Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

DFT study on the effect of oxygen vacancy and H_2O in Mn-MOF-74 on SCR reaction

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Table S1 Charge transfer of four concerned molecules after adsorption on carboxyl oxygen vacancy.

Atomic species	Mulliken charge (|e|)				
	Framework of Mn-MOF-74	NH_3	NO	O_2	NO_2
Mn	0.497	0.580	0.512	0.615	0.540
O*	-0.539	-0.549	-0.551	-0.552	-0.559
N	-	-0.434	0.024	-	0.302
O	-	-	-0.162	-	-
O1	-	-	-	-0.158	-0.285
O2	-	-	-	-0.127	-0.288
Net charge	-	0.144	-0.138	-0.285	-0.271

Notes：O* is hydroxyl oxygen, O is O atom of NO; O1 and O2 represent the oxygen atoms in the O_2 and NO_2, respectively.

Table S2 Charge transfer situation of four concerned molecules after adsorption on hydroxyl oxygen vacancy.

Atomic species	Mulliken charge (|e|)				
	Framework of Mn-MOF-74	NH_3	NO	O_2	NO_2
Mn	0.473	0.657	0.584	0.684	0.621
O*	-0.551	-0.465	-0.454	-0.449	-0.491
N	-	-0.433	0.021	-	0.293
O	-	-	-0.171	-	-
O1	-	-	-	-0.157	-0.291
O2	-	-	-	-0.133	-0.286
Net charge	-	0.129	-0.150	-0.290	-0.284

Table S3 Changes of Mn-O bond lengths before and after H_2O adsorption.

Key name	Bond length /Å		
	Framework of Mn-MOF-74	Adsorption of two H_2O molecules	Adsorption of six H_2O molecules
Mn-O1*	2.019	2.166	2.117
Mn-O2*	1.956	2.045	2.078

Table S4 Lattice parameter changes of Mn-MOF-74 (hexagonal) before and after H_2O adsorption.

Mn-MOF-74 Lattice parameter	Before adsorption	Adsorption of two H_2O molecules	Adsorption of six H_2O molecules
a (Å)	15.1065	15.3229	15.3410
b (Å)	15.1065	15.0376	15.3231
c (Å)	15.1065	15.6279	15.4401
a (degree)	117.8214	117.9977	118.0588
b (degree)	117.8214	119.8679	118.1399
γ (degree)	117.8214	115.4766	117.1774

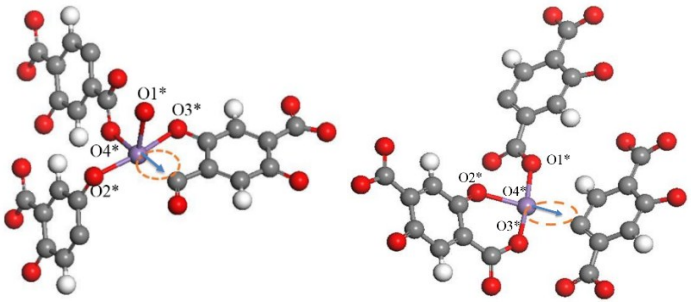
The effect of H_2O on oxygen vacancy

The adsorption of H_2O on metal sites containing oxygen vacancies were calculated. Table S5 lists the changes of Mn-O bond lengths before and after H_2O adsorbed in MOF-74-$O_{Vcarboxyl}$ and MOF-74-$O_{Vhydroxyl}$. Different from the bond length stretching after H_2O adsorption in perfect crystals, in the oxygen vacancies containing structure, only the Mn-O4* bond was elongated and the other bonds were shorten. It indicates that the metal sites moves closer to oxygen vacancies after the adsorption of H_2O. The movement of metal sites is shown in the Fig.S1. The effect of H_2O on two kinds of oxygen vacancy are almost the same.

Table S5 changes of Mn-O bond lengths before and after H2O adsorption.

Bond name	Bond length /Å			
	Carboxyl oxygen vacancy		Hydroxyl oxygen vacancy	
	Before adsorption	After adsorption	Before adsorption	After adsorption
Mn-O1*	2.064	1.930	2.030	1.968
Mn-O2*	1.934	2.048	2.034	1.975
Mn-O3*	2.156	2.095	2.060	2.032
Mn-O4*	2.195	2.284	2.114	2.304

Fig.S1 Change of the position of Mn metal site (a) carboxyl oxygen vacancy (b) hydroxyl oxygen vacancy.



(a) (b)