

Supporting Information

Controlling Selectivity in Unsaturated Aldehyde Hydrogenation Using Single-Site Alloy Catalysts

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- Figure S1. Kinetic data for the hydrogenation of CMA with CuPt_x/SBA-15 catalysts as a function of nanoparticle composition for P(H₂) = 12.5 and 37.5 bar.
- Figure S2. Additional time-dependent kinetic data for the hydrogenation of CMA with CuPt_x/SBA-15 catalysts.
- Table S1. Estimated Pt content in our CuPt_x/SBA-15 catalysts.
- Figure S3. IR spectra of crotonaldehyde adsorbed on CuPt_x/SBA-15 catalysts.
- Figure S4. DFT calculations of the adsorbate structures and adsorption energies for crotonaldehyde on Cu(111) and Pt(111) surfaces.
- Figure S5. TPD and IsoTPD for the hydrogenation of cinnamaldehyde with atomic hydrogen on clean Cu(110) single-crystal surfaces.
- Figure S6. Kinetic data from catalyst recycling experiments on the conversion of CMA with Cu/SBA-15 and CuPt_{0.005}/SBA-15 catalysts.

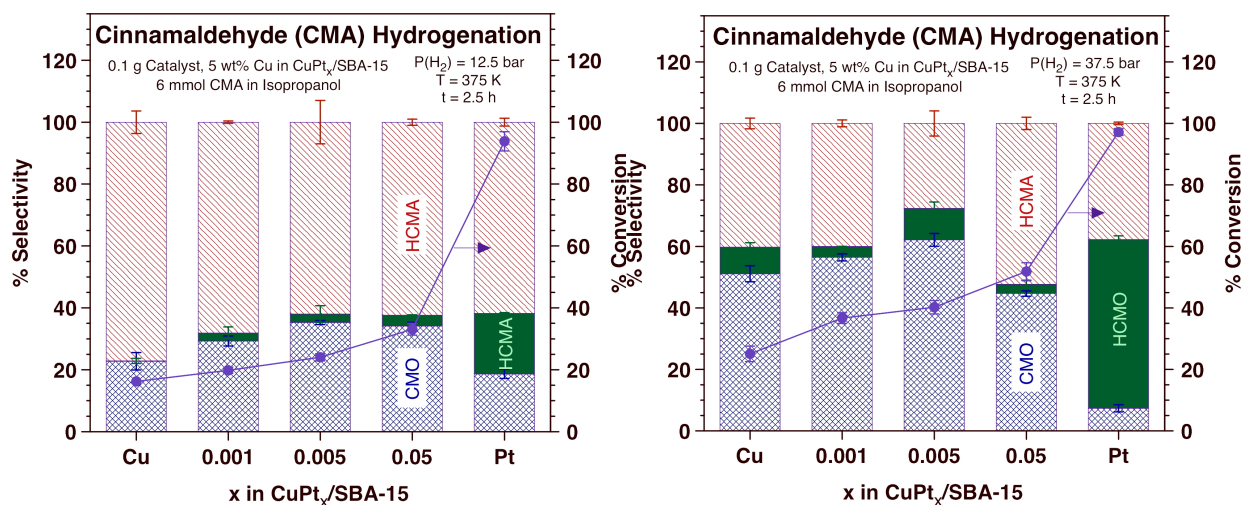


Figure S1. Total conversion (after 2.5 h of reactions) and selectivity for the hydrogenation of cinnamaldehyde using Cu-Pt bimetallic nanoparticle catalysts supported on SBA-15 as a function of their metal composition. Data are provided for reactions carried out with hydrogen pressures of 12.5 (left panel) and 37.5 (right) bar, to complement the results reported in Figure 1 for $P(H_2) = 25$ bar. In all cases, optimum selectivity toward CMO production is seen for Cu-Pt bimetallic nanoparticles with 0.5 mol% Pt. This is due mainly to a suppression of the hydrogenation of CMA to HCMA and HCMO that is so favorable with Pt. Conversion numbers for each individual product can be estimated from Figure 1 and Supplementary Figure S1 by multiplying the total conversion, purple filled circles, times the selectivities provided in the bar portion of the plots.

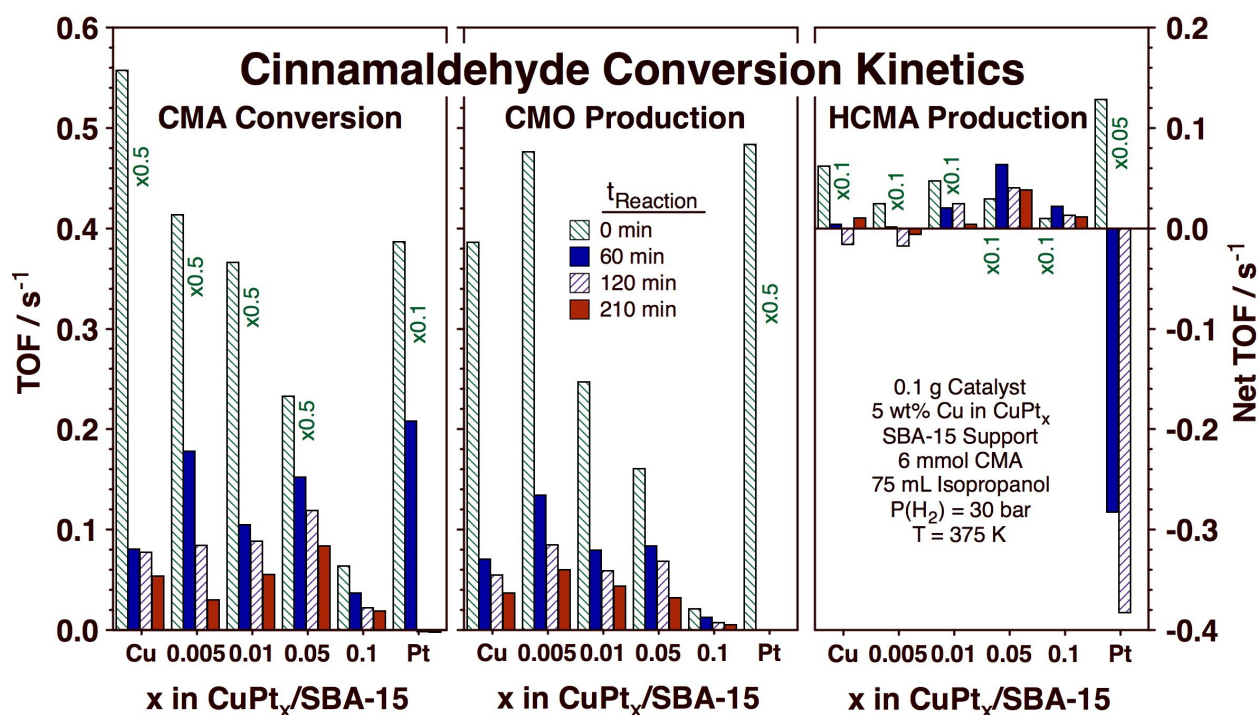


Figure S2. Net turnover frequencies (TOF, in units of molecules converted or produced per metal atom per second) for the consumption of CMA (left) and for the production of CMO (center) and HCMA (right) at several times during the hydrogenation of CMA using Cu-Pt bimetallic nanoparticle catalysts supported on SBA-15. Data are reported as a function of bimetallic nanoparticle composition. The negative values seen after long times of reaction for HCMA are due to its further hydrogenation to HCMO. One thing to note here, in addition to the maximized selectivity toward CMO for CuPt_x with $x \sim 0.005$, is the increase in CMO selectivity seen in all cases with increasing time of reaction (increased conversion in our batch reactor).

Table S1. Estimated Pt content in our CuPt_x/SBA-15 catalysts.

Sample	Nominal %Pt	%Pt from ICP-AES^a	%Pt from XPS	<d> / nm^b	%Surface Atoms^c
CuPt _{0.001} /SBA-15	0.100	0.105 ± 0.005	2.3 ± 0.8	6.7 ± 0.8	2.6 ± 0.3
CuPt _{0.005} /SBA-15	0.500	0.494 ± 0.005	2.1 ± 0.8	6.6 ± 0.8	3.3 ± 0.4

^a Measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

^b Average metal nanoparticle diameter, measured by transmission electron microscopy (TEM).

^c Estimated by assuming spherical nanoparticles of <d> diameter and the placement of all Pt atoms on the surface.

The bimetallic nanoparticle compositions estimated by XPS are about an order of magnitude larger than those measured by bulk techniques such as ICP-AES, and close to the estimates for the total number of Pt atoms within individual bimetallic nanoparticles. This suggests that the Pt atoms are all located in the near-surface region.

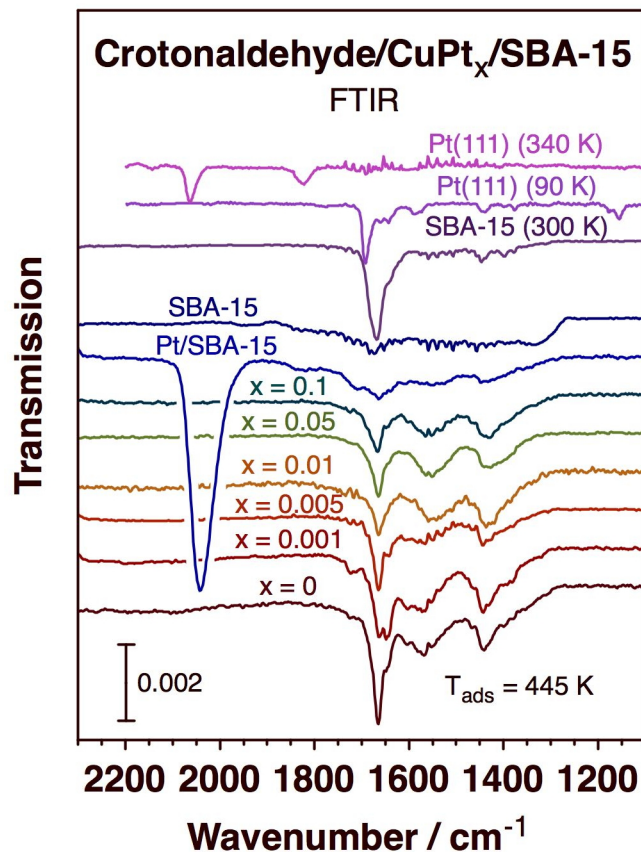


Figure S3. Transmission infrared absorption spectra of crotonaldehyde adsorbed on $\text{CuPt}_x/\text{SBA-15}$ catalysts after annealing to 445 K as a function of the composition of the dispersed metal nanoparticles (the value of x). Adsorption is molecular in all cases other than on the pure Pt catalyst, in which case decomposition and the formation of adsorbed CO (indicated by the large C–O stretching peak at 2044 cm^{-1}) is observed. It is also seen that adsorption on the $\text{CuPt}_x/\text{SBA-15}$ catalysts is likely through the oxygen atom of the aldehyde, as only the peaks associated with the C=O moiety are affected by bonding on the surface; the frequency of the C=C stretching mode remains about the same as in the free molecule.

Crotonaldehyde Adsorption DFT Calculations

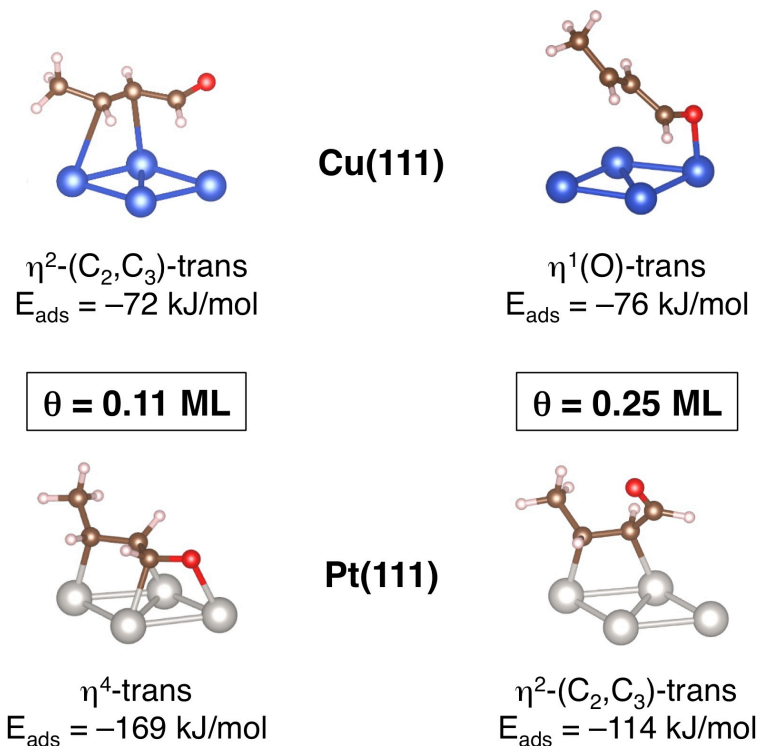


Figure S4. DFT calculations of the adsorption structures and energies for crotonaldehyde on Cu(111) (top) and Pt(111) (bottom) surfaces. The most stable bonding configurations are shown for two different surface coverages, a ninth (corresponding to one molecule per (3 x 3) surface cell, left) and a quarter (for a (2 x 2) cell, right) of a monolayer. On Pt, multiple coordination is favored, and that is easier and more energetically favorable at low coverages. On Cu, on the other hand, a single bond via the oxygen atom at high coverages is preferred (several configurations with different coordinations were found to have the same energy, within the accuracy of the calculations, at low coverages, but none proved to be more stable than the high-coverage structure shown here). This may explain the differences in hydrogenation selectivity seen in catalysis between the two metals.

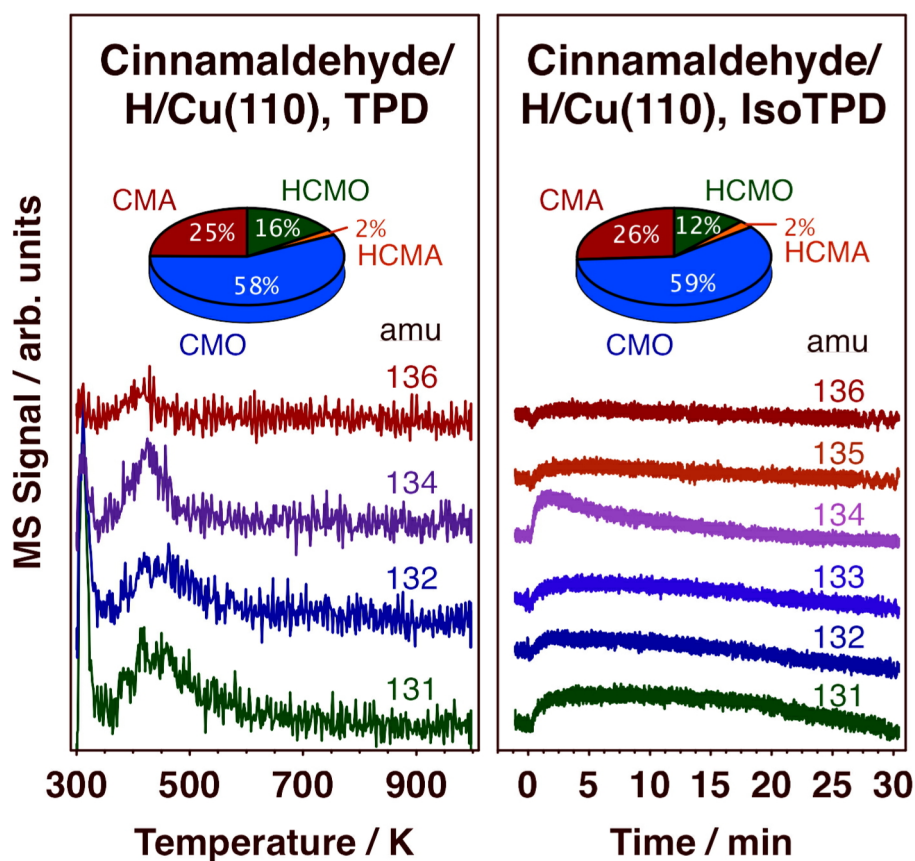


Figure S5. Regular (temperature ramped, left panel) and isothermal (right) temperature programmed desorption (TPD) traces from hydrogenation experiments with cinnamaldehyde on clean Cu(110). These experiments were performed in a similar manner as those with oxygen-predosed Cu(110) reported in Figure 5. Slightly lower CMA conversions and full hydrogenation to HCMO are seen on this clean-Cu surfaces compared to the surface pretreated with oxygen, but an equally high selectivity toward CMO formation was seen in both cases.

Cinnamaldehyde Hydrogenation Kinetics

Catalyst Recycling Tests

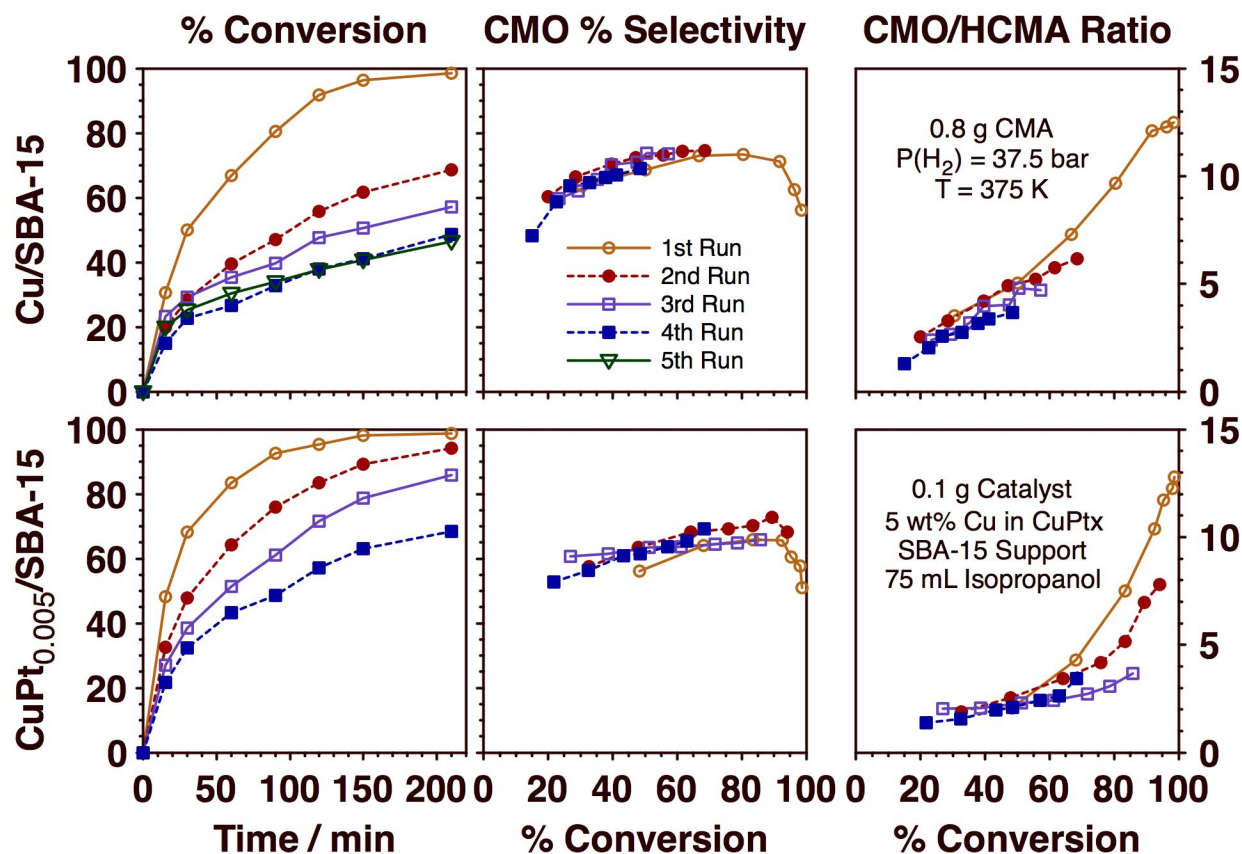


Figure S6. Kinetic data for the conversion of CMA with Cu/SBA-15 (top row of panels) and CuPt_{0.005}/SBA-15 (bottom) catalysts. Shown are the temporal evolution of the total conversion (left), the selectivity toward CMO production (center), and the CMO/HCMA ratio (right) for five consecutive runs performed with the same catalysts, each starting with a fresh reaction mixture but without any additional treatment of the catalyst in between runs. These catalyst recycling experiments indicate that the large drop in activity and the increase in CMO selectivity seen as a function of reaction time is not due to long-term catalyst poisoning with strongly-bonded organic fragments, but rather to the preferential adsorption of HCMA on the surface once produced.