Supporting Information

Catalytic Oxidation of Formaldehyde over Manganese Oxides with Different Crystal Structure

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Experimental Section

Raman spectra of the catalysts were recorded at room temperature on a UV resonance Raman spectrometer (UVRDLC-P-DL-03), which consisted of three optional exciting lasers (244, 325, and 532 nm), a three-stage grating spectrograph, and a CCD detector cooled by liquid nitrogen. The instrument was calibrated against the Stokes Raman signal of Teflon at 1378 cm$^{-1}$. A continuous diode pumped solid state (DPSS) laser beam (532 nm) was used as the exciting radiation, and the power output was about 48 mW. The diameter of the laser spot on the sample surface was focused at 25 μm.

HRTEM was performed on a FEI Tecnai G² F20 electron microscope operating at 200 kV with a supplied software for automated electron tomography. Typically, a drop of the sample solution was dispensed onto a 3-mm carbon-coated copper grid. Excess solution was removed by an absorbent paper, and the sample was dried at room temperature.

CO$_2$-TPD measurement was similar to that of HCHO-TPD. In detail, the catalysts were saturated by 4.99 % CO$_2$ containing mixture balanced by nitrogen at ambient temperature for 0.5h. Then the flow gas was changed to pure helium for 0.5 h to remove the excessive CO$_2$, followed by the temperature ramping to 250 °C at a linear rate of 10 °C min$^{-1}$. The CO$_2$ was monitored by mass spectrometer at the m/z ratio of 44.
Results

Fig. S1 Raman shift patterns of α-, β-, γ- and δ-MnO$_2$ samples.
Fig. S2 HRTEM images of α-, β-, γ- and δ-MnO₂ samples, 1, 2 refer to different magnifications of one sample.
Fig. S3 XRD patterns of $\alpha$-, $\beta$-, $\gamma$- and $\delta$-MnO$_2$ samples after reaction.

Fig. S4 XPS spectra for Mn2p of $\alpha$-, $\beta$-, $\gamma$- and $\delta$-MnO$_2$ samples.
Fig. S5 CO\textsubscript{2}-TPD results for α-, β-, γ- and δ-MnO\textsubscript{2} samples.