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Preparation of Monosodium 2-Sulfoterephthalate to Make MIL-101(Cr)-SO₃H Catalyst

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General information: The lab-synthesized sTA-Na was characterized and compared with the commercial sTA-Na by the following analyses. The FT-IR (Fourier-transform infrared) spectra were recorded from KBr pellets in range 4000~400 cm^{-1} on a PerkinElmer Spectrometer one spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded by a PANalytical X'Pert diffractometer (Cu $K\alpha$ radiation with $\lambda = 0.15405$ nm) with 2θ from 5° to 40° and a step of 0.02° for sTA-Na samples, but 2θ from 2° to 12° for MIL-101(Cr)- SO_3H samples. The ^{13}C and ^1H NMR (Nuclear Magnetic Resonance) spectroscopies were performed on Bruker Advance III HD, and MS (Mass spectrometry) spectroscopy was analyzed on Thermo Q Exactive plus.

FT-IR spectrum of the prepared 2-sulphonate para-xylene monosodium (spX-Na):

The p-xylene was sulfonated with fuming H_2SO_4 (~98%) at 95°C for 12 h, having a yield of 99.6%. The filter cake of p-xylene-2-sulphonate was dissolved in water and titrated with 8N $\text{NaOH}_{(\text{aq})}$ until $\text{pH}\sim 10$ to precipitate powder spX-Na, having a yield of 78%. In Fig. S1., the FT-IR spectrum of the prepared spX-Na shows that the absorption bands at around 1240 and 1185 cm^{-1} can be corresponded to $\text{O}=\text{S}=\text{O}$ symmetric and asymmetric stretching, while the peaks at 1028 and 620 cm^{-1} corresponded to the $\text{S}-\text{O}$ and $\text{C}-\text{S}$ stretching vibrations, respectively. Moreover, the stretching vibrations of $\text{C}=\text{C}$ of the benzene ring are appeared at 1600 and 1475 cm^{-1} , and the weak vibrations of methyl $-\text{CH}_3$ are at 2983, 2923, and 2859 cm^{-1} , indicating that spX-Na has been successfully prepared.

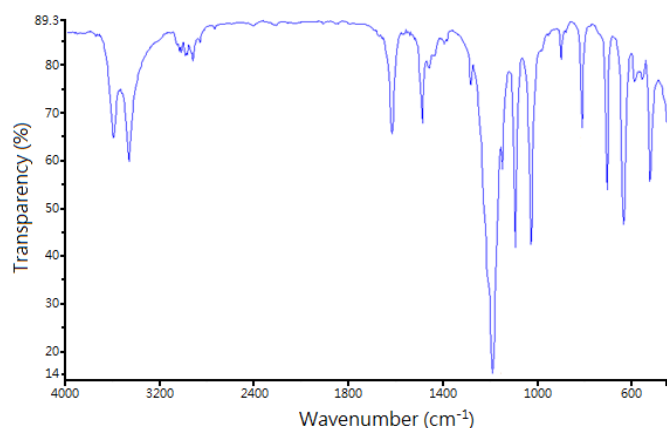


Fig. S1. FT-IR spectrum of the prepared spX-Na by the sulfonation of para-xylene at 95°C for 12 h followed with acid-base neutralization with 8N $\text{NaOH}_{(\text{aq})}$ until $\text{pH}\sim 10$.

FT-IR spectra and PXRD patterns of the products of monosodium 2-sulfoterephthalate (sTA-Na) precipitated at $\text{pH}\sim 0.5$ and 2.09: The spX-Na of 25 g was oxidized by KMnO_4 of 76g at its boiling state in a three-necked flask to form sTA-

Na ions., followed with adding 12M HCl to acidify solution to pH~0.5 or 2.09 and precipitate sTA-Na, having a yield of 60% and 56%, respectively. The FT-IR spectra of the sTA-Na products precipitated at pH=0.5 and pH=2.09 are compared in Fig. S2., showing that both have the same functional groups. The absorption peaks at 1225, 1190, and 1029 cm^{-1} can be corresponded to $-\text{SO}_3^-$ stretching vibrations and the peak at 1714 cm^{-1} can be attributed to $-\text{C}=\text{O}$ of the carboxyl group.

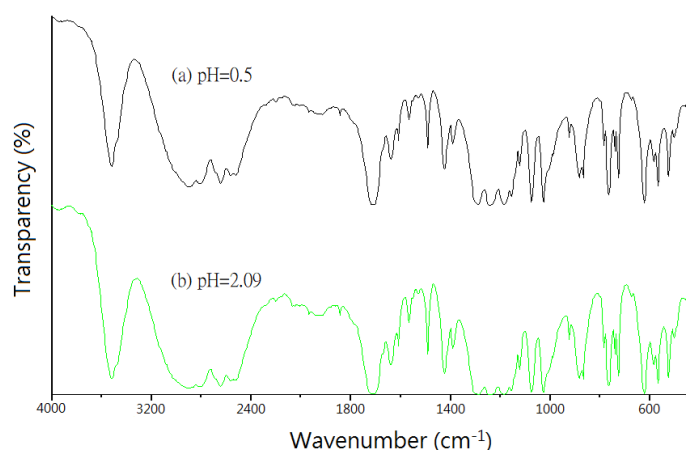


Fig. S2. FT-IR spectra of the sTA-Na products precipitated at (a) pH=0.5 and (b) pH=2.09, acidified with 12M HCl.

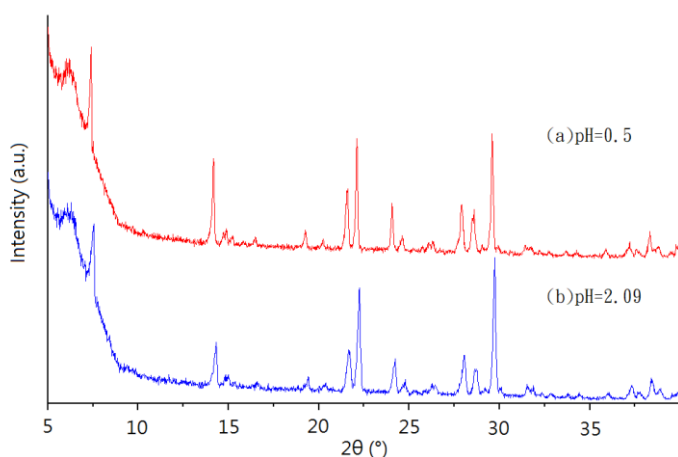
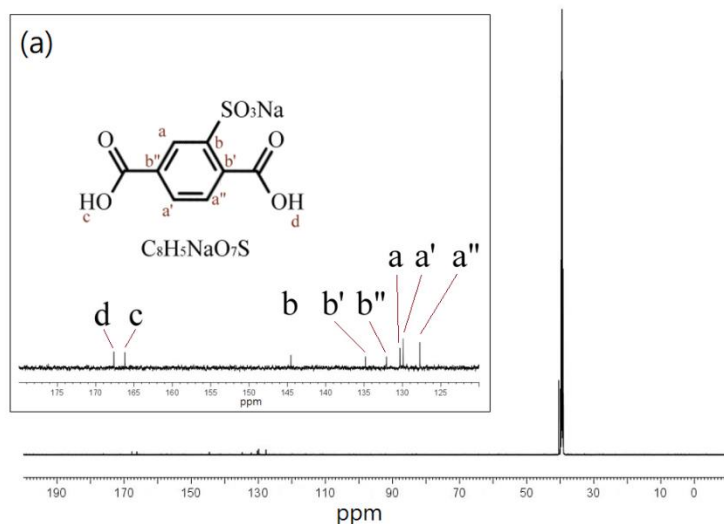


Fig. S3. PXRD patterns of the sTA-Na products precipitated at (a) pH=0.5 and (b) pH=2.09, acidified with 12M HCl.

¹³C NMR and ¹H NMR spectra of the lab-synthesized and the commercial sTA-Na: Fig. S4(a)~(d) are ¹³C and ¹H NMR spectra of the lab-synthesized and the commercial sTA-Na, recorded at 150MHz and 600MHz respectively and referenced to the solvent deuterated DMSO (dimethyl sulfoxide), showing that both has the same molecular structure. As shown in the insets of Fig. S4(a) and (b), the molecular structure of sTA-

Na has three kinds of carbons: the tertiary carbon in the benzene ring (marked with a, a', and a''), the quaternary carbon in the benzene ring (marked with b, b', and b''), and the primary carbon in the carboxylate group (marked with c and d). The component carbons of each type have different degrees of influence due to their relative positions from the functional groups, resulting in the different chemical shifts, δ parts per million (ppm), expected for the carbon atom resonances of these guests. In Fig. S4(a) of the ^{13}C NMR spectrum of the lab-synthesized sTA-Na, resonance peaks at δ 130.32, 129.92, and 127.73 ppm are characteristic of the tertiary carbon atoms; at δ 144.55, 134.81, and 132.09 ppm are the quaternary carbon atoms; at δ 166.18 and 167.63 ppm are the carbon atoms in the carboxylate group. The very strong peaks at δ 40.41 and 39.50 ppm are the carbons of the solvent deuterated DMSO. The ^{13}C NMR spectrum of the commercial sTA-Na in Fig. S4(b) is almost the same as that of the lab-synthesized sTA-Na, shown in Fig. S4(a). In the ^1H -NMR analyses, the molecular structure of sTA-Na has two kinds of hydrogens: the hydrogen bonded to the carbon of benzene ring (marked with a, b, and c), and the hydrogen of the carboxylate group (marked with d and e). As shown in Fig. S4(c) and (d), the resonance peaks at δ 8.35, 7.97 and 7.72 ppm are assigned to the hydrogens of the benzene ring; at δ 13.83 and 13.31 ppm are the hydrogens of the carboxylate group. The peak intensities shown below their peaks in Fig. S4(c) and (d) have a ratio about 1 : 1 : 1 : 1 : 1, which is consistent with the number ratio of the five different hydrogens presented in the molecular structure of sTA-Na.



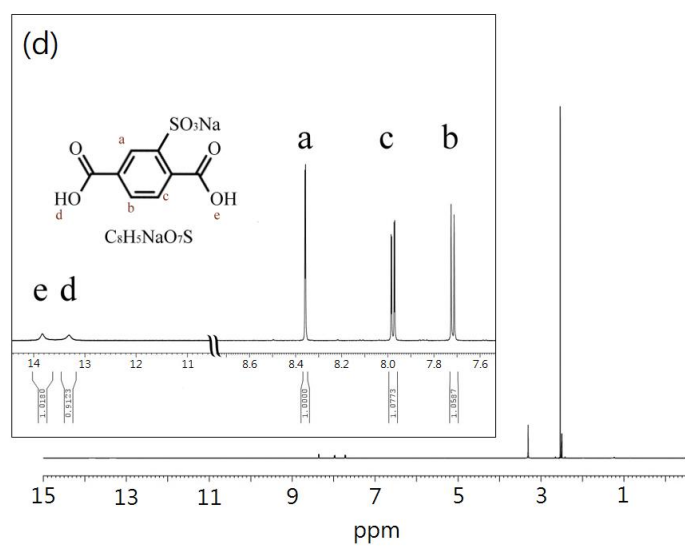
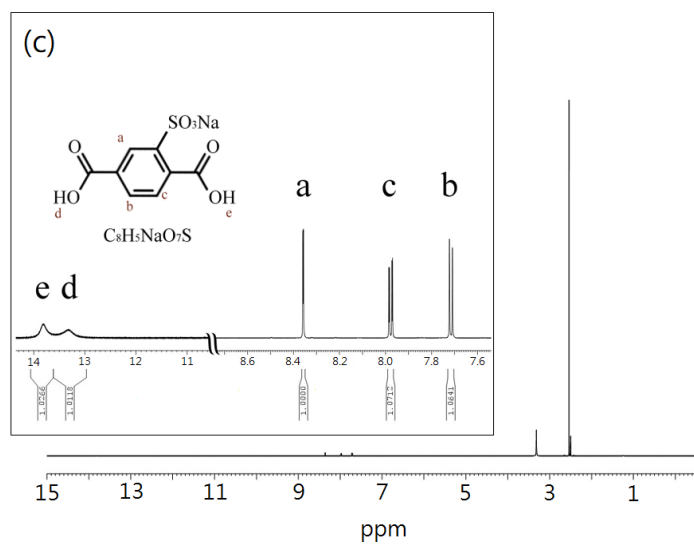
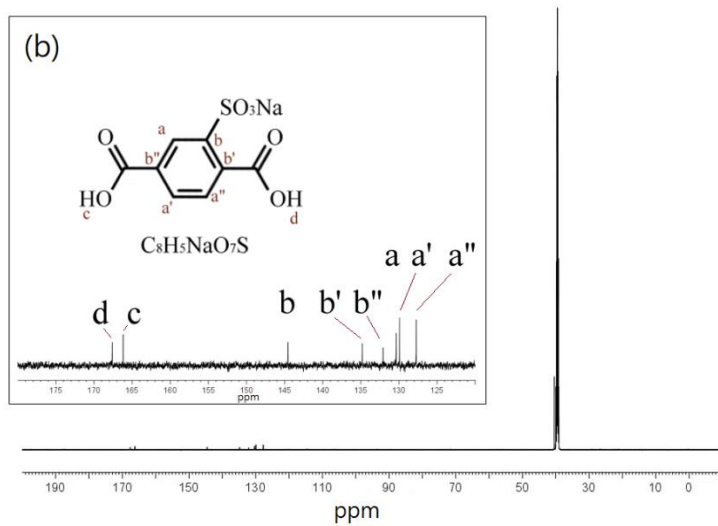


Fig. S4. ^{13}C NMR spectra of (a) the lab-synthesized and (b) the commercial sTA-Na;

^1H NMR spectra of (c) the lab-synthesized and (d) the commercial sTA-Na. The signals were clearly assigned, and the integrals also fit. The signals at around 40 ppm in ^{13}C NMR spectra and at around 2.5 ppm in ^1H NMR spectra were assigned to solvent DMSO.

Mass spectrometry of the lab-synthesized and the commercial sTA-Na: Ion mass spectrometry indicated their parent-ion masses while performed on the liberated guest vapors as the sample was heated. MS spectra of the negative ion mode in Fig. S5(a) and (b) show that the molecular weights of the lab-synthesized and the commercial sTA-Na both are 267.965, which corresponds to the molecular weight of $\text{C}_8\text{H}_5\text{O}_7\text{SNa}$ (monosodium 2-sulfoterephthalate, sTA-Na). The m/z 244.9753 and 266.9576 are caused by the heating and dissociation of $\text{C}_8\text{H}_5\text{O}_7\text{SNa}$ into negative ions of $\text{C}_8\text{H}_5\text{O}_7\text{S}^{-1}$ and $\text{C}_8\text{H}_4\text{O}_7\text{SNa}^{-1}$. The error values respectively are 1.0720 and 2.0896 ppm in the lab-synthesized sTA-Na, and 0.9686 and 1.7054 ppm in the commercial sTA-Na, which all are lower than a reasonable error of 5 ppm.

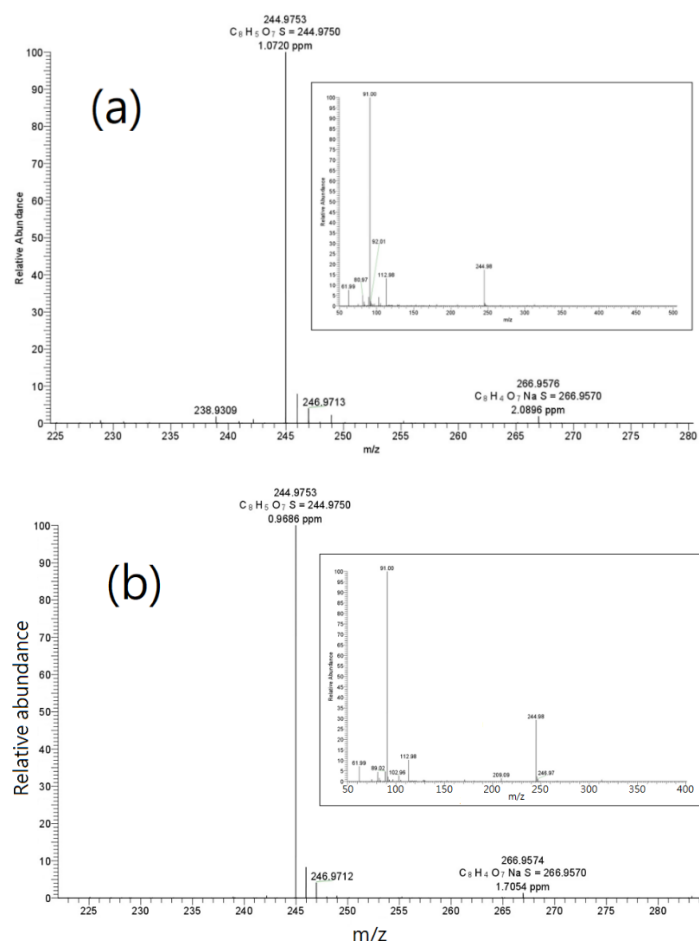


Fig. S5. Mass spectrometry of negative ion mode: (a) the lab-synthesized and (b) the commercial sTA-Na. The spectra from 225 to 280 are the enlarged view of the inset.