

Electronic Supplementary Information

Covalent anchoring of N-hydroxyphthalimide on silica via robust imide bonds as a reusable catalyst for selective aerobic oxidation of ethylbenzene to acetophenone

Guojun Shi, Ya Feng, Sihao Xu, Qiuting Lu, Yuxin Liang, Enxian, Yuan, Lijun Ji

1. Characterization methods

FT-IR was applied to clarify the structure of the prepared immobilized NHPI catalyst and related intermediates on a spectrometer (Tensor 27, Bruker). The spectra were recorded with a resolution of 4 cm^{-1} and a scanning scope of $400\text{--}4000\text{ cm}^{-1}$. The self-supporting wafer diluted by KBr was prepared with a sample concentration of 1%.

Thermogravimetric analyses were carried out on a thermal gravimetric analyzer (Pyris 1 TGA, PerkinElmer) to investigate the grafting concentration and the thermal stability of the prepared SiO_2 -bound NHPI catalyst. A temperature range $30\text{--}1000\text{ }^\circ\text{C}$ and a scan rate of $10\text{ }^\circ\text{C}/\text{min}$ were adopted under a N_2 atmosphere.

The concentrations of C, H and N elements of prepared immobilized NHPI catalyst and related intermediates were determined by an element analyzer (Vario EL Cube, Elementar). The samples with an accurate mass was burned using oxygen (99.999) in the presence of CuO as a catalyst, the resulting gaseous mixture was analyzed by a gas chromatographer and calculated to determine the concentration of C, H and N elements in the synthesized catalysts.

XPS measurements were performed to probe the chemical of N element in the catalyst on an ESCALAB electron spectrometer. Monochromatic Al $K\alpha$ (1486.6 eV, 15 kV) was used as incident radiation. The obtained binding energies were determined with an overall resolution better than 0.05 eV. The C 1s binding energy from adventitious hydrocarbon was applied as a charge reference and fixed at 284.6 eV.

The resulting reaction mixture was analyzed qualitatively by GC-MS (Trace ISQ,

ThermFisher) equipped with a capillary column (length: 30 m, i. d.: 0.25 mm, stationary phase thickness: 0.25 μm). The organic components extracted were identified by the means of NIST database.

2. Supplementary results

Table S1 Textural properties of SiO_2 , SiO_2 -APTES-PMDA-NOH and SiO_2 -APTES-PMDA-NOH-R4.

Catalyst	S_{BET} (m^2/g) ^a	Pore volume (cm^3/g) ^b	Average pore diameter (nm) ^c
SiO_2	372	0.85	9.1
SiO_2 -APTES-PMDA-NOH	139	0.26	7.4
SiO_2 -APTES-PMDA-NOH-R4	161	0.29	7.2

^a Determined by the BET method. ^b BJH desorption cumulative volume of pore between 0.85 nm and 150 nm. ^c Calculated according to $4V_{\text{pore}}/S_{\text{BET}}$.

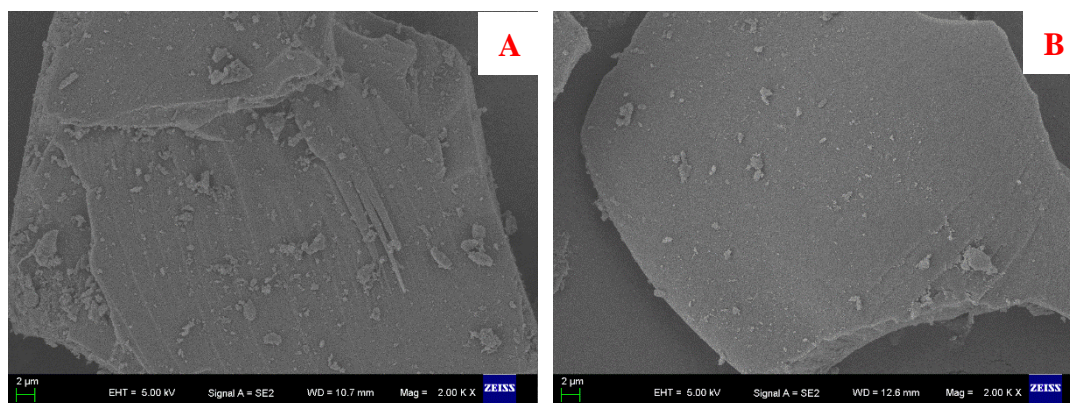


Figure S1 SEM images of the fresh catalyst SiO_2 -APTES-PMDA-NOH (A) and the retrieved catalyst SiO_2 -APTES-PMDA-NOH-R4 (B).

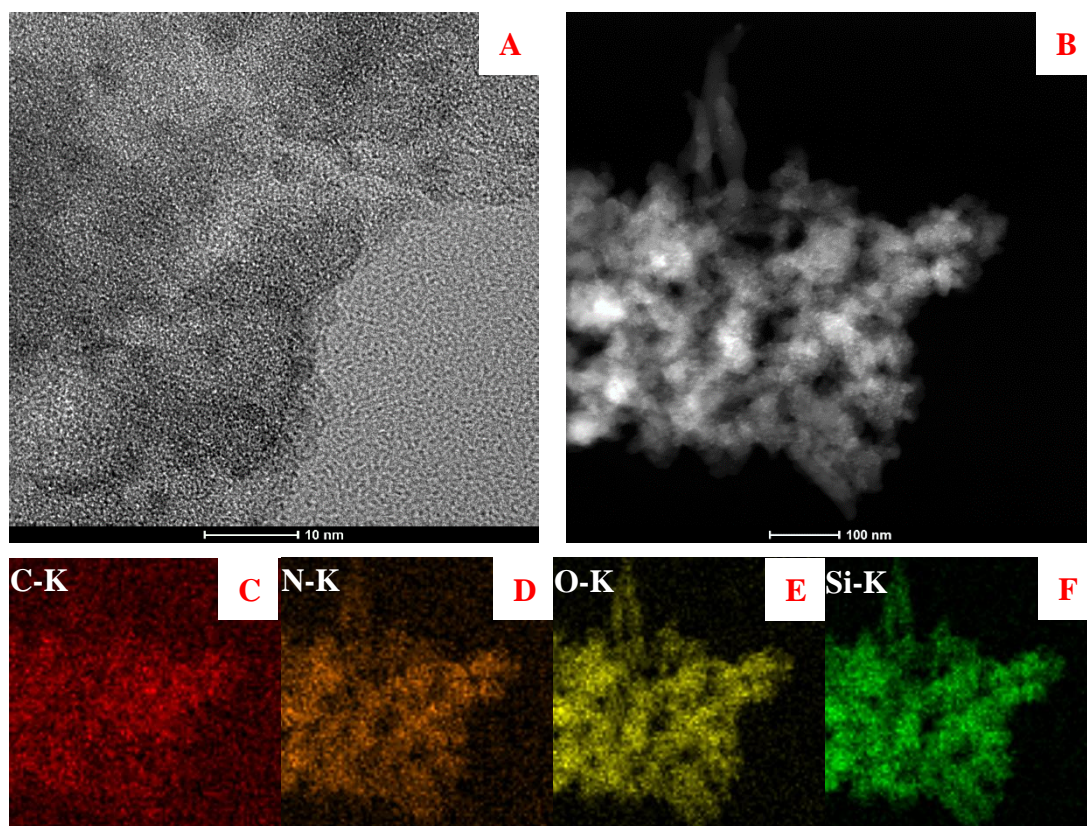


Figure S2. HRTEM (A), HAADF STEM (B) images and elemental mapping images (C-F) of the fresh catalyst SiO_2 -APTES-PMDA-NOH.

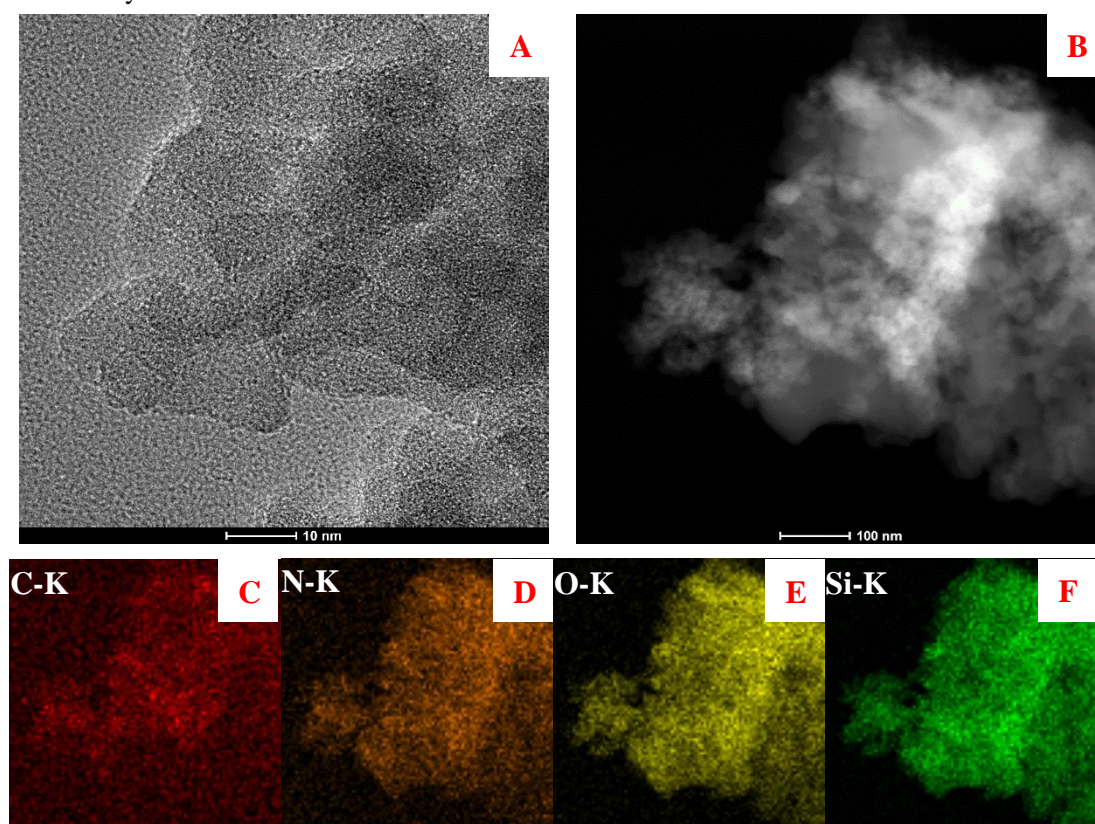


Figure S3. HRTEM (A), HAADF STEM (B) images and elemental mapping images (C-F) of the retrieved catalyst SiO_2 -APTES-PMDA-NOH-R4.

Table S2 Effect of solvents on ethylbenzene oxidation over immobilized NHPI catalyst ^a

Solvent	Conv. (%)	Selectivity (%)				
		AP	BAC	BA	1-PATE	Others
CH ₃ CN	0	-	-	-	-	-
CH ₃ CH ₂ OH	0	-	-	-	-	-
CCl ₄	2.10	100	0	0	0	0
CH ₃ COOH	31.5	79.4	0	2.0	18.0	0.6

^a Reaction conditions: ethylbenzene (3 mmol), immobilized NHPI catalysts (0.3 g), Co(OAc)₂•4H₂O (0.06 mmol), O₂ (2 MPa), solvent (6 mL), 90 °C, 5 h. AP: acetophenone, BAC: benzoic acid, BA: benzaldehyde, 1-PATE: 1-phenylvinyl acetate.

Table S3 Catalytic performance of the immobilized NHPI catalyst for ethylbenzene oxidation at 150 °C in acetic acid ^a

Catalyst	Conv. (%)	Selectivity (%)				
		AP	BAC	BA	1-PATE	Others
Co(OAc) ₂ ^b	2.8	100.0	0.0	0	0	0
Co(OAc) ₂	23.5	39.4	0.0	6.5	51.0	3.2
SiO ₂ -APTES-PMDA-NOH/Co(OAc) ₂	84.5	50.6	42.5	0.8	5.5	0.5
SiO ₂ -APTES-PMDA-NOH/Co(OAc) ₂ ^c	47.9	25.0	18.5	3.7	52.4	0.4

^a Reaction conditions: ethylbenzene (3 mmol), immobilized NHPI catalysts (0.3 g), Co(OAc)₂•4H₂O (0.06 mmol), O₂ (2 MPa), acetic acid (6 mL), 150 °C, 5 h. AP: acetophenone, BAC: benzoic acid, BA: benzaldehyde, 1-PATE: 1-phenylvinyl acetate. ^b 90 °C. ^c the 2nd run.