Electronic Supplementary Information (ESI)

Liquid Phase Oxidation of Alkylaromatics to Aromatic Ketones with Molecular Oxygen over Mn-based Metal-organic Framework

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Procedures for adsorption test

An adsorption experiment using Mn-MOF-74 as an adsorbent and ethylbenzene/diphenylmethane as smaller/bigger model substrates was carried out in order to evaluate the accessibility of substrates to the interior pores of Mn-MOF-74. The adsorption experiment was carried out according to the following procedures: In a glass vessel, substrates (0.3 mmol), *m*-dichlorobenzene as a solvent (5 mL) and the Mn-MOF-74 as an adsorbent (50 mg) were placed. The mixture was stirred at room temperature with magnetic stirring. After 24 h of adsorption, the mixture was withdrawn, filtered and analyzed by using a gas chromatograph (Shimadzu GC-14B) with a flame ionization detector equipped with a capillary column (Zebron ZB-FFAP; 0.32 mm×50 m). The amounts of substrates adsorbed were determined by using biphenyl as an internal standard.

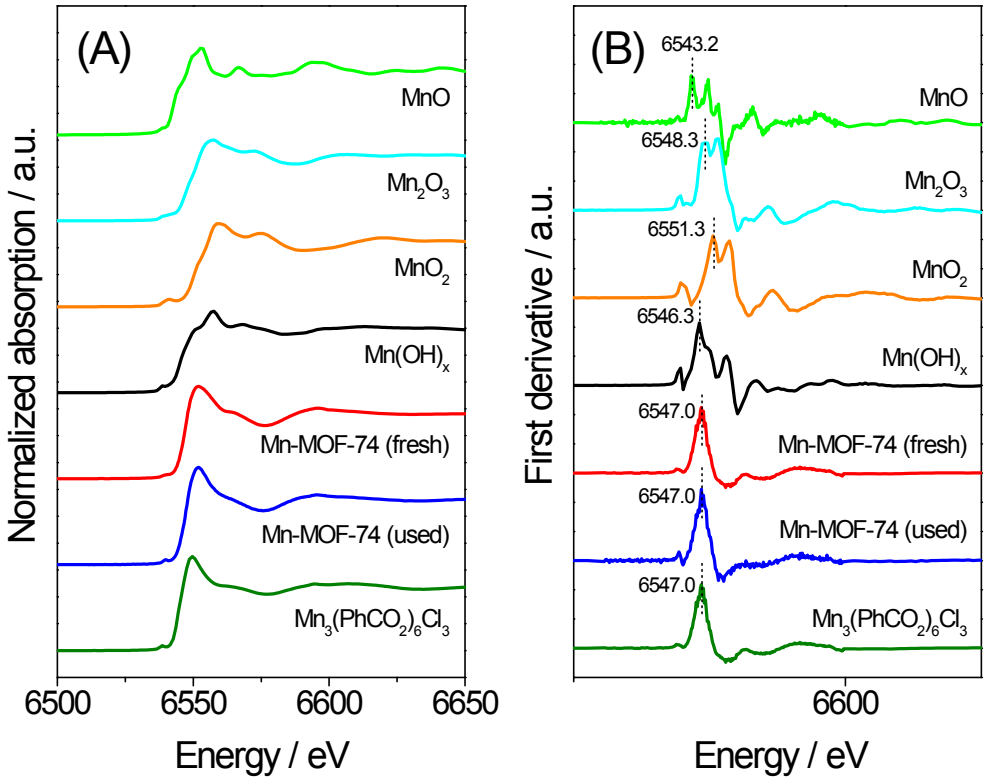

Fig. S1 (A) Mn K-edge XANES spectra and (B) their first derivatives of Mn-MOF-74, used Mn-MOF-74 and $Mn_3(PhCO_2)_6Cl_3$ together with some reference Mn oxide/hydroxide compounds.

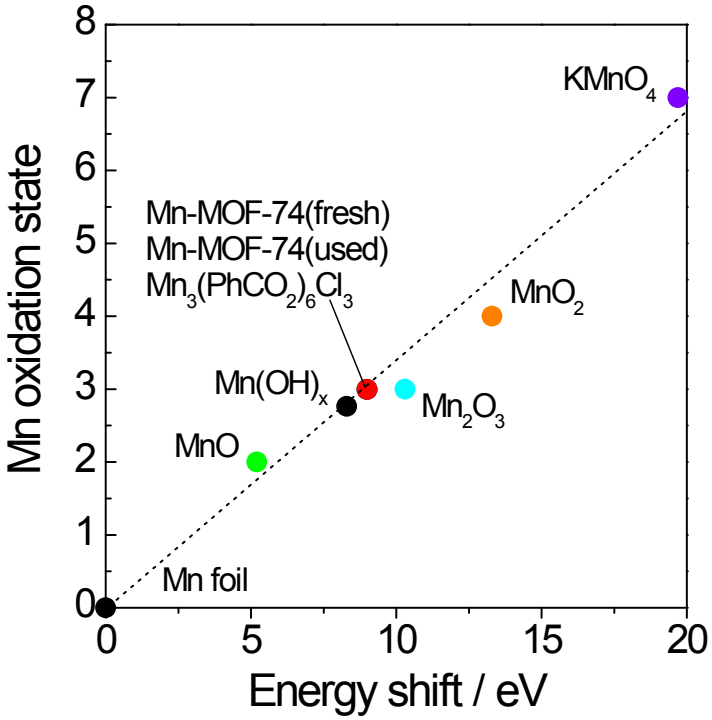

Fig. S2 Correlation between the energy shift and oxidation state of Mn atoms in the experimental samples and reference Mn oxide/hydroxide compounds.

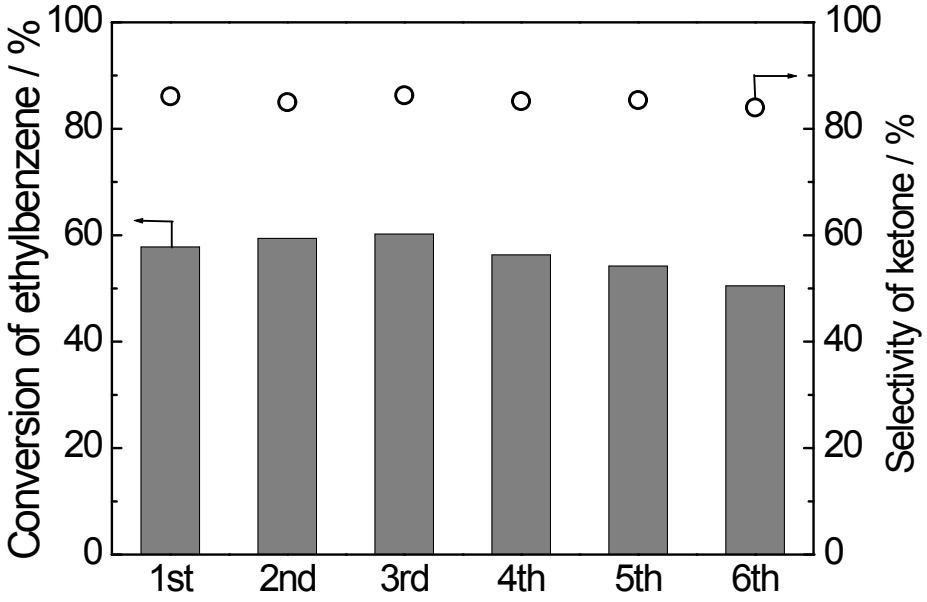

Fig. S3 Reusability tests of Mn-MOF-74 catalyst in the liquid-phase oxidation of ethylbenzene with molecular O_2. Reaction conditions: catalyst (Mn 0.03 mmol), ethylbenzene (40 mmol), O_2 flow (5 mL/min), 135 ºC, 9 h.

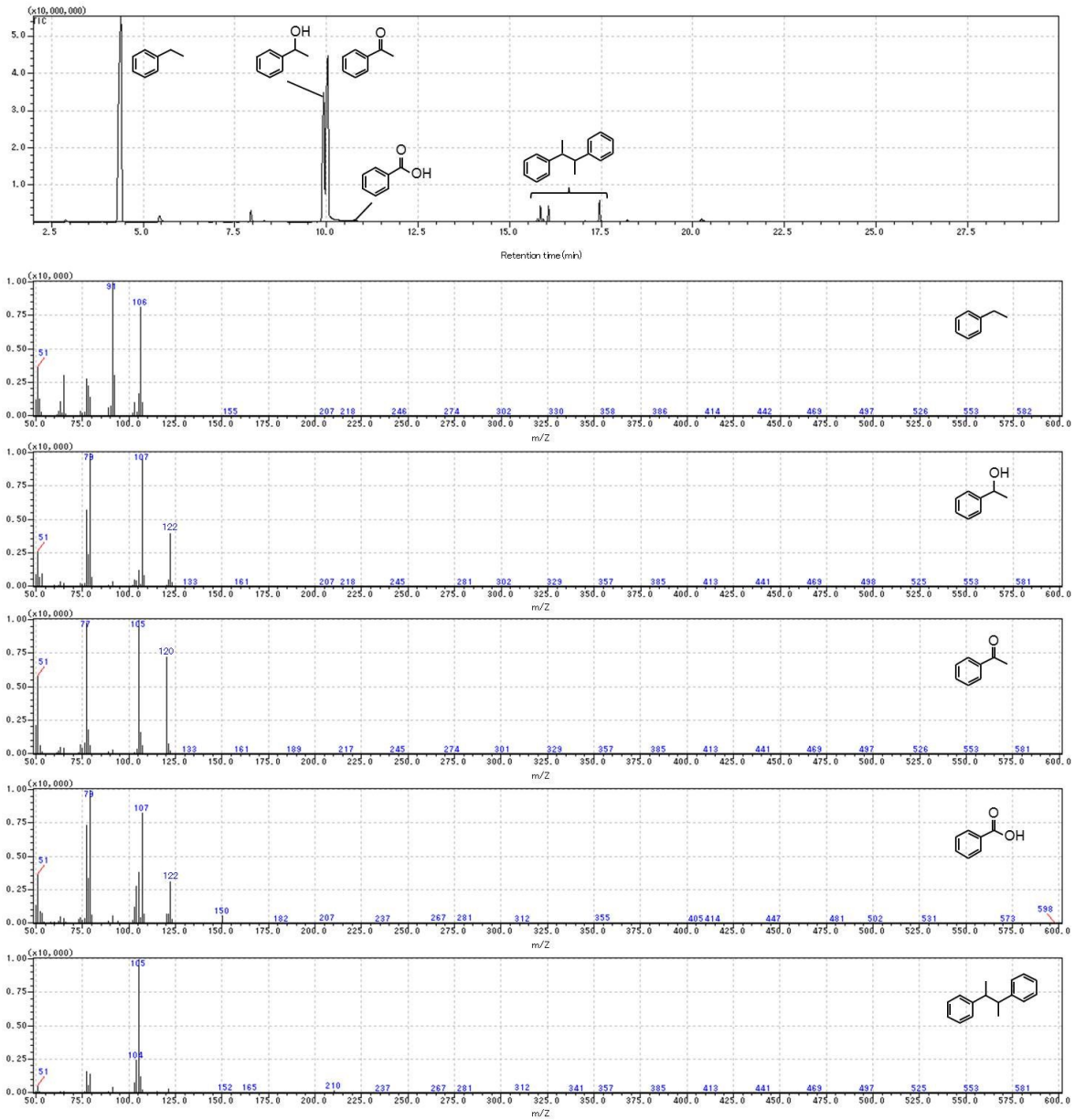

Fig. S4 GC-MS spectra of the reaction mixtures obtained in the liquid-phase oxidation of ethylbenzene (Reaction conditions: catalyst (Mn 0.03 mmol), substrate (40 mmol), O_2 flow (5 mL/min), 135 ºC, 9 h). The spectra shown below are the MS fragment charts corresponding to each GC peak.

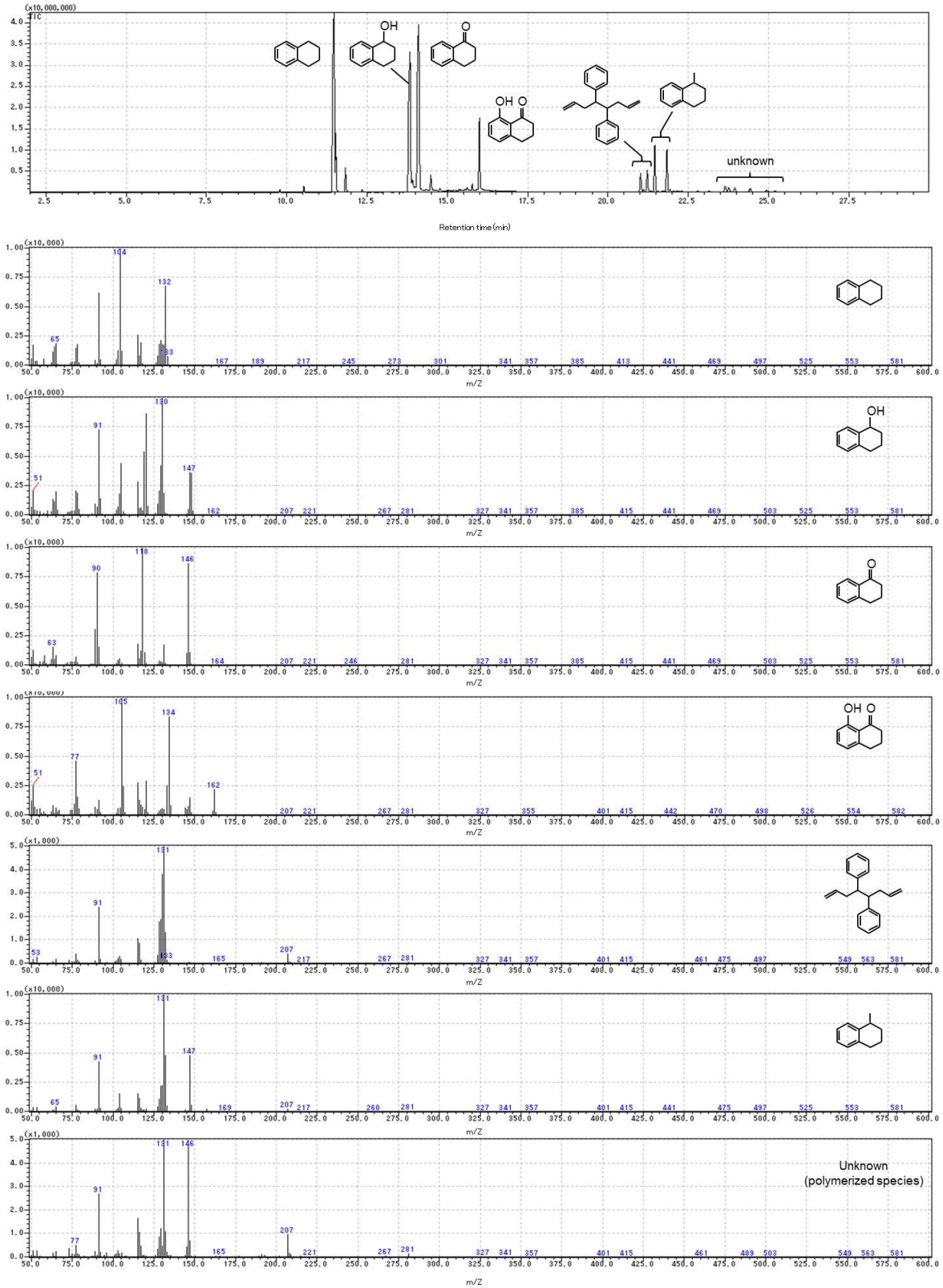

Fig. S5 GC-MS spectra of the reaction mixtures obtained in the liquid-phase oxidation of tetralin (Reaction conditions: catalyst (Mn 0.03 mmol), substrate (5 mmol), solvent (*m*-dichlorobenzene, 5 mL), O_2 flow (5 mL/min), 135 ºC, 9 h). The spectra shown below are the MS fragment charts corresponding to each GC peak.