Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

On the mechanism of methanol photooxidation to methylformate and carbon dioxide on TiO_2: An operando-IR study

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Supporting Information

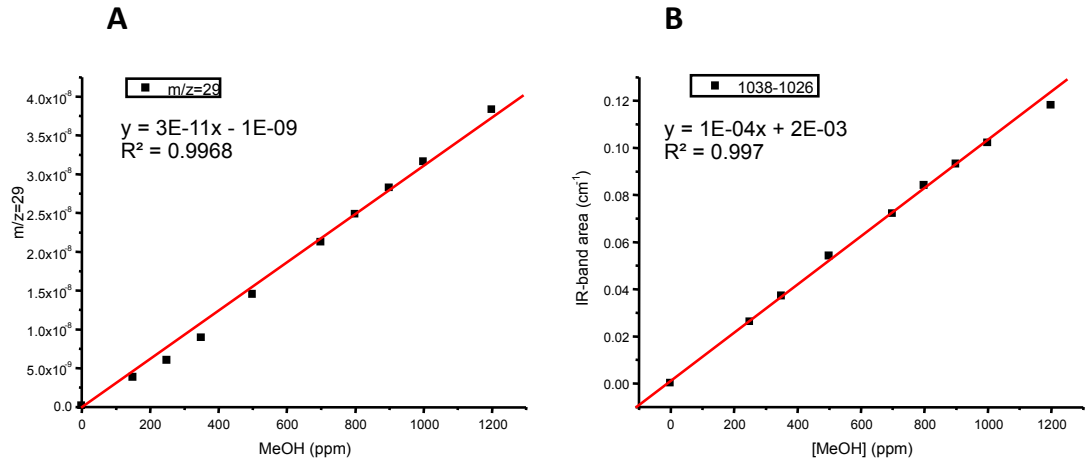

Figure S-1. Methanol calibration curve using the MeOH-MS signal (at m/z=29) (A) and characteristic MeOH-IR band area (at 1038-1026 cm^{-1}) (B).

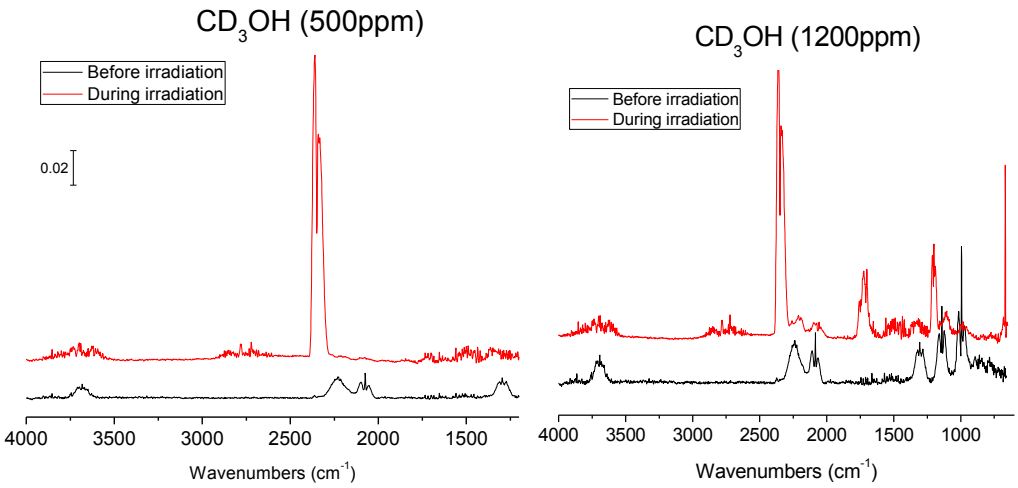

Figure S-2. IR spectra of the reaction gas phase before (black) and during (red) the photooxidation of 500 ppm and 1200 ppm of CD_3OH. This figure shows a total photooxidation and conversion of methanol for 500 ppm initial concentration. For 1200 ppm, the methanol conversion is 75% with CO_2-selectivity = 60%. (T=28 °C; flow=20 cm^3/min; 20% O_2/Ar v/v; □□□365 nm; I_0=15 mW/cm^2).

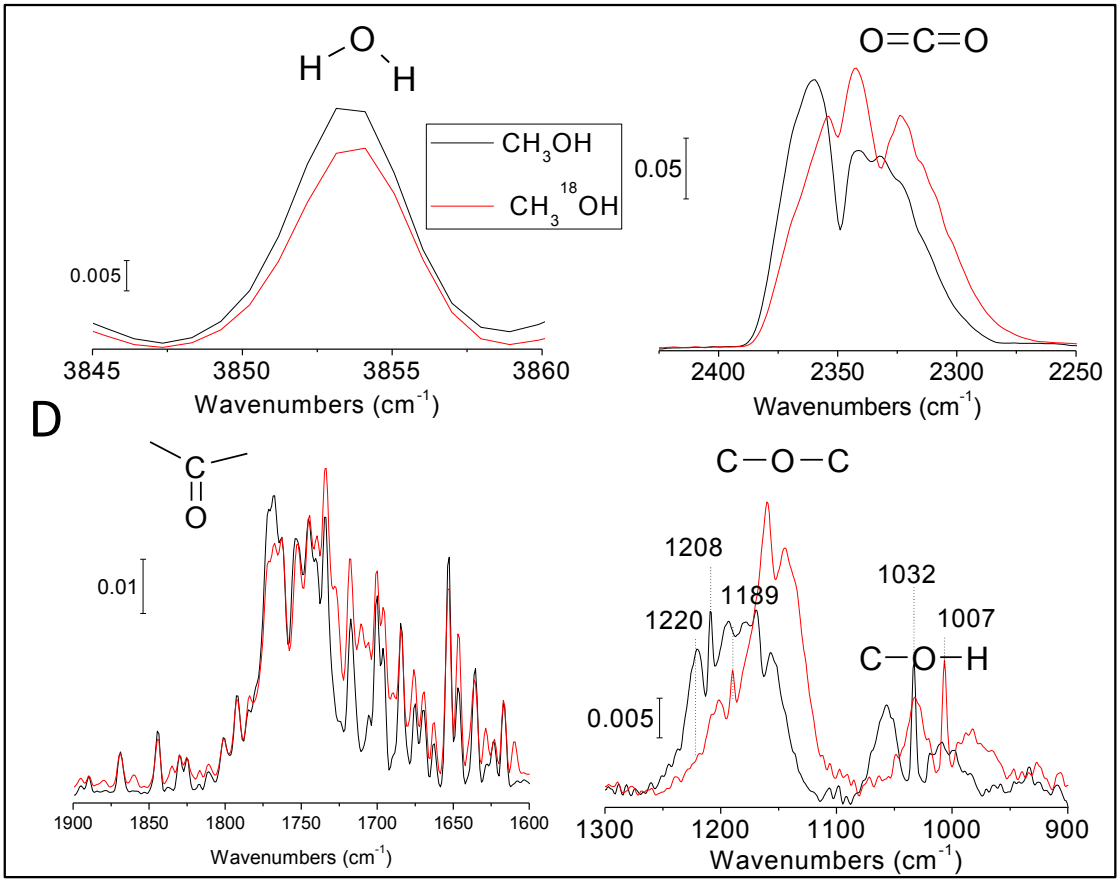

Figure S-3. IR spectra (in the water, carbon dioxide, carbonyl and -C-O- vibration zones) of the reaction gas phase during photooxidation of 1200 ppm of $CH_3{}^{16}OH$ (black) and $CH_3{}^{18}OH$ (red) under the same conditions.

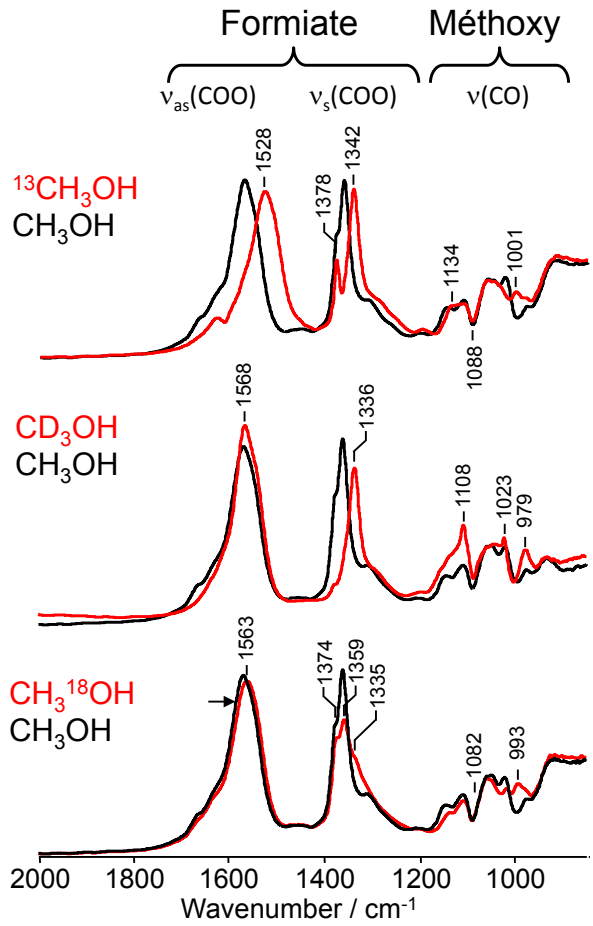

Figure S-4. IR spectra of TiO_2 surface during the photooxidation of natural methanol and of different methanol labeled molecules (methanol concentration = 1200 ppm).

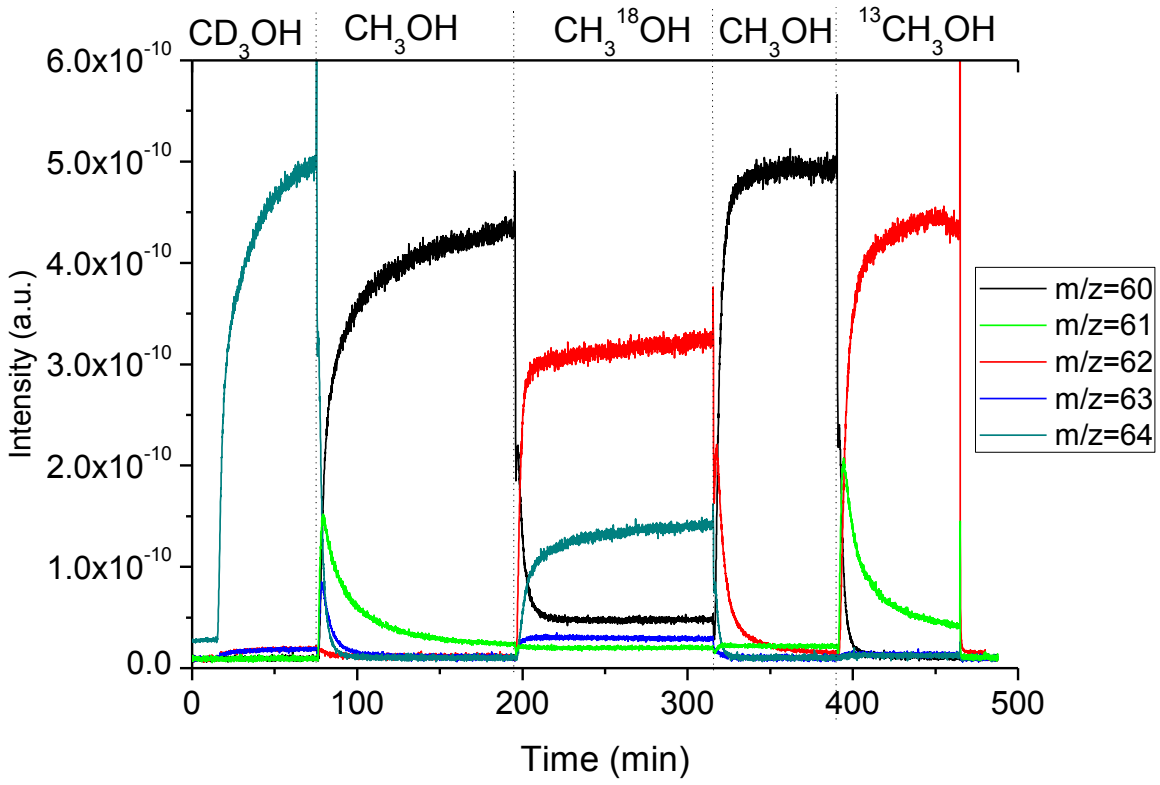

Figure S-5. Evolution of the MS signals of unlabeled and labeled methyl format produced during the photooxidation of different methanol molecules. The dotted line corresponds to the time of the isotopic transition and t=0 min is the starting irradiation moment.

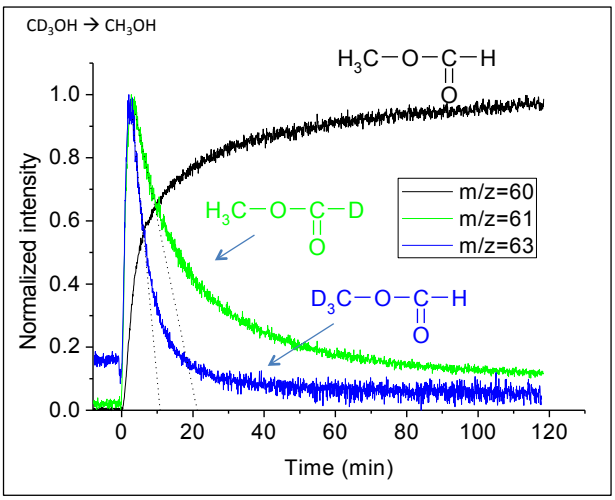

Figure S-6. Evolution of the normalized MS signals, versus irradiation time, of unlabeled and labeled methyl format produced during the isotopic exchange of CD_3OH/CH_3OH. t=0min correspond to the isotopic exchange moment.

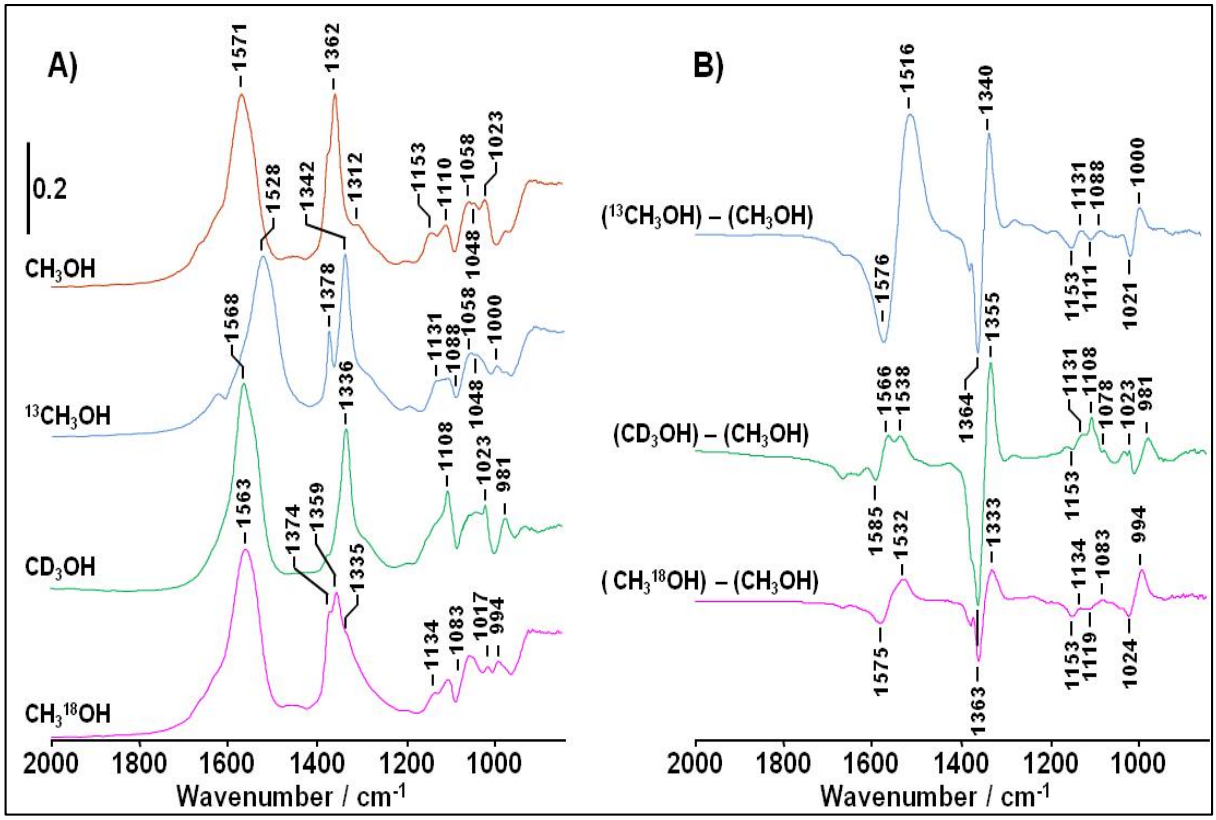

Figure S-7. Part A: IR spectra of adsorbed species on TiO_2-P25 after 60 minutes of UV irradiation of 1200 ppm of labeled methanol in synthetic air (flow=20 cm^3/min; 25°C; $I_{0(366)}$~15 mW/cm^2; λ=366 nm). Part B: spectra of difference of labeled spectra minus non-labeled methanol spectrum.

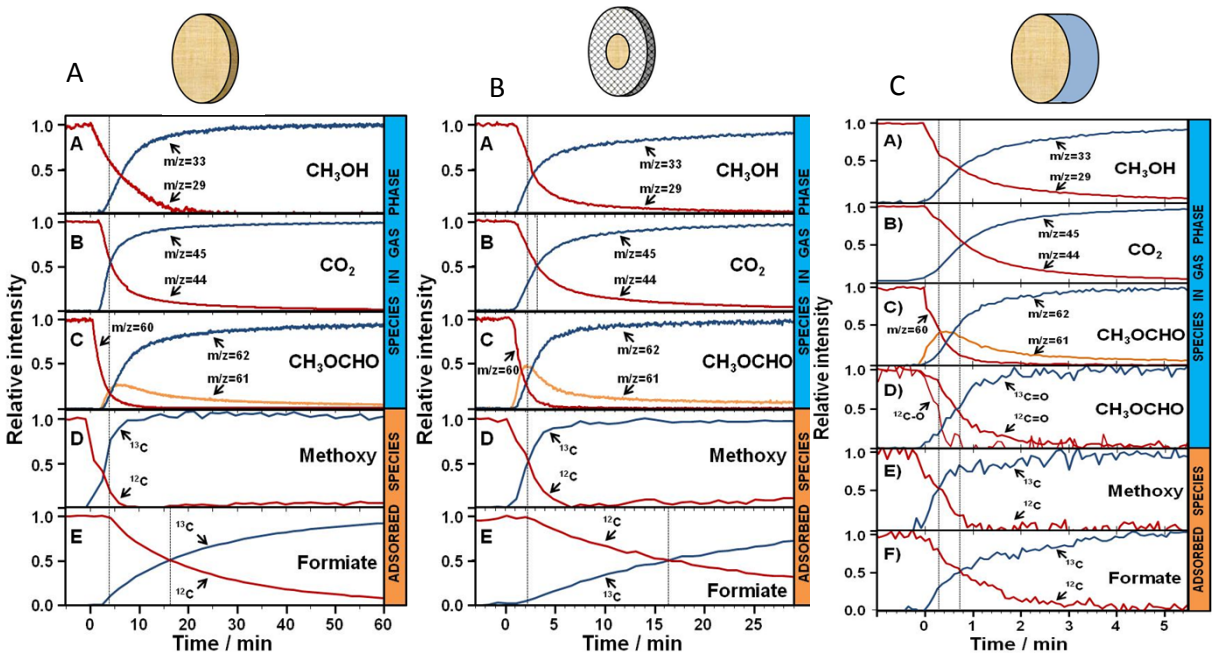

Figure S-8. Evolution of adsorbed species on TiO_2 surface and in gas phase during methanol photooxidation versus time of the $^{12}CH_3OH/^{13}CH_3OH$ SSITKA experiment (t = 0 min correspond to the $^{13}CH_3OH/CH_3OH$ exchange).[1] A: 20 mg of self supported TiO_2 pellet (16 mm of diameter and 50-70 µm of thickness), methanol concentration = 1200 ppm; B: 5 mg TiO_2 supported on INOX grid (6 mm; 50-70 µm of thickness), methanol concentration = 500 ppm; C: TiO_2 supported-TiO_2 powder deposited on a KBr window (16 mm; <10 µm of thickness), methanol concentration = 100 ppm.

[1] MS signal of species in gas phase: A) methanol ($^{12}CH_3OH$ (m/z=33), $^{13}CH_3OH$ (m/z=29)), B) carbon dioxide ($^{12}CO_2$ (m/z=44), $^{13}CO_2$ (m/z=45), C) methyl formate ($^{12}CH_3O^{12}CHO$ (m/z=60), $^{13}CH_3O^{12}CHO$ and $^{12}CH_3O^{13}CHO$ (m/z=61), $^{13}CH_3O^{13}CHO$ (m/z=62)). IR signal of adsorbed species: D) methoxy (area of 1033 and 998 cm^{-1} bands for labeled ^{12}C and ^{13}C, respectively) and E) formate (area of 1359 and 1338 cm^{-1} bands for labeled ^{12}C and ^{13}C, respectively).