

Supporting Information for

Synergetic Effect in Heterogeneous Acid Catalysis by a Porous Ionic Crystal Based on Al(III)-Salphen and Polyoxometalate

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Experimental details

Materials: Distilled water, methanol, ethanol, *p*-xylene, acetone, ammonium hydroxide solution, *o*-phenylenediamine, aluminum(III) nitrate nonahydrate, 2,6-lutidine, pinacol, and naphthalene were purchased from Kanto Chemicals. Salicylaldehyde was purchased from TCI. Solvents were dried over molecular sieves. $[\text{Al}(\text{salphen})(\text{H}_2\text{O})_2](\text{NO}_3)^{\text{S1}}$ and $\text{Na}_3[\alpha\text{-PW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}^{\text{S2}}$ were synthesized according to the reported procedure.

Characterizations: Inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent Technologies, ICP-OES720) was used for the quantitative analysis of inorganic elements in **I**. Prior to the ICP-OES measurements, ammonium hydroxide solution (1 mL) was added to ca. 10 mg of **I** to dissolve the solid completely into water (100 mL). CHN analysis was performed on Elementar vario MICRO cube at the Elemental Analysis Center of School of Science of the University of Tokyo. FT-IR spectra were measured with a JASCO FT/IR 4100 spectrometer (JASCO) equipped with a TGS (Figure S1) or a MCT (Figure S7) detector. The sample was mounted on a CaF_2 plate (20 mm diameter) and placed in the center of an IR cell in Ar atmosphere. After measuring a background spectrum of the sample, pyridine was dropped on the sample in Ar atmosphere to measure an IR spectrum of pyridine-adsorbed sample. Thermogravimetry was conducted with a Thermo Plus 2 thermogravimetric analyzer (Rigaku) with $\alpha\text{-Al}_2\text{O}_3$ as a reference under a dry N_2 flow (100 mL min^{-1}) in the temperature range of 303–1273 K. Powder XRD patterns were measured with a New advance D8 X-ray diffractometer (Bruker) by using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$, 40 kV-40 mA) at 1.8 deg min^{-1} . N_2 (77 K) adsorption isotherm was measured using a Belsorp-max volumetric adsorption apparatus (BEL Japan). Prior to the measurement, about 0.1 g of crystals were ground and treated in vacuo at 373 K. Solid state magic angle spinning (MAS) NMR spectra with cross polarization (contact time = 2 ms) was recorded with an AVANCE 400WB spectrometer (Bruker) with a resonance frequency of 100.6 MHz (^{13}C). MAS rate was 10 kHz and adamantane (^{13}C : 28.8 and 38.3 ppm) was used as an external standard for the calibration of chemical shifts. Monte Carlo (MC) based simulations were carried out using the Sorption tool of Materials Studio package

(Accelrys Inc.) by the Metropolis MC method with universal forcefield.^{S3,S4} Prior to the MC simulations, partial atomic charges of the components of the host structure (i.e., POM and Al(III)-salphen) were derived from DFT calculations as follows: Template structures of POM and Al(III)-salphen were cut out from the crystal structure, and geometrical optimization followed by Mulliken charge analysis^{S5} were carried out using the Dmol³ tool^{S6} of Materials Studio package. GGA-PBE exchange-correlation function^{S7} and double-numerical plus polarization (DNP) function were used as the basis sets for all atoms. Partial atomic charges of pinacol were also derived from the Dmol³ tool.^{S6} During the MC simulation of the location of pinacol in **I**, positions of all atoms of the hosts were fixed, pinacol were treated as rigid bodies, and only translational degrees of freedom were considered (otherwise the calculation did not converge).

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(S3) N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, E. Teller, *J. Chem. Phys.*, **1953**, *21*, 1087-1092.

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(S6) B. Delley, *J. Chem. Phys.*, **2000**, *113*, 7756-7764.

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Table S1. Crystallographic data of **I**

Formula	[Al(salphen)(H ₂ O) ₂] ₃ [α -PW ₁₂ O ₄₀] \cdot 7CH ₃ COCH ₃ (C ₇₂ H ₇₈ N ₆ Al ₃ O ₅₆ PW ₁₂)
Crystal system	Monoclinic
Space group	<i>P2/c</i>
Unit cell dimensions	<i>a</i> = 32.127(7), <i>b</i> = 15.117(4), <i>c</i> = 26.528(7), β = 92.984(4)
Volume	12866(5)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	2.279
<i>F</i> (000)	8152
<i>h, k, l</i> range	-32/38, -15/18, -31/31
μ (Mo K α) (mm ⁻¹)	10.810
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0782
<i>wR</i> ₂ (all data)	0.2066
GOF on <i>F</i> ²	1.094

Table S2. Selected bond distances (Å), angles (°), and atomic numbering schemes

Compound I					
W1-O5	1.7	W10-O40	1.89(3)	Al3-O303	1.78(1)
W1-O6	1.86	W10-O41	1.68(2)	Al3-N300	1.98(2)
W1-O7	1.93	W10-O42	1.89(2)	Al3-N301	1.99(2)
W2-O28	1.85(2)	W10-O45	1.88(2)	O100-Al1-O101	175.1(7)
W2-O30	1.93(2)	W11-O29	1.86(2)	O100-Al1-O102	90.4(7)
W2-O31	1.88(2)	W11-O30	1.87(2)	O100-Al1-O103	93.3(7)
W2-O39	1.69(2)	W11-O31	1.93(2)	O100-Al1-N100	85.9(7)
W2-O42	1.93(2)	W11-O37	1.67(2)	O100-Al1-N101	90.7(7)
W3-O28	1.90(2)	W11-O40	1.89(2)	O101-Al1-O102	93.8(7)
W3-O29	1.90(2)	W12-O7	1.87(2)	O101-Al1-O103	89.0(6)
W3-O32	1.91(2)	W12-O10	1.87(2)	O101-Al1-N100	89.7(7)
W3-O33	1.89(2)	W12-O12	1.67(2)	O101-Al1-N101	86.4(7)
W3-O36	1.69(2)	W12-O14	1.84(2)	O102-Al1-O103	93.6(7)
W4-O9	1.92(2)	W12-O22	1.89(2)	O102-Al1-N101	94.0(7)
W4-O11	1.67(2)	W13-O6	1.94(2)	O103-Al1-N100	92.0(7)
W4-O13	1.89(2)	W13-O8	1.67(2)	N100-Al1-N101	80.7(7)
W4-O19	1.88(2)	W13-O9	1.85(2)	O200-Al2-O201	174.7(7)
W4-O20	1.90(2)	W13-O10	1.91(2)	O200-Al2-O202	93.4(6)
W5-O32	1.87(2)	W13-O21	1.89(2)	O200-Al2-O203	88.4(6)
W5-O34	1.89(2)	P1-O1	1.48	O200-Al2-N200	88.4(7)
W5-O35	1.68(2)	P1-O2	1.53	O200-Al2-N201	87.9(7)
W5-O43	1.92(3)	P1-O3	1.54	O201-Al2-O202	91.6(6)
W5-O45	1.89(2)	P1-O4	1.54	O201-Al2-O203	93.5(6)
W6-O13	1.89(2)	P2-O24	1.54	O201-Al2-N200	86.5(7)
W6-O14	1.92(2)	P2-O25	1.48	O201-Al2-N201	89.8(7)
W6-O15	1.68(2)	P2-O26	1.51	O202-Al2-O203	91.4(6)
W6-O17	1.90(2)	P2-O27	1.51	O202-Al2-N201	94.1(7)
W6-O18	1.91(3)	Al1-O100	1.95(2)	O203-Al2-N200	93.5(7)
W7-O16	1.68	Al1-O101	1.93(2)	N200-Al2-N201	81.1(7)
W7-O17	1.9	Al1-O102	1.81(2)	O300-Al3-O301	175.5(7)
W7-O19	1.93	Al1-O103	1.83(1)	O300-Al3-O302	91.4(7)
W8-O18	1.89(3)	Al1-N100	2.01(2)	O300-Al3-O303	92.1(7)
W8-O20	1.87(2)	Al1-N101	2.00(2)	O300-Al3-N300	90.2(7)
W8-O21	1.93(2)	Al2-O200	1.93(1)	O300-Al3-N301	89.9(7)
W8-O22	1.92(2)	Al2-O201	1.98(2)	O301-Al3-O302	90.9(7)
W8-O23	1.66(2)	Al2-O202	1.83(1)	O301-Al3-O303	91.7(6)
W9-O33	1.89(2)	Al2-O203	1.81(1)	O301-Al3-N300	85.8(7)
W9-O34	1.88(2)	Al2-N200	2.00(2)	O301-Al3-N301	87.4(7)
W9-O41	1.92(2)	Al2-N201	1.97(2)	O302-Al3-O303	92.3(7)
W9-O43	1.89(3)	Al3-O300	1.94(1)		
W9-O44	1.68(2)	Al3-O301	1.97(2)		
W10-O38	1.92(2)	Al3-O302	1.84(2)		

Symmetry Codes: (1) x, y, z, (2) -x, y, 1/2-z, (3) -x, -y, -z, (4) x, -y, 1/2+z

Table S3. Possible hydrogen bonds and their distances (Å)

Compound 1	
O103(Al-salphen)-O200(Al-salphen,H ₂ O)	2.601
O101(Al-salphen, H ₂ O)-O203(Al-salphen)	2.632
O201(Al-salphen, H ₂ O)-O302(Al-salphen)	2.629
O202(Al-salphen)-O300(Al-salphen, H ₂ O)	2.676
O301(Al-salphen, H ₂ O)-O400(acetone, O)	2.676
O201(Al-salphen, H ₂ O)-O401(acetone, O)	2.763
O300(Al-salphen, H ₂ O)-O402(acetone, O)	2.604
O101(Al-Salphen, H ₂ O)-O403(acetone, O)	2.646
O100(Al-Salphen, H ₂ O)-O404(acetone, O)	2.590
O100(Al-Salphen, H ₂ O)-O405(acetone, O)	2.676
O301(Al-Salphen, H ₂ O)-O406(acetone, O)	2.780

Table S4. Pinacol to pinacolone rearrangement over various solid catalysts and conditions

Catalyst	Temp [K]	Solvent	Time [h]	Conv. [%]	Selec. ^a [%]	Reference
H-ZSM-5	393	-	4	80	90	1
Ca-HY	393	-	4	70	88	1
La-HY	393	-	4	68	82	1
Nafion-H	448	-	0.6	92	75	2
Fe-AlPO	383	Toluene	3	69	81	3
Ni-AlPO	383	Toluene	3	50	80	3
Cu-AlPO	383	Toluene	3	54	80	3
Fe-ZSM-5	383	Toluene	6	0	-	4
Fe-MCM-41	383	Toluene	6	33	64	4
MCM-41	383	Toluene	6	13	14	4
Phosphonate-polysilsesquioxane	413	-	12	-	80 ^d	5
Fe-Na-montmorillonite ^b	398	-	1	34	100	6
Al ₁₃ -montmorillonite ^b	398	-	1	100	100	6
Fe-Al ₁₃ -montmorillonite ^b	398	-	1	100	100	6
None	573–723	scH ₂ O	-	100	100	8
H ₄ SiMo ₁₂ O ₄₀	423	-	1	100	44 ^c	9
H ₃ PMo ₁₂ O ₄₀	423	-	1	100	43 ^c	9
H ₄ SiW ₁₂ O ₄₀	423	-	1	100	71	9
H ₃ PW ₁₂ O ₄₀	423	-	1	100	78	9
[Cr ₃ O(OOCPh) ₆ (H ₂ O)] ₄ [SiW ₁₂ O ₄₀]	373	Toluene	12	100	79	10
[Fe ₃ O(OOCPh) ₆ (H ₂ O)] ₄ [SiW ₁₂ O ₄₀]	373	Toluene	6	100	80	10
[ε-Al ₁₃ O ₄ (OH) ₂₅ (H ₂ O) ₁₁][α-CoW ₁₂ O ₄₀] · 34H ₂ O (needle polymorph)	373	Toluene	40	31	58	11
[ε-Al ₁₃ O ₄ (OH) ₂₅ (H ₂ O) ₁₁][α-CoW ₁₂ O ₄₀] · 42H ₂ O (plate polymorph)	373	Toluene	40	76	78	11
Al ₂ O ₃	473	-	1	62	44	12
Aluminum phosphate	473	-	1	62	46	12
SiO ₂	473	-	1	34	42	12
ZrO ₂	473	-	1	31	44	12

a: by-product is 2,3-dimethyl-1,3-butadiene. b: catalyst : reactant = 5 : 1. c: by-product is acetone.

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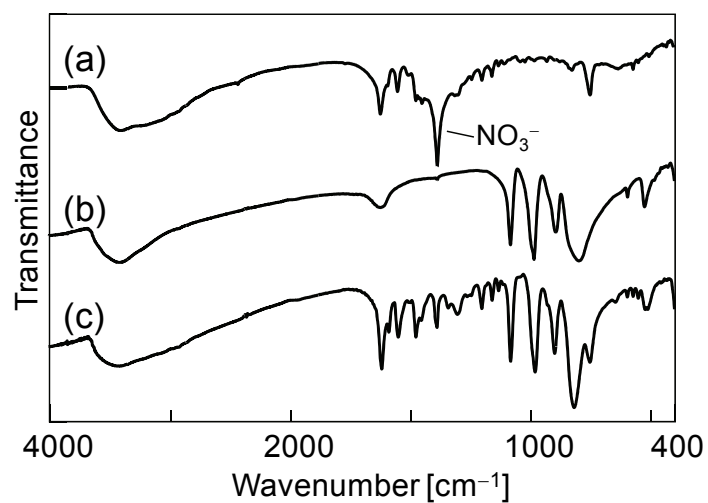


Figure S1. IR spectra of (a) $[\text{Al}(\text{salphen})(\text{H}_2\text{O})_2](\text{NO}_3)$, (b) $\text{Na}_3[\alpha\text{-PW}_{12}\text{O}_{40}]$, and (c) **I**. Note that the signal assigned to nitrate in (a) is absent in (c), showing that NO_3^- has been replaced by $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$.

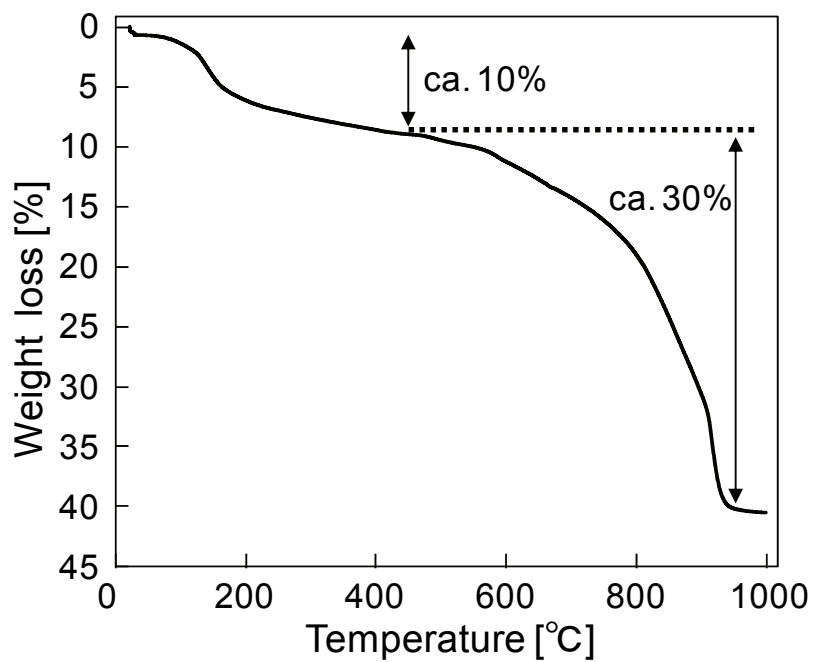


Figure S2. Thermogravimetry of **I** under a dry N₂ flow (100 mL min⁻¹). The weight loss (ca. 10%) between rt and 450 °C (723 K) can be assigned to the desorption of solvent molecules (four *p*-xylene molecules). The weight loss (ca. 30%) between 450–1000 °C (1273 K) can be assigned to the removal of salphen ligands.

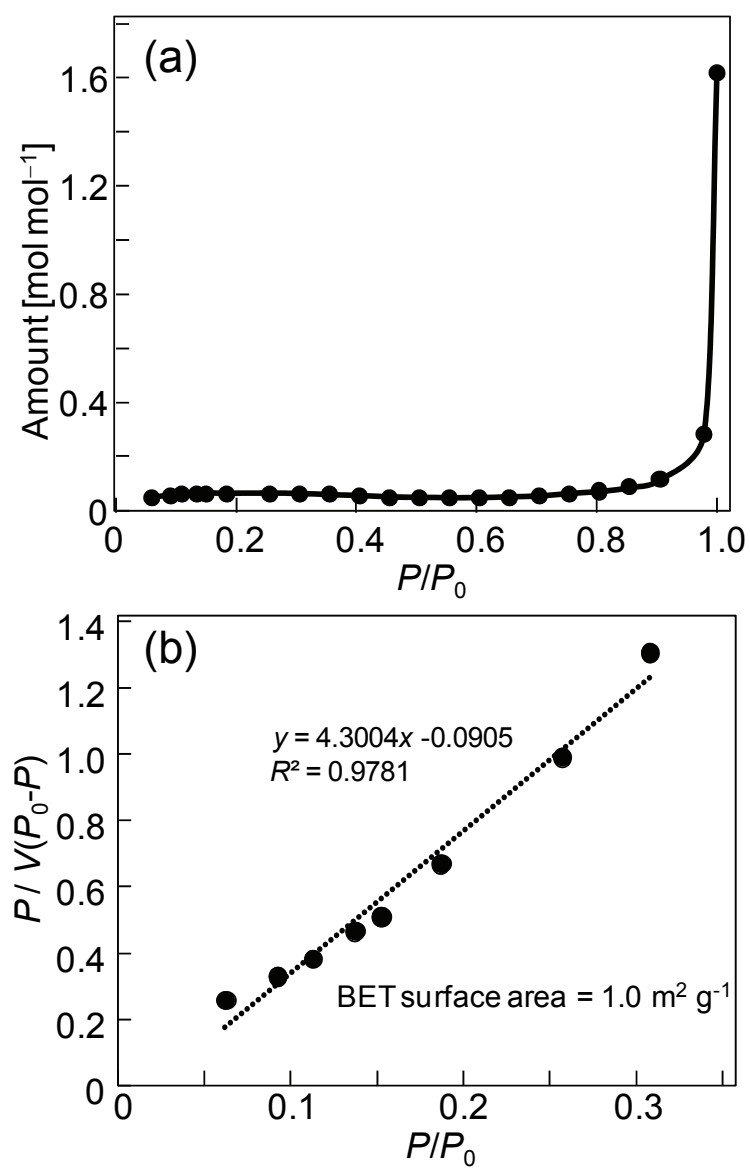


Figure S3. (a) N₂ adsorption isotherm (77 K) and (b) BET plot of **I** (pretreatment: evacuation at 373 K).

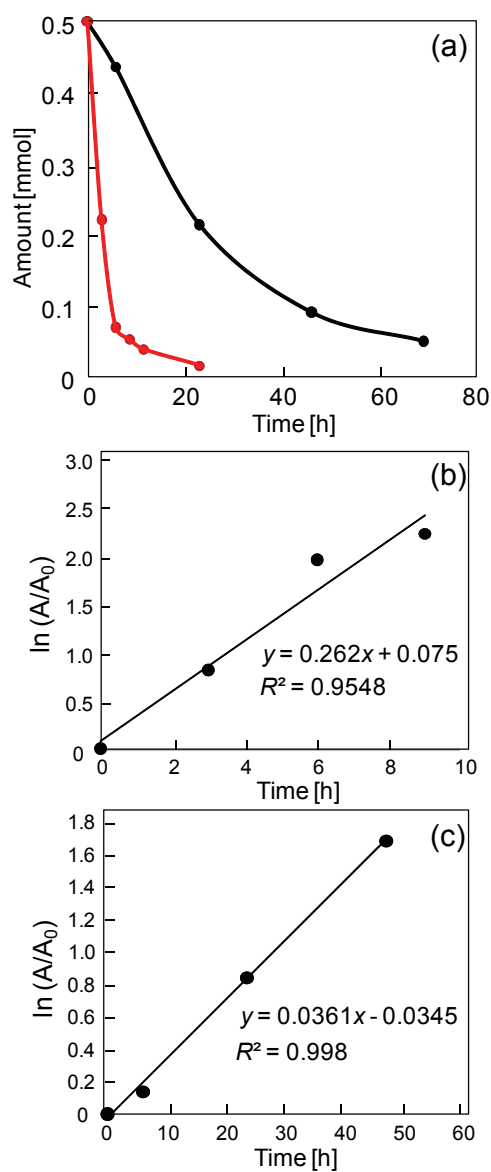


Figure S4. (a) Time courses of changes in amounts of pinacol with **I** (porous crystalline compound, red) or **I** after evacuation at 373 K (non-porous amorphous compound, black) as catalysts. Reaction rates of (b) **I** (porous crystalline compound) and (c) **I** after evacuation at 373 K (non-porous amorphous compound). It was assumed that the reaction is first-order in pinacol.

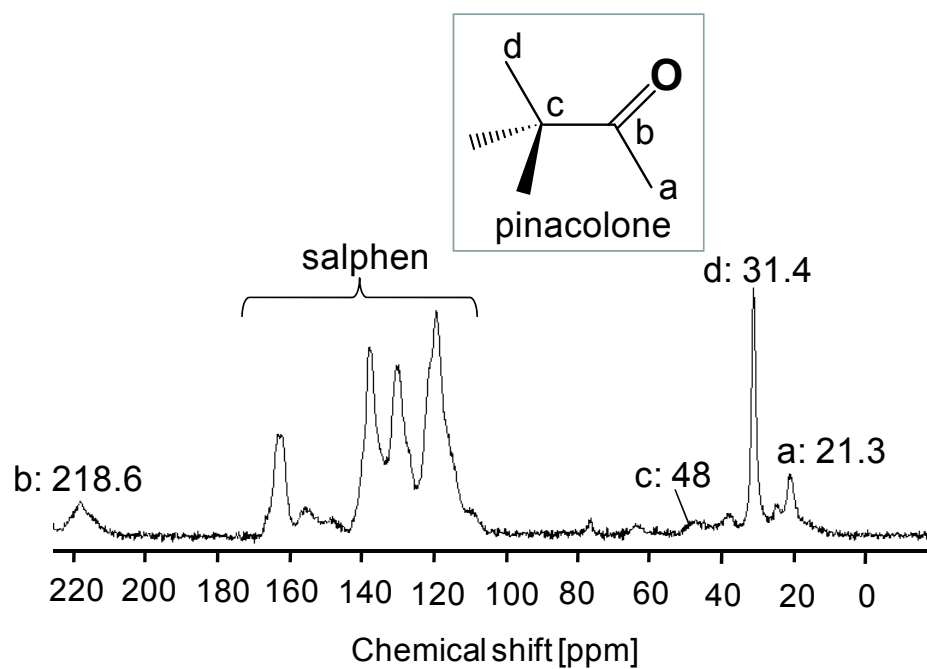


Figure S5. ^{13}C -CPMASNMR spectrum of **I** after the reaction. Pinacolone is the main product of this reaction. ^{13}C -NMR spectrum of pinacolone in CDCl_3 shows peaks at 213.8, 44.3, 26.4, and 24.6 ppm for b, c, d, and a, respectively.^{S8}

(S8) Spectral database for organic compound (SDBS) at National institute of Advanced Industrial Science and Technology (AIST).

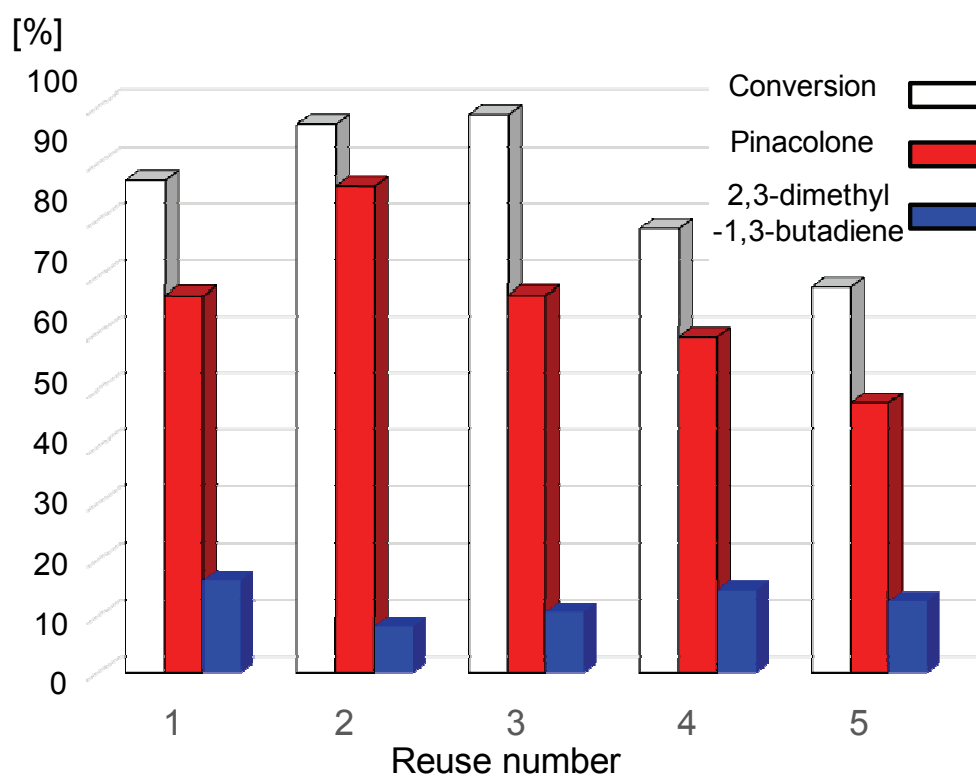


Figure S6. Catalytic activities of **I** after successive reuse experiments. Compound **I** was washed with *p*-xylene before the next reuse experiment. The increase in the catalytic activities for the second and third runs is probably due to the products which remained in the pore after the first and second runs, respectively. On the other hand, the decrease for the fourth and fifth runs is probably due to the difficulty in collecting the solid catalyst, which sticks to the glass reactor and magnetic stirrer, and/or slight changes in the crystal structure of **I**.

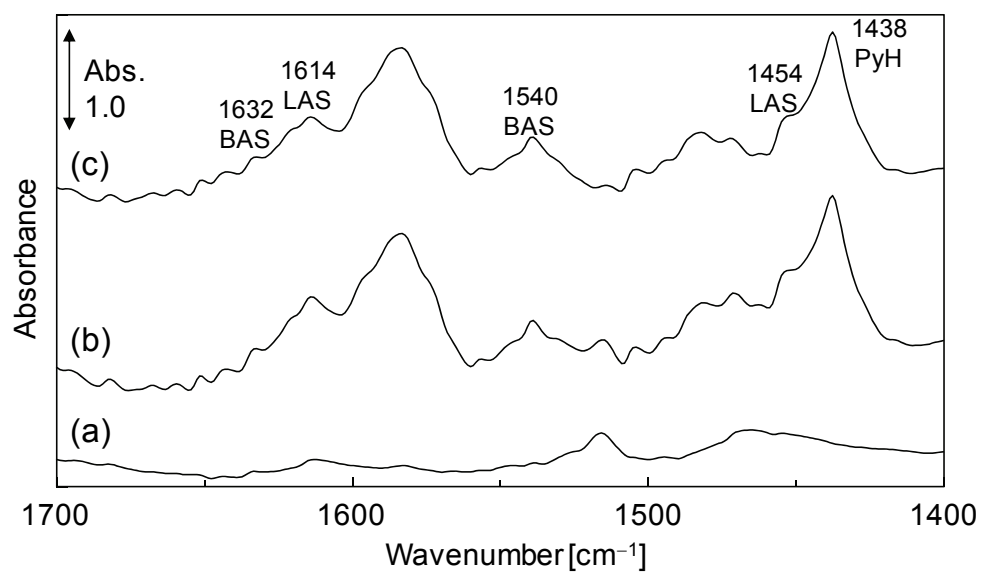


Figure S7. IR spectra of (a) **I**, (b) **I** treated with pyridine as a basic probe molecule, and (c) difference spectrum (b – a). BAS: pyridine adsorbed on Lewis acid site; LAS: pyridine adsorbed on Lewis acid site; PyH: hydrogen-bonded pyridine.