

Supplementary information

General

Unless otherwise noted, materials were purchased from Wako Pure Chemicals, the Tokyo Kasei Co., Aldrich Inc., Combi-Blocks, or Enamin BB, and were used after appropriate purification. Montmorillonite (Na-mont; Kunipia F; Na, 2.73; Al, 10.3; Fe, 1.35; Mg, 1.97%) was purchased from the Kunimine Industry Co. The SiO₂/Al₂O₃ (JRC-SAH-1), SO₄²⁻/ZrO₂ (JRC-SZ-1), and H⁺-mordenite (JRC-Z-HM20) were supplied by the Catalysis Society of Japan. The ¹H and ¹³C NMR spectra were acquired on a Jeol JNM-ECS400 spectrometer with TMS as the internal standard. The GC analyses were performed using a Shimadzu GC-1700 instrument equipped with an FID detector and a capillary column (Inertcap 17, 30 m × 0.25 mm i.d., 0.25 μm). The GC-MS analyses were conducted on a Shimadzu GCMS-QP50560 instrument equipped with an Inertcap 17 column. Powder X-ray diffraction patterns were recorded using a Philips X' PertMPD with Cu-Kα radiation.

Preparation of various cation-exchanged montmorillonite catalysts

Various cation-exchanged montmorillonite catalysts were prepared from Na⁺-mont and aqueous solution containing TiCl₄,^{S1} AlCl₃·6H₂O,^{S2} HCl,^{S2} Cu(NO₃)₂·3H₂O^{S3} and La(OTf₃),^{S4} respectively, through cation-exchange method.

Typical procedure for depolymerization of PTMG with benzoic anhydride

A pressure tube was charged with Ti⁴⁺-mont (0.2 or 0.05 g), PTMG (M_n ≈ 2,000, 0.3 mmol per oxytetramethylene unit), and an aromatic compound (8 mL). The resulting

mixture was stirred in a preheated oil bath at 150 or 160 °C for a specified time. After reaction, the pressure tube was cooled in an ice bath and biphenyl was added as an internal standard.

Ti⁴⁺-mont reuse experiment

After reaction, the reaction mixture was centrifuged and Ti⁴⁺-mont was washed with diethyl ether in the pressure tube, dried under vacuum, and then reused for depolymerization of PTMG with benzene.

XRD measurements of Ti⁴⁺-mont treated with PEG

The Ti⁴⁺-mont (0.1 g) and PEG (M_n ≈ 2,000, 0.13 g) were thoroughly mixed in an agate mortar, formed into a pellet, and heated at 40°C. After heating, the pellet obtained was ground and analyzed using XRD.

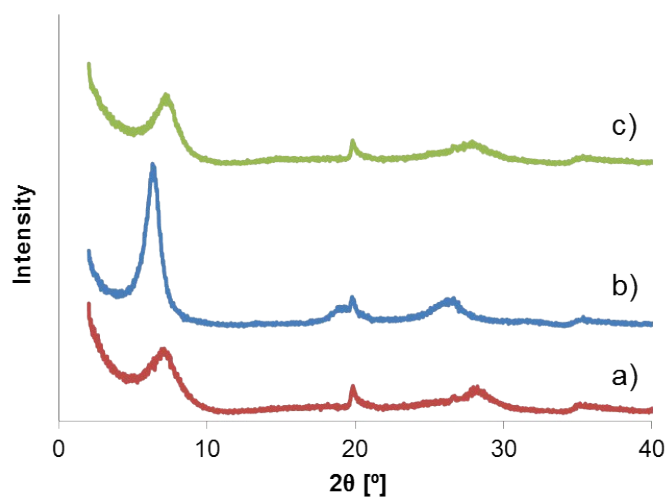


Figure S1. XRD patterns of Ti⁴⁺-mont (a) before treatment, (b) after treatment with PTMG, and (c) after depolymerization of PTMG with benzene.

Product identification

Tetralin, 5-methyltetralin, 6-methyltetralin, 5,6,7,8-tetrahydroxynaph-1-ol, 5,6,7,8-tetrahydroxynaph-2-ol, 1,2,3,4,5,6,7,8-octahydroanthracene, 1,2,3,4,5,6,7,8-octahydrophenanthrene, and *N*-phenylpyrrolidine were identified by GC and GC-MS. The GC retention times were identical with those of authentic samples. 5,7-Dimethoxy-1,2,3,4-tetrahydronaphthalene was isolated and identified by ¹H and ¹³C NMR.

5,7-Dimethoxy-1,2,3,4-tetrahydronaphthalene [CAS No. 20875-62-1]

¹H NMR (400 MHz, CDCl₃, 30°C): δ = 6.27 (d, *J* = 1.8 Hz, 1H; Ar), 6.21 (d, *J* = 1.8 Hz, 1H; Ar), 3.75-3.81 (6H; OCH₃), 2.70 (t, *J* = 4.5 and 6.4 Hz, 2H; CH₂), 2.57 (t, *J* = 4.5 and 6.4 Hz, 2H; CH₂), 1.75 (m, 4H; CH₂); ¹³C NMR (100 MHz, CDCl₃, 30°C): δ = 158.3, 158.1, 130.8, 118.4, 104.4, 95.8, 55.3, 55.2, 30.1, 23.0, 22.9, 22.6 ppm ; MS (70 eV, EI) : m/z (%): 192 (100) [M⁺], 177 (25), 164 (74), 149 (38).

References

- [S1] T. Mitsudome, T. Matsuno, S. Sueoka, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Green Chem.*, 2012, **14**, 610-613.
- [S2] K. Motokura, N. Nakagiri, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Org. Chem.*, 2007, **72**, 6006-6015.
- [S3] T. Kawabata, M. Kato, T. Mizugaki, K. Ebitani, K. Kaneda, *Chem. Eur. J.*, 2005, **11**, 288-297.
- [S4] T. Mizugaki, R. Arundhathi, T. Mitsudome, K. Jitsukawa, K. Kaneda, *ACS Sustainable Chem. Eng.*, 2014, **2**, 574-578.