

Supporting information

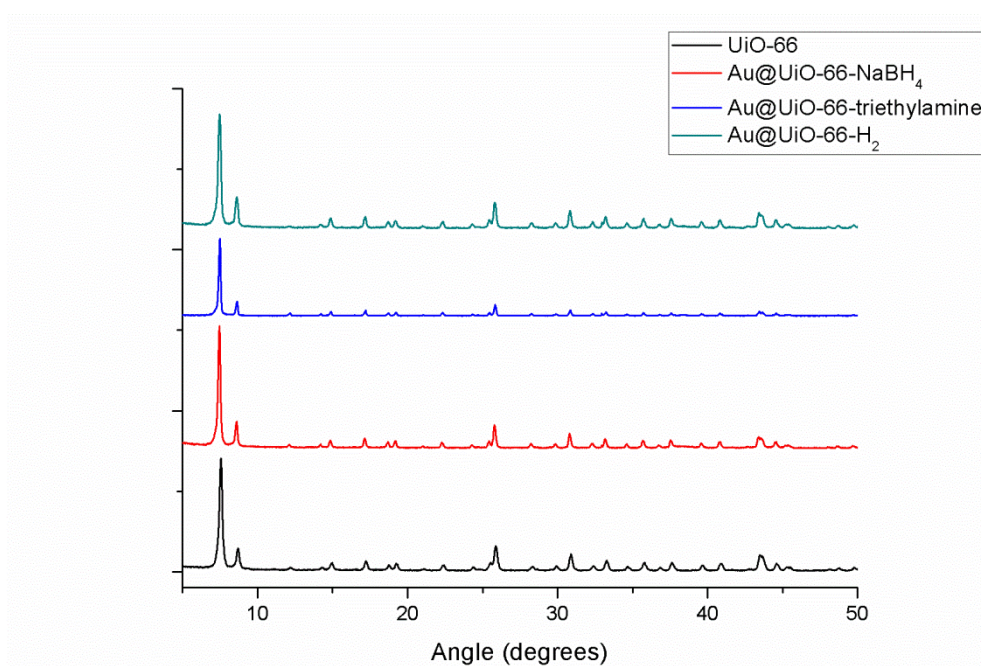


Fig S.1 XRPD patterns of the UiO-66 and Au@UiO-66 materials.

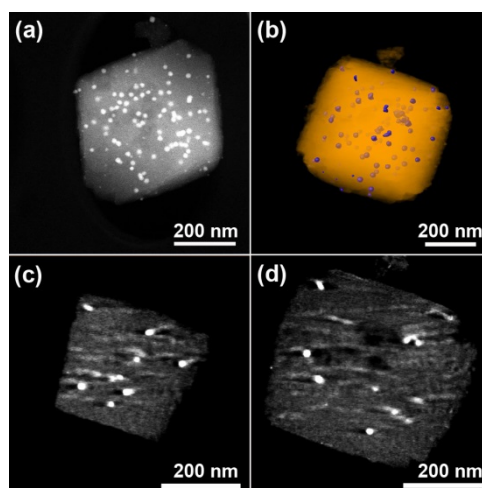


Fig S.2 . HAADF-STEM electron tomography reconstruction of the Au@UiO-66-H₂ material. (a) HAADF-STEM image of the Au-loaded UiO-66 crystal used for tomographic reconstruction. (b) Reconstructed volume, with the UiO-66 matrix rendered in Orange, and the Au nanoparticles in Blue. (c)&(d) Orthoslices through the reconstructed volume, evidencing that the bright-contrast Au nanoparticles are spread throughout the UiO-66 matrix.

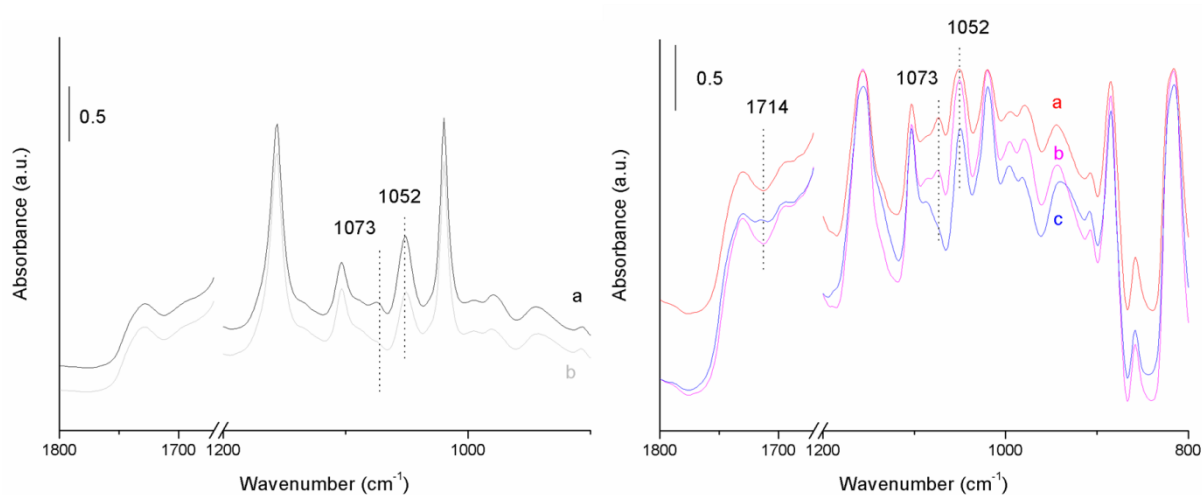
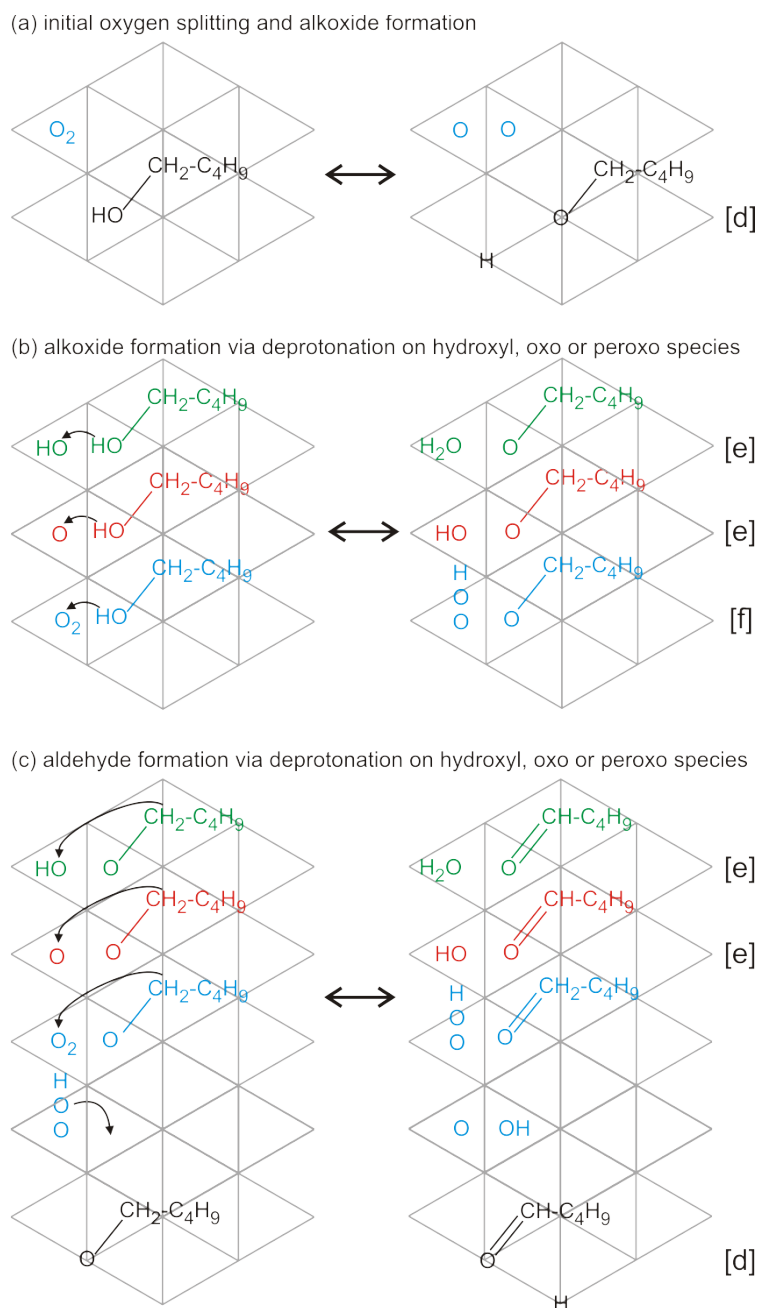


Fig S.3 Left: IR spectra of pentanol (3mbar) adsorbed on the Au@UiO-66-NaBH₄ sample in the absence of O₂ at 25°C (a) and 60°C (b). Right: IR spectra of pentanol (3mbar) adsorbed on the Au@UiO-66-NaBH₄ sample in the presence of 15mbar O₂ at 25°C (a), 60°C (b) and 100°C (c).



Scheme S. 1. Plausible oxidation mechanism on the Au Nanoparticles, schematically shown on a Au(111) surface. The symbols refer to articles where similar reaction pathways are postulated: [d]¹, [e]² and [f]³.

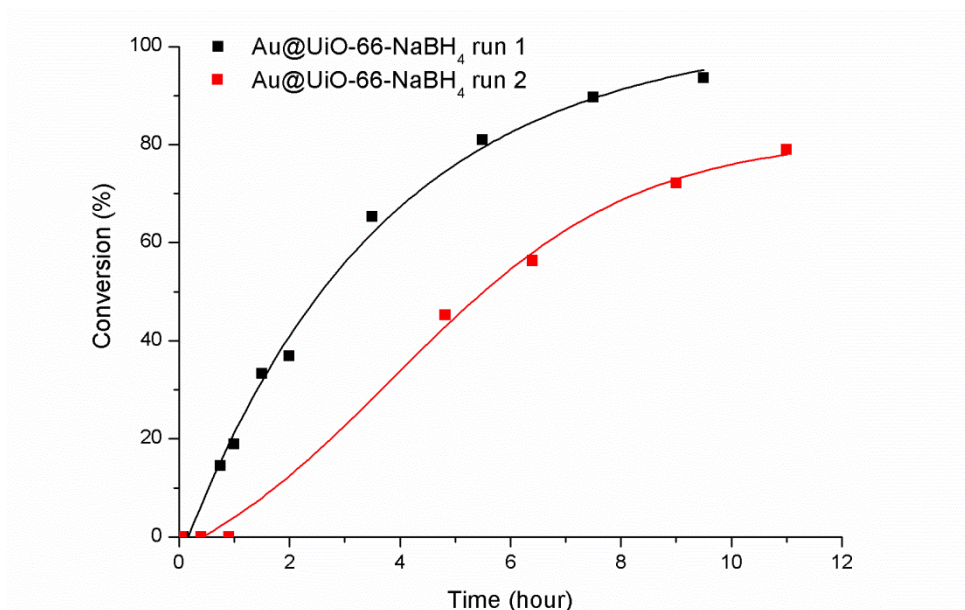


Fig S.4 Benzyl alcohol conversion in the first and second run using Au@UiO-66-NaBH₄ as catalyst

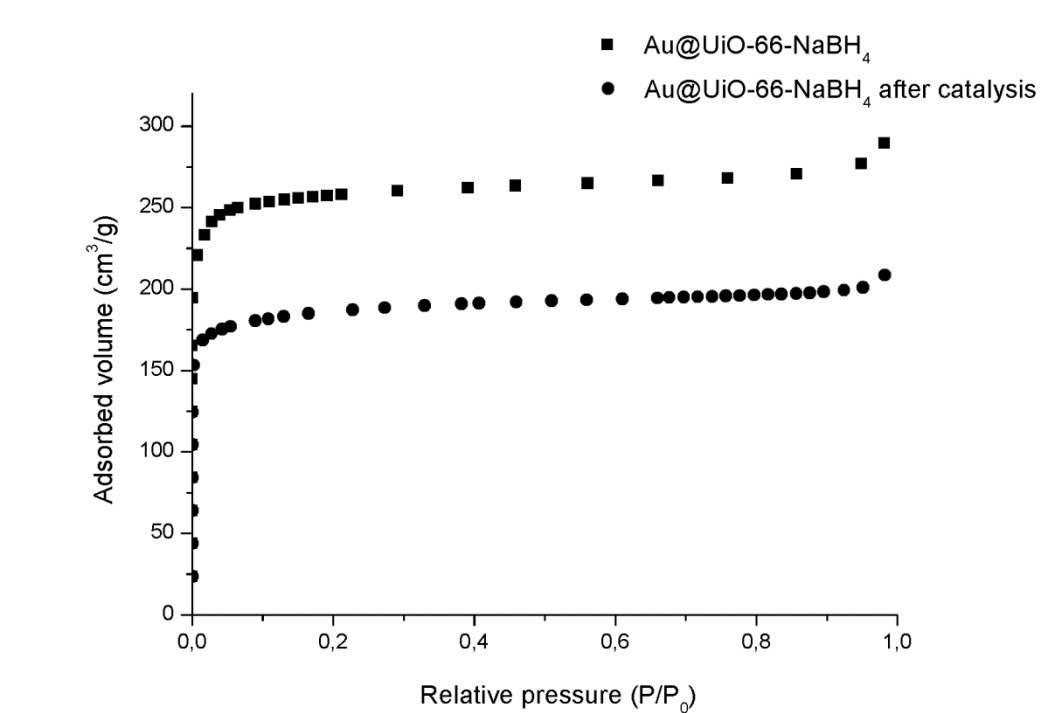


Fig S.5 N₂ sorption isotherm of Au@UiO-66-NaBH₄ before (■) and after catalysis (●)

Cluster calculations

The cluster model used in this paper is the same as applied earlier in the paper of Vermoortele et al.⁴ (**Figure S.6**). Geometry optimizations were performed with the Gaussian09 package⁵ using the B3LYP hybrid functional.⁶ The double-zeta Pople basis set 6-31g(d) was used for all atoms except for Zr, for which the LANL2DZ effective core potential and basis set were applied.⁷ Afterwards single point energy refinements at the B3LYP/6-311++g(d,p) level of theory were performed to account for the electronic energy effects of the substituents on the terephthalate linkers, employing the LANL2TZ(f) effective core potential and basis set for Zr⁸. Furthermore, van der Waals corrections of the type D3 as developed by Grimme⁹ in conjunction with the B3LYP functional were computed. Using the standard notation “LOT-E”//“LOT-G” (LOT-E and LOT-G being the electronic levels of theory used for the energy and geometry optimizations, respectively), all cluster results discussed in this paper are obtained with the method denoted as “B3LYP/6-311++g(d,p)*-D3//B3LYP/6-31g(d)*”. The PHVA method¹⁰, applied also previously for kinetics^{4, 11}, was then used to investigate the kinetics of the pentoxide formation on the extended UiO-66 cluster.

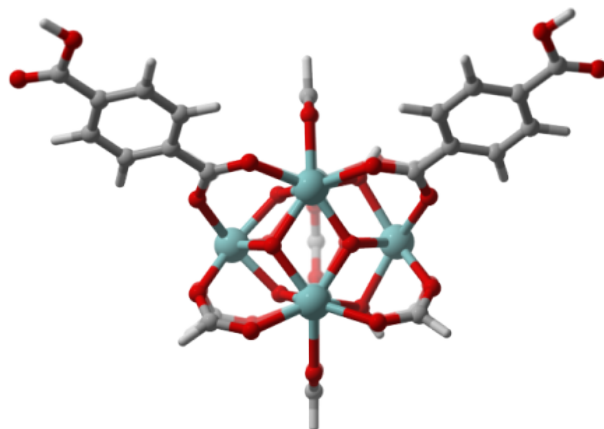
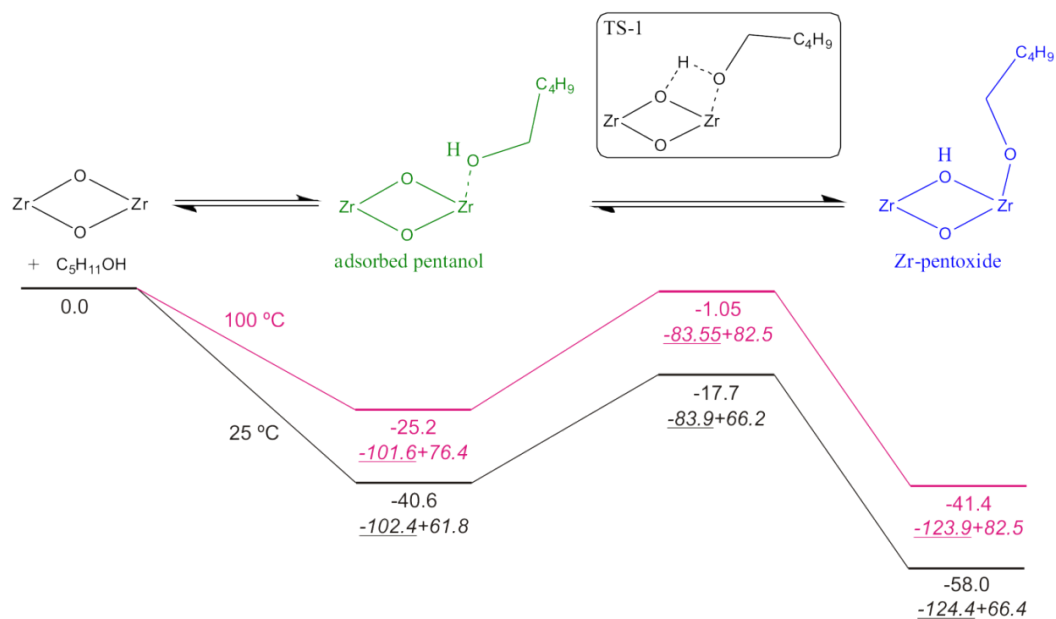


Fig S.6 Extended cluster model for UiO-66. The terephthalic linkers closest to the considered active site are maintained.

Accessible Zr-sites form strong Lewis acid adsorption sites, and experimentally, after loading of pentanol an equilibrium between gas phase and adsorbed pentanol will be installed. Pentanol can either be physisorbed or chemisorbed on the Zr-defect sites within the UiO-66 (Scheme S.2). A free energy profile was determined based on the extended UiO-66 cluster model, as displayed in Figure S.9.⁴ Gibbs free energy differences are reported in Scheme S.2, as well as the enthalpy and entropy contributions. At 25 °C, the adsorption free energy of a linearly adsorbed pentanol is -40.6 kJ/mol but this decreases with increasing temperature due to a large entropic penalty. Furthermore, the pentoxide formation from (linearly) adsorbed pentanol is both exergonic and exothermic, and only a small free energy barrier needs to be overcome, which probably can even decrease when the environment is fully taken into account.



Scheme S.2. Equilibrium between gas phase pentanol, adsorbed pentanol (physisorption) and Zr-pentoxide (chemisorption). Free energy profile at 25 °C (black) and at 100 °C (red) with a pentanol pressure of 3mbar. *Enthalpy* and *entropy* contributions to the free energies are also given in kJ/mol. Extended cluster (Fig. S.6) results at B3LYP/6-311++g(d,p)*-D3//B3LYP/6-31g(d)*.

Molecular dynamics simulations

Construction of the models

We performed calculations on a fully periodic UiO-66 model with unit cell formula $[\text{Zr}_6\text{O}_5(\text{OH})_2(\text{RCOO})_{10}][\text{Zr}_6\text{O}_4(\text{OH})_4(\text{RCOO})_{12}]$ (one BDC linker consists of two RCOO units). The structure exhibits one missing BDC linker, which leads to a topology with straight parallelogram shaped channels throughout the material (**Fig S.7**, pore size ~ 10 - 11 Å). The unit cell was then optimized with the Vienna Ab Initio Simulation Package (VASP 5.2.12)¹². We applied a plane wave kinetic energy cutoff of 600 eV, employing the PBE exchange-correlation functional¹³ with D3-dispersion corrections including Becke–Johnson damping¹⁴. Subsequently, we ran molecular dynamics simulations starting from two different placements of pentanol (adsorbed pentanol and chemisorbed pentanol or Zr-pentoxide).

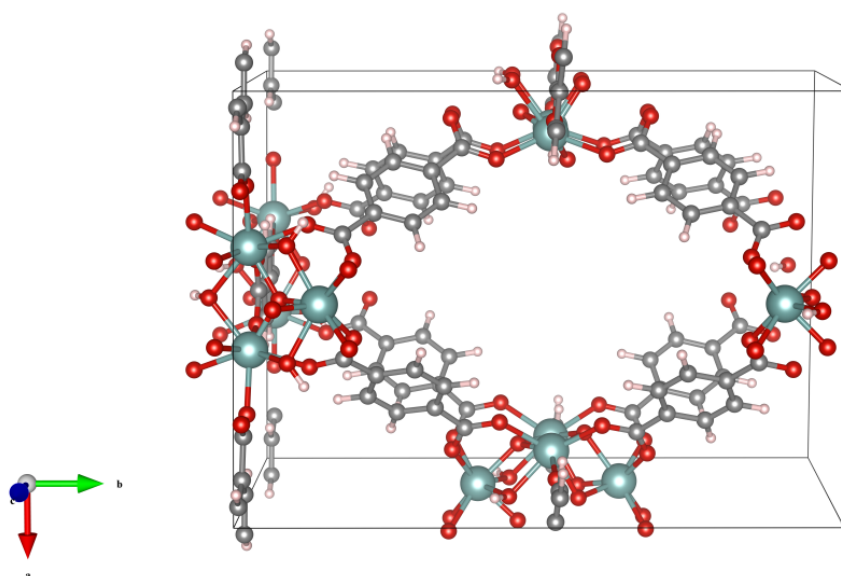


Fig S.7 Applied periodic model for the UiO-66 with one missing linker.

Au nanoparticles were generated using the program OpenMD (www.openmd.org) applying the Sutton-Chen formulation of the Finnis-Sinclair metallic potential using quantum corrections according to Kimura et al¹⁵. We generated a NP of 55 atoms,¹⁶ and removed one atom to obtain a NP of 54 atoms. Having an even number of Au-atoms makes it possible to model the system without spin polarization, an approach that is frequently used when Au-NP are considered². Similar to the UiO-66 case, adsorbed and chemisorbed states of pentanol were constructed for further investigation by molecular dynamics simulations.

Computational Methodology

AIMD simulations were performed with the CP2K simulation package¹⁷ on the DFT level of theory and with Gaussian Plane Wave basis sets (GPW)¹⁸. The BLYP functional¹⁹ was chosen including Grimme D3 dispersion corrections^{14a}. The DZVP-GTH basis set²⁰ was applied for all atoms except for Zr and Au, in which we opted for the MOLOPT-DZVP-GTH basis set²¹. The time step for integration of the equations of motion was set to 0.5 fs. The simulations were performed within the NVT ensemble ($P=1$ bar, $T=298$ K). The

velocities are updated each time step during the *ab initio* molecular dynamics run (see computational details in the Supporting Information). The Velocity Power Spectrum (VPS) was generated with MD-tracks.²² The analysis was performed on 126000 MD-steps of 1 fs, starting from an equilibrated structure (obtained after an initial MD run of 1 ps). The input velocities were divided in 12 blocks and subsequently a Fourier transform of each block was calculated and the final VPS was constructed from the average over all the blocks. Remark that a larger number of blocks leads to an improved statistical accuracy of the amplitudes, however, a reduced resolution of the frequency scale.²³

Furthermore, the wavenumbers were scaled (scaling factor = 0.98) to obtain a good comparison with experimental data. An overview of all VPS spectra plotted together is given in **Fig. S.8**, while the standard deviation on the amplitudes is given in **Figures S.9-S.12**.

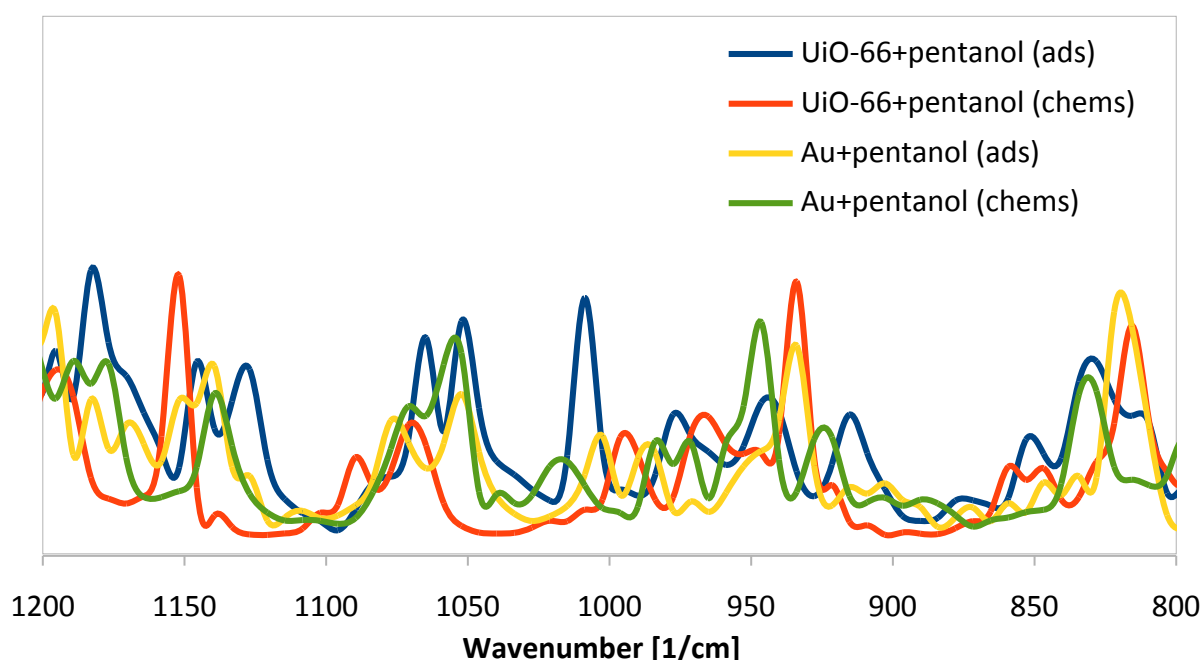


Fig S.8 Smoothed velocity power spectra of pentanol for the 4 systems that were used.

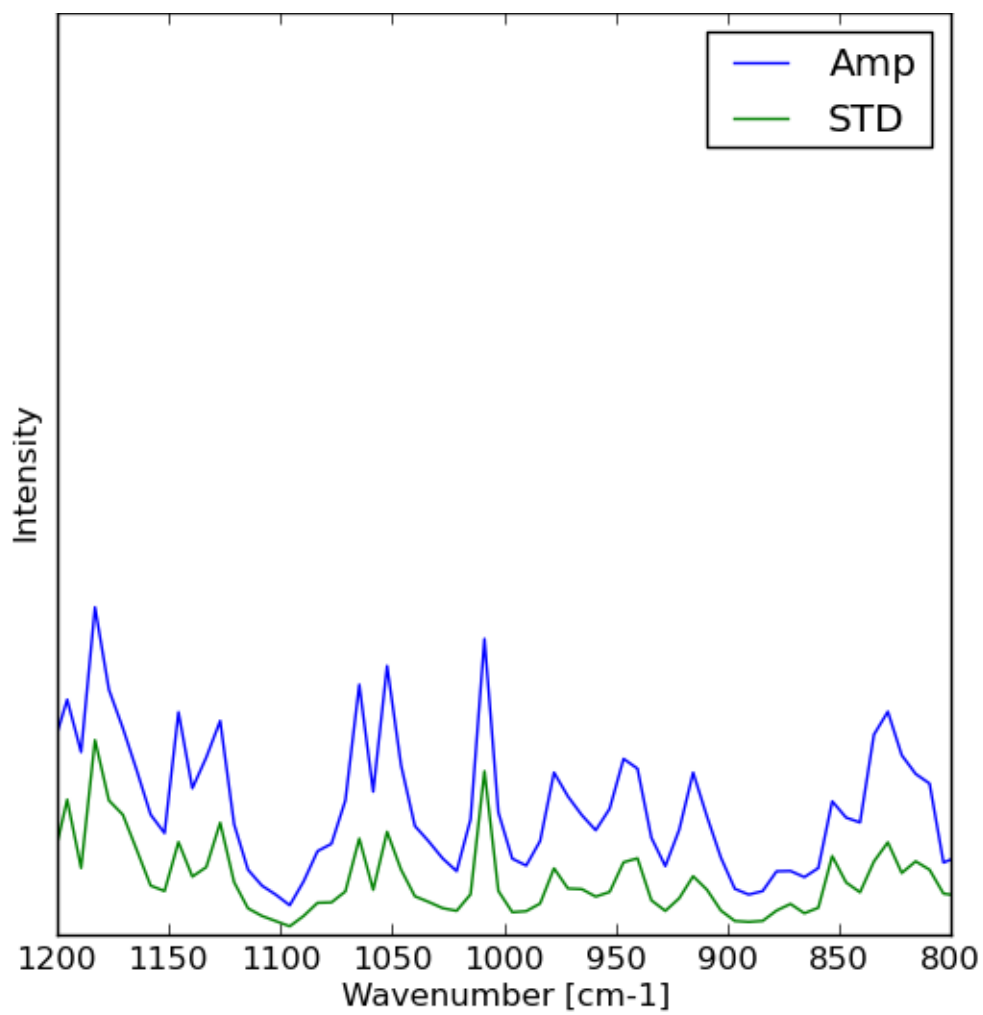


Fig S.9 Velocity power spectra of pentanol for the UiO-66 model with adsorbed pentanol.²³

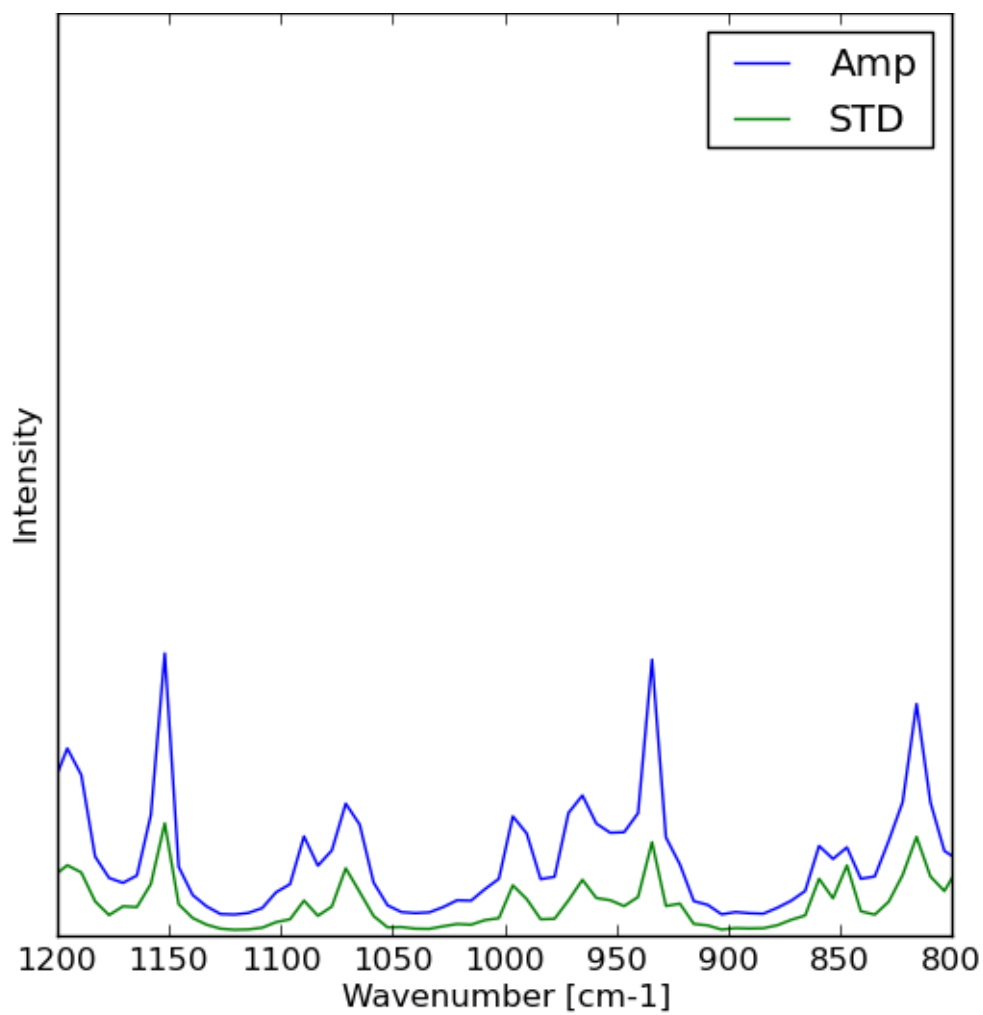


Fig S.10 Velocity power spectra of pentanol for the UiO-66 model with chemisorbed pentanol.²³

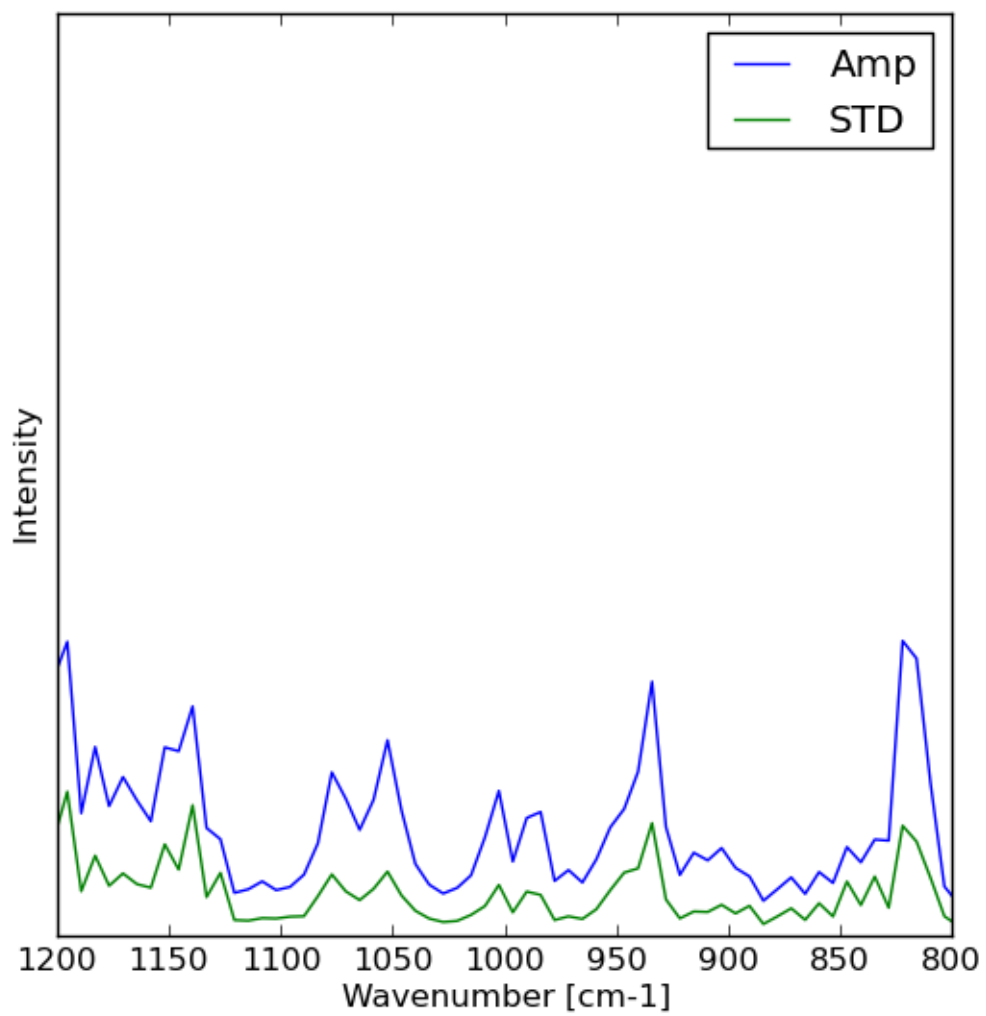


Fig S.11 Velocity power spectra of pentanol for the Au model with adsorbed pentanol.²³

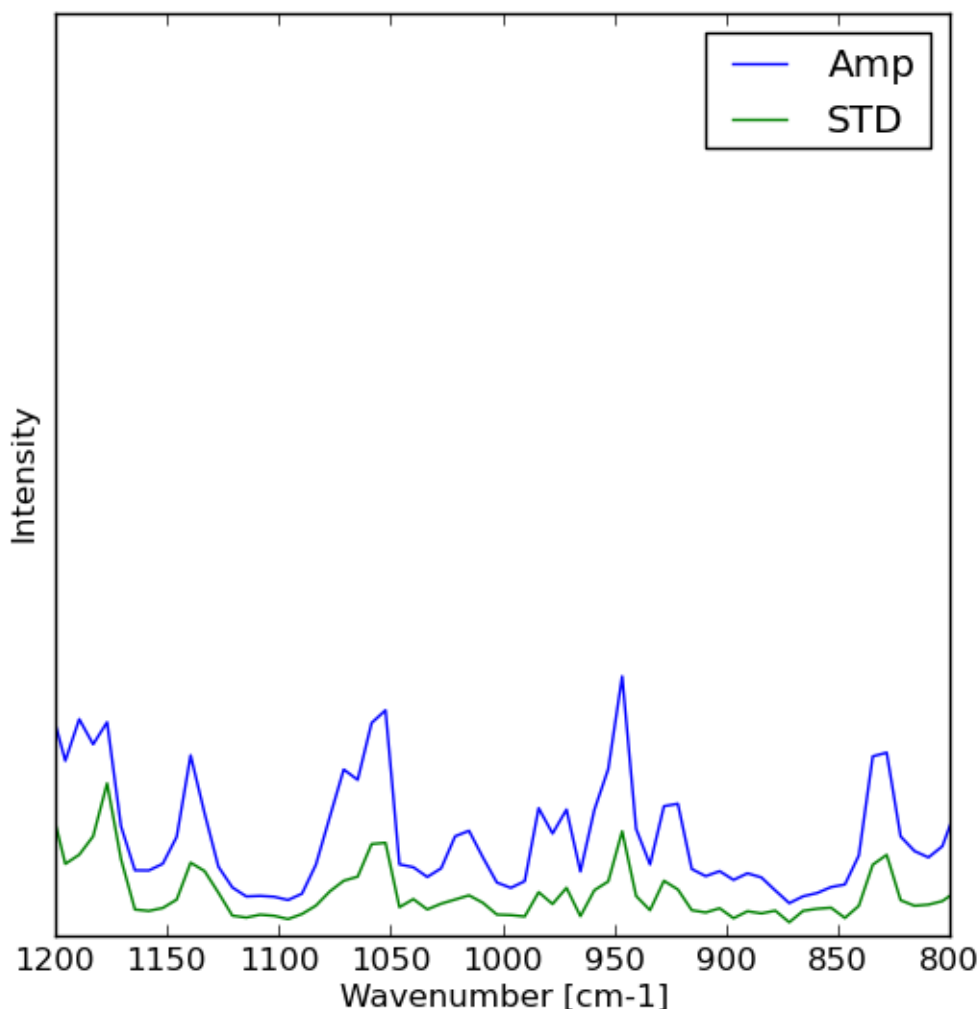


Fig S.12 Velocity power spectra of pentanol for the Au model with chemisorbed pentanol.²³

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