

Supporting Information

Formaldehyde Selectivity in Methanol Partial Oxidation on Silver: Effect of Reactive Oxygen Species, Surface Reconstruction and Stability of Intermediates

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SI-1 Temperature Programmed Reaction Spectroscopy for Methanol on O/Ag(111)

Temperature programmed reaction spectroscopy (TPRS) results were obtained after 0.06 L of methanol exposure (equivalent to 2 ML at 100 K) at 200 K on pre-oxidized Ag(111) surfaces with various oxygen coverages (Fig. S1). Oxygen is accumulated by ozone decomposition method at 140 K prior to methanol dosage. In TPRS experiments given in Figure S1, desorption channels of $m/z=2$, 18, 28, 29, 30, 31, 32 and 44 were simultaneously monitored.

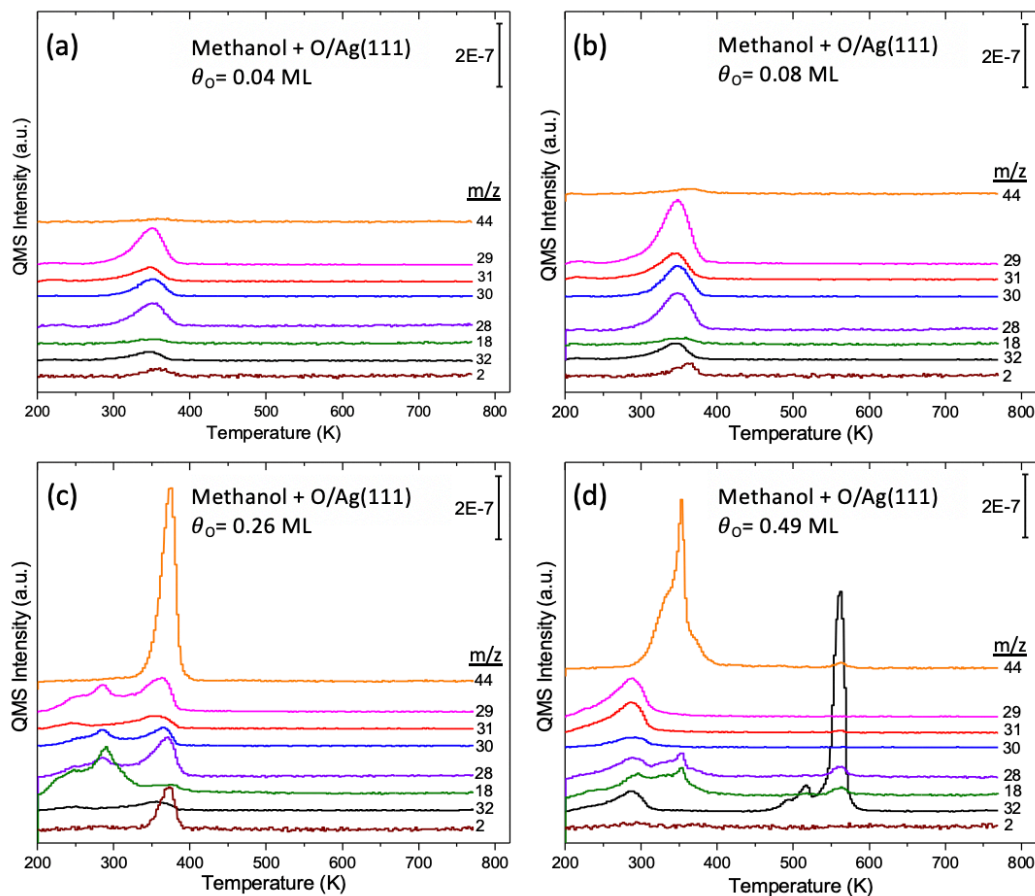


Figure S1. TPRS profiles for the reaction of methanol with oxygen on Ag(111). Methanol (0.06 L) was exposed at 200 K for all cases on pre-oxidized Ag(111) prepared by (a) 0.04, (b) 0.08, (c) 0.26 and (d) 0.49 ML of oxygen accumulation at 140 K. (Heating rate: 1 K/s)

For quantitative analysis of methanol oxidation products reported in the main text in Figures 1c and 1d, fragmentation patterns of pure formaldehyde and methanol molecules in the gas phase were obtained by utilizing the currently used quadrupole mass spectrometer (QMS). The fragmentation patterns of these pure molecules are given in Table 1.

Table 1. QMS fragmentation patterns of pure methanol and formaldehyde.

m/z	28	29	30	31	32
Methanol	35	86	14	100	65
Formaldehyde	59	100	73	3	-

Quantification of the formaldehyde yield ($Q_{\text{Formaldehyde}}$) is calculated from $m/z=30$ signal instead of the most intense fragment of formaldehyde ($m/z=29$) due to a significant methanol contribution to the $m/z=29$ signal (Eq. 1). Fraction of $m/z=30$ signal, I_{30} , to the sum of all QMS fragmentation signals of formaldehyde in the gas phase is found to be 0.31. Therefore, the integrated $m/z=30$ signal is divided by a factor of 0.31 to quantify the total formaldehyde molecules produced. In addition, the methanol contribution in the $m/z=30$ desorption signal ($I_{31} \times 0.14$) is also subtracted.

$$Q_{\text{Formaldehyde}} = [(\int I_{30} \cdot \Delta T) \div 0.31] - [(\int I_{31} \cdot \Delta T) \times 0.14] \quad (\text{Eq. 1})$$

For CO_2 production, integrated $m/z=44$ signal was used. Only formaldehyde and carbon dioxide yields were considered for selectivity calculations in the main text in Figure 1.

SI-2. Methanol Adsorption on Clean Ag(111)

Temperature programmed desorption (TPD) of methanol was performed on clean Ag(111) at 100 K as a function of methanol exposure and the most intense fragment of methanol, $m/z=31$, was monitored (Fig. S2). Methanol was found to desorb molecularly from the clean Ag(111) surface in all of the TPD experiments. In Figure S2, a desorption signal at 155 K (β_1) is observed for the lowest methanol coverage (0.1 MLE). With increasing methanol coverage, the β_1 signal grows in intensity and another signal (β_2) at 160 K appears. These signals (β_1 and β_2) converge to a saturation before a new feature at 138 K (α_2) arises and the integrated signal of this saturation coverage is used to estimate $\theta_{\text{methanol}} = 1.0$ MLE. Therefore, β_1 and β_2 signals are attributed to methanol molecules adsorbed on Ag(111) surface in the first monolayer. For higher coverages, α_1 and α_2 signals appear and they can be assigned to multilayer methanol overlayers. Former vibrational spectroscopy results indicate that a crystalline phase of methanol forms on top of amorphous methanol layers on Pt(111) and desorbs at 125 K.¹ Thus, the α_1 and α_2 signals in Figure S2 are attributed to a crystalline and an amorphous methanol phase, respectively. TPD profiles of methanol on Ag(111) in Figure S2 are in a perfect agreement with the literature.²

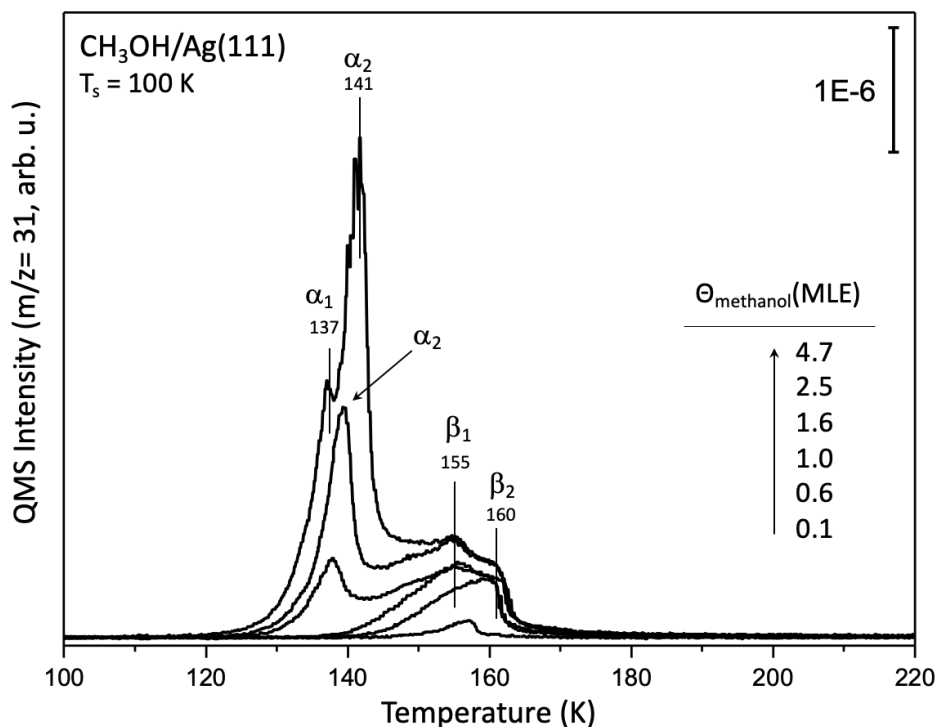


Figure S2. Temperature programmed desorption profiles ($m/z=31$) obtained after methanol adsorption on a clean Ag(111) at 100 K as a function of increasing methanol coverage.

SI-3. Infrared Spectra of Methoxy on O(0.04 ML)/Ag(111) at 100 and 300 K

Infrared reflection absorption spectroscopy (IRAS) was used to establish that methoxy species created on O(0.04 ML)/Ag(111) at 100 K were stable on the surface at 300 K. The characteristic vibrational signals of methoxy species were obtained at 100 K after 0.03 L of methanol exposure on O(0.04 ML)/Ag(111) at 100 K (Fig. 4b and Fig. S3a). Subsequently, the methoxy containing Ag(111) was heated to 300 K and almost no change in the infrared signals was observed (Fig. S3b). These results indicate that methoxy species were stable at 300 K on the Ag(111) surface.

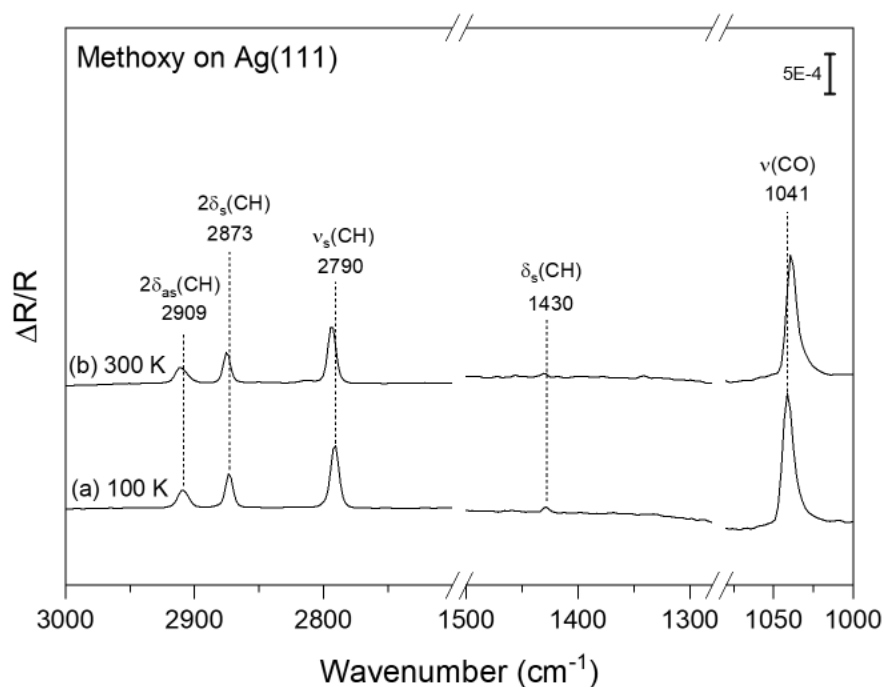


Figure S3. (a) Infrared reflection absorption spectra of methoxy species on Ag(111) obtained by 0.03 L of methanol exposure onto O(0.04 ML)/Ag(111) at 100 K. (b) spectrum acquired after increasing the temperature to 300 K for the same surface given in (a).

SI-4. Temperature Programmed Reaction of Formate on O(0.10 ML)/Ag(111)

Temperature programmed reaction of formate species on Ag(111) was performed after acquisition of the IRAS spectrum given in Figure 4d in the main text. Based on the infrared spectrum in Figure 4d, bridging bidentate formate species forms after 0.03 L of methanol exposure on O(0.10 ML)/Ag(111) at 300 K. Following TPD spectra in Figure S4 show that bidentate formate decomposes predominantly into CO₂ and H₂ at ~370 K. Water desorption at the same temperature is attributed to the reaction of H atoms with the excess oxygen on the surface.

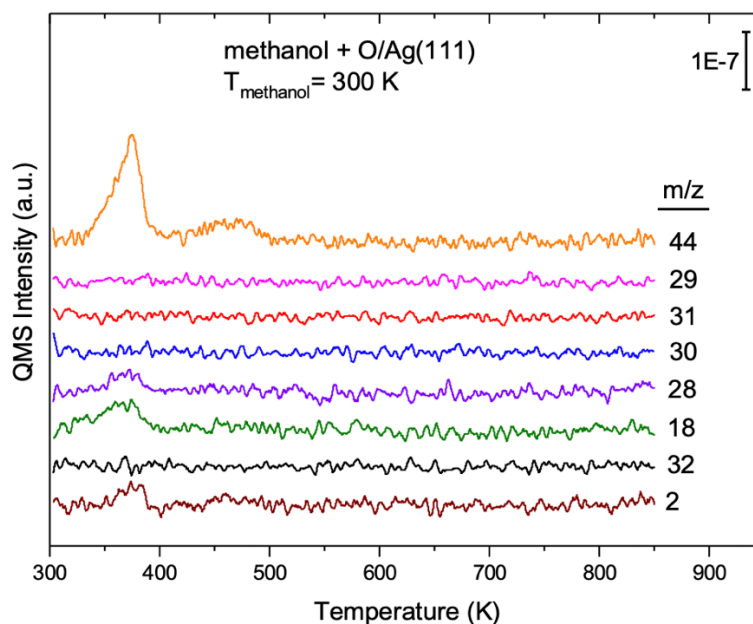


Figure S4. Temperature programmed reaction spectra obtained after the IRAS acquisition in Figure 3d in the main text for O(0.10 ML)/Ag(111) exposed to 0.03 L of methanol at 300 K.

References

¹ Ehlers, D.H.; A. Spitzer A.; Liith H. The adsorption of methanol on Pt(111). An IR reflection and UV photoemission study. *Surf. Sci.* **1985**, 160, 57-69

² Jenniskens, H. G.; Dorlandt, P. W.; Kadodwala, M. F.; Kley, A. W. The adsorption of methanol on Ag(111) studied with TDS and XPS. *Surf. Sci.* **1996**, 357, 624-628.