

Supporting information for manuscript titled:

Oxygen precursor to the reactive intermediate in methanol synthesis by Cu-ZSM-5

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UV-vis:

The setup consists of a plug-flow reactor (i.d.=8 mm) fitted inside a furnace, a UV-Vis light source (Top Sensor Systems DH-2000 deuterium-halogen light source) and a photodiode array detector (Ocean Optics SD 2000) connected to the catalyst bed via optical fiber technology (Top Sensor Systems FCB-UV400-ME cable and FCB-UV400G-0.1-XHT high-temperature probe). Each spectrum is the result of the superposition of 300 scans in the 38000-12000 cm^{-1} region, each 50 ms in duration.

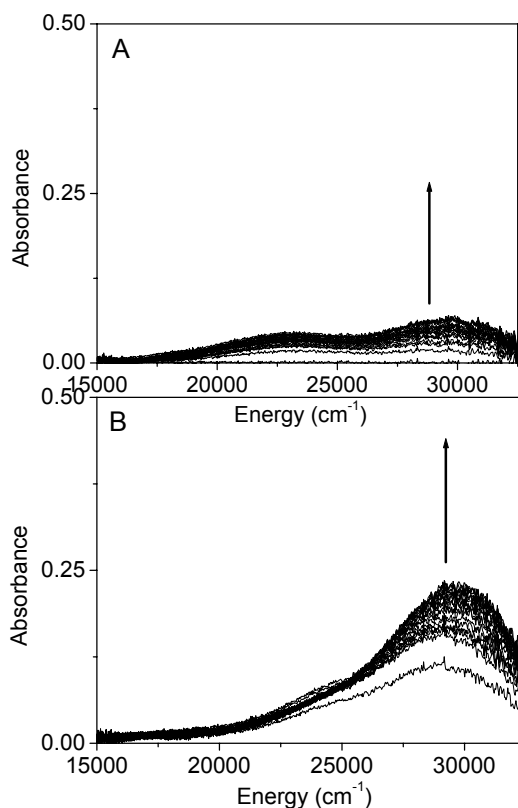


Figure S1: UV-vis spectra recorded of auto-reduced (He at 450°C) Cu-ZSM-5 with Cu/Al=0.2 (A) and 0.3 (B) during $^{16}\text{O}_2$ treatment at RT. Spectra recorded every 40 seconds for 14 min after opening O_2 flow.

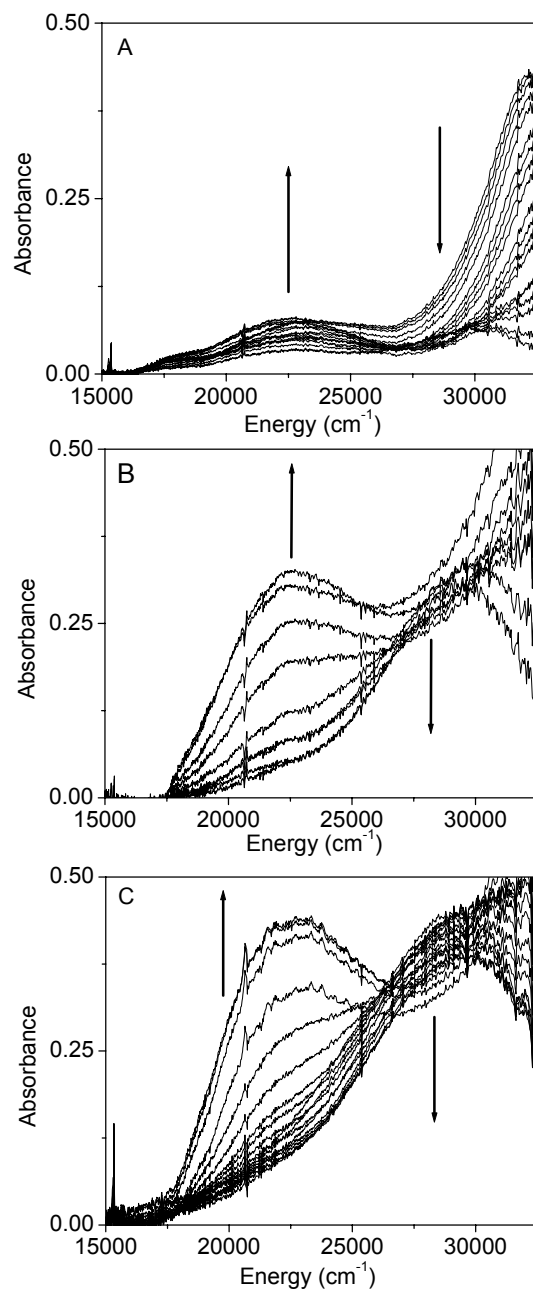


Figure S2: UV-vis spectra recorded during the subsequent heating (2°C/min) of O₂ RT treated Cu-ZSM-5 with Cu/Al=0.2 (A) and 0.5 (B) after flushing for 15 min in He at RT. (C) UV-vis spectra recorded during the subsequent heating (2°C/min) of O₂ RT treated Cu-ZSM-5 with Cu/Al= 0.5 in closed O₂ atmosphere. Spectra recorded every 20°C.

Resonance Raman spectroscopy

Resonance Raman (rR) spectra were recorded using a Spex 1877 CP triple monochromator with 1200, 1800, and 2400 grooves/mm holographic spectrograph gratings and an Andor Newton CCD cooled to -80°C . Excitation was provided by either a Coherent I90C-K Kr^+ ion laser ($\lambda_{\text{ex}} = 413.1 \text{ nm}$) or an Innova Sabre 25/7 Ar^+ CW ion laser ($\lambda_{\text{ex}} = 351.1 \text{ nm}, 363.8 \text{ nm}, 379.5 \text{ nm}, 457.9 \text{ nm}$). The spectral resolution was $\sim 2 \text{ cm}^{-1}$. Spectra were recorded at room temperature at a power of 5mW at the sample. Sample preparation was the same as for the samples prepared for UV-vis measurements. After UV-vis measurement, the catalyst pellets were mounted in the quartz side arm of the U-tube, ensuring that the conditions for UV-vis and resonance Raman measurements were identical. Baseline spectra were collected using ground, activated charcoal in a quartz U-tube side arm.

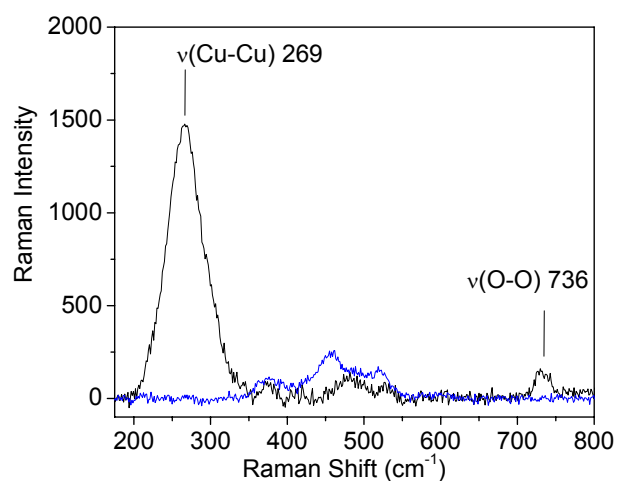


Figure S3: rR spectra (363.8 nm , 5mW) of the oxygen precursor formed at RT (black) and after heating the oxygen precursor to 300°C (blue).

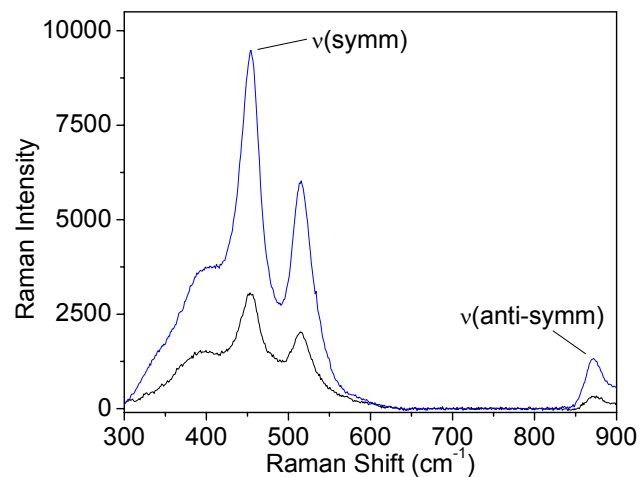


Figure S4: rR spectra (457.9 nm, 5mW) of the oxygen precursor formed at RT (black) and after heating the oxygen precursor to 300°C (blue). Note: there is some small amount of activated in the precursor sample and any amount present will be observed in the rR experiment with 457.9 nm laser excitation. The key to this Figure is the large overall intensity increase between the RT precursor (black) and the heated precursor sample (blue).