

## Electronic Supplementary Information

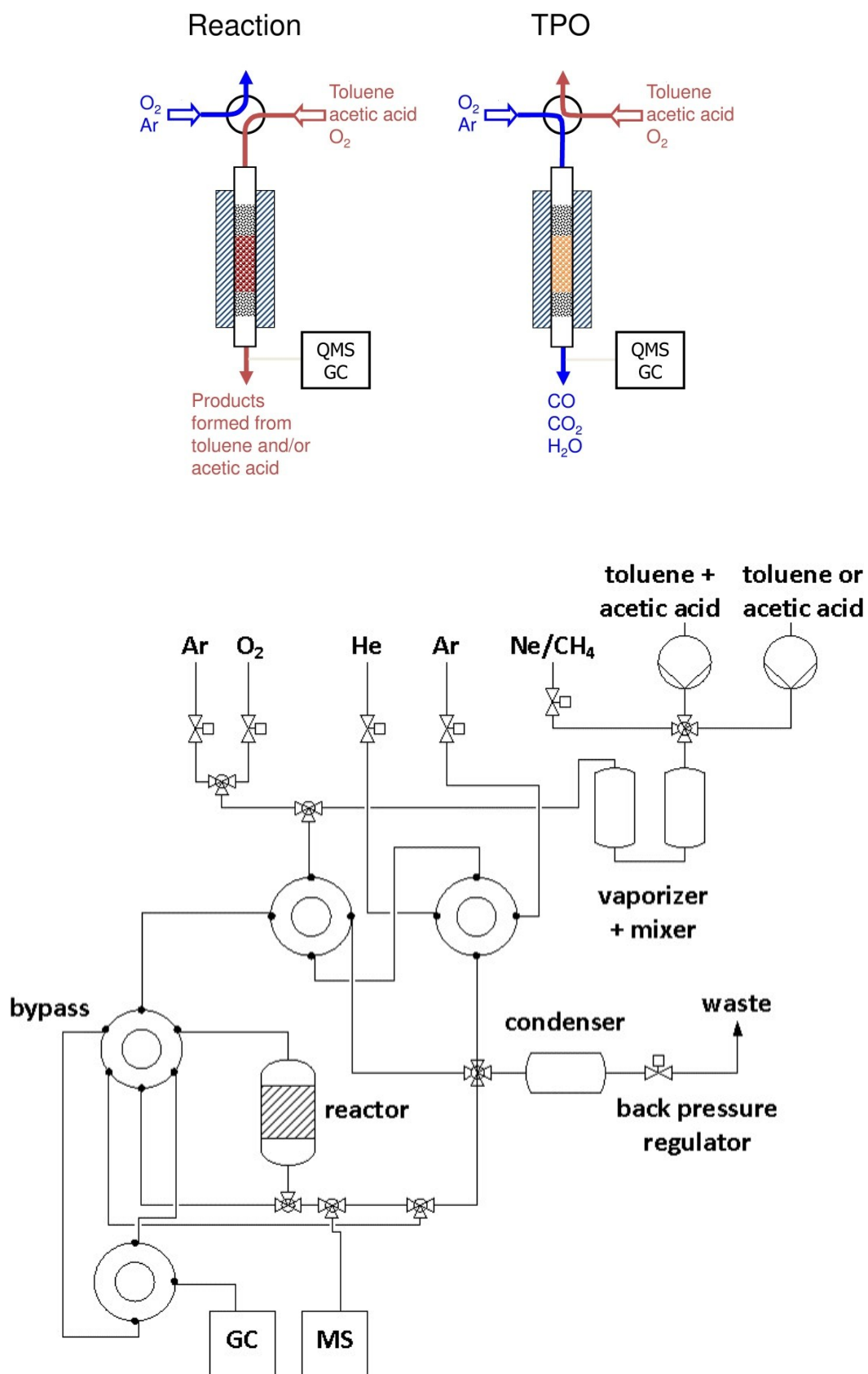
### **Nature of surface carbon species and pathways of their formation in the heterogeneously catalysed acetoxylation of toluene**

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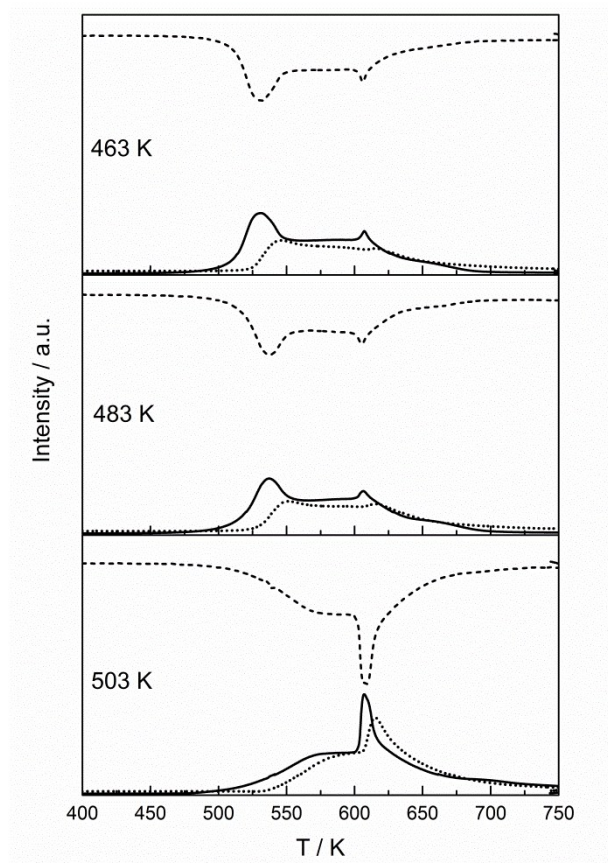
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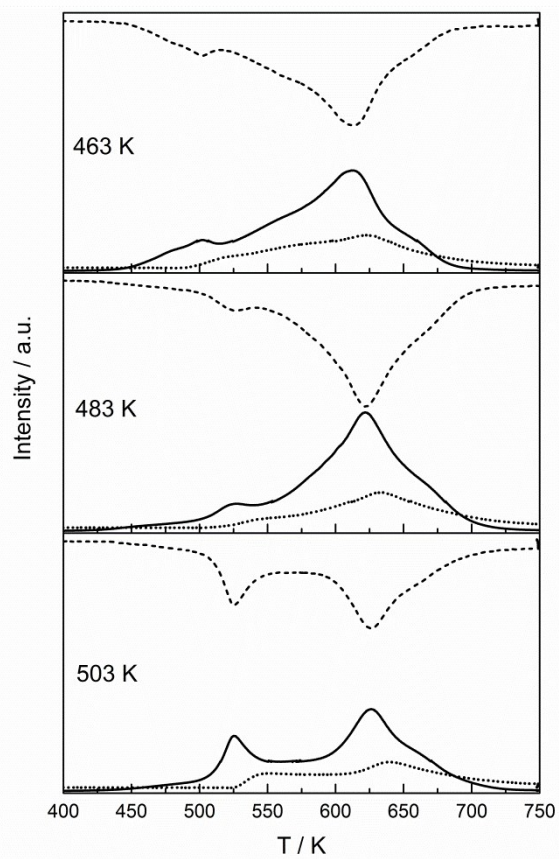
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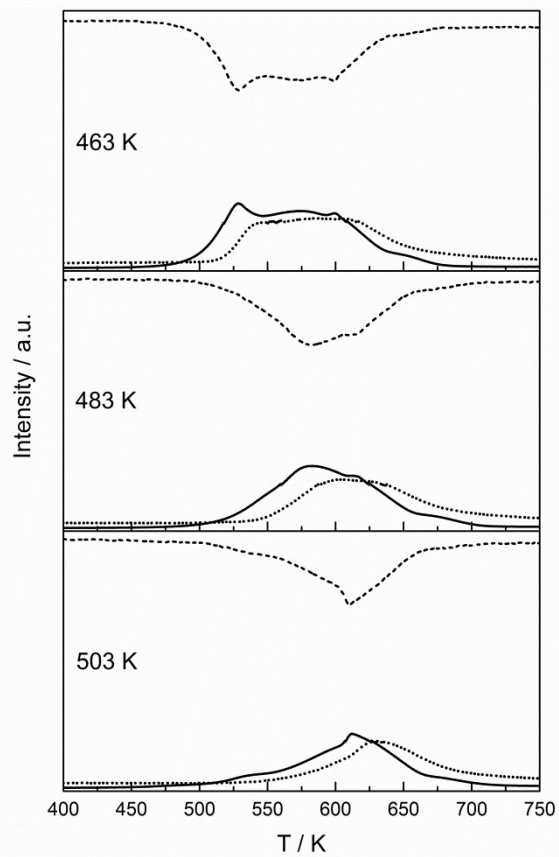
**Figure S1.** Schematic representation of in situ TPO tests and detailed set-up scheme.



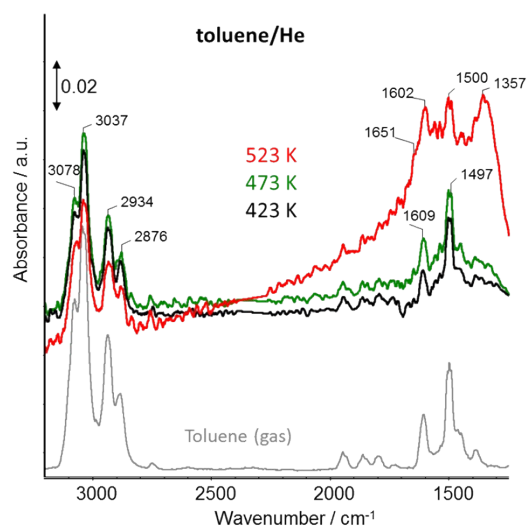
**Figure S2.** Profiles of CO<sub>2</sub> (solid line) and H<sub>2</sub>O (dotted line) liberated and O<sub>2</sub> (dashed line) consumed upon TPO of Pd-Sb/TiO<sub>2</sub> initially pre-treated in a toluene/acetic acid/O<sub>2</sub> feed and subsequent treatment in toluene/acetic acid/O<sub>2</sub> feed at 463 K, 483 K or 503 K.



**Figure S3.** Profiles of CO<sub>2</sub> (solid line) and H<sub>2</sub>O (dotted line) liberated and O<sub>2</sub> (dashed line) consumed upon TPO of Pd-Sb/TiO<sub>2</sub> initially pre-treated in a toluene/acetic acid/O<sub>2</sub> feed and subsequent treatment in toluene/O<sub>2</sub> feed at 463 K, 483 K or 503 K.

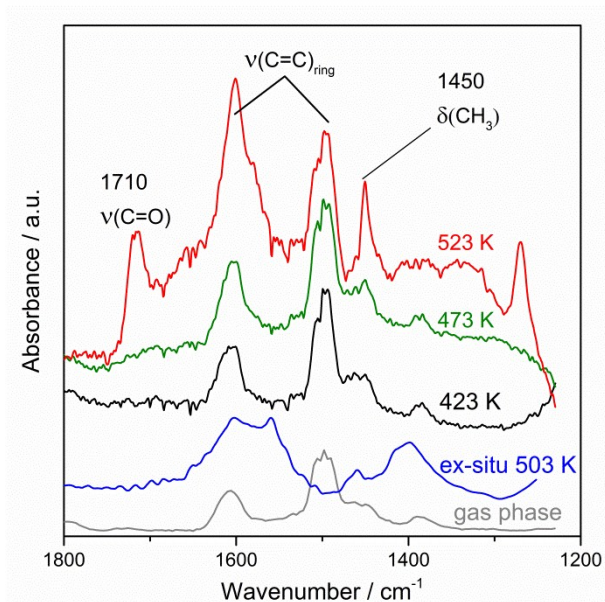


**Figure S4.** Profiles of CO<sub>2</sub> (solid line) and H<sub>2</sub>O (dotted line) liberated and O<sub>2</sub> (dashed line) consumed upon TPO of Pd-Sb/TiO<sub>2</sub> initially pre-treated in a toluene/acetic acid/O<sub>2</sub> feed and subsequent treatment in acetic acid/O<sub>2</sub> feed at 463 K, 483 K or 503 K.



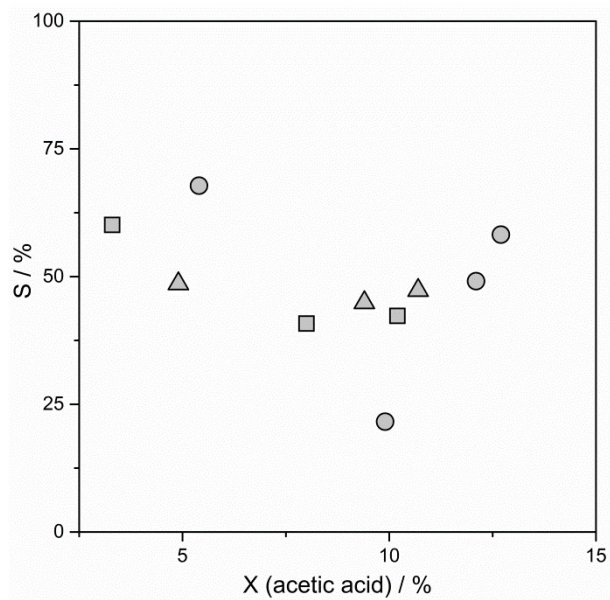
**Figure S5.** In-situ IR spectra recorded after dosing toluene/He over Pd-Sb/TiO<sub>2</sub> at 423 K, 473 K, 523 K, and gas phase toluene as reference.

Figure S5 shows the IR absorption spectra of toluene in the absence of gas phase O<sub>2</sub> at different temperatures. The vibration bands at 1651 and 1357 cm<sup>-1</sup> are assigned to the interaction of the methyl group with the catalyst. The band at 1651 cm<sup>-1</sup> indicates the formation of an adsorbed benzaldehyde species. The band at 1357 cm<sup>-1</sup> is assigned to the deformation of the methyl group caused by an interaction with the catalytic surface.



**Figure S6.** In situ IR spectra at 423 K, 473 K, 523 K, and ex situ IR spectrum after dosing toluene/O<sub>2</sub> at 503 K; gas phase toluene is given as reference.

The original profiles of CO<sub>2</sub>, H<sub>2</sub>O, and O<sub>2</sub> obtained from TPO experiments are shown in Figures S2-S4. The CO<sub>2</sub> and H<sub>2</sub>O profiles were integrated and the calculated areas were divided by the calculated areas obtained from TPO after activation of the catalyst under toluene/acetic acid/O<sub>2</sub> feed for 6 h. The corresponding areas to the latter profiles are 0.264 for CO<sub>2</sub>/Ar and 0.171 for H<sub>2</sub>O/Ar.



**Figure S7.** Selectivity to benzyl acetate as a function of acetic acid conversion at 463 K ( $\square$ ), 483 K ( $\Delta$ ) or 503 K ( $\circ$ ) and 2 bar under toluene/acetic acid/ $O_2$  feed with a molar concentration of 1/4/3.