Supporting Information

Methanol Oxidation to Formate on ALD Prepared VO_x/θ-Al_2O_3 Catalysts: a Mechanistic Study

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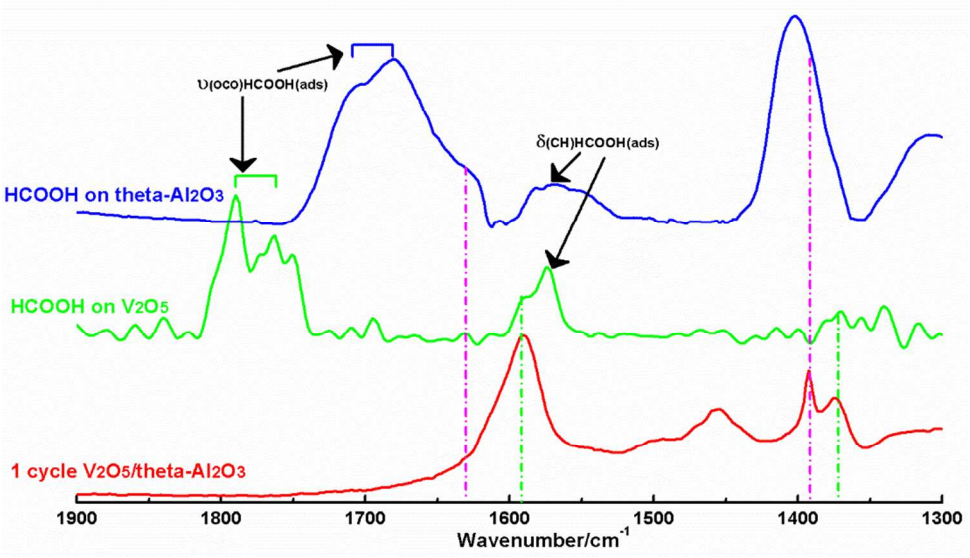


Figure S1. FTIR spectra of formic acid adsorbed on theta-Al_2O_3 and V_2O_5.

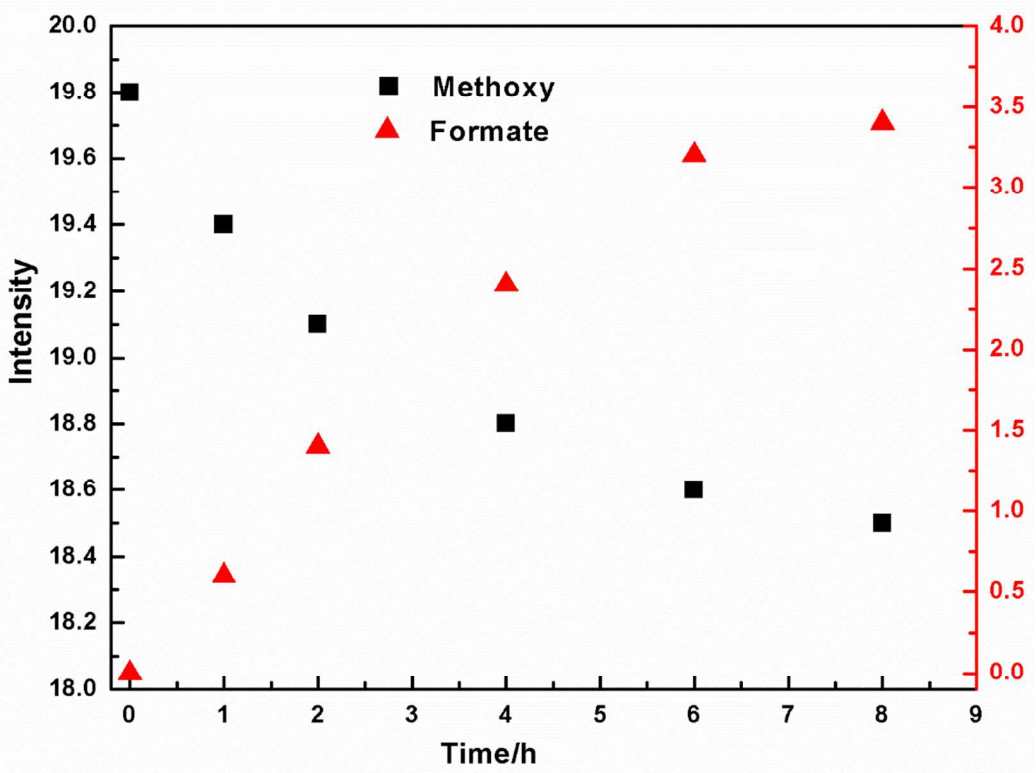


Figure S2. A plot of the integrals of the absorption of formates and methoxy on 1c VO_x/θ-Al_2O_3 (0.48 wt%) versus time at 200 ^oC. The formate absorption centered at ~1590 cm^{-1} was integrated to obtain the indicated format "intensity". The indicated methoxy intensity was obtained from an integration of a portion of a deconvolution of the C-H stretching region. The peak that was integrated is centered at 2940 cm^{-1} and is shown in Figure S3.

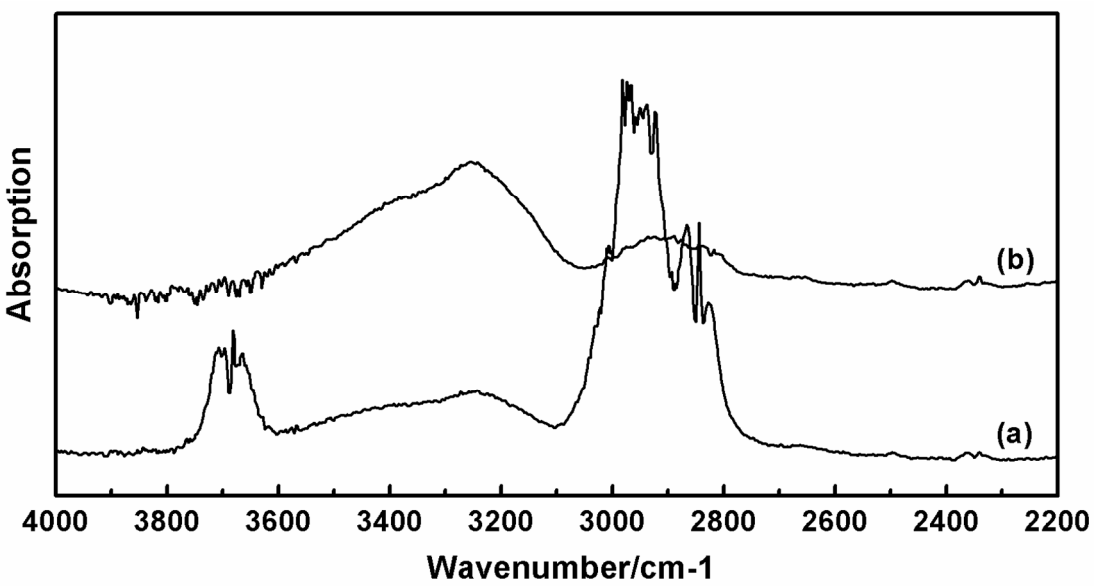


Figure S3. *In-situ* FTIR spectra of methanol on θ-Al_2O_3, (a), after dosing with gas phase methanol for 5 min at 110 ^oC; (b) after subsequent evacuation for 30 min at 200 ^oC.

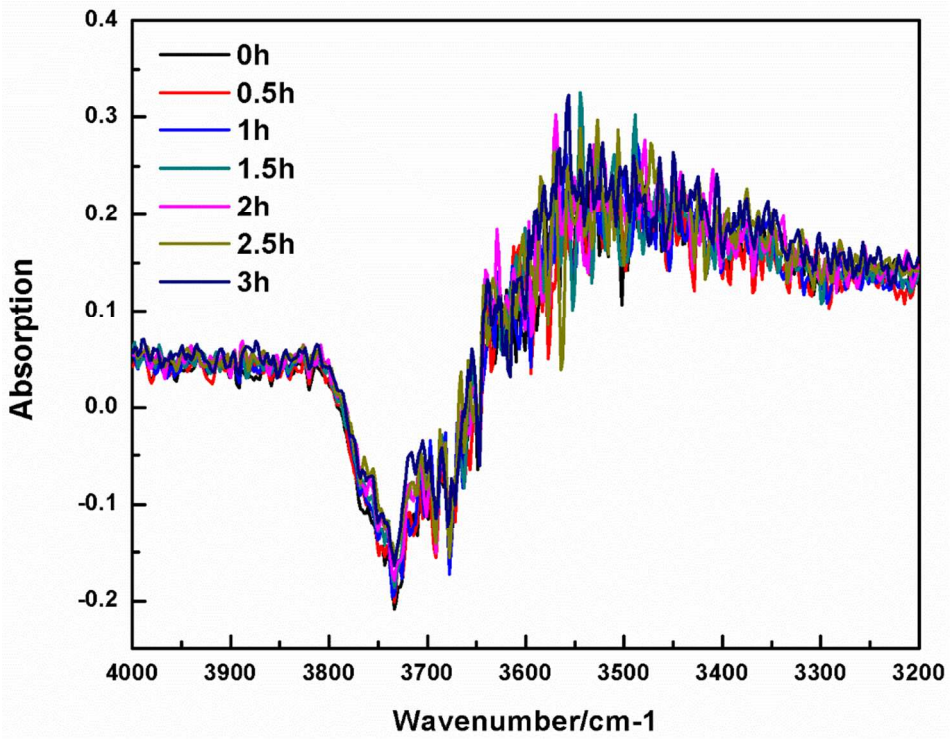


Figure S4. *In-situ* FTIR spectra of methanol on 1c VO_x/θ-Al_2O_3 in the OH stretch region at 200 ^oC.

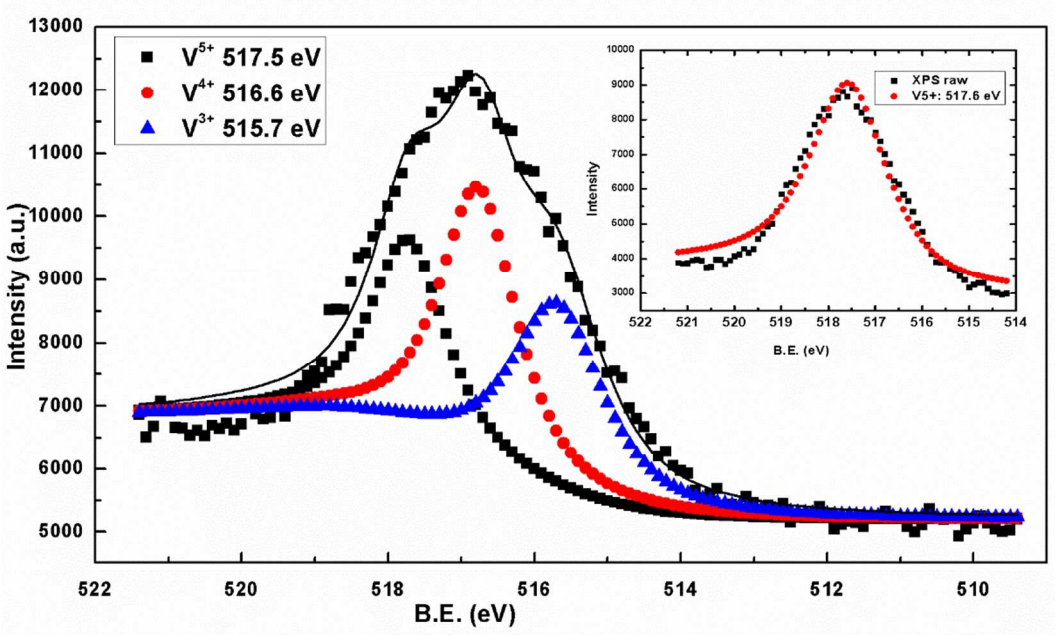


Figure S5. Deconvolution of the fit of the V $2p_{3/2}$ signal from 1c VO_x/θ-Al_2O_3 (0.48 wt%) after reduction with 20 Torr of H_2 at 350 ^oC for 3 hours and oxidation at 350 ^oC with 20 Torr of O_2 for 3 hours. All of the hydrogen was carefully removed by pumping on the system before any oxygen was introduced into the system.

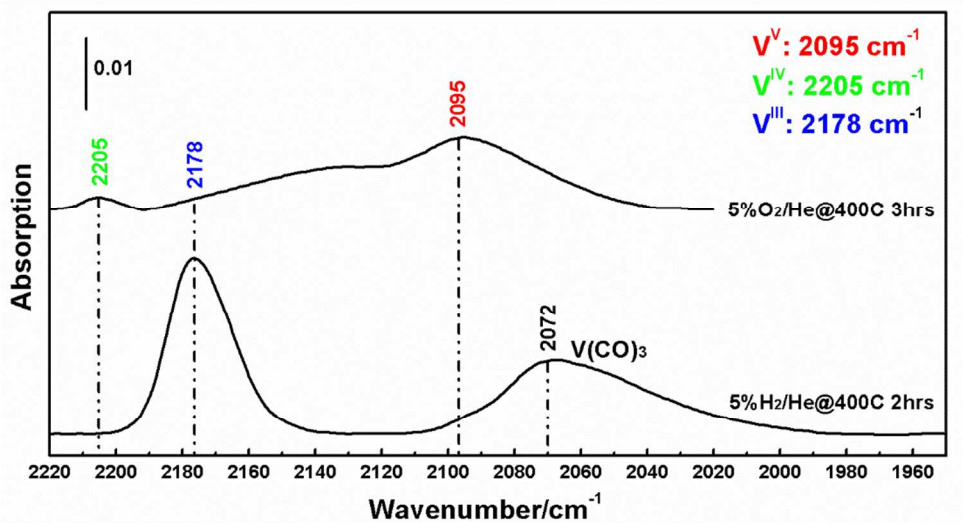


Figure S6. *In-situ* FTIR spectra of CO adsorption on oxidized and then reduced 1c VO_x/Al_2O_3.

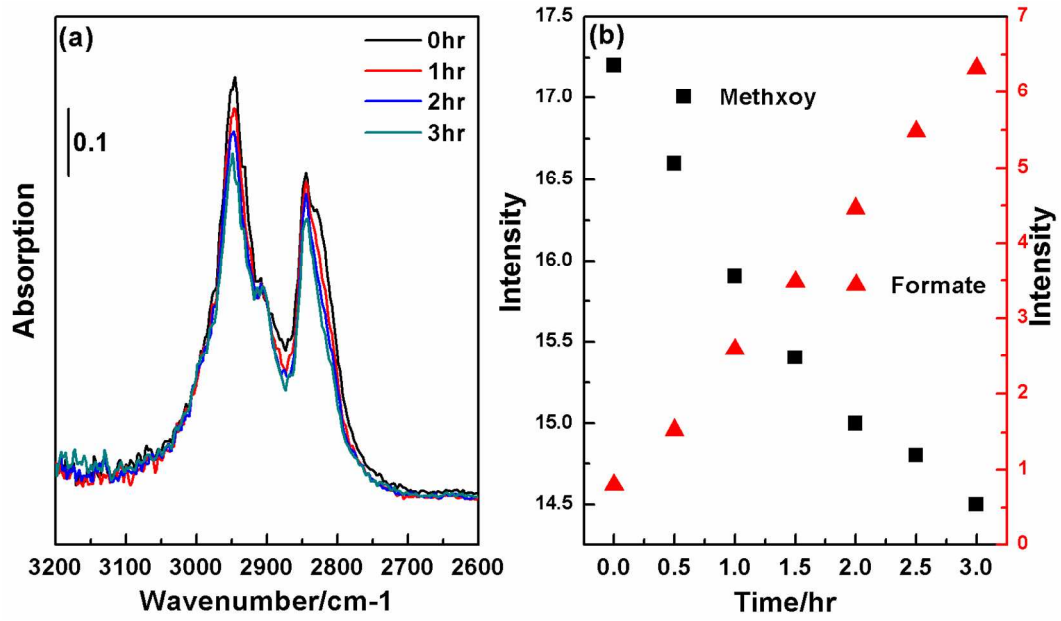
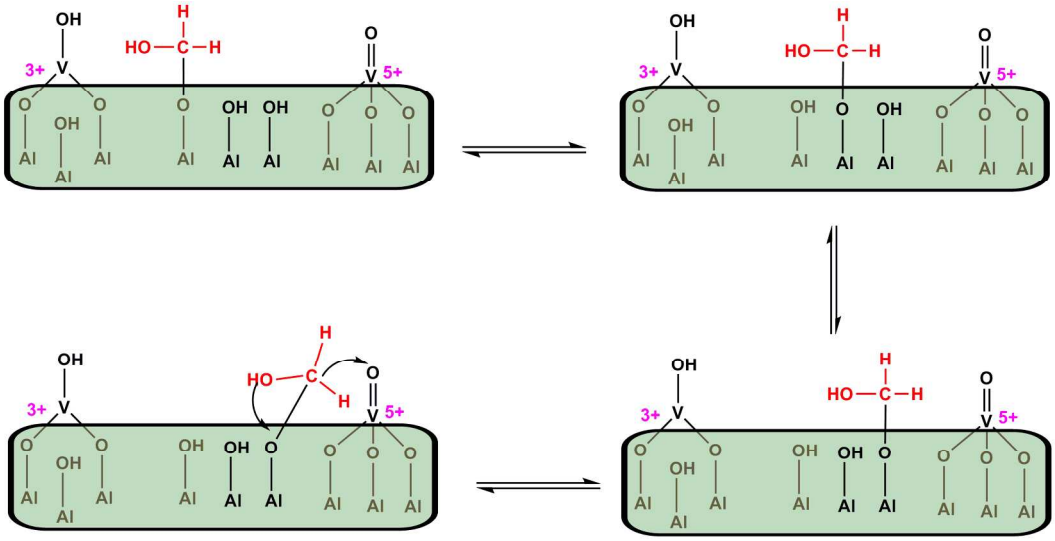


Figure S7. (a) *In-situ* FTIR spectra in the methoxy region (3200-2600 cm^{-1}) after methanol oxidation on 1c VO_x/Al_2O_3 (0.48 wt%) as a function of reaction time at 200 ^oC; (b) Time profile of the intensities of the formate and methoxy absorptions. The indicated methoxy intensity was obtained from an integration of a portion of a deconvolution of the C-H stretching region. The peak that was integrated is shown in Figure S3 and is centered at 2940 cm^{-1}.



Scheme S1. A schematic of a proposed mechanism for the migration of hydroxymethyl on the surface of 1c $VO_x/\theta\text{-}Al_2O_3$ (0.48 wt%)