

Electronic Supplementary Information

Selective hydroxylation of benzene derivatives and alkanes with hydrogen peroxide catalysed by a manganese complex incorporated in mesoporous silica-alumina

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Experimental method

Materials. All chemicals used for synthesis were obtained from chemical companies and used without further purification. Tetraethyl orthosilicate, cetyltrimethylammonium bromide, sodium aluminate, sodium hydroxide, diethyl ether, benzene, chlorobenzene, nitrobenzene and an aqueous solution of hydrogen peroxide (30 wt%) were purchased from Wako Pure Chemical Industries. Tris(2-pyridylmethyl)amine and methoxybenzene was supplied from Tokyo Chemical Industry. Manganese(II) perchlorate hydrate, *n*-hexane and iodobenzene diacetate were delivered by Sigma-Aldrich. Acetonitrile was obtained from Nacalai tesque. Purified water was provided by a water purification system, Millipore Direct-Q3 UV, where the electronic conductance was 18.2 MΩ cm. $[\text{Mn}^{\text{III/IV}}_2(\mu\text{-O})_2(\text{TPA})_2](\text{ClO}_4)_3$ was synthesized by the literature method.^{S1}

Synthesis of $[(\text{tpa})\text{Mn}^{\text{II}}(\text{CH}_3\text{CN})(\text{H}_2\text{O})](\text{ClO}_4)_2$.^{S2} An acetonitrile solution (20 mL) of manganese(II) perchlorate hydrate (830 mg, 2.29 mmol) was slowly added to an acetonitrile solution (20 mL) of tris(2-pyridylmethyl)amine (666 mg, 2.29 mmol) for 1 h on a magnetic stirrer. Diethyl ether (200 mL) was added dropwise to the resultant solution with stirring. The obtained white precipitate was collected by filtration and dried in vacuo. The crude complex was recrystallised from acetonitrile-diethyl ether. Anal. Calcd (%): for $\text{C}_{20}\text{H}_{23}\text{Cl}_2\text{MnN}_5\text{O}_9$: C, 39.82; H, 3.84; Cl, 11.75; N, 11.61. Found: C, 40.07; H, 4.13; Cl, 11.76; N, 11.78. (Yield 469 mg, 34 %)

Synthesis of Al-MCM-41.^{S3} Al-MCM-41 was synthesized by a reported method with modifications. Cetyltrimethylammonium bromide (18.4 g) was dissolved in an aqueous solution (1.0 L) of NaOH (8.40 g). Tetraethylorthosilicate (87.5 g, 420 mmol) was added dropwise to the aqueous solution for 2 h at 35 °C and magnetically stirred for further 30 min at the temperature. Then, sodium aluminate (0.484 g, 5.90 mmol) was added to the aqueous suspension and stirred for 4 h. The obtained white precipitates were filtered and washed with deionized water. After drying at 333 K in an oven, the precipitate was calcined at 773 K in air for 6 h with a ramp rate of 1 K min⁻¹. The obtained powder was characterized by N₂ adsorption-desorption at 77 K and powder X-ray diffraction.

Preparation of $[(\text{tpa})\text{Mn}]^{2+}@\text{Al-MCM-41}$. $[(\text{tpa})\text{Mn}]^{2+}@\text{Al-MCM-41}$ was prepared by a cation exchange method in an acetonitrile solution. A typical procedure is

as follows: Al-MCM-41 (200 mg) was suspended in an acetonitrile solution (10 mL) of $[(\text{tpa})\text{Mn}^{\text{II}}]^{2+}$ (1.1 mg, $[(\text{tpa})\text{Mn}^{\text{II}}]^{2+}$: 0.18 mM) and magnetically stirred for 2 h at room temperature. The obtained solid was collected by centrifugation and washed with acetonitrile two times and dried in *vacuo*. The amount of incorporated $[(\text{tpa})\text{Mn}^{\text{II}}]^{2+}$ was determined to be 3.9×10^{-6} mol g^{-1} by the UV-vis absorbance change of the supernatant. The amount of incorporated $[(\text{tpa})\text{Mn}^{\text{II}}]^{2+}$ can be increased to 3.6×10^{-5} mol g^{-1} by increasing the concentration (1.7 mM) of $[(\text{tpa})\text{Mn}^{\text{II}}]^{2+}$ in an acetonitrile solution.

Preparation of $[(\text{tpa})_2\text{Mn}_2(\mu\text{-O})_2]^{3+}@$ Al-MCM-41 and $\text{Mn}^{2+}@$ Al-MCM-41. $[(\text{tpa})_2\text{Mn}_2(\mu\text{-O})_2]^{3+}@$ Al-MCM-41 and $\text{Mn}^{2+}@$ Al-MCM-41 were prepared by the same procedure for the preparation of $[(\text{tpa})\text{Mn}^{\text{II}}]^{2+}@$ Al-MCM-41 as described in the main text by employing $[(\text{tpa})_2\text{Mn}_2(\mu\text{-O})_2](\text{ClO}_4)_3$ and $\text{Mn}(\text{ClO}_4)_2$ instead of $[(\text{tpa})\text{Mn}^{\text{II}}(\text{CH}_3\text{CN})(\text{H}_2\text{O})](\text{ClO}_4)_2$.

N_2 adsorption for BET surface area determination. Nitrogen adsorption-desorption at 77 K was performed with an instrument for volumetric adsorption measurement, Belsorp-mini II (BEL Japan, Inc.), within a relative pressure range from 0.01 to 101.3 kPa. The mass of a sample was as much as ca. 50 mg for adsorption analysis after pretreatment at 393 K for ca. 4.0 h under vacuum conditions and kept in N_2 atmosphere until N_2 -adsorption measurements. The sample was exposed to a mixed gas of He and N_2 with a programmed ratio and adsorbed amount of N_2 was calculated from the change of pressure in a cell after reaching the equilibrium (at least 5 min).

Physical measurements. UV-vis absorption spectra of solutions were recorded on a Hewlett Packard 8453 diode array spectrometer. UV-vis diffused reflectance spectra were measured by a Jasco V-670 spectrometer equipped with an SIN-768 attachment. The EPR spectra were taken on a JEOL X-band spectrometer (JES-REIXE) with a quartz EPR tube (4.5 mm i.d.) at 77 K or 4 K. The g values were calibrated using an Mn^{2+} marker. The surface acidity of Al-MCM-41 was determined by a colorimetric titration using Hammett indicators. A small portion of Al-MCM-41 was immersed to a nitrobenzene solution containing the indicator (anthraquinone). After keeping at room temperature for 8 hours, the colour change of anthraquinone adsorbed on Al-MCM-41 was measured by UV-vis diffused reflectance spectroscopy.

Catalysis measurements. A typical procedure for a catalysis measurement is as follows: $[(\text{tpa})\text{Mn}^{\text{II}}]^{2+}@$ Al-MCM-41 (17 mg, $[(\text{tpa})\text{Mn}^{\text{II}}]^{2+}$: 23 μM) was suspended to

acetonitrile (1.6 mL). Benzene (0.40 mL) and aqueous hydrogen peroxide (30 wt%, 0.40 mL) were successively added to the suspension with vigorous stirring at room temperature. An aliquot of the reaction solution was taken out and injected to GC/MS (Shimadzu QP-5000) to analyze products.

References

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- S2 A. L. Ward, L. Elbaz, J. B. Kerr and J. Arnold, *Inorg. Chem.*, 2012, **51**, 4694.
- S3 E. G. Vaschetto, G. A. Monti, E. R. Herrero, S. G. Casuscelli and G. A. Eimer, *Appl. Catal., A*, 2013, **453**, 391.

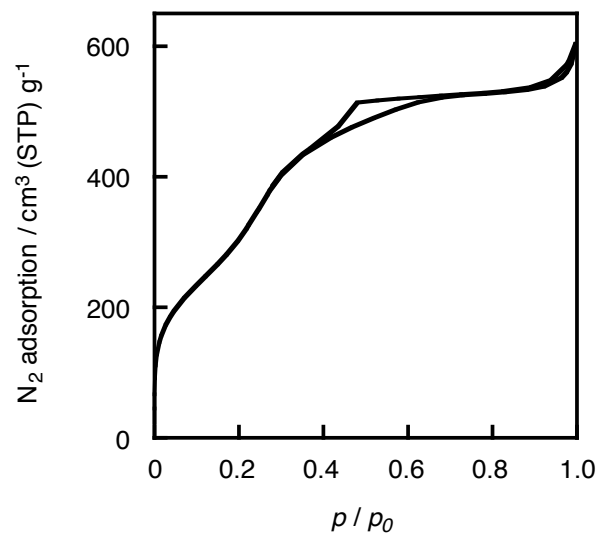


Fig. S1 N₂-adsorption and desorption isotherm of Al-MCM-41 at 77 K.

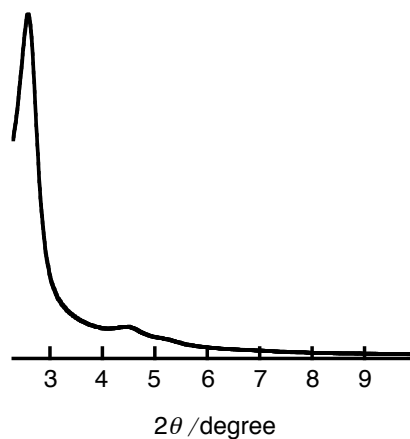
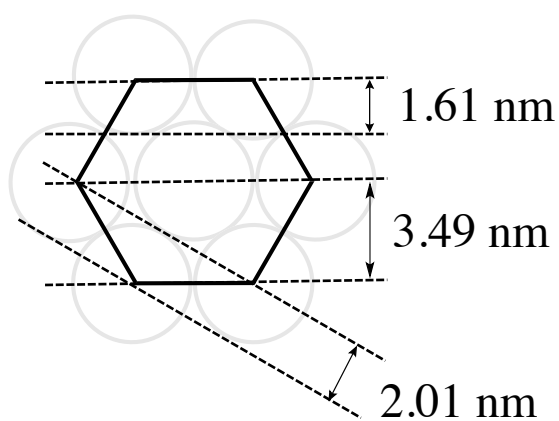


Fig. S2 Powder X-ray diffraction pattern of Al-MCM-41

Pore-size estimation from powder X-ray diffraction. A powder X-ray diffraction pattern was recorded on a Rigaku MiniFlex 600. Incident X-ray radiation was produced by a Cu X-ray tube, operating at 40 kV and 15 mA with Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The scan rate was 1° min^{-1} from $2\theta = 2\text{--}10^\circ$. Three obtained peaks appeared at 2.6° , 4.4° and 5.3° are characteristic for the hexagonal crystal structure. The calculated lattice spacing values (d) based on these angles were 3.49, 2.01 and 1.61 nm.



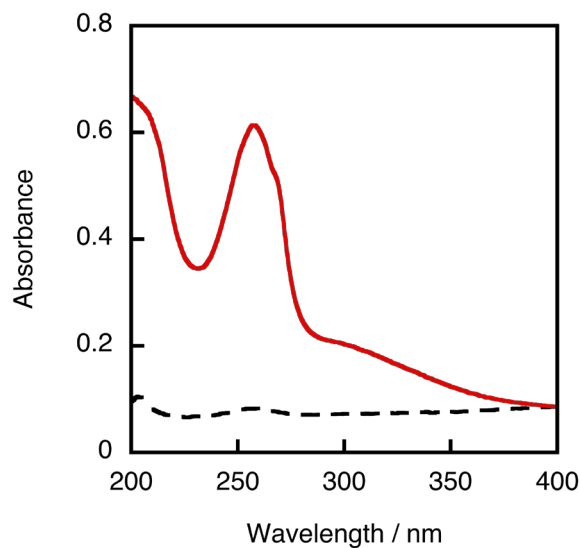


Fig. S3 UV-vis diffuse reflectance spectra of $[(\text{tpa})\text{Mn}^{\text{II}}]^{2+}@$ Al-MCM-41 (red solid line) and Al-MCM-41 (black dashed line).

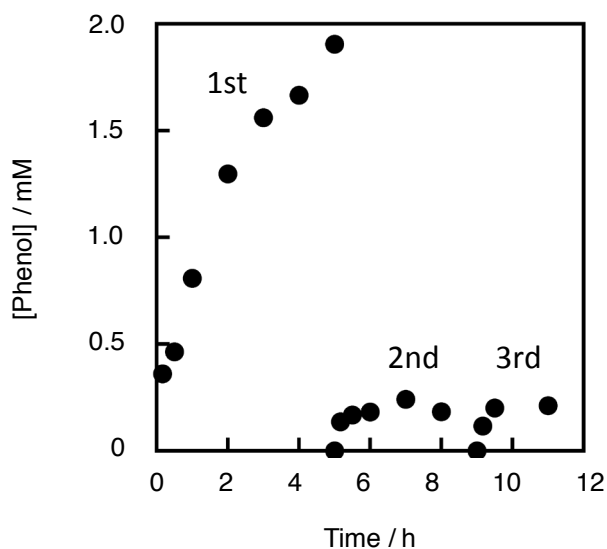


Fig. S4 Time course of formation of phenol in hydroxylation of benzene with aqueous H_2O_2 catalyzed by $[(\text{tpa})\text{Mn}^{\text{II}}]^{2+}@$ Al-MCM-41 (7.0 mg, $[(\text{TPA})\text{Mn}^{\text{II}}]^{2+}$: 23 mM). The reaction was performed in a mixed solution (1.2 mL) composed of benzene, aqueous H_2O_2 and MeCN [0.20:0.20:0.8 (v/v/v)]. The concentrations of benzene, H_2O_2 and an Mn complex in the starting solutions are 1.9 M, 1.5 M and 23 μM , respectively. The catalyst was recovered from the reaction solution and washed with MeCN by using centrifugation for repeated catalysis measurements.

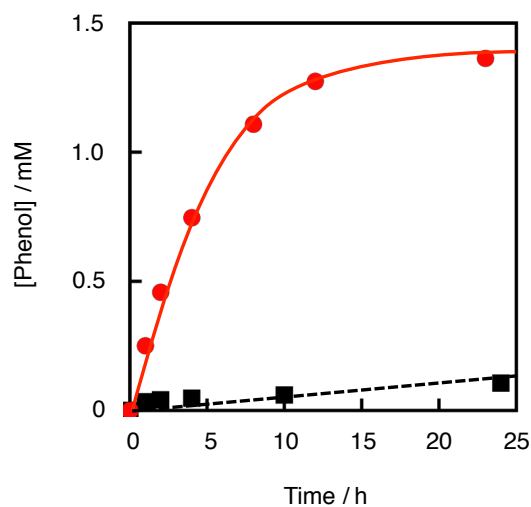


Fig. S5 Time courses of formation of phenol (red circle) in hydroxylation of benzene (0.40 mL) and *p*-benzoquinone (black square) in hydroxylation of phenol (434 mg) with aqueous H₂O₂ (30 wt%, 0.40 mL) catalysed by [(tpa)Mn^{II}]²⁺@Al-MCM-41 ([Mn]: 23 μM) in MeCN at 298 K. The concentrations of benzene or phenol and H₂O₂ in the starting solutions are 1.9 M and 1.5 M, respectively.

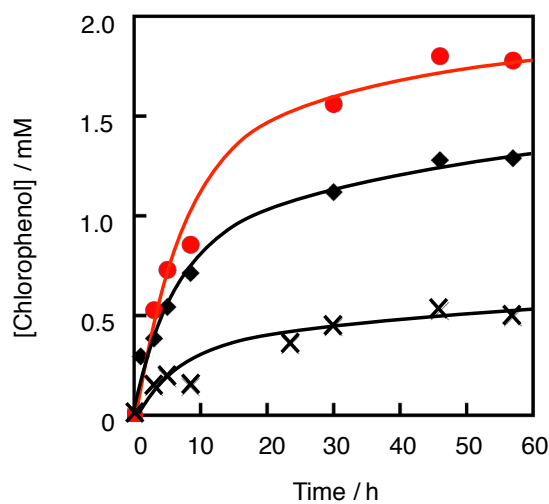


Fig. S6 Time courses of formation of chlorophenol (red circle) [*o*- (diamond), *m*- and *p*-chlorophenol (cross)] in hydroxylation of chlorobenzene (0.40 mL) with H₂O₂ (30 wt%, 0.40 mL) catalysed by [(tpa)Mn^{II}]²⁺@Al-MCM-41 ([[(tpa)Mn^{II}]²⁺]: 23 μM) at 298 K. The concentrations of chlorobenzene and H₂O₂ in the starting solution were 1.7 M and 1.5 M, respectively.

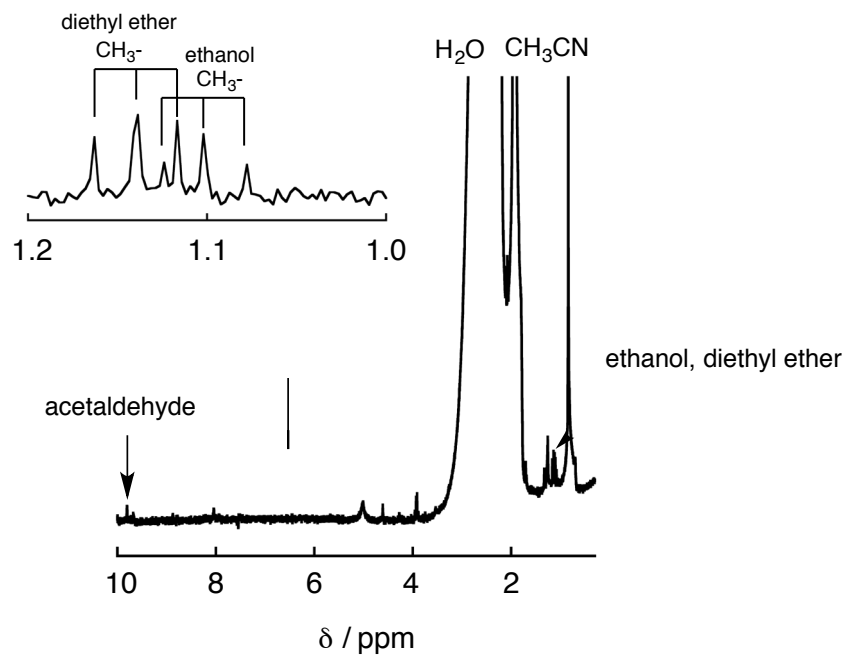


Fig. S7 ¹H-NMR spectrum of formation of ethanol, diethyl ether and acetaldehyde in hydroxylation of ethane (19 mM) with an aqueous H₂O₂ (30 wt%, 20 μL) catalysed by [(tpa)Mn^{II}]²⁺@Al-MCM-41 ([[(tpa)Mn^{II}]²⁺]: 890 μM) in CD₃CN (1.0 mL) at 298 K.

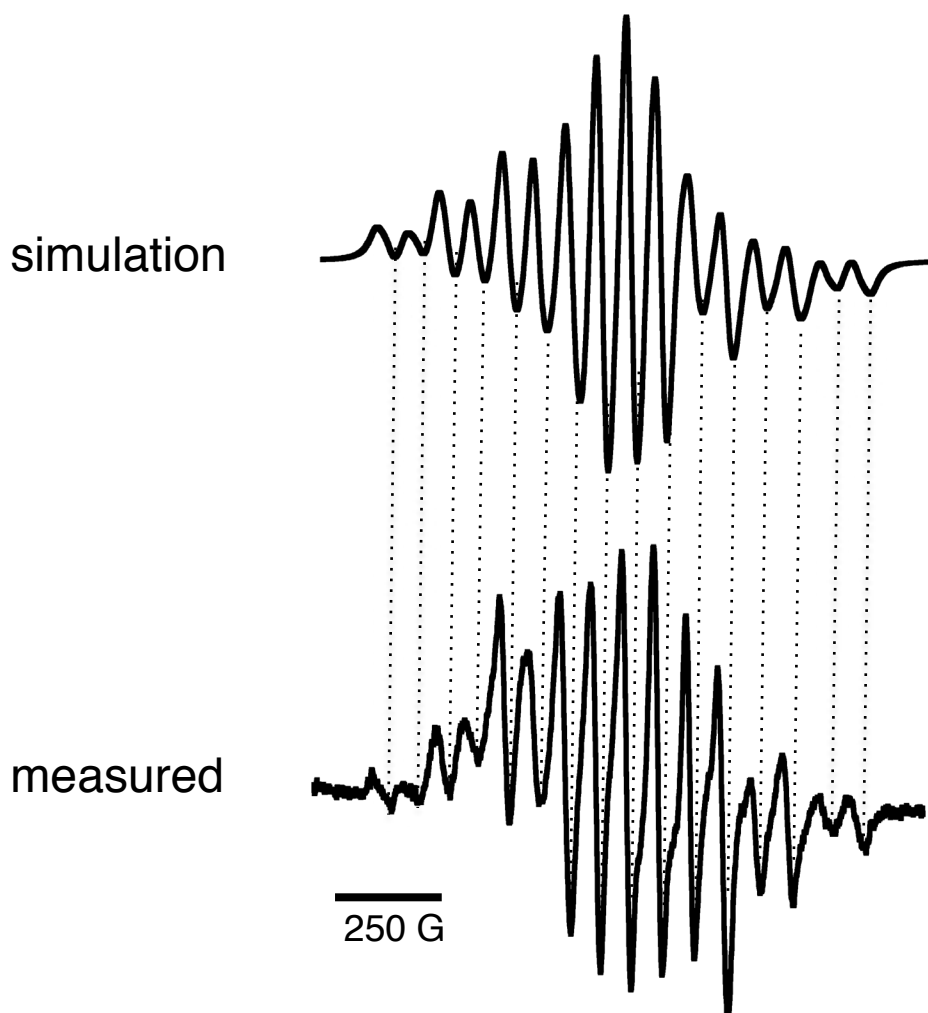


Fig. S8 An EPR simulation spectrum of binuclear $[(tpa)_2Mn_2(\mu-O)_2]^{3+}$.

The obtained parameters by the simulation are as follows: $g_x = 2.037$, $g_y = 2.037$, $g_z = 2.027$, $A_{1x} = 158$ G, $A_{1y} = 145$ G, $A_{1z} = 101$ G, $A_{2x} = 73$ G, $A_{2y} = 73$ G, $A_{2z} = 54$ G, line width $dx = dy = dz = 22$ G.

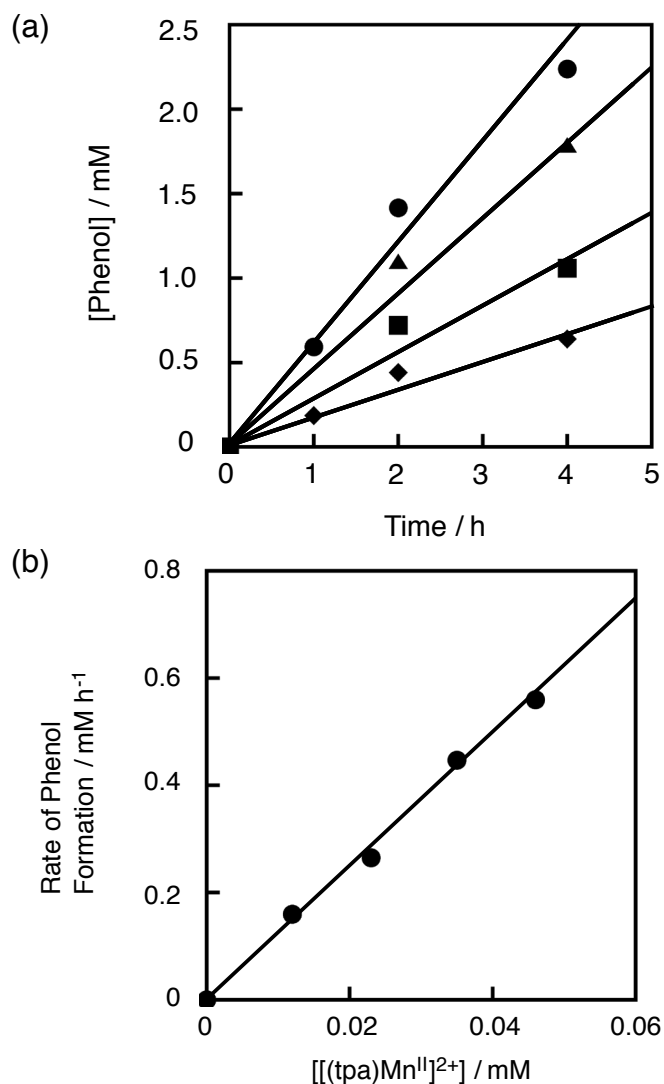


Fig. S9 (a) Time courses of formation of phenol in hydroxylation of benzene (0.40 mL) with an aqueous H₂O₂ (30 wt%, 0.40 mL) catalysed by [(tpa)Mn^{II}]²⁺@Al-MCM-41 {[[(tpa)Mn^{II}]²⁺]: 12 mM (diamond), 23 mM (square), 35 mM (triangle), and 46 mM (circle)} in MeCN (1.6 mL) at 298 K. (b) Plots of formation rates of phenol vs concentration of [(tpa)Mn^{II}]²⁺. The concentrations of benzene and H₂O₂ in the starting solutions were 1.9 M and 1.5 M, respectively.

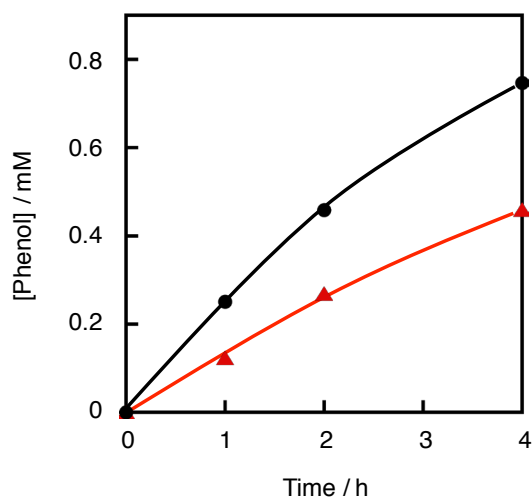


Fig. S10 Time courses of formation of phenol in hydroxylation of benzene [0.40 mL (black circle) and 0.20 mL (red triangle)] with an aqueous H₂O₂ (30 wt%, 0.40 mL) catalysed by [(tpa)Mn^{II}]²⁺@Al-MCM-41 ([[(tpa)Mn^{II}]²⁺]: 23 μM) in MeCN at 298 K. The total volume of the reaction solution was 2.4 mL and the concentrations of benzene and H₂O₂ in the starting solutions were 1.9 (black circle) or 0.86 M (red triangle) and 1.5 M, respectively.

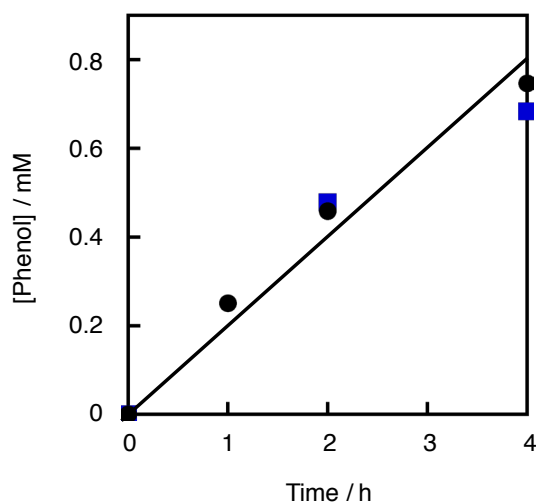


Fig. S11 Time courses of formation of phenol in hydroxylation of benzene (0.40 mL) with an aqueous H₂O₂ [30 wt%, 0.40 mL (black circle) and 0.20 mL (blue square)] catalysed by [(tpa)Mn^{II}]²⁺@Al-MCM-41 ([[(tpa)Mn^{II}]²⁺]: 23 μM) in MeCN at 298 K. The total volume of the reaction solution was 2.4 mL and the concentrations of H₂O₂ in the starting solutions were 1.5 (black circle) and 0.75 M (blue square), respectively.