Electronic Supplementary Information (ESI)

Excellent catalytic oxidation performance on toluene and benzene over OMS-2 with hierarchical pore structure synthesized by one-pot facile method: Modifying surface property by introducing different K amount

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The detail information of the chemicals and characterizations

1.1 The manufacturers of chemicals

KMnO$_4$ (FuChen Chemical Reagents Co., Ltd), PVP (polyvinylpyrrolidone, Tianjin GuangFu Fine Chemical Research Institute), 50 wt.% Mn(NO$_3$)$_2$ solution (Shanghai Aladdin Biochemical Technology Co., Ltd.), KOH (FuChen Chemical Reagents Co., Ltd), Quartz (Tianjin GuangFu Fine Chemical Research Institute).

1.2 Characterization of catalysts

X-ray diffraction (XRD) was performed on Bruker D8 Advance X-ray diffractometer with a Cu Kα (λ = 1.5418 Å) source (40 kV, 40 mA), and the 2θ angle was in the range of 5-80°. N$_2$ adsorption-desorption tests were executed at -196 ^{o}C using Micromeritics physical adsorption apparatus (ASAP 2020) in order to obtain BET surface area (S$_{BET}$) and the pore characterization of the samples. The catalyst was pretreated in pure N$_2$ at 300 ^{o}C for 4 h and then at 90 ^{o}C for 1 h before the test for purpose of removing the physically adsorbed impurities. The bulk chemical composition of the catalysts was acquired by X-Ray fluorescence (XRF) spectrum conducted on Bruker S4 Explorer. The morphology of the samples was obtained through scanning electron microscope (SEM) (Hitachi S-4800 microscope) and transmission electron microscope (TEM) (Tecnai G2 F30) at 15 and 300 kV, respectively. The surface composition and properties were tested by X-ray photoelectron spectroscopy (XPS) on Kratos-AXIS ULTRADLD by using an Al Kα radiation source, and the binding energy of C1s at 284.7 eV was considered as internal reference. The outlet gas was analyzed by an on-line gas monitoring mass spectrometry (MS)(QIC-20, Hidden) with the m/z = 32 fragment (O$_2$ signal).

AutoChem TP5080 instrument (Xianquan, China) with a TCD detector was used to obtain the curves of temperature programmed reduction with H$_2$ (H$_2$-TPR) and temperature programmed desorption of O$_2$ (O$_2$-TPD). For H$_2$-TPR test, 0.020 g catalyst was pre-treated in pure O$_2$ at 300 ^{o}C for 1 h and then cooled down to room temperature. Afterwards, the catalyst was heated from room temperature to 550 ^{o}C in 5% H$_2$/N$_2$ mix atmosphere at a rate of 30 mL/min. For O$_2$-TPD test, 0.100 g sample was pre-treated at 300 ^{o}C in pure O$_2$ for 1 h. After the sample was cooled down to room temperature, the pure He with a rate of 30 mL/min was

introduced into the system and then heated from room temperature to 850 °C.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was recorded on Nicolet 6700 with a high-sensitive MCT detector cooled by liquid N_2. The catalyst mixed with KBr powder was put into the diffuse reflection cell (Harrick) and pre-treated in pure N_2 or 20% O_2/N_2 at 300 °C. Thereafter, the sample was cooled down to different reaction temperature to collect the background. Then, 1000 ppm toluene/benzene and N_2 as the carrier with or without O_2 were introduced into the reaction cell at the total flow of 100 mL/min.

1.3 Activity evaluation of catalysts

0.300 g catalyst (40-60 mesh) was mixed with 0.600 g quartz (Tianjin GuangFu Fine Chemical Research Institute), and put into a fixed bed Quartz tube reactor together. The feed includes 18 vol% O_2/N_2 and 1000 ppm toluene/benzene introduced by pure N_2 with the rate of 8 mL/min at 5 °C, the total flow velocity of 100 mL/min. The weight hourly space velocity (WHSV) is 20,000 mL h^{-1} g^{-1}. The catalytic activity measurement was performed on an online gas chromatograph (GC2100, Beifen Ruili, Beijing, China) with FID detector and KB-1 capillary column (30 m × 0.25 mm × 0.25 μm). The on-line mass spectrometer (MS) (QC20, Hidden) was used to analyze the products. The conversion of the reactant (toluene and benzene) was calculated as follows:

Conversion = [c(Reactant)$_{inlet}$-c(Reactant)$_{outlet}$]/c(Reactant)$_{inlet}$×100% (1)

Whereas, c(Reactant)$_{inlet}$ and c(Reactant)$_{outlet}$ represent the inlet and outlet concentration of toluene/benzene, respectively.

The reaction rate (r) and the apparent activation energy (Ea) for the oxidation of toluene and benzene are calculated based on the general formula (2) and (3), respectively:

$r = -kc^m$ (2)

$k = -A \exp(-E_a/RT)$ (3)

Where, k, c, m, A and T stand for the rate constant, concentration of toluene/benzene, reaction order, pre-exponential factor and reaction temperature, respectively.
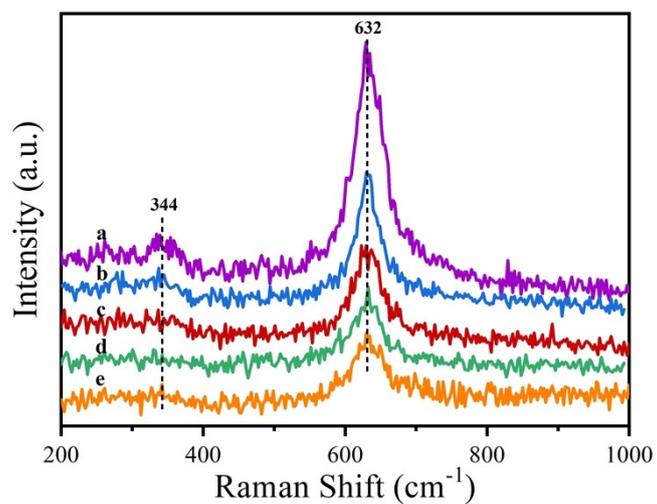
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Fig. S1 Raman spectra of OMS-2 (a), OMS-2-1A(b), OMS-2-1.5A(c), OMS-2-2.5A(d) and OMS-2-3.5A(e)
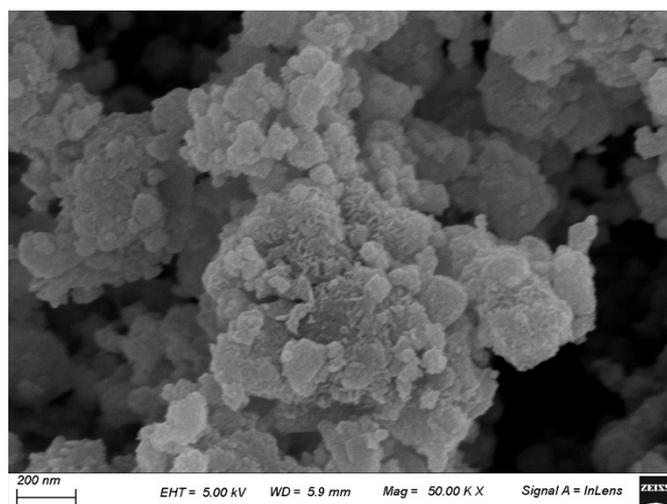
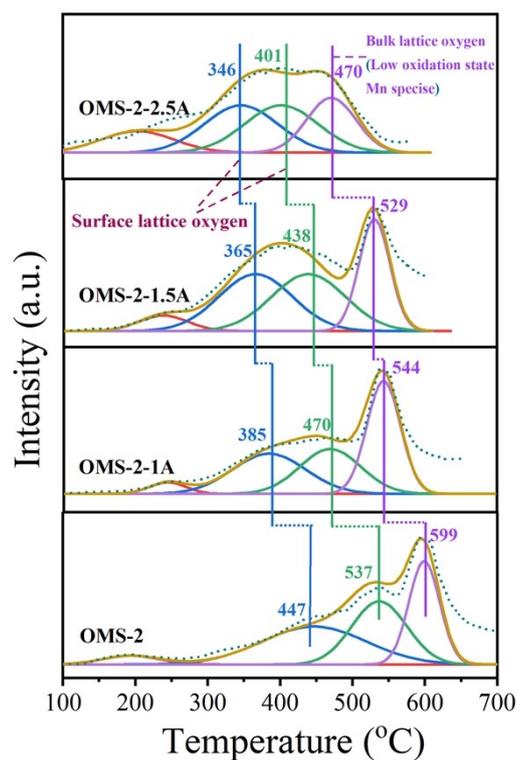

Fig. S2 SEM image of OMS-2-3.5A

Fig. S3 The fitting peaks of O_2-TPD curves in the range of 100-700 °C for OMS-2 and OMS-2-xA samples

Table S1 O_2 desorption amount of OMS-2 and OMS-2-xA samples

Catalyst	O_2 desorption amount (μmol/g) [a]				
	O_{ad} (Peak I)	Surface O_{latt} (Peak II$_1$, II$_2$)	low oxidation state Mn O_{latt} (Peak III)	Mn^{4+} O_{latt} (Peak IV)	Total
OMS-2	40.8	153.1	157.3	154.9	506.1
OMS-2-1A	31.1	161.7	101.1	192.2	486.1
OMS-2-1.5A	25.9	163.5	54.2	196.2	439.8
OMS-2-2.5A	21.4	170.8	34.9	210.6	437.7

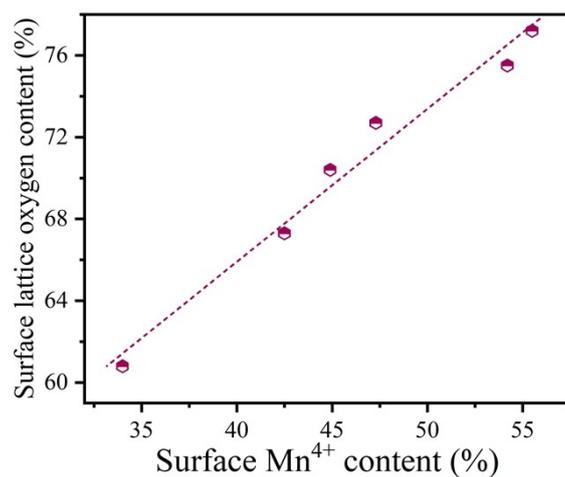[a] Calculated from the peaks of O_2-TPD profiles

Fig. S4 The relationship between surface Mn^{4+} and lattice oxygen species.

Table S2 The catalytic toluene and benzene oxidation results of the prepared four samples.

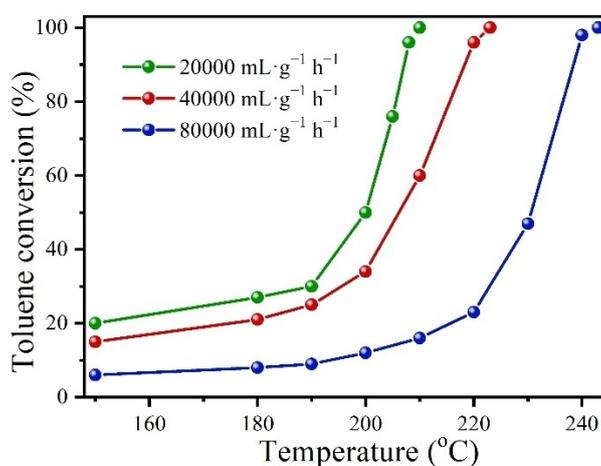| Catalyst	Toluene oxidation (WHSV:20000 h^{-1})				Benzene oxidation (WHSV:60000 h^{-1})			
	T_{50}	T_{90}	$r_{210} \times 10^{-6}$ [b]	Ea	T_{50}	T_{90}	$r_{210} \times 10^{-6}$ [c]	Ea
	(°C)	(°C)	(mol/g·min)	(kJ/mol)	(°C)	(°C)	(mol/g·min)	(kJ/mol)
OMS-2	227	238	4.78	42.3	257	-	3.03	50.1
OMS-2-1A	217	229	5.14	32.8	221	255	3.43	39.3
OMS-2-1.5A	213	220	5.60	31.5	215	241	4.09	37.2
OMS-2-2.5A	200	207	6.43	19.8	205	233	4.53	30.9

Fig. S5 The activity of OMS-2-2.5A with different WHSVs during toluene oxidation process

Table S3 Comparison of catalytic performance over different K modified OMS-2 catalysts for VOC oxidation

| Catalyst	Preparation method	Toluene/ Benzene	T_{90} (^{o}C)	Concentration (ppm)	Space velocity (mL g^{-1} h^{-1})	Reference
KMn2	One-pot hydrothermal	Benzene	240	2000	48000	21
4-K/MnO$_2$	Two- step hydrothermal	Toluene	216	1000	50000	27
Post-K/MnO$_2$	Impregnation	Toluene	228	1000	50000	28
Pre-K/MnO$_2$	Two-step Hydrothermal	Toluene	242	1000	50000	28
KOH/MnO$_2$	Two- step hydrothermal	Toluene	226	1000	50000	36
KCl/MnO$_2$	Two- step hydrothermal	Toluene	243	1000	50000	36
K$_2$SO$_4$/MnO$_2$	Two- step hydrothermal	Toluene	236	1000	50000	36
KNO$_3$/MnO$_2$	Two- step hydrothermal	Toluene	319	1000	50000	36
OMS-2-2.5A	One-pot hydrothermal	Toluene	207	1000	20000	This work
OMS-2-2.5A	One-pot hydrothermal	Toluene	218	1000	40000	This work
OMS-2-2.5A	One-pot hydrothermal	Benzene	233	1000	60000	This work
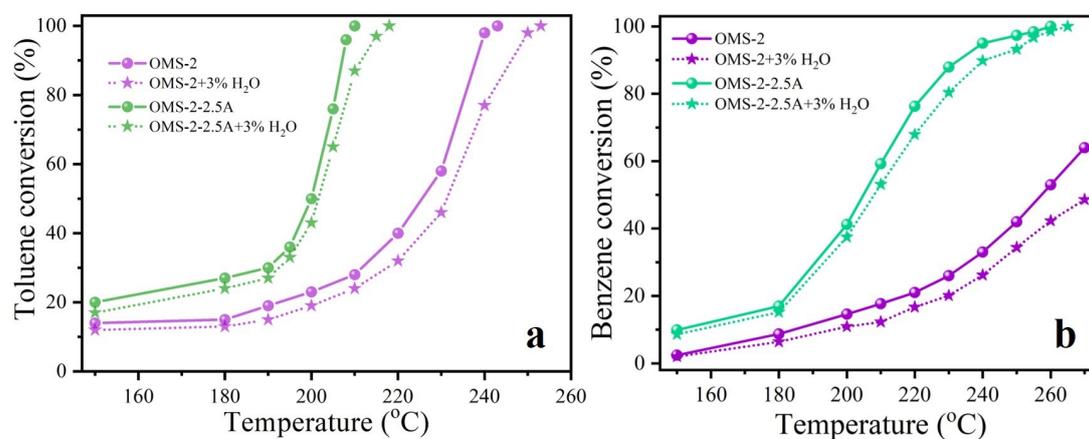
Fig. S6 Catalytic performance with 3% H$_2$O addition of toluene oxidation (a) and benzene oxidation (b)
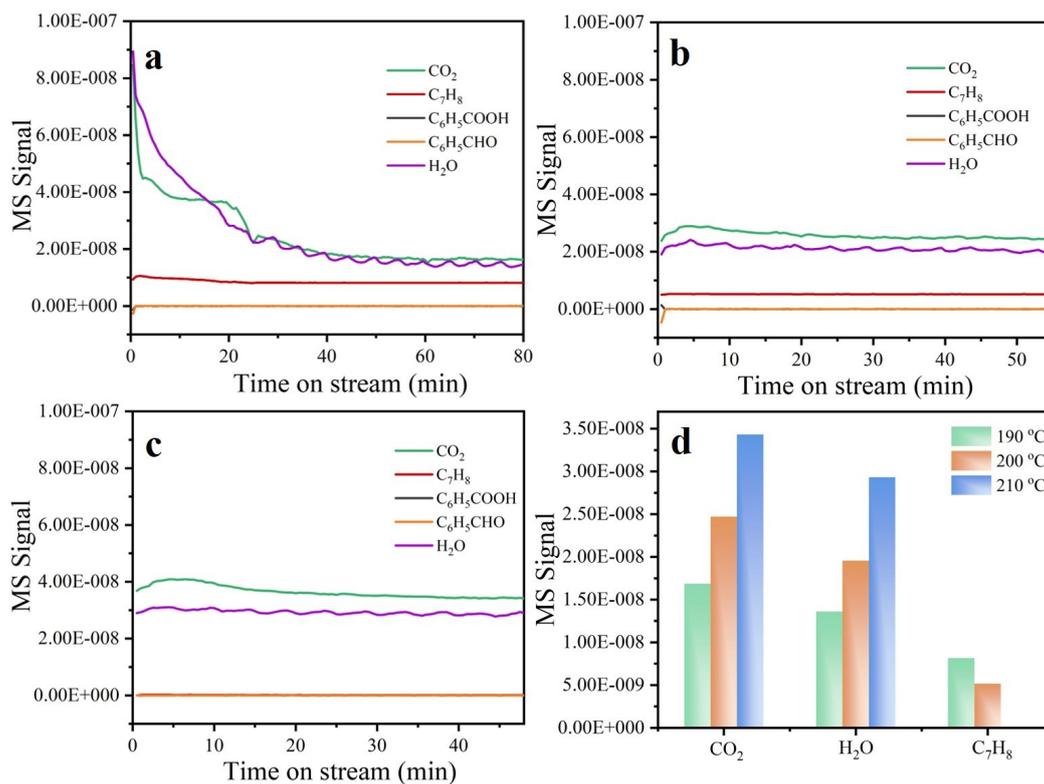
Fig. S7 The MS signal of the CO_2, C_7H_8, C_6H_5COOH, C_6H_5CHO and H_2O at different reaction temperature (a: 190 °C, b: 200 °C, c: 210 °C) and the comparison of CO_2, H_2O and C_7H_8 at 190, 200 and 210 °C (d) for OMS-2-2.5A.
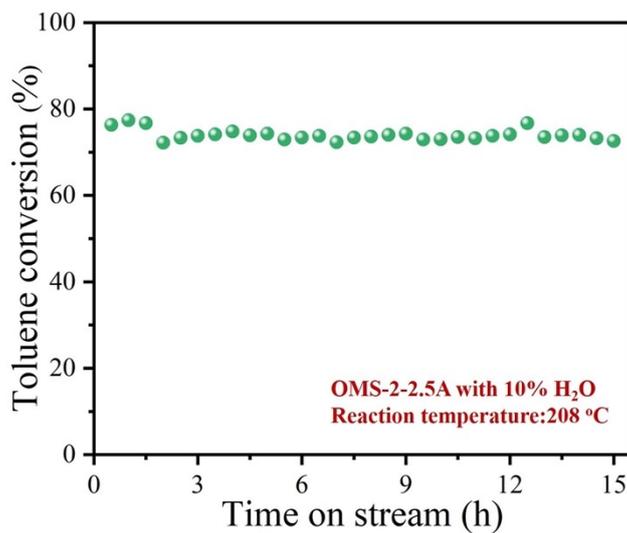

Fig. S8 Activity stability as a function of time with 10% H_2O at 208 °C of OMS-2-2.5A during catalytic toluene oxidation process
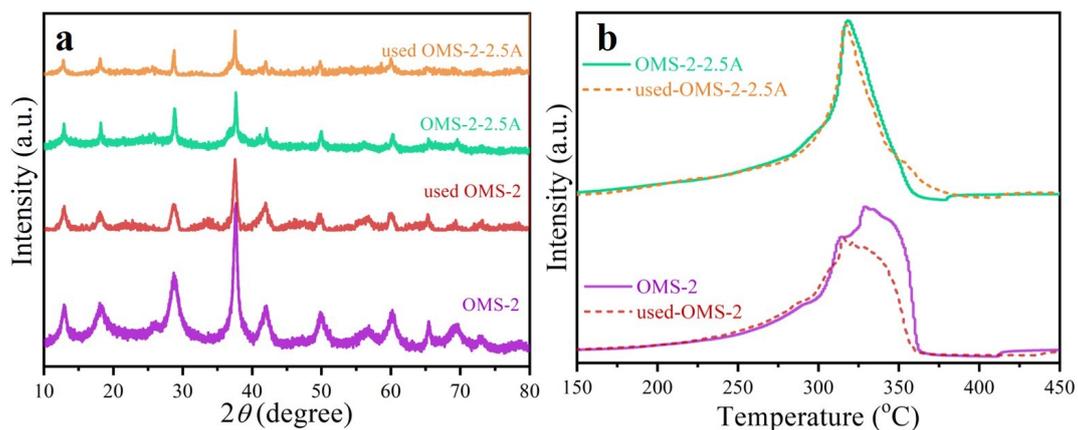
Fig. S9 XRD patterns(a) and H$_2$-TPR(b) curves of OMS-2, used OMS-2, OMS-2-2.5A and used OMS-2-2.5A
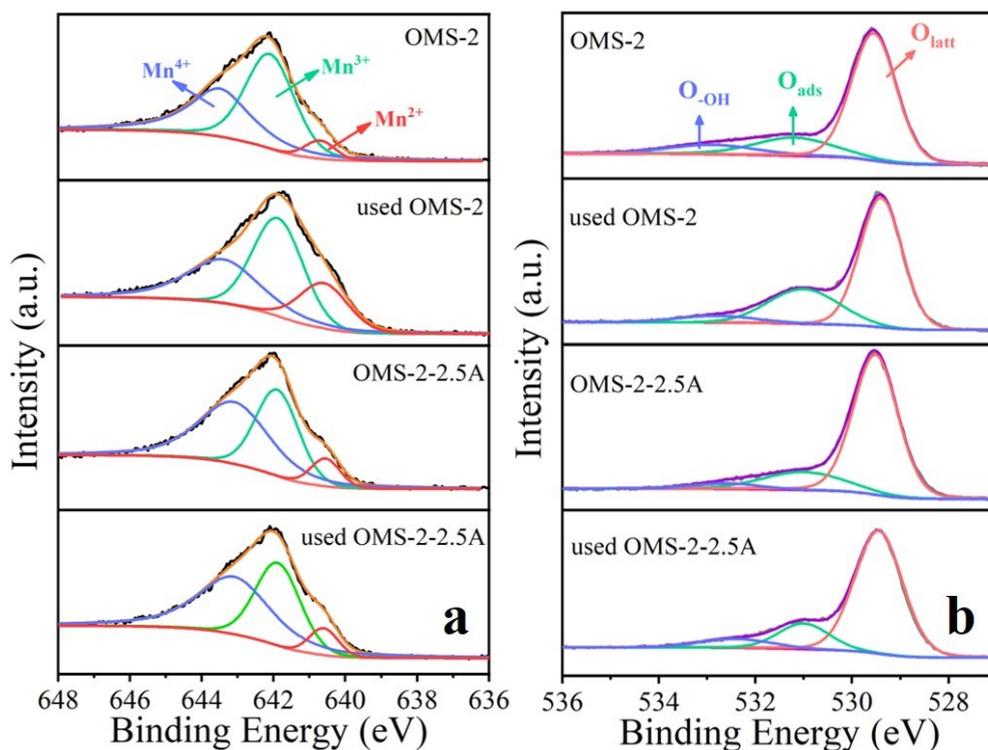

Fig. S10 XPS for Mn2p (a), O1s (b) of fresh and used catalysts (OMS-2 and OMS-2-2.5A)

Table S4 Assignment of IR bands of toluene and benzene adsorption process

Position/cm^{-1}	Assignment
1170, 1136, 1196, ~1340	-C-O- of benzyl alcohol
1339, 1390, ~1396, ~1489	-CH$_3$ methyl group
1316, ~1429, 1521	maleate
1373, ~1539	-COO$^-$ of benzoate
1594, ~1452, ~1510, ~1619	C=C of aromatic ring
~1645	-CHO of benzaldehyde
~1712, ~1681	benzoquinone
1730	quinone
~1795, ~1745, ~1865	Five-membered cyclic anhydride
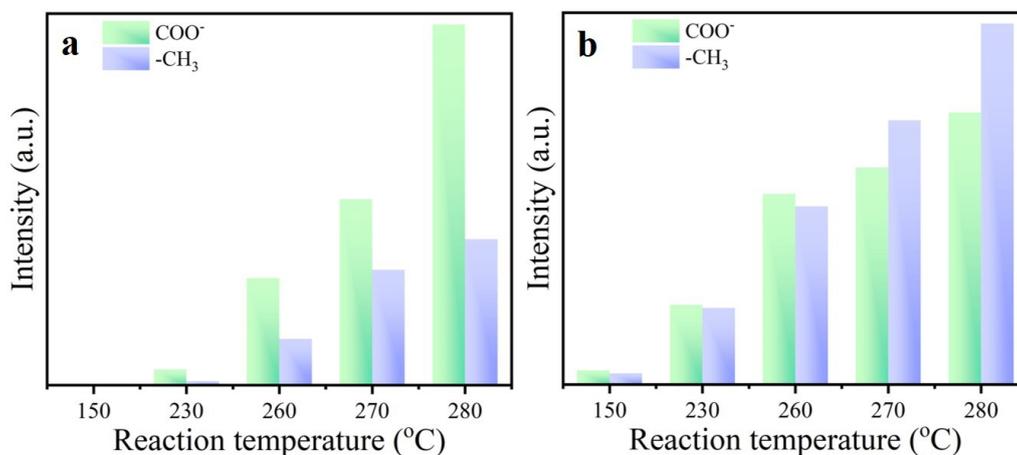
Fig. S11 The amount of -COO$^-$ and -CH$_3$ species at different temperature for OMS-2-2.5A without (a) and with (b) adsorbed oxygen species.