

Fig. S1 A series of 3 “low flux” ISS spectra followed by 10 “high flux” ISS spectra were performed to determine the Pt/(Al+O) intensity as a function of 1 keV He⁺ exposure for the as deposited Pt₂ model catalyst. The fit passes through the down-sloping signal only in order to extrapolate back to 0 He⁺ exposure which determines the as deposited value for each cluster size. The inset shows an example of a “high flux” ISS spectrum.

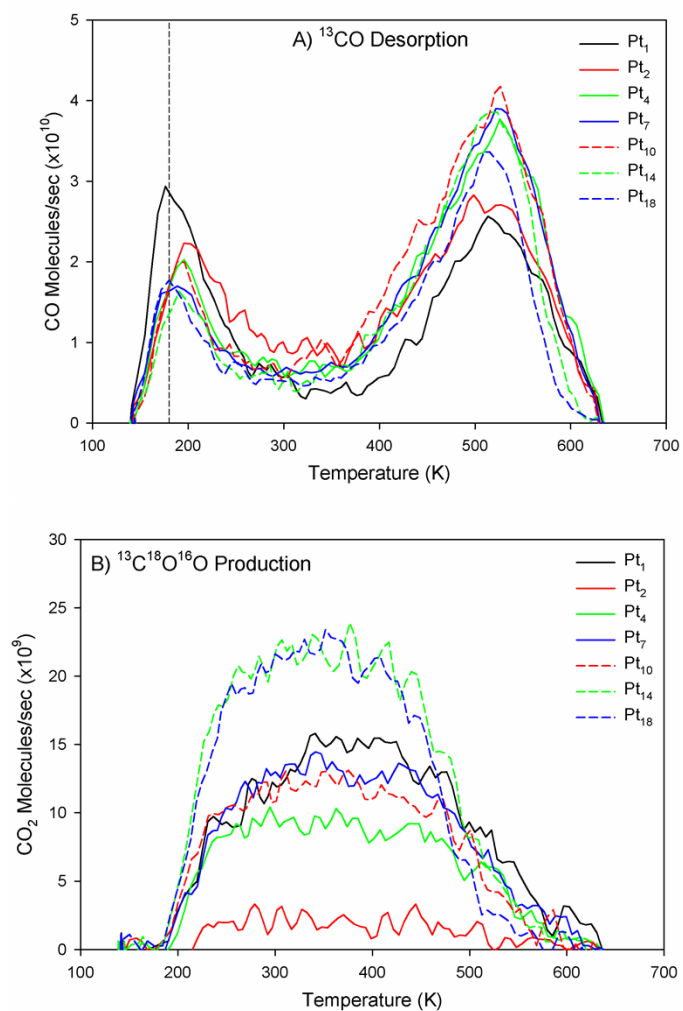


Fig. S2 ^{13}CO desorption (a) and $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ production (b) as a function of cluster size for 180 K oxidation. Notice the strong size dependence for CO_2 formation. The dashed line indicates the CO dose temperature (180 K).

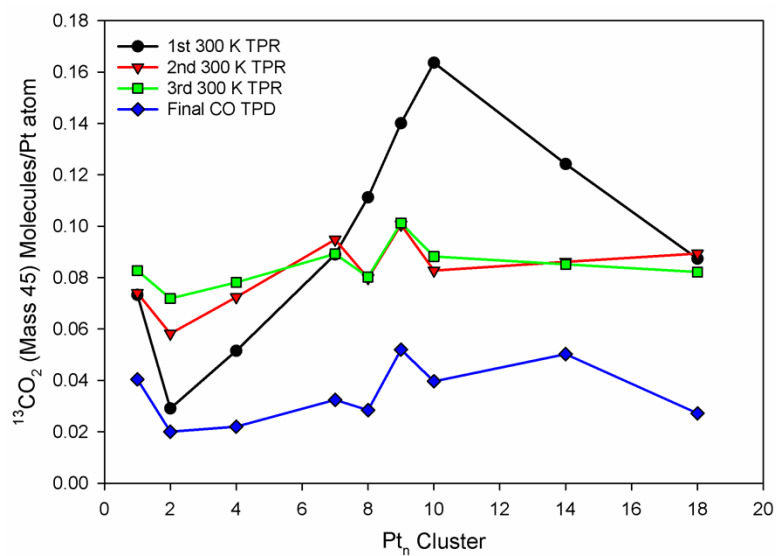


Fig. S3 The integrated $^{13}\text{CO}_2$ signal during 3 TPRs ($T_{\text{oxidation}} = 300\text{ K}$) and a final CO TPD. Notice the trend is very similar for the main product channel of $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ (mass 47), even for the final CO TPD, suggesting mass 45 is indeed $^{13}\text{CO}_2$ production.

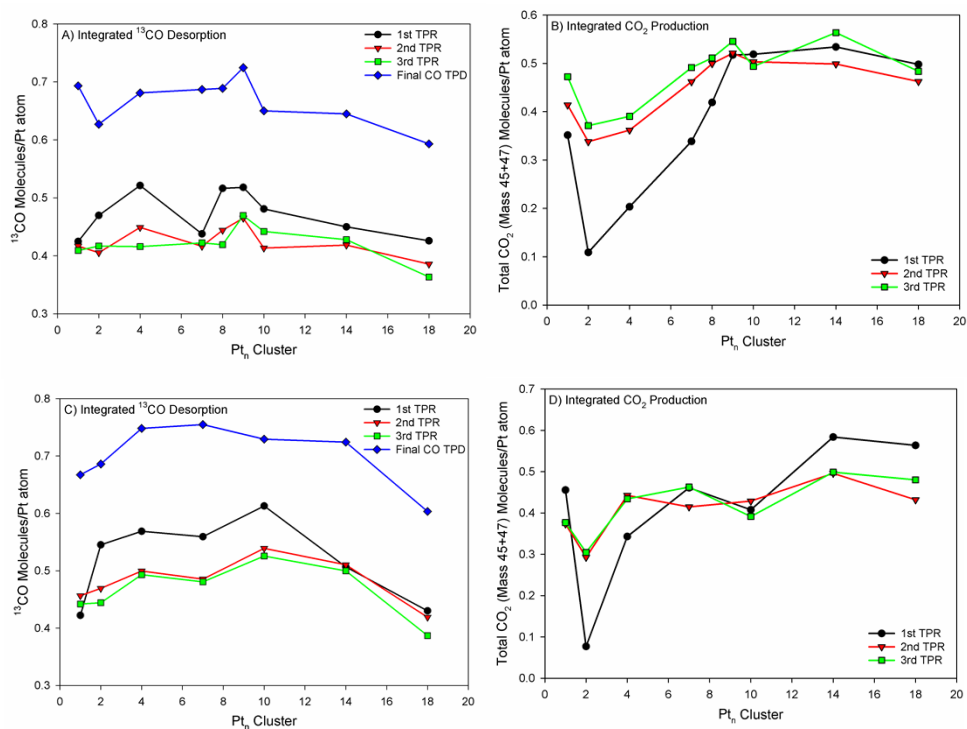


Fig. S4 The main text shows the integrated CO and CO₂ desorption as an average of the 180 K and 300 K oxidation TPR experiments. Here they are shown separately with CO and CO₂ shown for 300 K in (a) and (b) respectively. 180 K oxidation is shown in (c) and (d).

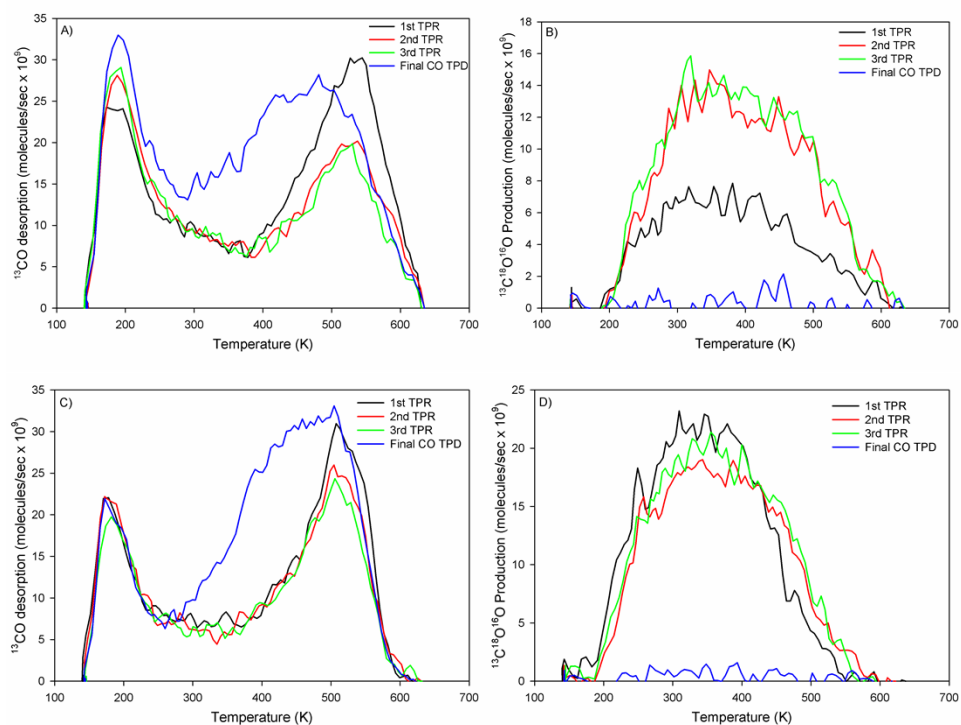


Fig. S5 A series of 3 TPRs followed by a final CO TPD was performed for each cluster size studied. Here are the CO and CO₂ desorption for Pt4 (a,b) and Pt18 (c,d) respectively.