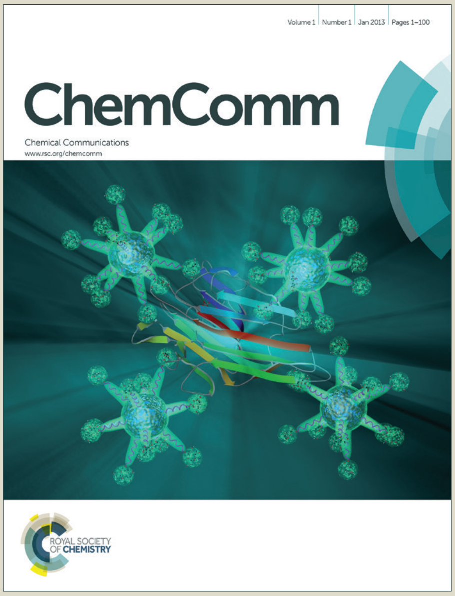
ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Y. Aratani, Y. Yamada and S. Fukuzumi, *Chem. Commun.*, 2015, DOI: 10.1039/C4CC09967B.



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

View Article Online
DOI: 10.1039/C4CC09967B

Chem. Commun.

RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

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

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Yusuke Aratani, Yusuke Yamada* and Shunichi Fukuzumi*

Selective hydroxylation of benzene derivatives and alkanes to the corresponding phenol and alcohol derivatives with hydrogen peroxide was efficiently catalysed by a manganese tris(2-pyridylmethyl)amine (tpa) complex ($[(\mathrm{tpa})\mathrm{Mn}^{\mathrm{II}}]^{2+}$) incorporated in mesoporous silica-alumina with highly acidic surfaces in contrast to the reactions in a homogeneous solution where $[(\mathrm{tpa})\mathrm{Mn}^{\mathrm{II}}]^{2+}$ was converted to catalytically much less active bis(μ-oxo)dimanganese(III,IV) complex.

High-valent manganese-oxo complexes play pivotal roles as reactive intermediates in oxygen-evolving centre (OEC) in photosystem II[1,2] as well as in biomimetic oxidation of substrates.[3-7] In this context, manganese(IV)-oxo complexes bearing pentadentate N5 ligands have been isolated and the reactivity of manganese(IV)-oxo complexes has been studied for oxidation of various substrates.[8-11] The reactivity of manganese(IV)-oxo complexes is expected to be enhanced by using tetradentate N4 ligand such as tris(2-pyridylmethyl)amine (tpa), which is less electron donating. However, the oxidation of $[(\mathrm{tpa})\mathrm{Mn}^{\mathrm{II}}]^{2+}$ with hydrogen peroxide in a solution is known to result in formation of the bis(μ-oxo)dimanganese(III,IV) complex.[12] Such bis-μ-oxo dimer formation may be prevented when the location of the mononuclear manganese complex is fixed on a solid support. However, the catalytic reactivity of the mononuclear manganese complexes supported on solid as a heterogeneous catalyst has yet to be reported, although manganese-substituted mesoporous silicas without ligands are known to exhibit the catalytic activity for hydroxylation of benzene with hydrogen peroxide (H_2O_2) at high temperatures (e.g., 345 K).[13]

We report herein that $[(\mathrm{tpa})\mathrm{Mn}^{\mathrm{II}}]^{2+}$ incorporated in mesoporous silica-alumina (Al-MCM-41) having a highly acidic property catalyses selective hydroxylation of benzene derivatives and alkanes with hydrogen peroxide (H_2O_2) to the corresponding phenols with hydrogen peroxide at ambient temperature. Although much efforts have been devoted, selective benzene hydroxylation is still a big challenge.[14] The catalytic activity of $[(\mathrm{tpa})\mathrm{Mn}^{\mathrm{II}}]^{2+}$ incorporated in mesoporous silica-alumina was compared with that of $[(\mathrm{tpa})\mathrm{Mn}^{\mathrm{II}}]^{2+}$ in a homogeneous solution and also with the bis(μ-oxo)dimanganese(III,IV) complex ($[(\mathrm{tpa})_2\mathrm{Mn}_2(\mu\text{-O})_2]^{3+}$) or Mn^{2+} ion incorporated in mesoporous silica-alumina.

Mesoporous silica-alumina was synthesized by using a mixture of tetraethyl orthosilicate and sodium aluminate as precursors under basic conditions (aqueous NaOH).[15] The acidity of Al-MCM-41 was determined to be $H_o < -8.1$ by using a Hammett indicator (anthraquinone). The Brunauer-Emmett-Teller (BET) surface area of Al-MCM-41 was determined to be 1200 $\mathrm{m}^2\ \mathrm{g}^{-1}$ based on the N_2 isotherm (Fig. S1†). The external surface area determined by the *t*-plot was as small as 32 $\mathrm{m}^2\ \mathrm{g}^{-1}$, suggesting that nearly all $[(\mathrm{tpa})\mathrm{Mn}^{\mathrm{II}}]^{2+}$ complexes seem to be incorporated inside mesopore. The powder XRD pattern of Al-MCM-41 indicates that the pore diameter is 3.5 nm (Fig. S2†), which is large enough to incorporate Mn complexes with the size smaller than 1.4 nm. $[(\mathrm{tpa})\mathrm{Mn}^{\mathrm{II}}]^{2+}$ was incorporated in Al-MCM-41 by Na^+ cation exchange to afford the supported catalyst ($[(\mathrm{tpa})\mathrm{Mn}^{\mathrm{II}}]^{2+}$@Al-MCM-41) in acetonitrile (MeCN). The adsorption of $[(\mathrm{tpa})\mathrm{Mn}^{\mathrm{II}}]^{2+}$ was confirmed by a UV-vis diffuse reflectance spectrum as shown in Fig. S3†, where the absorption band due to $[(\mathrm{tpa})\mathrm{Mn}^{\mathrm{II}}]^{2+}$ is observed. The amount of incorporated $[(\mathrm{tpa})\mathrm{Mn}^{\mathrm{II}}]^{2+}$ was determined to be $3.9 \times 10^{-6}\ \mathrm{mol}_{\text{-Mn}}\ \mathrm{g}^{-1}$, which corresponds to 1.5% of the cation exchange sites, by absorbance change of mother liquor. The amount of incorporated $[(\mathrm{tpa})\mathrm{Mn}^{\mathrm{II}}]^{2+}$ also determined by X-ray fluorescence measurement agreed well with that determined from the absorbance change within experimental error. The amount of incorporated $[(\mathrm{tpa})\mathrm{Mn}^{\mathrm{II}}]^{2+}$ can be increased up to $3.6 \times 10^{-5}\ \mathrm{mol}_{\text{-Mn}}\ \mathrm{g}^{-1}$ by increasing the concentration of $[(\mathrm{tpa})\mathrm{Mn}^{\mathrm{II}}]^{2+}$ in mother liquor.

View Article Online
DOI: 10.1039/C4CC09967B

Selective hydroxylation of benzene with H_2O_2 to yield phenol was catalysed by $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 at 298 K. Nearly 100% selectivity to phenol was obtained for the reaction system using $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 (3.6×10^{-5} $mol_{\text{-Mn}}$ g^{-1}, 100 mg, [Mn]: 1.8 mM) and benzene (5.6 mM) in an aqueous H_2O_2 solution (30%, 2.0 mL, 9.0 M) (Fig. 1a). Although the strong adsorption of both benzene and phenol onto the Al-MCM-41 support precluded the precise determination of benzene conversion, more than 0.6 mM phenol formation corresponding to 11% benzene conversion was confirmed. On the other hand, no benzene conversion was observed for the catalytic systems using Mn^{2+}@Al-MCM-41, $[(tpa)_2Mn_2(\mu\text{-}O)_2]^{3+}$@Al-MCM-41 and $[(tpa)Mn^{II}]^{2+}$ as catalysts under the same reaction conditions. To reduce the influence of the benzene adsorption, the benzene hydroxylation was also performed under conditions with reduced amount of the catalyst $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 (3.9×10^{-6} $mol_{\text{-Mn}}$ g^{-1}, 14 mg, [Mn]: 23 μM), increased amount of benzene (0.40 mL, 1.9 M) and aqueous 30% H_2O_2 (0.4 mL, $[H_2O_2]$: 1.5 M) diluted with acetonitrile (1.6 mL) (Fig. 1b). The turnover number of $[(tpa)Mn^{II}]^{2+}$ reached 60 in 12 h when the average turnover frequency was 5.0 h^{-1}. The catalytic activity of the recovered catalyst was significantly decreased (Fig. S4†). However, the change in Mn concentration of Mn(tpa)@Al-MCM-41 after the catalytic reaction for 12 h was negligible as evidenced by XRF measurements. Thus, a plausible reason for the deactivation may be oxidative degradation of the organic ligand of the Mn complex. No further oxidation of phenol to *p*-benzoquinone occurred at 298 K as evidenced by no hydroxylation of phenol under the same reaction conditions other than phenol was used instead of benzene (Fig. S5†). No hydroxylation of phenol would result from formation of oxonium ion,[16] which is more hardly oxidized than phenol, owing to the strongly acidic nature of silica-alumina.[17] Prevention of phenol oxidation in the presence of a strong acid has been reported in a homogeneous benzene hydroxylation.[18]

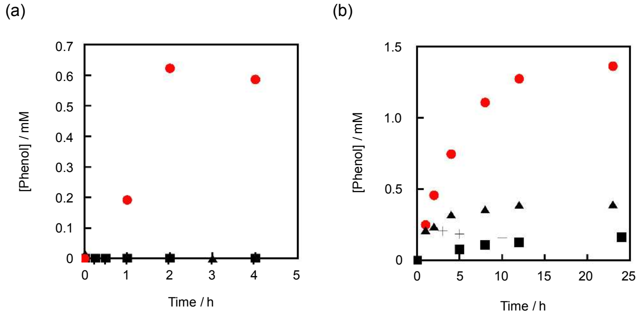


Fig. 1 Time courses of formation of phenol in hydroxylation of benzene with aqueous H_2O_2 catalyzed by $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 (red circle), Mn^{2+}@Al-MCM-41 (plus), $[(tpa)_2Mn_2(\mu\text{-}O)_2]^{3+}$@Al-MCM-41 (triangle) and $[(tpa)Mn^{II}]^{2+}$ (square) at 298 K. (a) The concentrations of benzene, H_2O_2 and Mn in the starting solution are 5.6 mM, 9.0 M, 1.8 mM, respectively. (b) The reaction was performed in a mixed solution (2.4 mL) composed of benzene, aqueous H_2O_2 and MeCN [0.40:0.40:1.6 (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 catalytic reactivity of $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 is significantly higher than that of $[(tpa)_2Mn_2(\mu\text{-}O)_2]^{3+}$@Al-MCM-41, Mn^{2+}@Al-MCM-41 prepared by a conventional ion-exchange method using manganese(II) perchlorate, and $[(tpa)Mn^{II}]^{2+}$ in a homogeneous solution (Fig. 1b).

Hydroxylation of methoxybenzene with H_2O_2 was also catalysed by $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 to yield mainly the corresponding *o*- and *p*-methoxyphenol with little *m*-methoxyphenol (Fig. 2). The electron-donating methoxy group directs the hydroxylation of the benzene ring at *ortho*- and *para*-positions as observed in electrophilic substitution of methoxybenzene.[18,19] The total turnover number of $[(tpa)Mn^{II}]^{2+}$ reached 174, which is ca. 3 times larger than that of the benzene hydroxylation. The catalytic hydroxylation of chlorobenzene with H_2O_2 also yielded mainly *o*- and *p*-chlorophenol (Fig. S6†) as observed in electrophilic substitution of chlorobenzene.[19,20] The observed regioselectivity for the position of hydroxylation of the benzene ring indicates that the reactive intermediate is most likely to be an electrophilic $Mn^{IV}(O)$ species ($[(tpa)Mn^{IV}(O)]^{2+}$@Al-MCM-41) produced by the reaction of $[(tpa)Mn^{II}]^{2+}$ with H_2O_2 inside Al-MCM-41. In general, oxygenation of phenol proceeds more readily than that of methoxybenzene.[21] However, only methoxybenzene oxygenation proceeds in the current reaction systems. This may be due to no formation of oxonium ion of methoxybenzene, because the methyl group of methoxybenzene may sterically disturb interaction with the Lewis acid site of the catalyst surface.

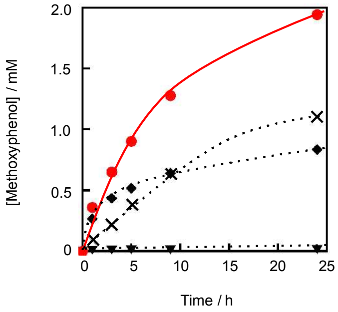


Fig. 2 Time courses of formation of methoxyphenol (red circle) [*o*- (diamond), *p*- (cross) and *m*-methoxyphenol (inverse triangle)] in hydroxylation of methoxybenzene (0.40 mL) with aqueous H_2O_2 (30 wt%, 0.40 mL) catalysed by $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 ($[[(tpa)Mn^{II}]^{2+}]$: 23 μM) in MeCN (1.6 mL) at 298 K. The concentrations of methoxybenzene and H_2O_2 in the starting solutions are 1.5 M and 1.5 M, respectively.

$[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 also catalysed the hydroxylation of electron deficient nitrobenzene with H_2O_2 at a higher temperature (323 K) as shown in Fig. 3. In contrast to the case of methoxy- benzene, *o*-nitrophenol was produced selectively.[22] This regioselectivity may result from a specific interaction of $[(tpa)Mn^{IV}(O)]^{2+}$ with the *ortho*-proton and the NO_2 group as reported for selective aerobic oxygenation of nitrobenzene to *o*-nitrophenol catalysed by $H_5PV_2Mo_{10}O_{40}$ polyoxometalate.[23]

Alkanes can also be hydroxylated by H_2O_2 with $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 in MeCN even at 298 K. 2-Hexanol was selectively produced in hydroxylation of *n*-hexane by H_2O_2 with $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 as shown in Fig. 4. In the reaction, 2-hexanol was selectively formed, although the reason

View Article Online
DOI: 10.1039/C4CC09967B

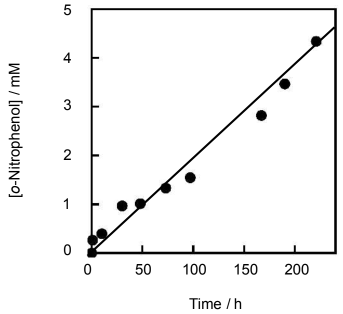


Fig. 3 Time courses of formation of *o*-nitrophenol in hydroxylation of nitrobenzene (0.40 mL) with aqueous H_2O_2 (30 wt%, 0.40 mL) catalysed by $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 ($[[(tpa)Mn^{II}]^{2+}]$: 75 μM) in MeCN (1.6 mL) at 323 K. The concentrations of nitrobenzene and H_2O_2 in the starting solutions are 1.6 M and 1.5 M, respectively.

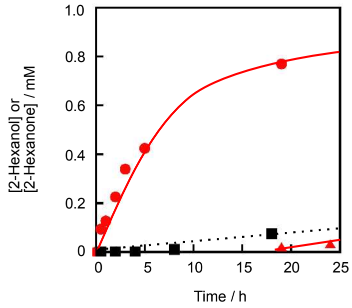


Fig. 4 Time courses of formation of 2-hexanol (red circle) and 2-hexanone (red triangle) in hydroxylation of *n*-hexane (0.10 mL) with aqueous H_2O_2 (30 wt%, 0.20 mL) catalysed by $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 ($[[(tpa)Mn^{II}]^{2+}]$: 69 μM) in MeCN (2.0 mL) at 298 K. Time course of formation of 2-hexanol with $[(tpa)Mn^{II}]^{2+}$ ($[[(tpa)Mn^{II}]^{2+}]$: 69 μM, black square) in a homogeneous solution. The concentrations of *n*-hexane and H_2O_2 in the starting solutions are 0.33 M and 0.77 M, respectively.

for the high selectivity has yet to be clarified. It should be again noted that almost no hydroxylation occurred with $[(tpa)Mn^{II}]^{2+}$ in a homogeneous solution under otherwise the same reaction conditions (Fig. 4). At prolonged reaction time 2-hexanone was produced via the oxidation of 2-hexanol (Fig. 4). When a CD_3CN solution (1.0 mL) of H_2O_2 (30 wt%, 20 □L; $[H_2O_2]$ = 0.17 M) and $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 ($[[(tpa)Mn^{II}]^{2+}]$: 890 μM) saturated with ethane (19 mM) was stirred for 23 h at room temperature, ethanol (35 μM) was produced by the hydroxylation of ethane together with acetaldehyde (75 μM) and diethyl ether (29 μM) (Fig. S7†).

The reaction of $[(tpa)Mn^{II}]^{2+}$ with H_2O_2 in a homogeneous solution afforded the bis(μ-oxo)dimanganese(III,IV) complex ($[(tpa)_2Mn_2(\mu\text{-}O)_2]^{3+}$) as shown in Fig. 6a, where the EPR spectrum exhibits hyperfine due to two Mn nuclei (the computer simulation spectrum is shown in Fig. S8†).[24] When $[(tpa)Mn^{II}]^{2+}$ is incorporated in mesoporous silica-alumina, the EPR spectrum of $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 after the catalytic hydroxylation of benzene with H_2O_2 still remains the signal due to the mononuclear species (Fig. 5b). Thus, formation of $[(tpa)_2Mn_2(\mu\text{-}O)_2]^{3+}$ was prohibited by the incorporation of $[(tpa)Mn^{II}]^{2+}$ in mesoporous silica-alumina.

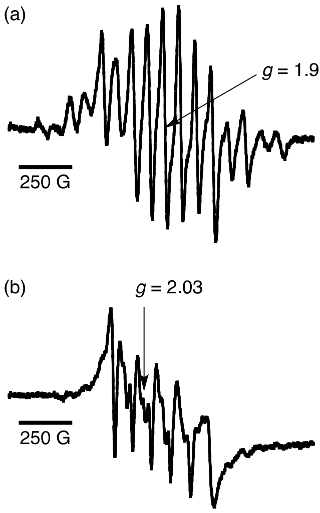


Fig. 5 EPR spectrum of (a) $[(tpa)_2Mn_2(\mu\text{-}O)_2]^{3+}$ produced by the reaction of $[(tpa)Mn^{II}]^{2+}$ with H_2O_2 in MeCN at 298 K and measured at 77 K and (b) $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 after the reaction with benzene and H_2O_2 in MeCN at 298 K and measured at 77 K.

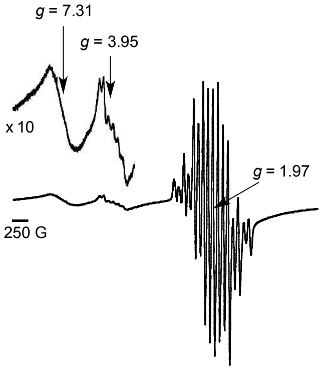


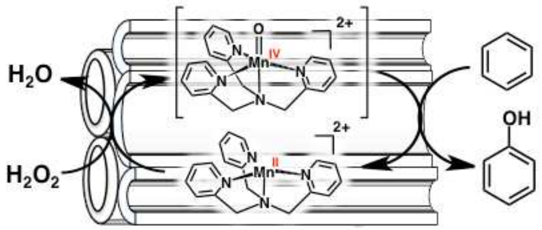
Fig. 6 EPR spectrum of (a) $[(tpa)_2Mn_2(\mu\text{-}O)_2]^{3+}$ produced by the reaction of $[(tpa)Mn^{II}]^{2+}$ with H_2O_2 in MeCN at 298 K and measured at 77 K and (b) $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 after the reaction with benzene and H_2O_2 in MeCN at 298 K and measured at 77 K.

We tried to detect $[(tpa)Mn^{IV}(O)]^{2+}$@Al-MCM-41 ($[[(tpa)Mn^{II}]^{2+}$: 3.6 × 10^{-5} mol g^{-1}), which may be produced by the reaction of $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 with iodobenzene diacetate. However, the amount of $[(tpa)Mn^{IV}(O)]^{2+}$ was too small to be detected by EPR because of the broad signal due to the $Mn^{IV}(O)$ species. When a large amount of $[(tpa)Mn^{II}]^{2+}$ (2.6 × 10^{-4} mol g^{-1}) was forcedly incorporated in Al-MCM-41, the treatment of the sample with iodobenzene diacetate gave a broad EPR signal due to the $Mn^{IV}(O)$ species at the low magnetic field region (g = 3.95 and 7.31) with hyperfine due to one Mn nucleus (Fig. 6).[8] In this case, however, the EPR signal due to $[(tpa)_2Mn_2(\mu\text{-}O)_2]^{3+}$ at g = 1.97 with hyperfine due to two Mn nuclei was also observed (Fig. 6). Thus, the formation of $[(tpa)_2Mn_2(\mu\text{-}O)_2]^{3+}$ cannot be avoided when the incorporated amount of $[(tpa)Mn^{II}]^{2+}$ was too large. Nevertheless the observation of the EPR signal due to the $Mn^{IV}(O)$ species suggests that $[(tpa)Mn^{IV}(O)]^{2+}$ is formed by the reaction of $[(tpa)Mn^{II}]^{2+}$ with iodobenzene diacetate and stabilized inside Al-MCM-41.

The rate of formation of phenol in the hydroxylation of benzene with H_2O_2 catalysed by $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 was proportional to concentrations of $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41 and benzene, but independent of concentration of H_2O_2 (Figs. S9, S10 and S11†) as given by eqn 1,

$$d[PhOH]/dt = k_{cat}[cat][benzene] \qquad (1)$$

where k_{cat} is the catalytic rate constant and [cat] is an Mn concentration in $[(tpa)Mn^{II}]^{2+}$@Al-MCM-41. Formation rates of phenol increased linearly with increasing concentration of $[(tpa)Mn^{II}]^{2+}$ in the presence of large excess of benzene (Fig. S9a†). The second-order rate constant (k_{cat}) was determined to be 6.5 M^{-1} h^{-1} from the slope of a linear plot of the formation rates of phenol vs. concentrations of $[(tpa)Mn^{II}]^{2+}$ (Fig. S9b†). The kinetic formulation in eqn 1 suggests that the rate-determining step in the catalytic hydroxylation of benzene with H_2O_2 may be the hydroxylation of benzene by $[(tpa)Mn^{IV}(O)]^{2+}$@Al-MCM-41, which is produced by the reaction of $[(tpa)Mn^{II}]^{2+}$ with H_2O_2 inside Al-MCM-41 as shown in Scheme 1.



Scheme 1 Catalytic cycle in hydroxylation of benzene with H_2O_2 catalysed by $[(tpa)Mn^{II}]^{2+}$ incorporated in Al-MCM-41.

In conclusion, selective hydroxylation of benzene derivatives and alkanes with H_2O_2 was efficiently catalysed by $[(tpa)Mn^{II}]^{2+}$ incorporated in Al-MCM-41 to yield the corresponding phenol and alcohol derivatives without further oxidation resulted from the highly acidic nature of silica-alumina surfaces at ambient temperature. The $Mn^{IV}(O)$ species ($[(tpa)Mn^{IV}(O)]^{2+}$), which is responsible for the hydroxylation of benzene derivatives and alkanes, is produced by the reaction of $[(tpa)Mn^{II}]^{2+}$ with H_2O_2 inside Al-MCM-41 and thus stabilized without formation of $[(tpa)_2Mn_2(\mu\text{-}O)_2]^{3+}$. The strategy to use Al-MCM-41 for stabilizing a reactive species, which would otherwise be converted to the much less reactive species, reported in this study provides a convenient way to develop efficient oxidation catalysts.

Notes and references

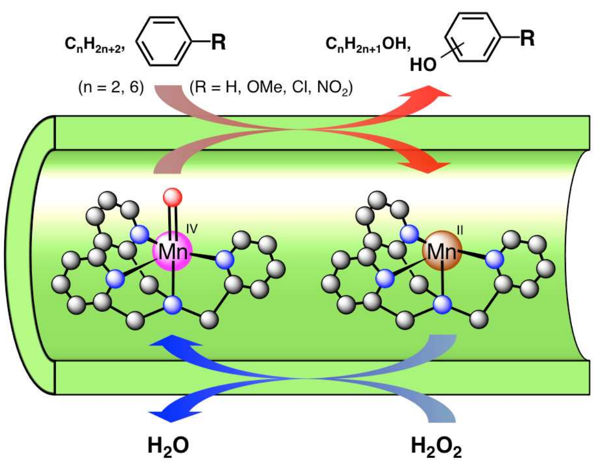
Department of Material and Life Science, Graduate School of Engineering, ALCA, Japan Science and Technology Agency (JST), Osaka University, Suita, Osaka 565-0871, Japan; E-mail: fukuzumi@chem.eng.osaka-u.ac.jp; Fax: +81-6-6879-7370

† Electronic Supplementary Information (ESI) available: Experimental details and N_2-adsorption desorption isotherm (Fig. S1), powder X-ray diffraction (Fig. S2), UV-vis DRS (Fig. S3), time courses of phenol derivatives (Figs. S4-S6, S9a, S10 and S11), ^{1}H NMR (Fig S7), EPR spectra (Fig. S8) and phenol formation rate (Fig. S9b). See DOI: 10.1039/c000000x/

1 (*a*) I. Rivalta, G. W. Brudvig and V. S. Batista, *Curr. Opin. Struct. Biol*., 2012, **16**, 11; (*b*) J. P. McEvoy and G. W. Brudvig, *Chem. Rev*., 2006, **106**, 4455.
2 Y. Umena, K. Kawakami, J. R. Shen and N. Kamiya, *Nature*, 2011, **473**, 55.
3 (*a*) C. W. Cady, R. H. Crabtree and G. W. Brudvig, *Coord. Chem. Rev*., 2008, **252**, 444; (*b*) C. S.Mullins and V. L. Pecoraro, *Coord. Chem. Rev*., 2008, **252**, 416.
4 (*a*) A. Sartorel, M. Bonchio, S. Campagna and F. Scandola, *Chem. Soc. Rev*. 2013, **42**, 2262; (*b*) E. Y. Tsui, J. S. Kanady and T. Agapie, T., *Inorg. Chem*. 2013, **52**, 13833.
5 (*a*) D. P. Goldberg, *Acc. Chem. Res*., 2007, **40**, 626; (*b*) K. A. Prokop, H. M. Neu, S. P. de Visser and D. P. Goldberg, *J. Am. Chem. Soc*., 2011, **133**, 15874; (*c*) S. Fukuzumi, H. Kotani, K. A. Prokop and D. P. Goldberg, *J. Am. Chem. Soc*., 2011, **133**, 1859.
6 (*a*) A. Kumar, I. Goldberg, M. Botoshansky, Y. Buchman and Z. Gross, *J. Am. Chem. Soc*., 2010, **132**, 15233; (*b*) T. P. Umile and J. T. Groves, *Angew. Chem., Int. Ed*., 2011, **50**, 695.
7 (*a*) J. Y. Lee, Y.-M. Lee, H. Kotani, W. Nam and S. Fukuzumi, *Chem. Commun*., 2009, **45**, 704; (*b*) Y. Han, Y.-M. Lee, M. Mariappan, S. Fukuzumi and W. Nam, *Chem. Commun*., 2010, **46**, 8160; (*c*) S. Fukuzumi, T. Kishi, H. Kotani, Y.-M. Lee and W. Nam, *Nat. Chem*., 2011, **3**, 38.
8 J. Chen, X. Wu, K. M. Davis, Y.-M. Lee, M. S. Seo, K.-B. Cho, H. Yoon, Y. J. Park, S. Fukuzumi, Y. N. Pushkar and W. Nam, *J. Am. Chem. Soc*., 2013, **135**, 6388.
9 H. Yoon, Y. Morimoto, K. Ohkubo, Y.-M. Lee, W. Nam and S. Fukuzumi, *Chem. Commun*., 2012, **48**, 11187.
10 H. Yoon, Y.-M. Lee, X. Wu, K.-B. Cho, Y. N. Pushkar, W. Nam and S. Fukuzumi, *J. Am. Chem. Soc*., 2013, **135**, 9186.
11 A manganese(VII) nitrido oxo species has recently been reported to be able to oxidize alkanes; see: L. Ma, Y. Pan, W.-L. Man, H.-K. Kwong, W. W. Y. Lam, G. Chen, K.-C. Lau and T.-C. Lau, *J. Am. Chem. Soc*., 2014, **136**, 7680.
12 A. R. Oki, J. Glerup and D. J. Hodgson, *Inorg. Chem*., 1990, **29**, 2435.
13 (*a*) W. Zhang, J. Wang, P. T. Tanev and T. J. Pinnavaia, *Chem. Commun*., 1996, 979; (*b*) Y. Xiong, J. Li, X. Yang and Y. Wu, *Z. Phys. Chem*., 2006, **220**, 315; (*c*) R. J. Kalbasi, A. R. Massah, F. Zamani, A. D. Bain and B. Berno, *J. Porous Mater*., 2011, **18**, 475.
14 (*a*) A. M. Eliasen, R. P. Thedford, K. R. Claussen, C. Yuan and D. Siegel, *Org. Lett*., 2014, **16**, 3628; (*b*) C. Yuan, Y. Liang, T. Hernandez, A. Berriochoa, K. N. Houk and D. Siegel, *Nature*, 2013, **499**, 192; (*c*) G. A. Olah, A. P. Fung and T. Keumi, *J. Org. Chem*., 1981, **46**, 4305.
15 E. G. Vaschetto, G. A. Monti, E. R. Herrero, S. G. Casuscelli and G. A. Eimer, *Appl. Catal., A*, 2013, **453**, 391.
16 (*a*) G. A. Olah, A. M. White and D. H. O'Brien, *Chem. Rev*., 1970, **70**, 561; (*b*) N. Solcà and O. Dopfer, *Chem. Phys. Lett*., 2001, **342**, 191.
17 (*a*) W. O. Parker, Jr. and S. Wegner, *Microporous Mesoporous Mater*., 2012, **158**, 235; (*b*) P. Gupta and S. Paul, *Catal. Today*, 2014, **236**, 153.
18 H. Guo, Z. Chen, F. mei, D. Zhu, H. Xiong and G. Yin, *Chem. Asian J*., 2013, **8**, 888.
19 S. Fukuzumi and J. K. Kochi, *J. Am. Chem. Soc*., 1981, **103**, 7240.
20 H. Yoshida, H. Yuzawa, M. Aoki, K. Otake, H. Itoh and T. Hattori, *Chem. Commun*., 2008, 4634.
21 R. Saladino, V. Neri, E Mincionea and P. Filippone, *Tetrahedron*, 2002, 58, 8493.
22 Small amount of *m*- and *p*-nitorophenol was formed at prolonged reaction time.
23 A. M. Khenkin, L. Weiner and R. Neumann, *J. Am. Chem. Soc*., 2005, **127**, 9988.
24 Y. Nishida, M. Nasu, T. Akamatsu and M. Tanno, *Chem. Lett*., 1992, 2325.

View Article Online
DOI: 10.1039/C4CC09967B

TOC



Selective hydroxylation of benzene to phenol with hydrogen peroxide was efficiently catalysed by a manganese complex incorporated in mesoporous silica-alumina.