Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information (ESI)

In situ-created Mn(III) complex active for liquid-phase oxidation of alkylaromatics to aromatic ketones with molecular oxygen

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Preparation of $Mn(PhCOO)_2^+$ complex

$Mn(PhCOO)_2^+$ complex was prepared as follows; a *N,N*-dimethylformamide (99.8%, Nacalai Tescue, Inc.) solution containing $MnCl_2 \cdot 4H_2O$ (98%, Nacalai Tescue, Inc.) and benzoic acid (99.5%, Nacalai Tescue, Inc.) with the molar ratio of 1:2 was magnetically stirred for 15 min, and then thermally reacted in the presence of O_2 at 135 ℃ for 12 h. The resulting solution was evaporated to remove the solvent and dried at 100 ℃ to yield $Mn(PhCOO)_2^+$ as a pale-red powder, which may containing Cl^- as a counter anion.

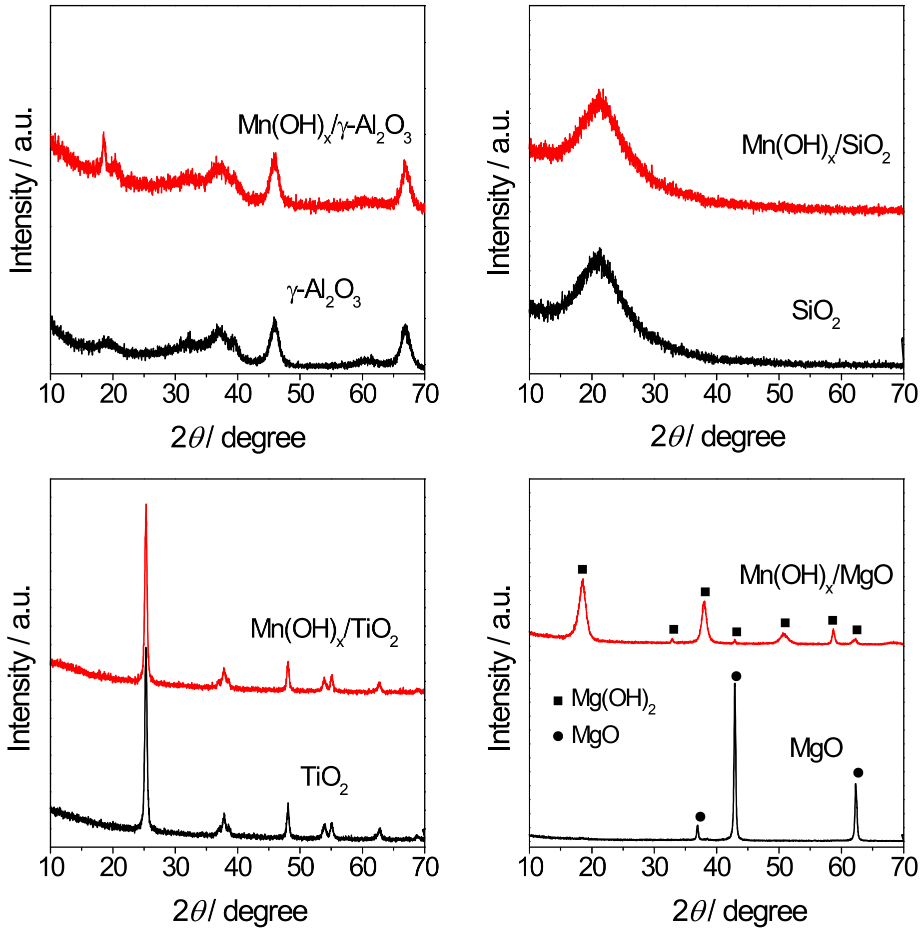

Fig. S1 XRD patterns of bare oxide supports (black line) and freshly-prepared supported $Mn(OH)_x$ catalysts (red line). $Mn(OH)_x/MgO$ shows diffraction patterns assignable to $Mg(OH)_2$ due to the hydration of MgO during the catalyst preparation.

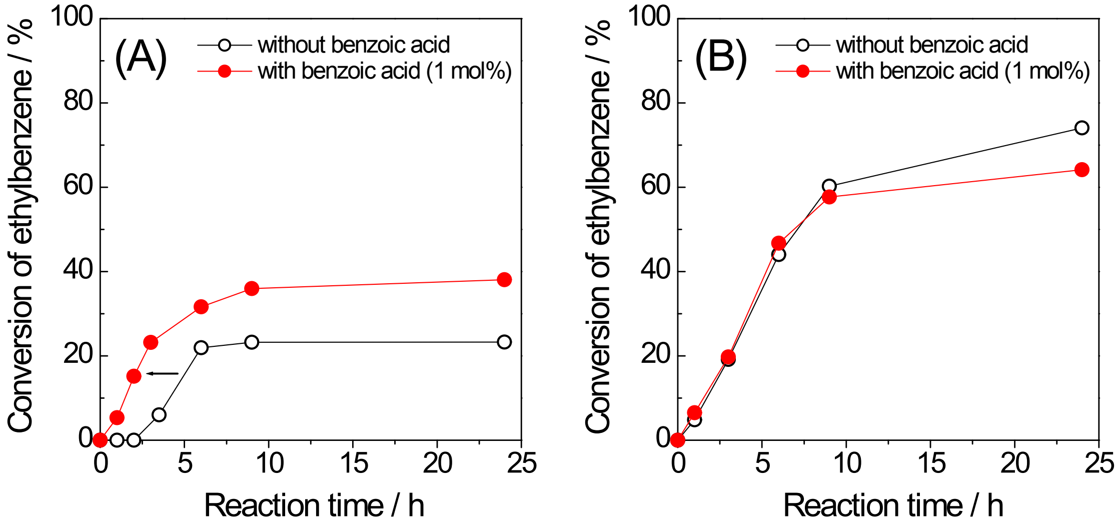

Fig. S2 Comparison of conversions of ethylbenzene over (A) $Mn(OH)_x/TiO_2$ and (B) $Mn(OH)_x/SiO_2$ with and without addition of 1 mol% of benzoic acid.

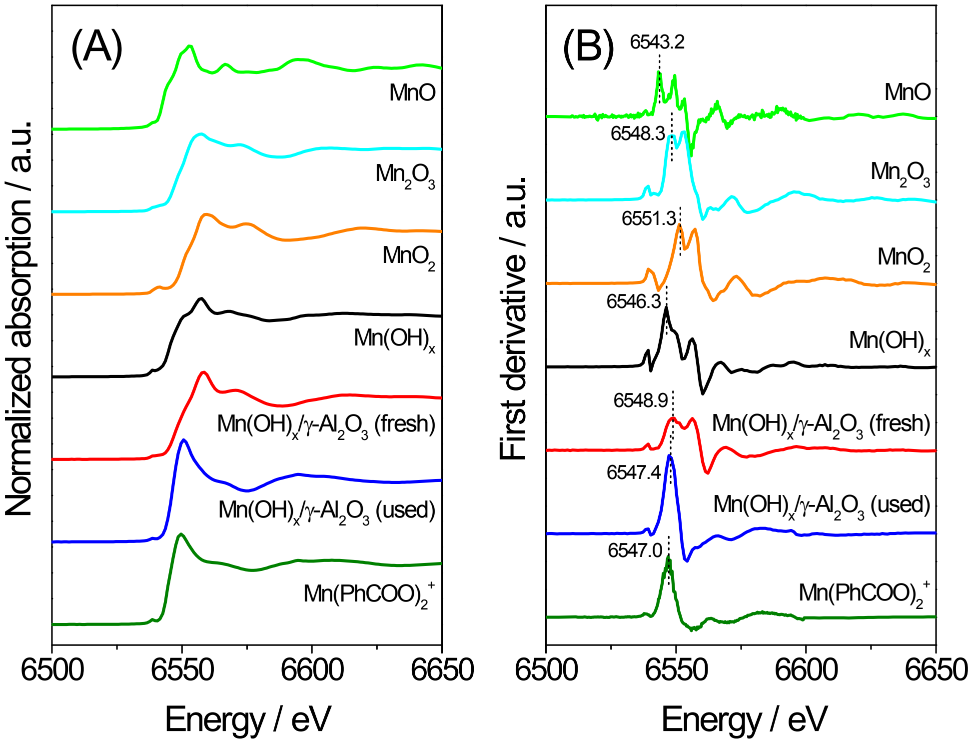

Fig. S3 (A) Mn K-edge XANES spectra and (B) their first derivatives of $Mn(OH)_x$, fresh $Mn(OH)_x/\gamma\text{-}Al_2O_3$, used $Mn(OH)_x/\gamma\text{-}Al_2O_3$, and $Mn(PhCOO)_2^+$ together with some reference Mn model compounds.

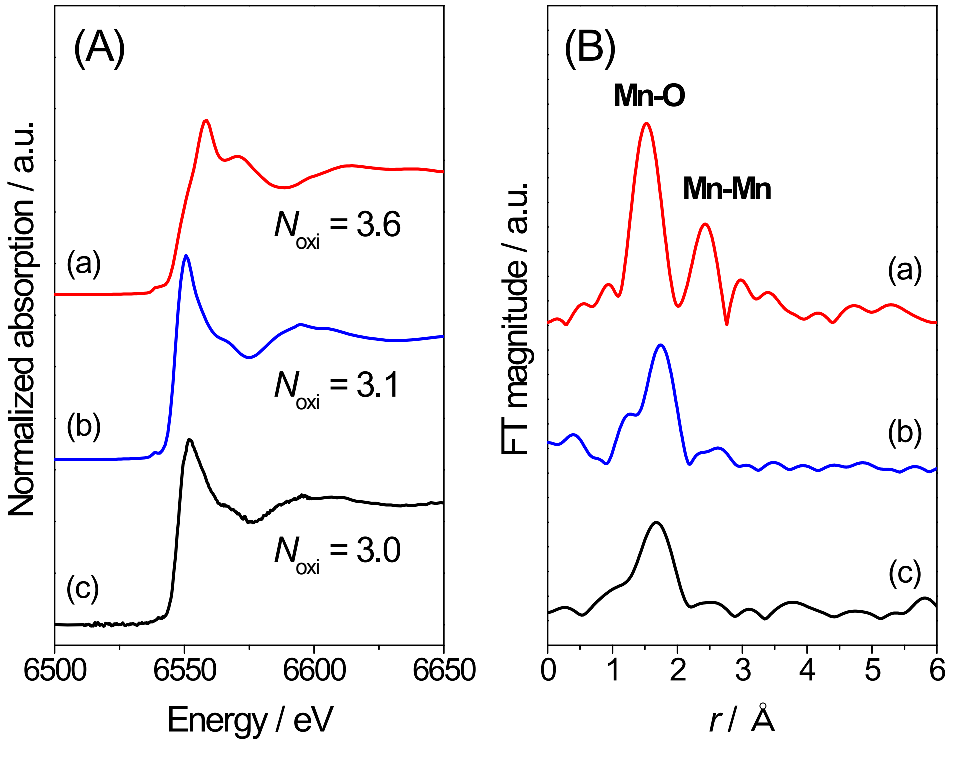

Fig. S4 Mn K-edge radial distribution functions of $Mn(OH)_x/\gamma\text{-}Al_2O_3$ catalyst (a) freshly-prepared, (b) after 1st catalytic use, and (c) after 2nd catalytic use.