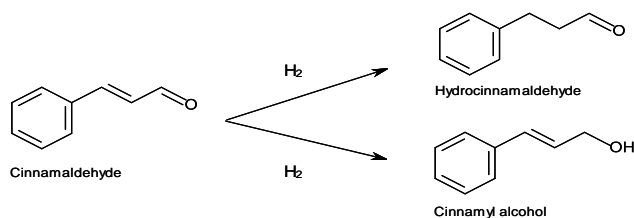


## Supporting Information

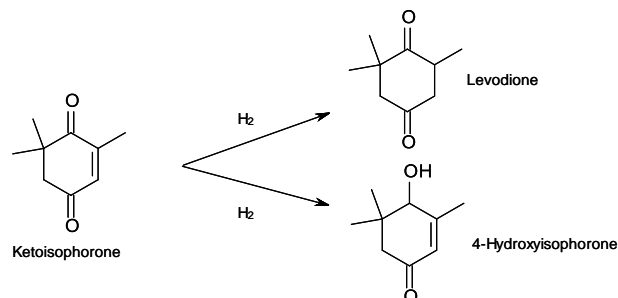
### Experimental

All chemicals were of AR grade and used without any further purification. Ketoisophorone, cinnamaldehyde, methanol, PtO<sub>2</sub> and Pt(acac)<sub>2</sub> were procured from Sigma-Aldrich. OMS-2 was synthesized via sol-gel method following the procedure reported by Duan *et al.*<sup>1</sup> 5 wt% Pt/OMS-2 was prepared by incipient wetness impregnation using platinum nitrate solution (assay 15.14%, Johnson-Matthey, UK), as the platinum precursor. After impregnation, the material was dried at 120 °C for 12 h followed by calcination at 500 °C for 4 h.

The hydrogenation data was taken using a 100 cm<sup>3</sup> Autoclave Engineers' high pressure reactor, which had a pressure range of 0-20 MPa and a maximum temperature limit of 573 K. In a typical experiment, the reactor was charged with 0.006 mol of substrate and 0.1 g of catalyst suspended in 60 cm<sup>3</sup> in 10 mol% methanol in water. The reactor was purged three times with N<sub>2</sub>, the mixture was agitated at 1500 rpm and heated to 373 K. After purging with H<sub>2</sub> three times, the reactor was pressurised to 1 MPa, which corresponded to time = 0. The reaction was monitored by sampling at regular time intervals, with analysis of the samples by GC equipped with a DB-1 capillary column and FID detector. The reaction schemes for the hydrogenation of cinnamaldehyde and ketoisophorone are shown in Figures S1 and S2, respectively.



**Figure S1** Reaction scheme for the hydrogenation of either C=C or C=O bond of cinnamaldehyde (the product resulting from the complete hydrogenation of both C=C and C=O double bond is not shown here).



**Figure S2** Simplified Reaction scheme for the hydrogenation of either C=C or C=O bond of ketoisophorone (the other products resulting from the further hydrogenation of the C=C and C=O double bond are not shown here).

*In situ* liquid phase HERFD-XANES (High-energy resolution fluorescence detection -X-ray absorption near edge spectroscopy)<sup>2</sup> was performed in a stainless steel autoclave reactor with a window made of 1 mm thick PEEK (polyether ether ketone).<sup>3</sup> The Pt L<sub>III</sub> edge was monitored using a Johan-type spectrometer recently installed at the SuperXAS beamline of the Swiss Light Source (SLS).<sup>4</sup> All the treatments were performed *in situ* using *ca.* 300 mg of catalyst and 20 cm<sup>3</sup> 10 mol% methanol in water at 373 K. Since, 5 wt% Pt/OMS-2 was prepared by incipient wetness impregnation followed by calcination in air at 500 °C for 4 h. For X-ray absorption spectroscopic measurements the catalyst was first reduced *in situ* in presence of H<sub>2</sub> (1 MPa) at 373 K and 20 cm<sup>3</sup> 10 mol% methanol in water. After reduction of the catalyst, the reactor was purged with He and cooled down to room temperature to remove the adsorbed hydrogen. Cinnamaldehyde or ketoisophorone or H<sub>2</sub> were then put in contact with the reduced catalyst. In each case, the Pt L<sub>III</sub> edge HERFD-XANES was measured with either 0.006 mol of cinnamaldehyde or ketoisophorone under He or 1 MPa H<sub>2</sub> at 373 K.

The energy position of inflection points was obtained from least squares fitting procedure by applying an analytical profile to extracted derivatives (Beta-function from PeakFit software). The corresponding estimation of the errors in the shifts shown in Table 1 was obtained from the fitting procedure. All measurements were from an average of 6 spectra. Although the data was taken every 0.45 eV, shifts were observed in the entire spectrum, meaning that resolution is primarily defined by the fitting. In practice this means that, with the current S/N data quality, it is possible to distinguish shifts as small as 0.01 eV.

### Computational details

All the density functional theory (DFT) calculations were performed with the VASP code in periodic slab models.<sup>5</sup> The electronic structure was calculated with the generalized gradient approximation (GGA) using the exchange-correlation functional PW91.<sup>6</sup> The projector augmented wave (PAW) method was employed to describe the interaction between the atomic cores and electrons.<sup>7</sup> The calculation details of Pt(111) and OMS-2(001) surfaces can be obtained in our previous work.<sup>8</sup> Four layer 2×2 unit cells were used for Pt(211) surface and the

upmost two layers were relaxed. A  $1 \times 2 \times 1$   $k$ -point sampling in the surface Brillouin zone was used for the Pt(211) surface. A cut-off energy of 400 eV and the force threshold on each relaxed atoms below  $0.05 \text{ eV } \text{Å}^{-1}$  were used in this work for all the structural optimizations.

In this system, it is not necessary to include the solvent effect in the DFT calculations as we have already shown<sup>8</sup> that, without explicitly including solvent effects, the chemistry including the selectivity can be adequately addressed using the framework of DFT we used in the current work. This is also consistent with a large volume of work in the literature for similar systems.<sup>9</sup> Specifically for hydrogenations, for example, it has been demonstrated that water does not affect the adsorption of  $\text{H}_2$ .<sup>10</sup>

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