

Exact-Stoichiometry High Surface-Area Mesoporous AlPO₄ Glass for Efficient Catalysis

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Supplementary Information

1. Collapse of mAlPO₄ mesoporous structure under the TEM electron beam

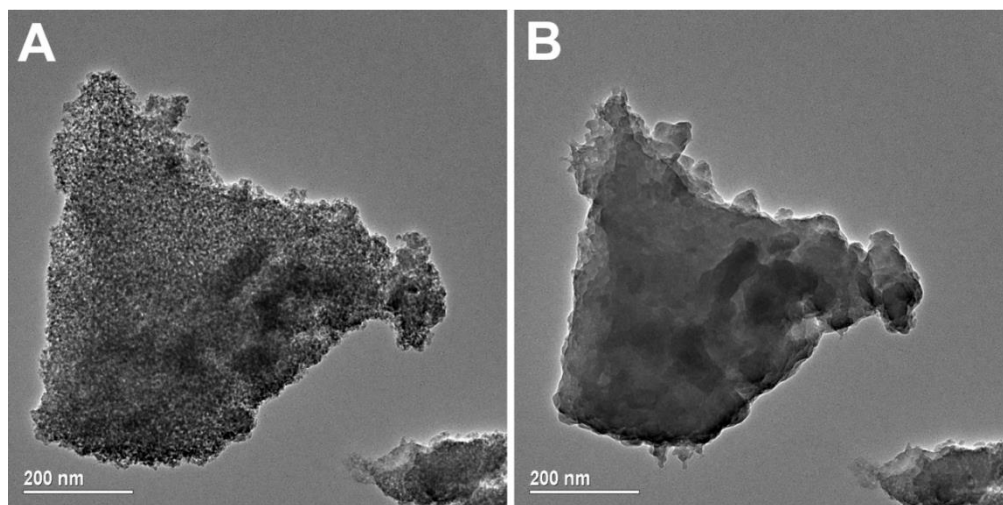


Figure S1. TEM image of mAlPO₄ (A) before and (B) after electron beam irradiation for 30s.

3. ²⁷Al and ³¹P MAS NMR of mAlPO₄ and Pd@mAlPO₄

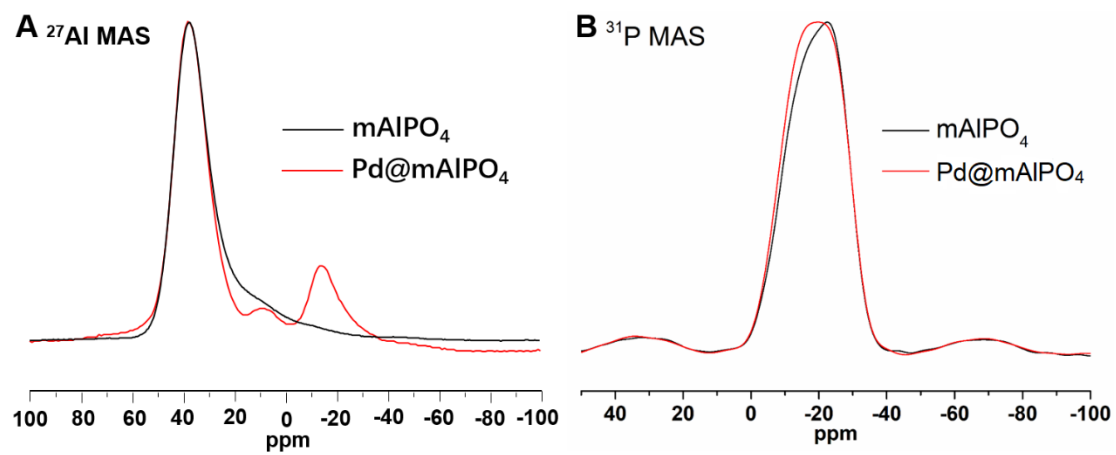


Figure S2. (A) ²⁷Al and (B) ³¹P MAS NMR spectra of mAlPO₄ and Pd@mAlPO₄.

4. Synchrotron X-ray Absorption Spectra of Rh@mAlPO₄

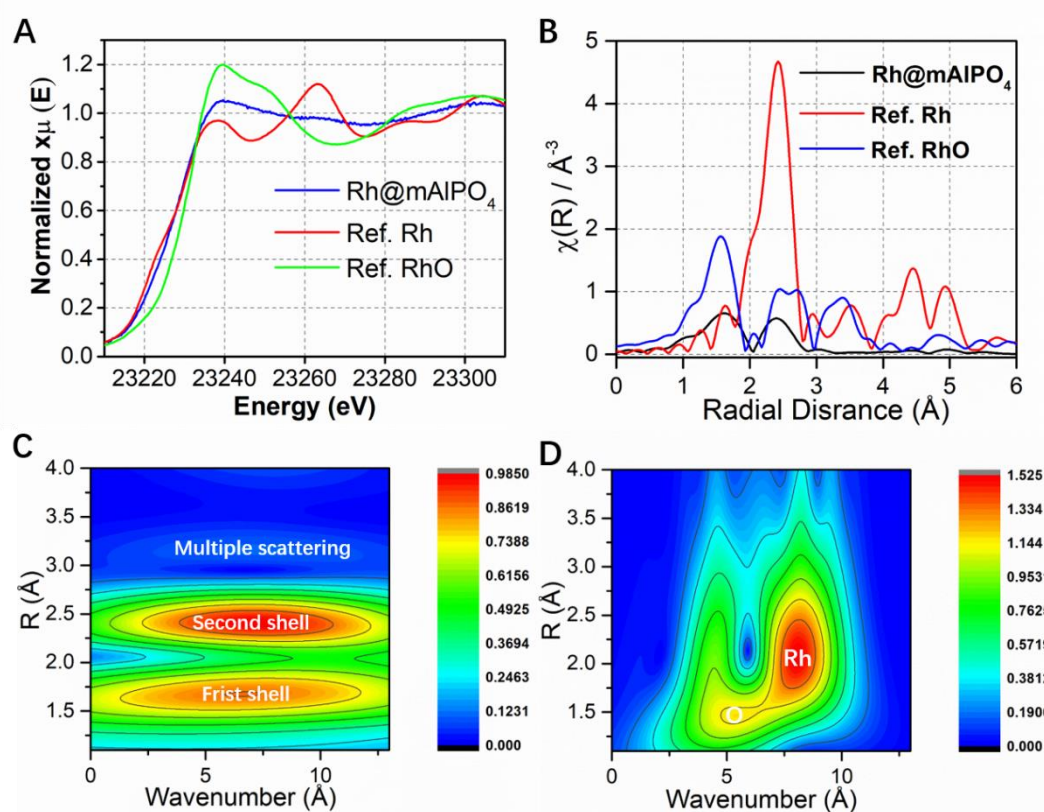


Figure S3. (A) XANES, (B) EXAFS, k_3 (C) Overview and (D) Detailed Rh k -edge

Morlet WT of Rh@mAlPO₄.

The XANES spectrum of Rh@mAlPO₄ (Figure S3A) shows an edge shifted by 0.6 eV toward higher energy relative to metallic Rh (3.2 eV shift for Rh³⁺), again indicating a slight increase in average oxidation although most Rh NPs are likely in the metallic state. The Fourier transformed EXAFS (Figure S3B) reveals the presence of first shell Rh-O bond and second shell Rh-h/P bond, and this is consistent with the Rh K-edge overview wavelet transform analysis shown in Figure S3C. The detailed wavelet transform analysis (Figure S3D) shows the second shell is dominated by Rh-Rh contribution and a reduced metal-(O-)P contribution relative to Pd@mAlPO₄. This is likely due to the lesser amount of Rh-O species present in the sample, which is evidenced by the also much reduced first shell Rh-O backscattering intensity, and smaller XANES edge shift.

2. Reactant-AlPO₄ interaction

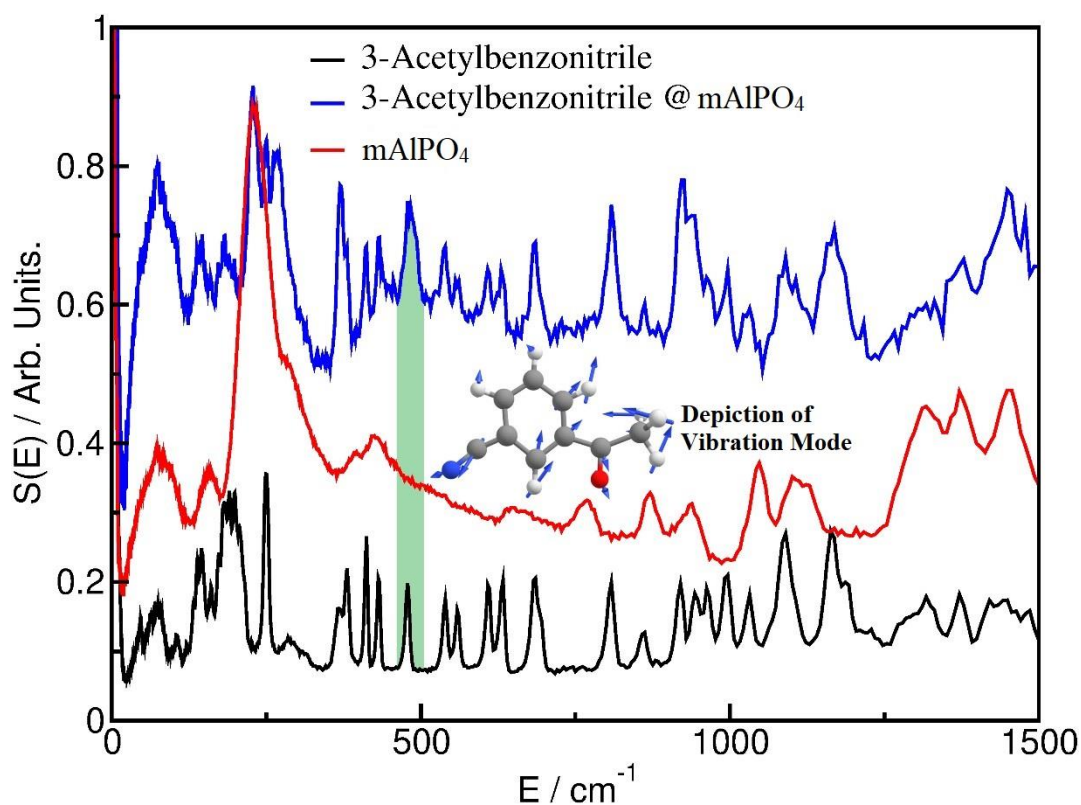


Figure S4. Inelastic neutron spectroscopy of blank mAlPO₄, 3-acetylbenzonitrile, and 3-acetylbenzonitrile@mAlPO₄

Inelastic neutron spectroscopy (INS) measurements were performed on the TOSCA instrument at the ISIS neutron and muon source, UK. Spectra were taken for empty AlPO₄, pure 3-acetylbenzonitrile, and 3-acetylbenzonitrile entrapped in AlPO₄. The first observation is that the peaks from pure 3-acetylbenzonitrile are clearly visible in the entrapped sample, showing that there is a sizeable portion of 3-acetylbenzonitrile molecules present. All these peaks are present except those at low wave number (< 200 cm⁻¹). Modes in this low energy region are typically intermolecular vibrations which exist in the crystal structure, therefore changes in this region upon entrapment points towards inclusion of single molecules within the matrix. Additional evidence for this

conclusion comes when the peak widths are carefully inspected. A very sizeable peak broadening is observed for the mode at $\sim 480\text{ cm}^{-1}$. A peak broadening in an INS measurement is indicative that a molecule is under the influence of a broad range of local potentials/environments, which supports the idea that individual molecules are entrapped within the matrix, with a range of different local environments. In order to get some qualitative insight into this broadened mode, we performed a single molecule density functional theory phonon calculation, using the B3LYP hybrid functional, and 6-311++G(d,p) basis set. The mode in question was identified as a collective bending of the entire molecule, meaning that changes in the local environments of every atom in the molecule will contribute to a shift in the peak, which again corroborates the conclusion that molecules are entrapped in the matrix in a range of local environments.

5. Pd@mAlPO₄ after recycling

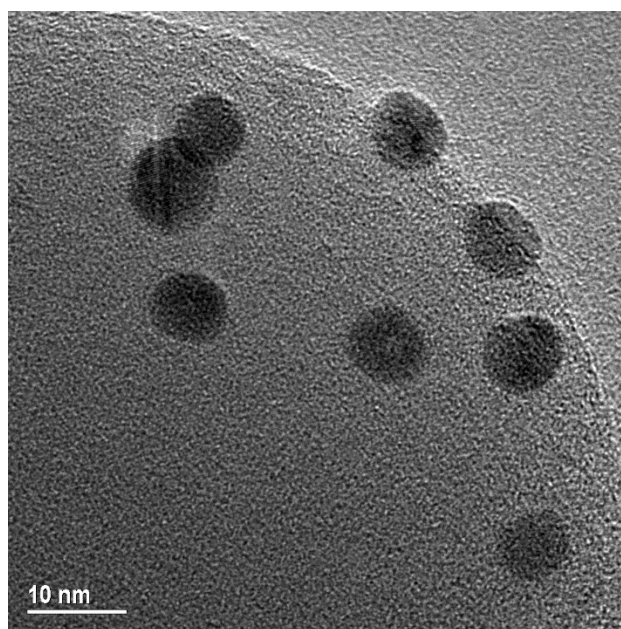


Figure S5. TEM image of Pd@mAlPO₄ after six cycles

6. Additional Recycling Test of mAlPO₄ and Rh-NPs@mAlPO₄

For both recycle test, the catalysts were recycled by filtration and washed by

corresponding solvents after each reaction. Then, the catalysts were dried and weighed before next recycle.

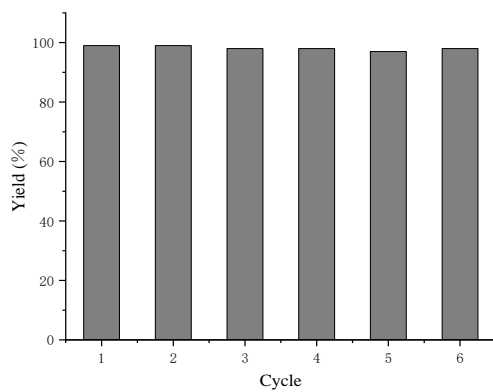


Figure S6. Recycling test of mAlPO₄ for [3 + 2] cycloaddition

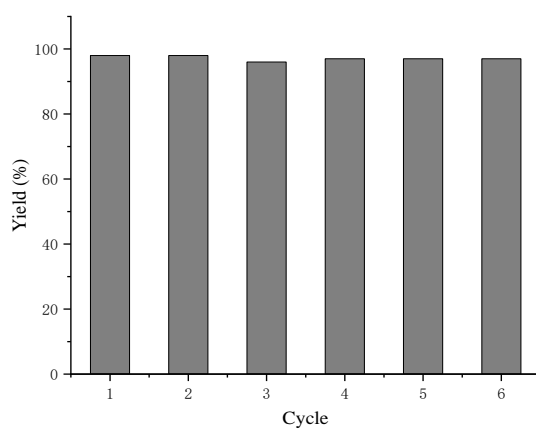


Figure S7. Recycling test of Rh-NPs@mAlPO₄ for hydrogenation of phenol (yield of cyclohexanol)