

Supplementary Information

Enhanced catalytic activity of MnCo-MOF-74 for highly selective aerobic oxidation of substituted toluene

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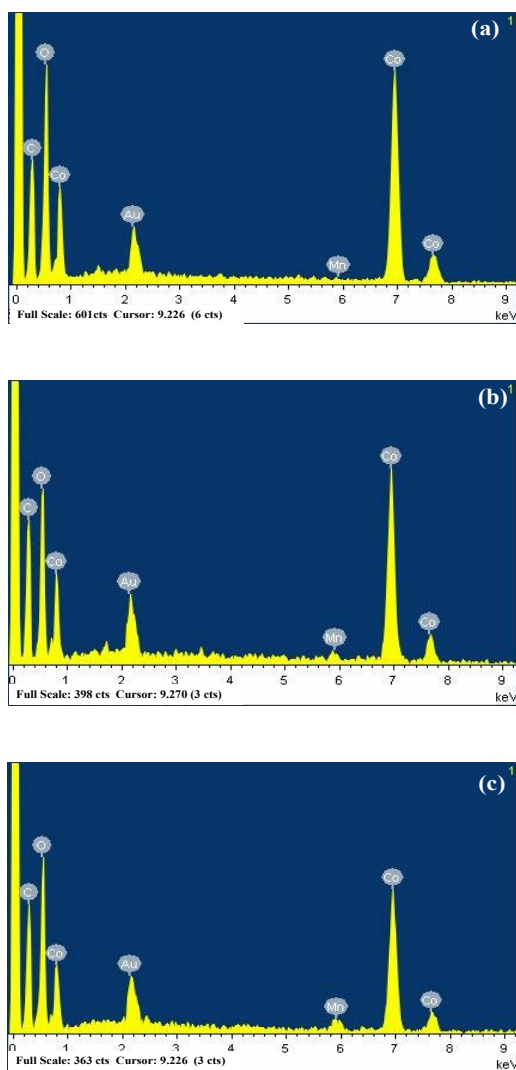


Fig. S1 EDS spectra of (a) MnCo-MOF-74-3, (b) MnCo-MOF-74-6, and (c) MnCo-MOF-74-9.

Table S1 Oxidation of toluene catalyzed over M-MOF-74 under different conditions^a

Entry	Catalyst	Time/ h	Conversion/%	Selectivity ^b /%		
				BAC	BA	BAL
1	Co-MOF-74	18	27.3	26.6	48.1	8.5
2	MnCo-MOF-74(dir)	6	12.5	-	95.4	1.4
3	MnCo-MOF-74-6	24	33.1	35.2	47.4	0.3

^aReaction condition: 30 mg of catalyst, 3 mL toluene (28 mmol), O₂ balloon, 10 mol% TBHP, 80 °C.

^b BAC = selectivity of benzoic acid, BA = selectivity of benzaldehyde, BAL = selectivity of benzyl alcohol.

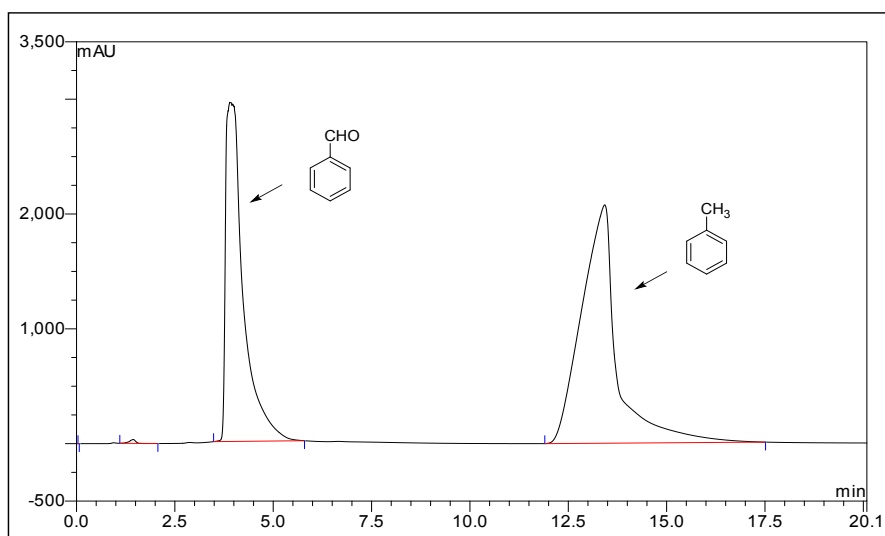


Fig. S2 HPLC spectrum of the results obtained for the toluene oxidation reaction by MnCo-MOF-74-6, reaction conditions: 30 mg of catalyst, 3.0 mL toluene (28 mmol), O₂ balloon, 10 mol% TBHP, 3 mL MeCN, 80 °C, 6 h.

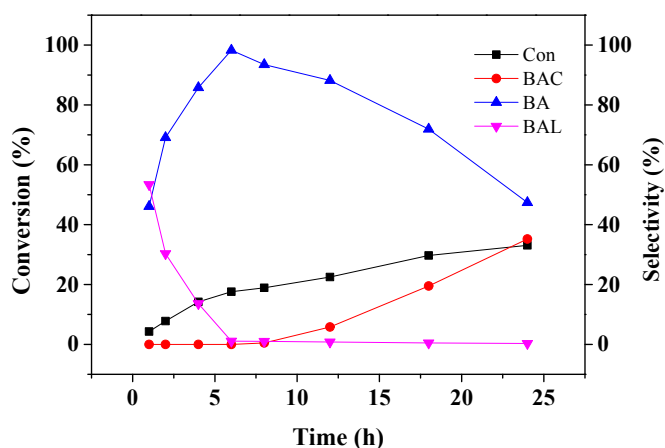
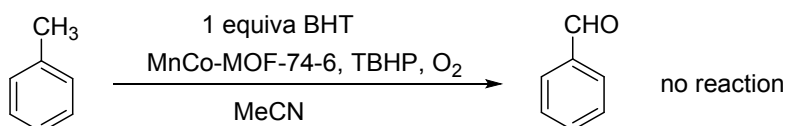
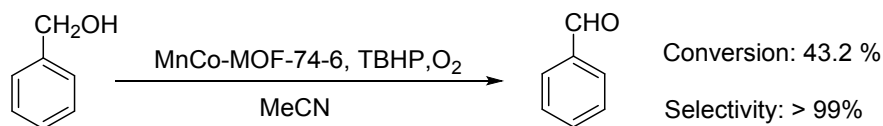


Fig. S3 Time-dependence plots of aerobic oxidation of toluene over MnCo-MOF-74-6. Reaction conditions: 30 mg of catalyst, 3.0 mL toluene (28 mmol), O₂ balloon, 10 mol% TBHP, 3 mL MeCN, 80 °C.



Scheme S1 Investigation into the reaction mechanism, reaction conditions: 15 mg of catalyst, 1.5 mL toluene (14 mmol), 3.1 g BHT (14 mmol), O₂ balloon, 10 mol% TBHP, 3 mL MeCN, 80 °C, 6 h.



Scheme S2 Aerobic oxidation of benzaldehyde over MnCo-MOF-74-6, reaction conditions: 30 mg of catalyst, 2.9 mL benzyl alcohol (28 mmol), O₂ balloon, 10 mol% TBHP, 3 mL MeCN, 80 °C, 6 h.

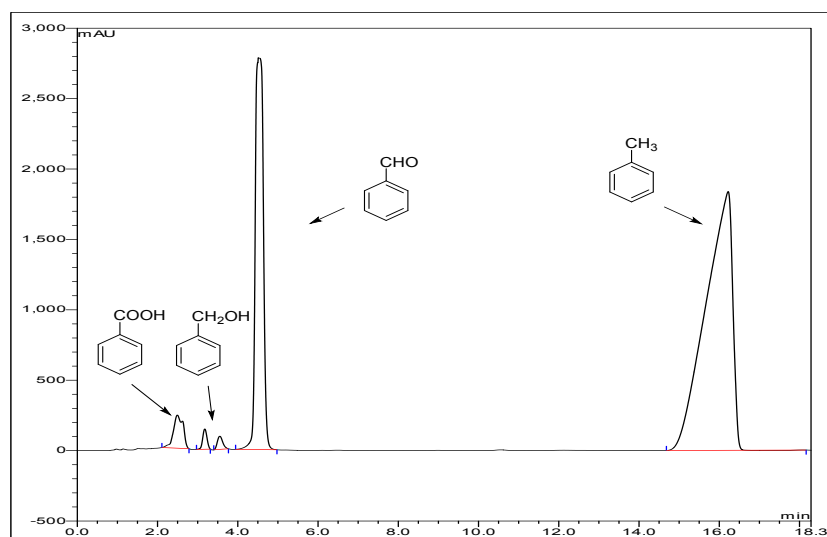


Fig. S4 HPLC spectrum of the results obtained for the toluene oxidation reaction by MnCo-MOF-74-6, reaction conditions: 30 mg of catalyst, 3.0 mL toluene (28 mmol), O₂ balloon, 10 mol% TBHP, 3 mL MeCN, 80 °C, 18 h.

Table S2 Summary of Co and Mn species leached in the solution after reaction

Entry	Catalyst	Co/mg·L ⁻¹	Mn/mg·L ⁻¹
1	Co-MOF-74	1.2	-
2	MnCo-MOF-74-6	0.9	0.2

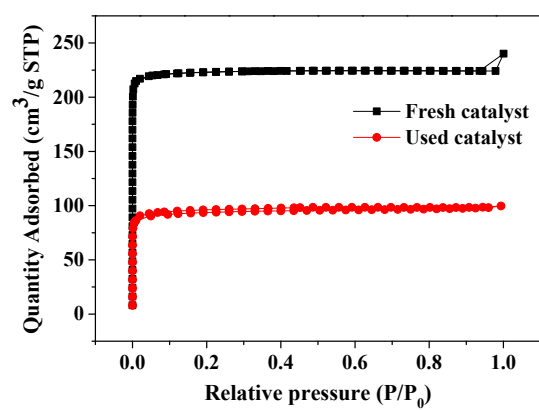


Fig. S5 Nitrogen adsorption-desorption isotherms of the fresh and used MnCo-MOF-74-6 catalyst in toluene oxidation.