SUPPLEMENTARY MATERIALS

A new series of tungstophosphoric acid-polymeric matrix catalysts: Application in green synthesis of 2-benzazepines and analogous rings

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Leaching analysis:

The content of W present in the final solution was determined by atomic absorption spectrometry using IL457 spectrophotometer (Instrumentation Laboratory Inc). The calibration curve method was used with standards prepared in the laboratory. The analyses were carried out at a wavelength of 255.1 nm; band width, 0.3 nm; lamp current, 15 mA; phototube amplification, 800 V; burner height, 4 mm, and acetylene-nitrous oxide flame (11:14). The results obtained revealed that the TPA was fully incorporated in the support.

Characterization details:

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX): The secondary electron micrographs of the samples were obtained by scanning electron microscopy (SEM) using Philips 505 equipment. The energy dispersive X-ray analysis (EDS) of the samples was performed using an EDAX 9100 analyzer at a working potential of 15 kV and graphite-supported samples metalized with gold.

X-ray diffraction analysis (XRD): Powder XRD patterns of the samples were recorded using a Philips PW-1417 with built-in recorder, with Cu Kα radiation, nickel filter, 20 mA and 40 kV in the high voltage source, and scanning angle between 5° and 60° 2θ at a scanning rate of 1°/min.

Fourier transform infrared spectroscopy (FT-IR): For FT-IR analysis, the spectra in the 400-4000 cm^{-1} range were recorded using KBr pellets in a Thermo Bruker IFS 66 IR spectrometer.

^{31}P nuclear magnetic resonance (P MAS-NMR): Spectra were recorded in Bruker MSL-300 equipment, using a 5 mm diameter and 10 mm high sample holder, 2.1 kHz spin rate, 5 μs pulses, 3 s of repetition time, and a frequency of 121.496 MHz for ^{31}P at room temperature, with resolution of 3.052 Hz per point. Several hundred pulse responses were collected. Phosphoric acid 85% was employed as external reference.

Acidity measurements: The total number of acid sites and the acid strength of the samples was measured by means of potentiometric titration. The solid (0.05 g) was suspended in acetonitrile (Merck, 90 mL) and stirred for 3 h. The suspension was then titrated with 0.05 N *n*-butylamine (Carlo Erba) in acetonitrile using a Hanna 11 pH meter with a double junction electrode. The initial electrode potential (E) indicates the maximum acid strength of the surface sites, and the total number of acid sites is given by the value (meq/g solid) where the plateau is reached. Acid strength can be assigned according to the E value as very strong site ($E > 100$ mV), strong site ($0 < E < 100$ mV), weak site ($-100 < E < 0$ mV), or very weak site ($E < -100$ mV).

Oxygen subscript meaning:

The subscripts indicate oxygen bridging W and the P heteroatom (a), corner sharing (b) and edge sharing (c) oxygen belonging toWO_6 octahedra, and terminal oxygen (d).

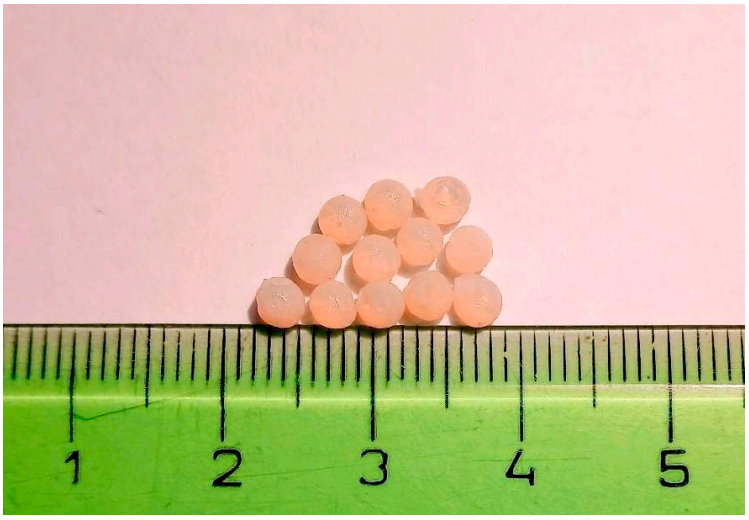


Figure S1. PLMTPA60/40$_{100}$ catalyst spheres.

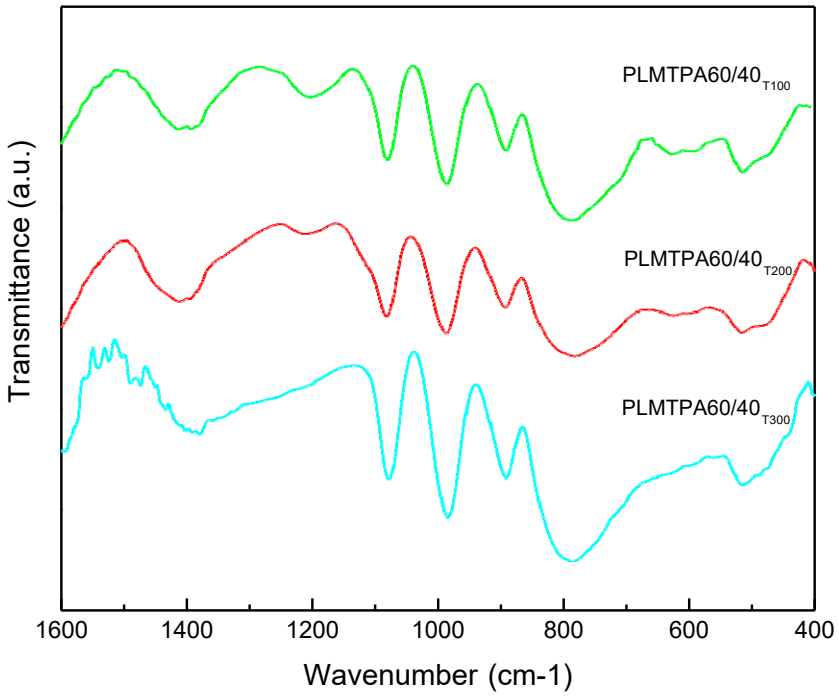


Figure S2. FT-IR spectrum of PLMTPA60/40 treated at 100 (PLMTPA40/60$_{T100}$), 200 (PLMTPA40/60$_{T200}$), and 300 °C (PLMTPA40/60$_{T300}$).

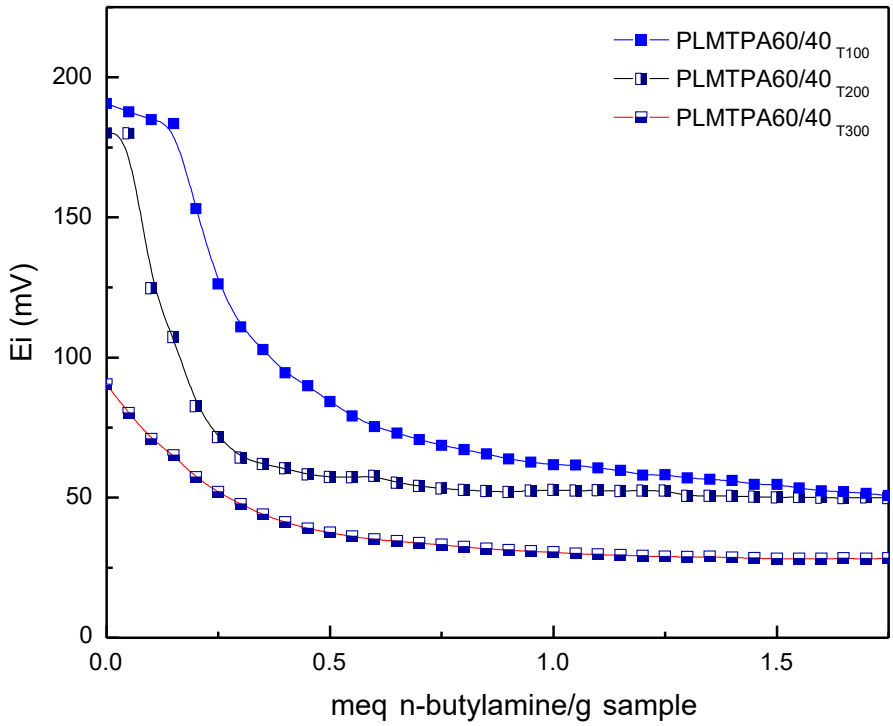
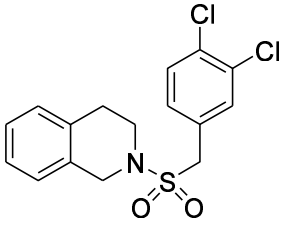


Figure S3. Potentiometric titration curves of PLMTPA60/40$_{T100}$, PLMTPA60/40$_{T200}$, and PLMTPA60/40$_{T300}$ samples.

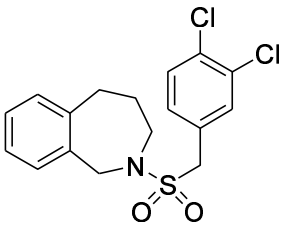
Table S1. Weight loss of the polymer and catalysts obtained by TGA.

Sample	**Weight loss (%)**		
	From 250-350 ºC	**From 350-460 ºC**	**Residue at 500 ºC**
PLM	22	64	14
PLMTPA20/80$_{T100}$	16	49	35
PLMTPA40/60$_{T100}$	13	44	43
PLMTPA60/40$_{T100}$	8	20	72

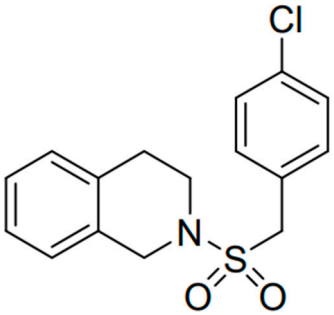
Product identification:



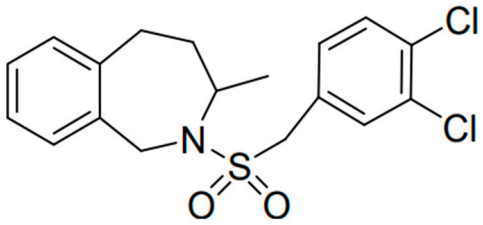
N-(3,4-dichlorobenzylsulfonyl)-1,2,3,4-tetrahydroisoquinoline: m.p. = 191-192 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.83 (t, 2H, J = 6.0 Hz), 3.47 (t, 2H, J = 6.0 Hz), 4.17 (s, 2H), 4.39 (br s, 2H), 6.99 (br d, 1H, J = 8.8 Hz), 7.13 (br d, 1H, J = 8.8 Hz), 7.18 (m, 1H), 7.18 (dd, 1H, J = 8.3 Hz, 2.1 Hz), 7.19 (m, 1H), 7.36 (d, 1H, J = 8.3 Hz), 7.41 (d, 1H, J = 2.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.9, 43.8, 47.3, 56.2, 126.1, 126.6, 127.1, 129.1, 129.9, 130.7, 131.8, 132.4, 132.9, 133.2.



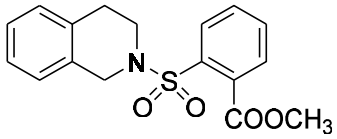
N-(3,4-dichlorobenzylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepine: m.p. = 147-149 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.49 (m, 2H), 2.92 (dd, 2H 3.60 J = 7.0 Hz, J = 4.3 Hz (br t, 2H, J = 5.1 Hz), 3.84 (s, 2H), 4.45 (br s, 2H), 6.94 (dd, 1H, J = 8.7 Hz, J = 2.1 Hz), 6.95 (d, 1H, J = 2.1 Hz), 7.19 (br d, 1H, J = 7.2 Hz), 7.22 (m, 1H), 7.25 (m, 2H), 7.32 (d, 1H, J = 8.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.3, 34.7, 52.3, 53.1, 58.3, 126.7, 128.6, 128.8, 129.2, 129.8, 130.0, 130.4, 132.4, 132.6, 132.9, 137.5, 141.9.



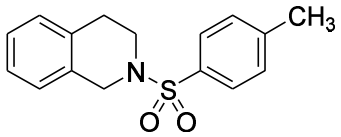
N-(4-chlorobenzylsulfonyl)-1,2,3,4-tetrahydroisoquinoline: m.p. = 190-192 °C ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.8 (t, 2H, J = 5.9 Hz), 3.42 (t, 2H, J = 6.0 Hz), 4.21 (s, 2H), 4.35 (br s, 2H), 6.97 (br d, 1H, J = 8.7 Hz), 7.10 (br d, 1H, J = 8.7 Hz), 7.17 (m, 1H), 7.19 (m, 1H), 7.28 (br s, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 29.0, 43.7, 47.3, 56.7, 126.1, 126.5, 127.0, 127.4, 129.0, 131.9, 132.0, 133.3, 134.9.



N-(3,4-dichlorobenzylsulfonyl)-2,3,4,5-tetrahydro-3-methyl-1*H*-benzo[*c*]azepine: m.p. = 138-139 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.33 (m, 3H), 1.49 (m, 1H) 1.68 (m, 1H), 2.59 (m, 1H), 3.08 (m, 1H), 3.80 (s, 2H), 4.14 (m, 1H), 4.48 (s, 2H), 6.87 (m, 1H), 6.86 (d, 1H, J = 2.0 Hz), 7.17 (br d, 1H J = 7.3 Hz), 7.20 (m, 2H), 7.25 (m, 1H), 7.26 (d, 1H, J = 8.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.0, 30.0, 32.9, 45.4, 53.4, 58.3, 128.2, 128.5, 129.2, 129.8, 130.1, 130.3, 132.3, 132.4, 132.8, 137.1, 141.2, 162.4.



N-(2-metoxycarbonylphenylsulfonyl)-1,2,3,4-tetrahydroisoquinoline: m.p. = 153-154 °C ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.91 (t, 2H, J = 5.9 Hz), 3.54 (t, 2H, J = 5.9 Hz), 3.93 (s, 3H), 4.45 (s, 2H), 7.07 (br d, 1H J = 9.1 Hz), 7.09 (br d, 1H J = 9.3 Hz), 7.15 (m, 1H), 7.16 (m, 1H), 7.50 (dd, 1H, J = 7.4 Hz, J = 1.5 Hz), 7.56 (m, 1H), 7.60 (m, 1H), 7.89 (dd, 1H, J = 7.4 Hz, J = 1.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.8, 43.5, 47.2, 53.1, 126.3, 126.4, 126.8, 128.5, 128.9, 129.0, 130.2, 131.8, 132.4, 133.3, 133.6, 135.8, 168.4.



N-(4-tolylsulfonyl)-1,2,3,4-tetrahydroisoquinoline: m.p. = 143-145 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.42 (s, 3H), 2.92 (t, 2H, J = 5.9 Hz), 3.35 (t, 2H, J = 5.9 Hz), 4.24 (s, 2H), 7.02 (br d, 1H, J = 8.9 Hz), 7.07 (br d, 1H, J = 8.9 Hz), 7.13 (m, 1H), 7.14 (m, 1H), 7.32 (d, 3H, J = 8.2 Hz), 7.72 (d, 1H, J = 8.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.5, 28.9, 43.7, 47.5, 126.3, 126.4, 126.7, 127.7, 128.8, 129.7, 131.7, 133.1, 133.4, 143.7.