an ordered Ru(001)−(2×1)-O phase. The two spectra at 110 K in Figure 5 present a new band at 1341 and 1345 cm^{-1}, respectively, that may be reasonably assigned, on group frequency grounds, to the ν_sOCO mode of adsorbed formate

(HCOO).[51] On layer III, this band is accompanied by a weak C—H stretching band at 2918 cm^{-1}, also assignable to formate. It is the first time that this intermediate is detected in the decomposition of methanol on a Ru(001) surface, either clean or modified. The same modes of formate obtained by decomposition of formic acid on clean Ru(001) appear at 1361 and 2936 cm^{-1}, respectively.[51] The shifts observed on layers II and III may be explained by a chemical effect induced by the high concentration of coadsorbed oxygen atoms. Since the ν_{as}OCO mode of formate, expected at ∼1640 cm^{-1} for canted species, is not observed in the spectra of Figure 5, this species is probably adsorbed in the highly symmetric C_{2v} local symmetry, either in a bridging [μ_2-η^2(O,O)-HCOO] or in a chelating [μ_1-η^2(O,O)-HCOO] configuration. The bridged form has been proposed for formate on clean and oxygen covered Pt(111).[52] The reactivity toward formate seems enhanced on layer III, as the νCH mode becomes visible. A quantitative measure of the formate yield may be given by the following integrated intensities ratio

$$[\nu_s\text{OCO(formate)}]/[\nu\text{CO(methoxide)} + \nu\text{CO(formyl)} +$$
$$\nu\text{CO(formaldehyde)} + \nu_s\text{OCO(formate)}] \quad (1)$$

In the spectra at 110 K, this ratio increases from 0.09 on layer II to 0.19 on layer III. Since this intermediate was not detected on clean Ru(001) neither on modified Ru(001)−O with θ_O = 0.25 ML, it seems plausible that it proceeds from a methoxide reaction with surface oxygen, by a Langmuir−Hinshelwood mechanism. This direct involvement of oxygen can only occur on high-density oxygen layers, where it is more reactive. In fact, the adsorption energy of an oxygen atom on Ru(001) decreases with increasing O−O lateral interactions, from 3.5 eV on clean Ru(001) to 1.8 eV as the Ru(001)−(1×1)-O superstructure is approached.[53,54]

Upon annealing the previous surfaces to 130 K, the RAIR spectra reveal some residual methoxide (νCO mode at 984 and 988 cm^{-1} for θ_O = 0.5 and 0.6 ML, respectively), a significant amount of carbon monoxide, as shown by the strong bands at 2037 and 2053 cm^{-1}, and, on layer III, formyl (νCO mode at 1217 cm^{-1}). Apparently, formate decomposes, probably into CO$_2$ and CO,[55] the first not remaining on the surface.[51] This is a very low decomposition temperature when compared to that of formate resulting from formic acid on the clean surface (305 K),[55] pointing to a higher reactivity toward formate dehydrogenation induced by preadsorbed oxygen atoms and other coadsorbates. The oxygen coverage plays an important role, both in the formation and in the decomposition of this species. It is a difficult to detect intermediate, stable only in a narrow temperature range. At 190 K, just a small amount of adsorbed formyl may still be identified on layer III, with the νCO mode shifted to 1217 cm^{-1}. The fact that CO is no longer stable at this temperature on layers II and III is well understood in terms of the repulsive interactions with oxygen atoms.[42]

The assignment of the intermediate formate was confirmed by adsorbing a very low dose (0.05 L) of deuterated methanol-d_4 on layer III, at 110 K, yielding the RAIR spectrum presented in Figure 6.

The strong band at 1312 cm^{-1} is readily assigned to the ν_sOCO mode of deuterated formate in C_{2v} symmetry, slightly affected by isotopic substitution, and that at 2203 cm^{-1} to the νCD mode.[51] The band at 1045 cm^{-1} can only be assigned to the νCO mode of a less oxidized intermediate, namely η^2-formaldehyde. The formation of methoxide-d_3 is indicated by the shift of the νCO mode to 961 cm^{-1}, as opposed to 982 cm^{-1}
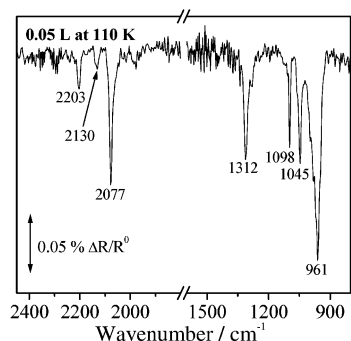
Figure 6. RAIR spectrum obtained after exposing layer III ($\theta_O = 0.6$ ML) to 0.05 L of methanol-d_4, at 110 K. The spectrum was scanned at 90 K.
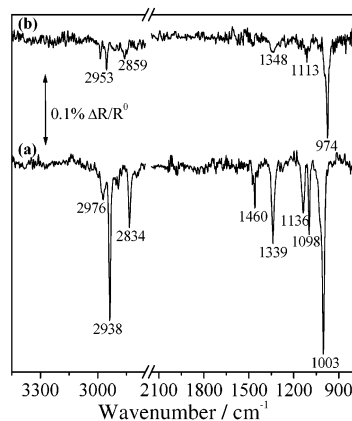
Figure 7. RAIR spectra recorded from (a) layer III ($\theta_O = 0.6$ ML) and (b) layer IV ($\theta_O = 0.75$ ML), dosed with 0.05 L of methanol at 100 K. The spectra were scanned at 90 K.

for the methanol-d_4 multilayer.[18,31,56] In the C–D stretching region, the main band, at 2077 cm^{-1}, corresponds to the $\nu_s CD_3$ mode of methoxide-d_3 in a C_{3v} local symmetry, and that at 2130 cm^{-1} corresponds to the $2 \times \delta_{as} CD_3$ mode. The band at 1098 cm^{-1} is assigned to the $\delta_s CD_3$ mode, enhanced by Fermi resonance with νCO (both A$_1$ species), although it may contain a contribution from the same mode of formyl.

To precisely define the temperature and oxygen coverage ranges at which methanol yields formate, different adsorption temperatures between 90 and 110 K were rehearsed on layers III and IV ($\theta_O = 0.75$ ML). The lowest temperature required to promote this oxidation on both surfaces was 100 K. The RAIRS data obtained for 0.05 L of methanol at this temperature are compared in Figure 7.

For layer III, the spectrum presents all of the characteristic features of a well-ordered C_{3v} methoxide layer, with narrow bands at 2976, 2938, 2834, and 1003 cm^{-1}, assigned to the $2 \times \delta_{as} CH_3$, $2 \times \delta_s CH_3$, $\nu_s CH_3$, and νCO modes, respectively. The organization of the layer is such that it is possible to observe, at 1460 cm^{-1}, the $\delta_s CH_3$ mode.[31,37] This result shows that the ordering is favored by adsorbing directly at 100 K rather than by annealing a disordered layer formed at 90 K. The band at 1339 cm^{-1} is assigned to the $\nu_s OCO$ mode of formate. Additionally, the spectrum evidences the presence of other intermediates, namely η^2-formaldehyde and η^2-formyl, identified by the corresponding νCO modes, at 1098 and 1136 cm^{-1}, respectively. For layer IV, the spectrum is very weak, showing a clear inhibition to all of the decomposition products. Formate may be identified by the feature at 1348 cm^{-1}. At this temperature, the ratio of integrated intensities given by eq 1 is 0.09 for layer IV versus 0.16 for layer III, showing that the

optimum oxygen coverage for formate production is approximately 0.6 ML.

A comparative assignment of the different intermediates in the decomposition of methanol as a function of the oxygen precoverage is made in Table 1.

Formaldehyde [μ_2-η^2(C,O)-H$_2$CO or μ_1-η^2(C,O)-H$_2$CO] and formyl [μ_3-η^2(C,O)-HCO] were essentially identified by the corresponding νCO mode, observed in the ranges 1090–1117 and 1136–1217 cm^{-1}, respectively. This wavenumber is dependent on coverage, on oxygen coverage, and on the presence of other coadsorbates. For formaldehyde η^2-coordinated in organometallic compounds,[57] the νCO mode is known to occur between 1017 and 1220 cm^{-1}. The probable reason for these shifts lies in different C–O bond strengths, a weaker CO bond resulting from a greater back-donation from the metal into the π_{CO}^* orbital of formyl or formaldehyde, that occurs for lower coverage.[50] This effect cannot be individualized in the present work, since, due to the complexity of the overlayers formed, it is coupled with the others.

The comparison between the intermediates yields on the different surfaces must be cautious, as it involves comparing different experiments.[28] Regarding the methoxide yield, the present results show that the oxygen chemical effect prevails for low coverages (up to $\theta_O = 0.25$ ML), roughly balancing with the site blocking effect for $\theta_O = 0.5–0.6$ ML. The latter predominates from there on, as for $\theta_O = 0.75$ ML only small amounts of methoxide and further intermediates coexist. This result differs from the conclusion drawn by Hrbek et al.,[37] who found an inhibiting site blocking effect at $\theta_O = 0.6$ ML. We believe that this divergence may be due to some uncertainty in their oxygen coverage calibration or to higher methanol exposures, resulting in molecular adsorption.

The surface species identified in this work in the decomposition of methanol (at low exposure) on the different Ru(001)–O layers are summarized in Figure 8.

Influence of the Methoxide Coverage on the Surface Intermediates. The relevance of the chemical effects of neighboring methoxide species is revealed by the dependence of its decomposition on coverage. This effect was studied on layer III ($\theta_O = 0.6$ ML), where the larger number of intermediates was observed. The starting surface was the mixed methoxide, formate, formyl and formaldehyde layer produced by dosing 0.05 L at 100 K (spectrum a in Figure 7). Increasing methanol exposure to 0.1 L leads to a RAIR spectrum with broad bands, none of them related to formate (Figure 9A).

This species may have been displaced by the incoming methanol, possibly by recombination with hydrogen. The absence of the other two intermediates, however, is not clear, since the band at 1128 cm^{-1} is too strong and broad to be assigned exclusively to the methyl rocking mode. It may also contain contributions from the νCO mode of formyl and formaldehyde. The predominant surface species is unquestionably methoxide, and the modifications in the spectrum from 0.05 to 0.1 L are compatible with a coverage increase, toward C_s or C_1 local symmetry. Warming this layer to 110 K, the spectrum evidences the re-ordering of the methoxide, the clear presence of formyl (νCO at 1148 cm^{-1}) and formaldehyde (νCO at 1094 cm^{-1}), and the appearance of formate ($\nu_s OCO$ mode at 1333 cm^{-1}). This spectrum resembles that of 0.05 L at 100 K, showing an increased stabilization of methoxide on a denser layer, since a thermal activation is needed to induce the same effects. At 130 K, along with some remaining methoxide, formyl, and formaldehyde, the strong band at 2002 cm^{-1}, assigned to on-top carbon monoxide, proves that the usual

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TABLE 1: Band Assignments for the Detected Intermediates in the Methanol Decomposition on Oxygen Modified Ru(001) Surfaces[a]

θ_O	0.25 ML	0.5 ML	0.6 ML		
T	90 K	90 K	90 K		band assignments
		2996	2997		$\nu_{as}CH_3/2\delta_{as}CH_3 + \nu_sCH_3$
	2926	2957/2842	2961		$\nu_{as}CH_3/2\delta_sCH_3 + \nu_sCH_3$
H_3CO (C_s)	2836	2863	2845		ν_sCH_3
	1117/1092	1098	1132		ρCH_3
	1015/991	1018/999	1020/990		νCO

| θ_O	0.25 ML	0.5 ML	0.6 ML	0.75 ML	
T	130 K	110 K	100 K	100 K	band assignments
	2976	2976	2976	2986	$2\delta_{as}CH_3 + \nu_sCH_3$
	2944	2942	2938	2953	$2\delta_sCH_3 + \nu_sCH_3$
H_3CO (C_{3v})	2837		2834	2859	ν_sCH_3
			1460		δ_sCH_3
	991	1001	1003	974	νCO
H_2CO	1090	1117	1098	1113	νCO
HCO	1165		1136		νCO
HCOO			2918		νCH
		1341	1339	1348	ν_sOCO

[a] For methoxide, only the bands observed for very low coverage (C_s and C_{3v} symmetries) are included. Only the lowest temperatures at which the species were observed in the present work are indicated.
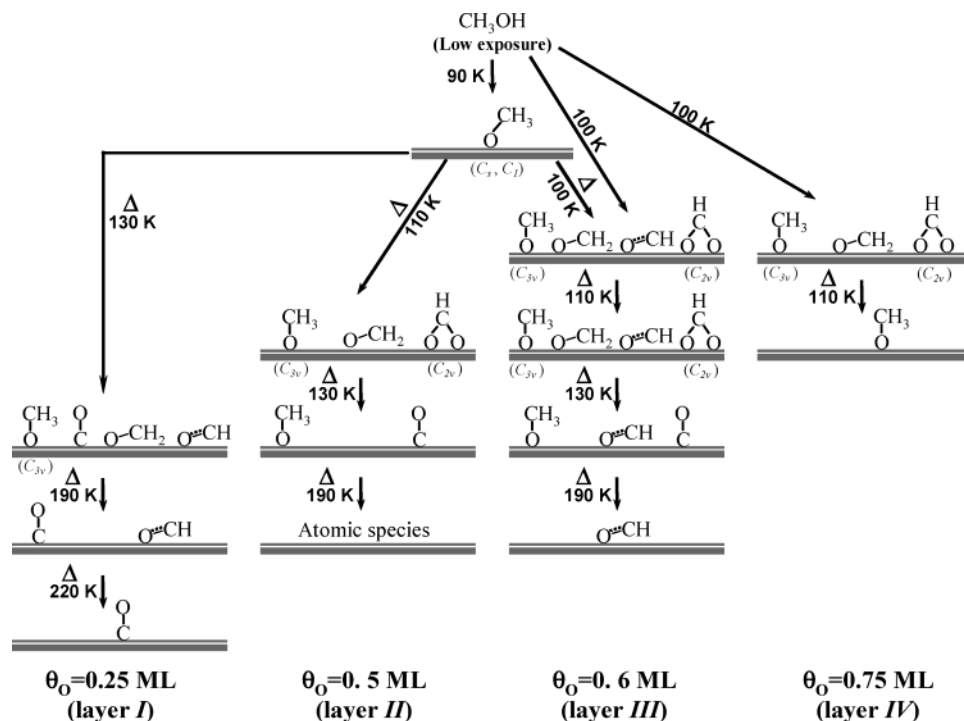
Figure 8. Schematic representation of the surface species identified by RAIRS in the thermal decomposition of methanol on oxygen modified Ru(001) surfaces.

decomposition by complete dehydrogenation of the intermediates is taking place. Similarly to methoxide, formaldehyde is also stabilized by an initial increased coverage. The stability of formate and formyl do not seem to be affected, since there is no evidence of adsorbed formate, as happened at this temperature for a lower methoxide coverage.

To produce a saturated layer of methoxide, a thick multilayer of methanol was built at 100 K, by exposing layer III to 10 L, and subsequently annealed. The very strong spectrum shown in Figure 9B correlates extremely well with that of solid-phase methanol.[18,58,59] By annealing to 110 K, a disordered methoxide layer was obtained, with no evidence for other decomposition products. Comparing with the corresponding spectra in Figures 5B and 9A, it becomes clear that the stability of methoxide

increases for saturation coverage on this layer. The agreement with previous results on oxygen modified Ru(001)[37] and on Ni-(110)[60] points to a stabilizing effect of neighboring methoxide species, independently from the surface. At 130 K, there is still methoxide coadsorbed with carbon monoxide (νCO at 2041 cm^{-1}), and the growing bands at 1209 and 1122 cm^{-1} indicate that the intermediates formyl and formaldehyde, respectively, start forming at this temperature. The band shapes in this spectrum suggest that several intermediates and the final product CO are coadsorbed in a disordered layer. Methoxide and formyl are still stable at 190 K. Only for saturation coverage is methoxide stabilized at such a high temperature, preventing the observation of any formate occasionally yielded.
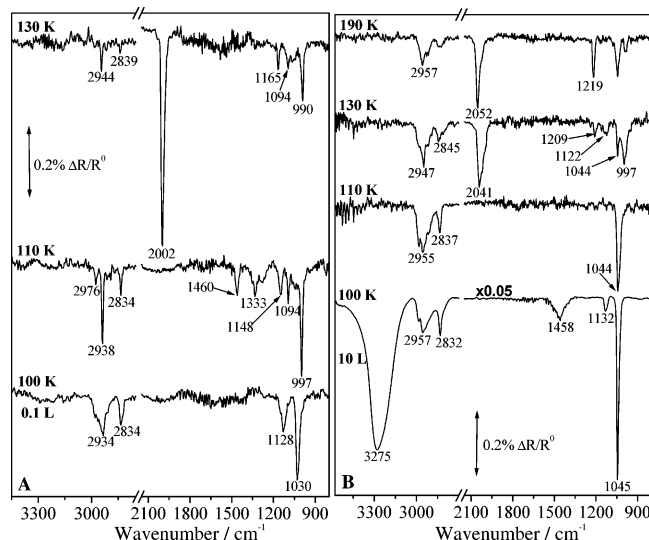
Figure 9. RAIR spectra obtained after exposing layer III ($\theta_O = 0.6$ ML) to 0.1 L (A) and 10 L (B) of methanol at 100 K, and subsequently annealing to the indicated temperatures. The spectra were scanned at 90 K.

IV. Conclusions

On oxygen modified Ru(001) surfaces, methanol adsorbs dissociatively as methoxide in C_s or C_1 local symmetry, for a low exposure (0.05 L) at 90 K. For this methanol dose, the methoxide yield is enhanced by increasing the oxygen coverage up to $\theta_O \approx 0.6$ ML, when the site blocking effect balances the chemical effect. By direct adsorption of methanol at higher temperatures (100 K $\leq T \leq$ 130 K) or by annealing the adsorbed methoxide, other surface intermediates may be observed, namely formaldehyde (H_2CO), formyl (HCO), and formate (HCOO).

The oxygen coverage determines the stability of the reaction intermediates in very specific ways. Formaldehyde is stable at 130 K for low oxygen coverages, whereas for $\theta_O \geq 0.5$ ML it desorbs or decomposes between 110 and 130 K. Formyl is sensitive to the presence of differently modified domains, forming probably at boundaries such as Ru(001)−(2×2)-O/clean Ru(001) or Ru(001)−(2×1)-O/Ru(001)−(2×2)-3O, and decomposing only above 190 K. Formate, as a methanol decomposition product, has been detected on these surfaces for the first time. It is stable in a narrow temperature range (100 K $\leq T <$ 130 K), with maximum yield for oxygen coverages within 0.5−0.6 ML, and forms only from low density methoxide layers, where methoxide itself is not so stabilized. These results point to the direct participation of preadsorbed oxygen in the deep oxidation of methanol. The low stability of formate is confirmed by the fact that, whenever formed by direct adsorption, it is easily displaced by additional incoming methanol molecules.

The effect of methoxide coverage on the decomposition intermediates and their stability was studied for two methanol exposures, 0.05 and 0.1 L, plus a saturated methoxide monolayer. It was proved that the oxidation temperature rises with increasing methoxide coverage and, if coverage is high enough, the intermediate formate is never stabilized on the surface: the temperature at which methoxide eventually reacts is above the range of formate stability.

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