

## Supporting Information

### **Polystyrene Sulfonate Threaded in MIL-101Cr(III) as Stable and Efficient Acid Catalysts**

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#### **Experimental**

##### **Chemicals and Regents.**

All chemicals were of analytical grade obtained from commercial sources and used without further purification. Sodium p-styrene sulfonate, and Amberlyst 15 were purchased from Sigma-Aldrich Company, Ltd. (USA).

##### **Synthesis.**

**Preparation of MIL-101:** In a typical experiment, 0.01 mol  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (4.00 g), 0.01 mol 1,4-benzene dicarboxylic acid (1.64 g), and 0.01 mol hydrofluoric acid (0.446 mL, 40 % in water) were dispersed in deionized water (48 mL) and stirred for 1 h, then the mixture was transferred to a 100mL Teflon-liner stainless steel autoclave and kept at 220 °C for 8 h. The autoclave was then left to cool down to room temperature. To obtain the pure crystals, the as-synthesized MIL-101 was further purified according to the following four-step processes: First, the reaction mixture was doubly filtered to remove the free terephthalic acid, washed thoroughly with deionized water; then, the MIL-101 using two subsequent solvent treatments such as boiling water at 70 °C for 5 h and hot ethanol at 60 °C for 3 h and collected by centrifugation; finally, the resulting solid (1 g) was dispersed in 30 mM of  $\text{NH}_4\text{F}$  aqueous solution (150 mL) at 60 °C for 10 h, and after cooling, the precipitate was filtered and washed several times with hot water to remove traces of  $\text{NH}_4\text{F}$ . For following processes, the prepared samples were dried at 120 °C for 2 h and stored under room temperature.

**Preparation of MIL-101~PSS-X:** The synthesis of MIL-101~PSS-X by following two-step processes: (1) synthesis of MIL-101~poly(sodium-4-styrene sulfonate) (MIL-

101~PSSNa). Typically, 0.2 g of sodium-4-styrenesulfonate (SS) and X mol % of divinyl benzene (DVB) (based on SS) were dissolved by 1 mL of DMSO. Then, 3 wt % AIBN (based on SS) was introduced as initiator. The obtained SS-AIBN in DMSO solution was mixed with 0.5 g of MIL-101 in a mortar. The polymerization was conducted at 80 °C for 2 days. The obtained powder was washed with DMF for 3 times to completely remove the unreacted monomer and the loosely attached polymer between MIL-101 particles. DMF was then removed by acetone soaking. Subsequently, the solids were treated with 500 mL of 1 M HCl solution for 1 h at 0 °C, then catalyst was centrifugally separated and washed several times with water and ethanol to remove HCl. The final product MIL-101~PSS-X was obtained after drying at 80 °C overnight.

### **Characterization.**

Scanning electron microscope (SEM) was undertaken on a JEOL JSM-7001F operating at an accelerating voltage of 0.5-30 kV. FT-IR spectra were collected with a Nicolet 6700 IR spectrometer (KBr pellets) in the range of 400-4000  $\text{cm}^{-1}$ . X-ray diffraction (XRD) patterns were obtained on a Bruker Advance D8 diffractometer with a lynxeye detector at 40 kV and 40 mA with a scanning rate of 4 °/min. The Brunauer–Emmett–Teller (BET) surface areas and porosity were measured by Micromeritics ASAP 2020 analyzer at 77 K. Each time, ~0.1 g sample was evacuated in a vacuum oven at 150 °C overnight. The sample was then transferred to preweighed quartz tube and degassed at 150 °C until the system pressure < 5  $\mu\text{mHg}$ . Afterwards, the tube was reweighed to obtain an accurate mass for BET surface area determination. BET surface area was calculated from the adsorption data in the relative pressure  $P/P_0$  in the range of 0.04 to 0.2. Pore size distributions were determined from the adsorption branches using the Barret-Joyner-Halenda (BJH) method. Pore volume was estimated at the relative pressure  $P/P_0$  of 0.99. Fourier transform infrared spectroscopy (FTIR, Shimadzu, KBr pellet) was performed at 20 °C at a 4  $\text{cm}^{-1}$  resolution. Thermogravimetric analyses were performed on a Mettler-Toledo TGA/SDTA851 instrument and recorded under air at a ramp of 5 °C  $\text{min}^{-1}$  up to 800 °C. The acid exchange capacity of the catalysts was determined by acid-base titration with standard NaOH solution. In a typical procedure, 50 mg of catalyst was suspended in 5 ml deionized water, while analyzed using a pH-meter, and subsequently titrated to an

end point at pH of 7 with 2.5 mM NaOH.

Determination of loading amount (C) of  $-\text{SO}_3\text{H}$  active sites:

$$C = \frac{3k}{989 + 3k \cdot \frac{18421 + 130.19x}{100 + x}} \quad (\text{Eq. S1})$$

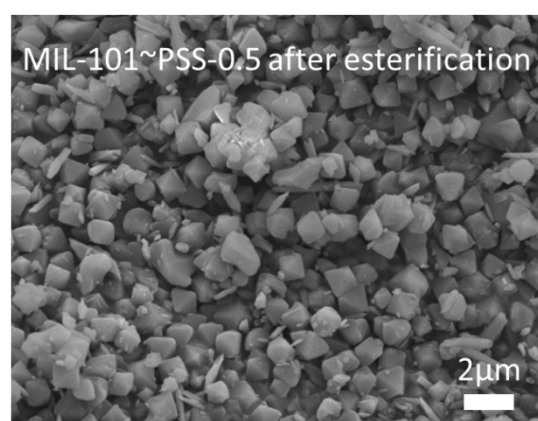
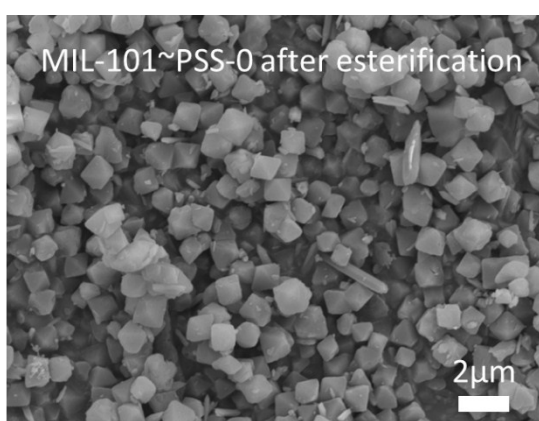
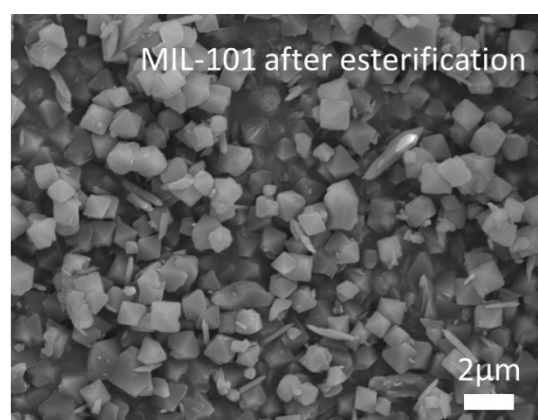
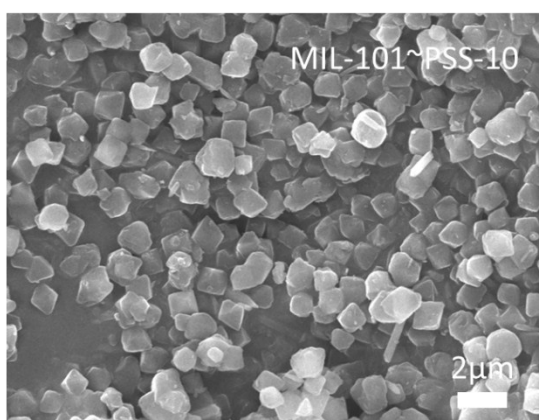
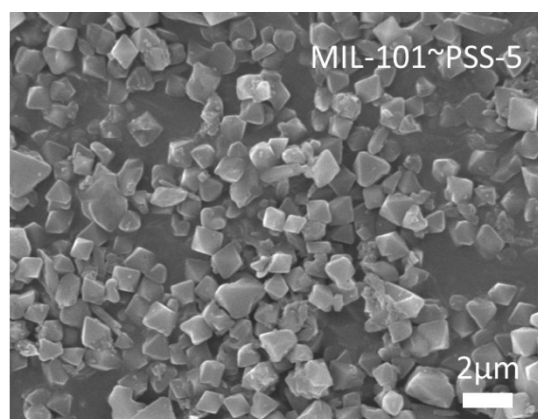
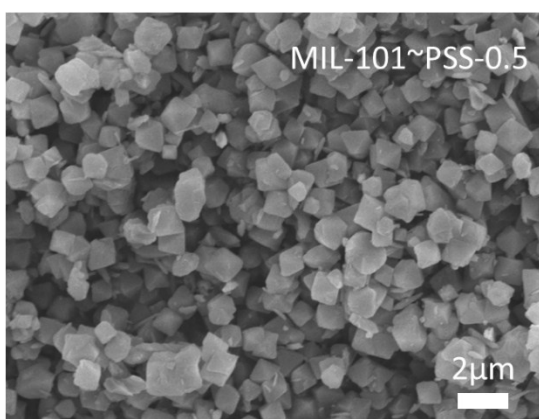
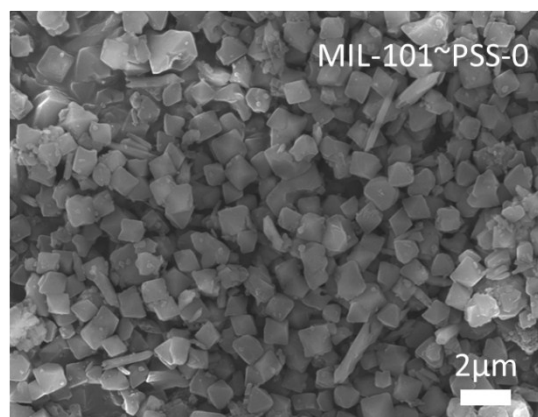
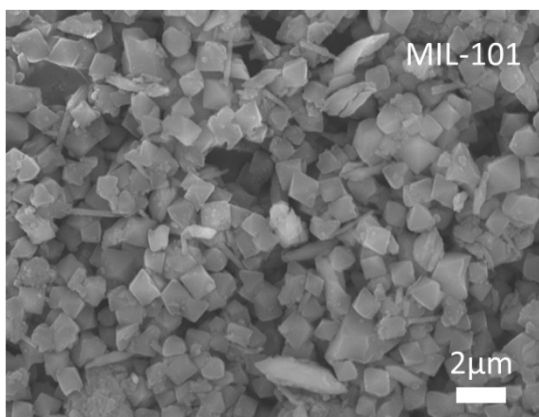
Where k stand for the molar ratio of S/Cr as determined by EDX; x is molar ratio of DVB/SS mixed for synthesis.

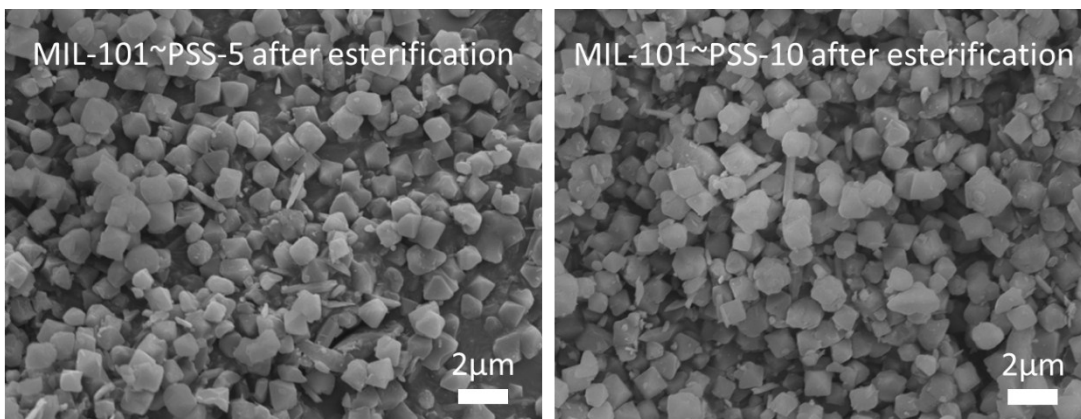
We explain why TGA curve is invalid for loading percentage estimation. The water content in both NaPSS~MIL-101 and MIL-101 are sensitive in environment, leading uncertainty for the weight loss. On the other hand, although contribution of water loss can be minimized by pretreating samples under vacuum, weight loss from TGA still cannot be only attributed to the decomposition of PSS polymer. The thermal decomposition temperature of PSS polymer is typically higher ( $\sim 450$  °C) than that of MIL-101, thus only the weight loss in the last plateau can be used to calculate the PSS content. Comparing to the TGA pleatue of the pristine MIL-101 with that of MIL-101~PSS-X, it shows that the weight loss increases by no more than 7% upon the loading of PSS. This value is much lower than the loading percentage estimated by EDX. We believe that the TGA weight loss cannot correctly reflect the loading ratio of PSS, because the heating treatment under air flow may not fully remove the polymeric PSS, because sulfur remain in the final products to form some sulfonated compounds with Cr as confirmed by EDX, the weight loss thus cannot correctly quantify the loading amount of PSS. To determine the water uptake, MIL-101~PSS-0 and pristine MIL-101 were fully dried under dynamic vacuum at 100 °C for 24 h. After drying, these were referred as “dry” samples and their mass was recorded to be  $W_{\text{dry}}$  by using microbalance. Then, these “dry” samples were equilibrated over different saturated salt solution in a well-sealed desiccator. After 72 h, the samples were taken out and quickly weight to record the mass as  $W_{\text{wet}}$ . Respective water uptakes of the samples were calculated from the following **Eq. S2**:

$$\text{Water uptake (\%)} = (W_{\text{wet}} - W_{\text{dry}}) \times 100 / W_{\text{dry}} \quad \text{Eq. S2}$$

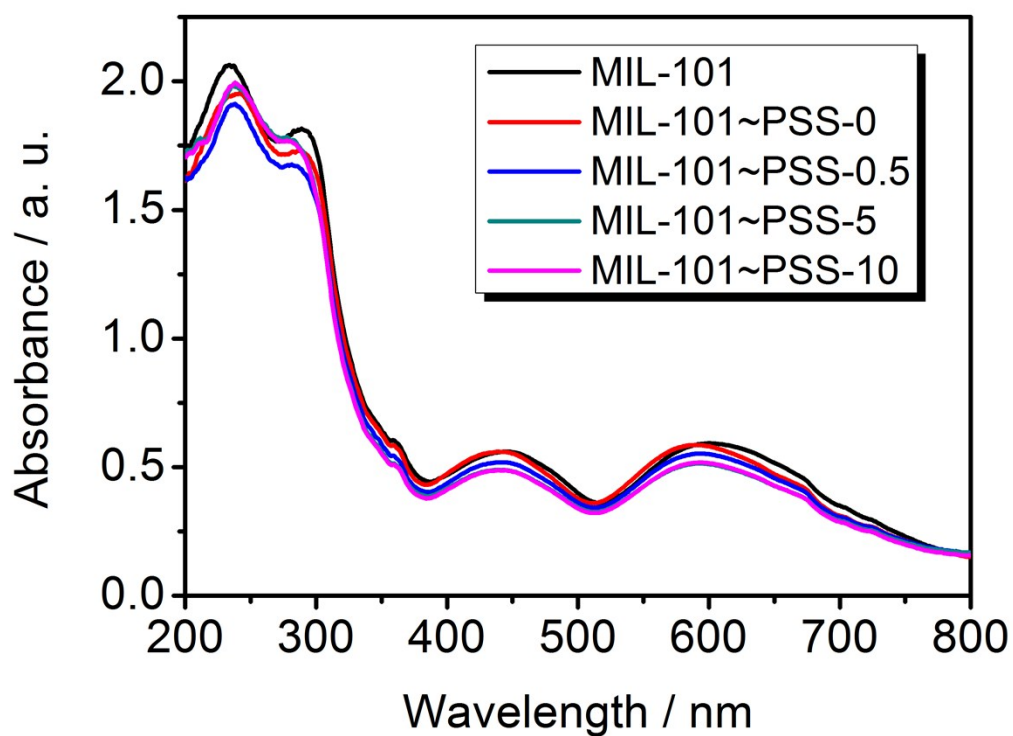
### **Esterification of acetic acid and *n*-butanol**

The reaction was conducted using a molar ratio mixture of 1:1 acetic acid:*n*-butanol. The reaction mixture (10 mL) was charged into a round bottom flask and kept stirring at 70 °C. A ratio of 3 g catalyst per mole of acetic acid was used. For recyclability testing, the catalysts were filtrated and treated with 1 M HCl at 0 °C before use in consecutive runs. GC-FID was used to quantify the yields of butyl acetate. Prior to use, GC-FID was carefully calibrated as shown in **Fig. S6**.

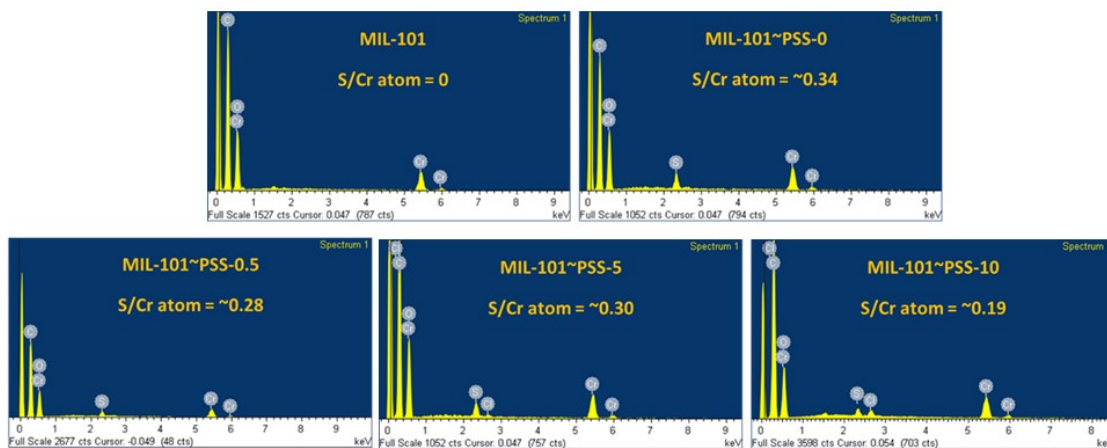




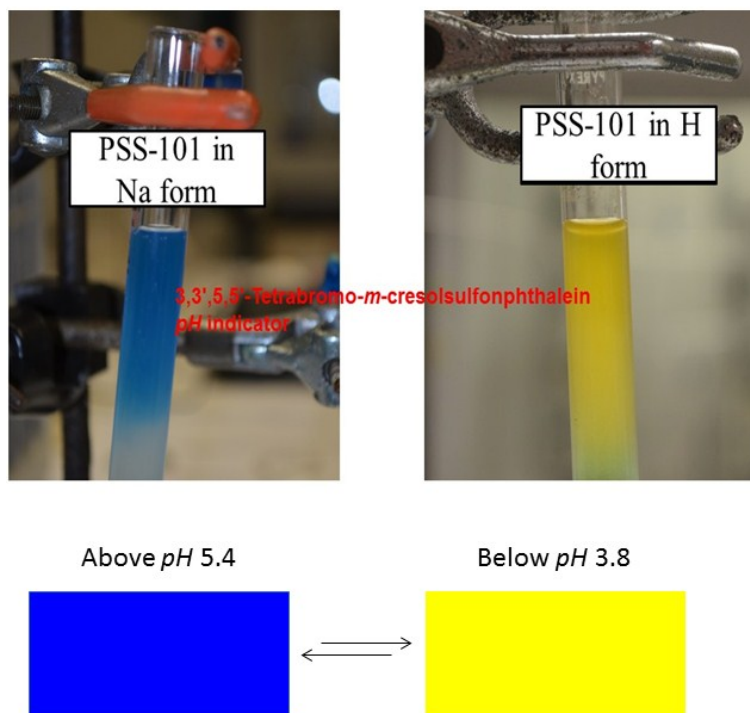
**Figure S1.** SEM images of MIL-101(Cr) and MIL-101~PSS-X samples before and after esterification.



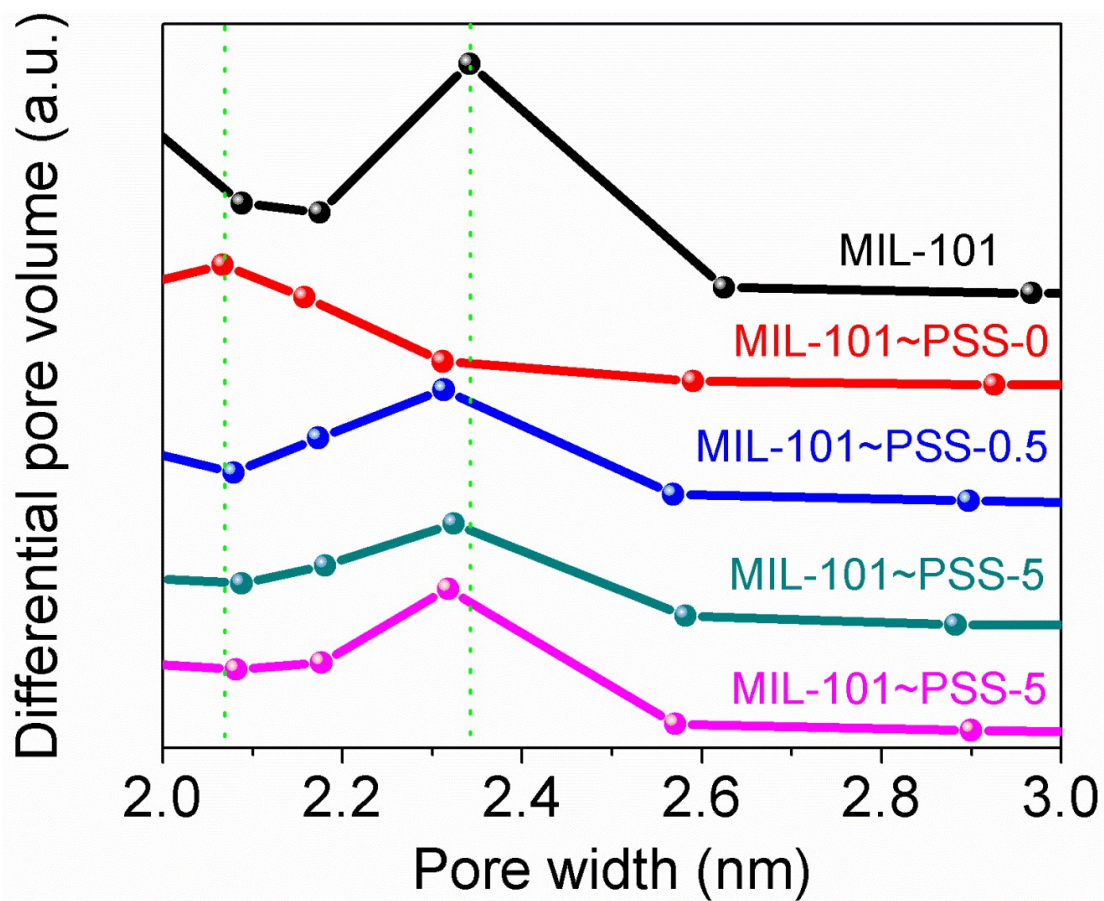
**Figure S2.** UV-vis absorption spectra of MIL-101 and MIL-101~PSS-X.



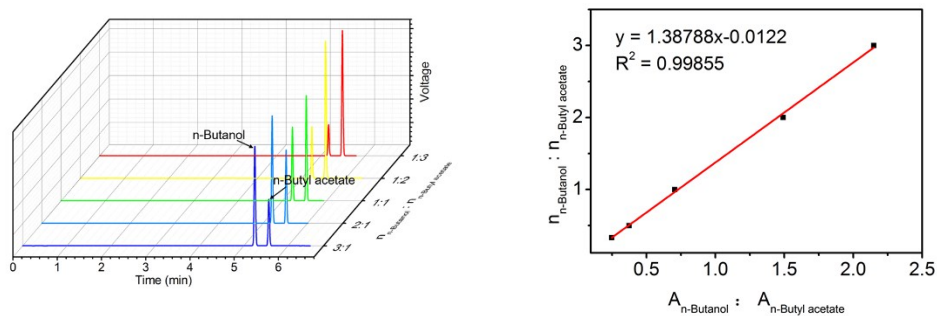
**Figure S3.** EDX spectra of MIL-101(Cr) and MIL-101~PSS-X samples.



**Figure S4.** The color change of 3,3',5,5'-tetrabromo-*m*-cresolsulphonphthalein upon contacting the MIL-101~PSS-0 power.

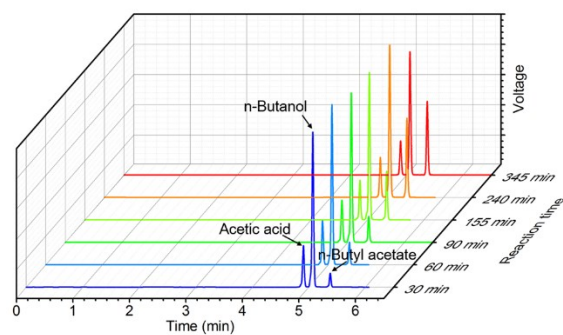


**Figure S5.** Pore size distribution of MIL-101 and MIL-101~PSS-X series. (Calculation method: BJH model on adsorption branch)

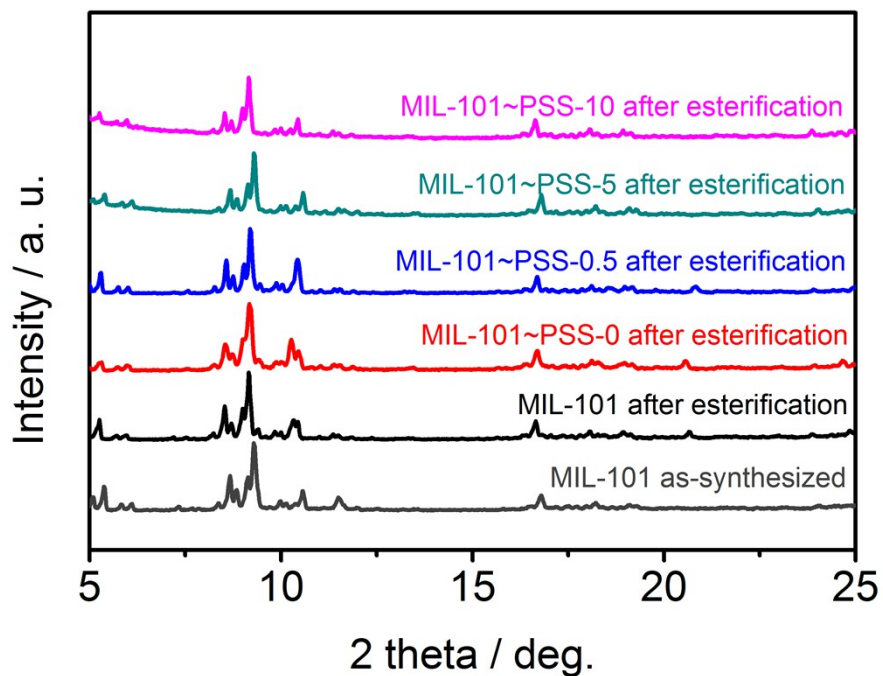


**Figure S6.** The calibration curve for GC-FID test.

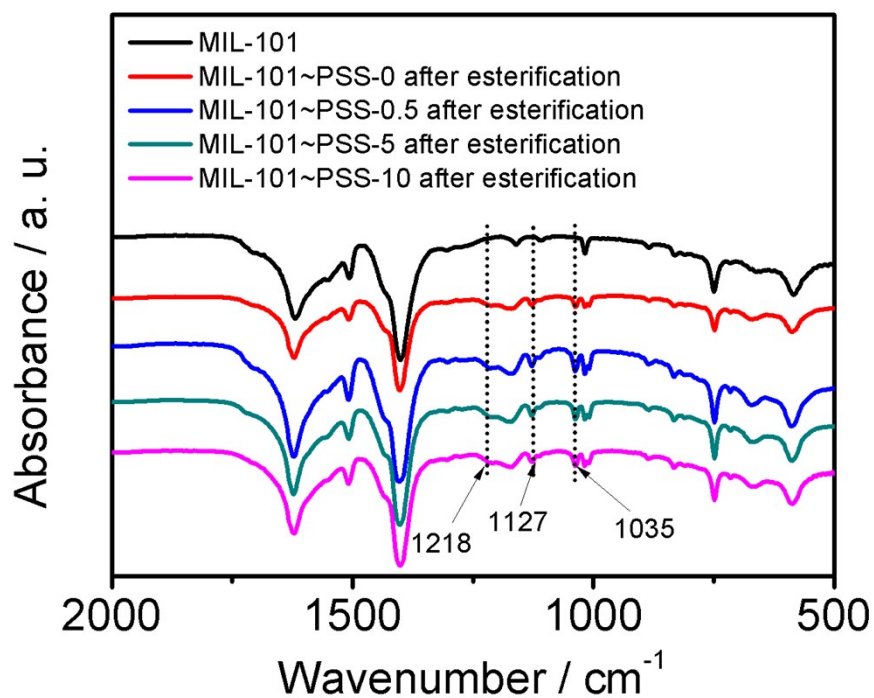




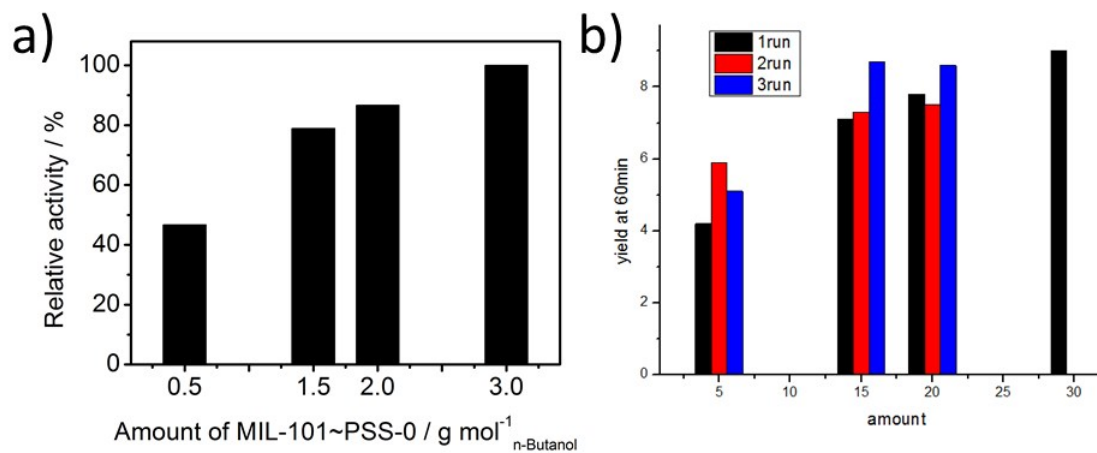
**Figure S7.** GC-FID results of esterification over MIL-101~PSS-0 as a function of time.



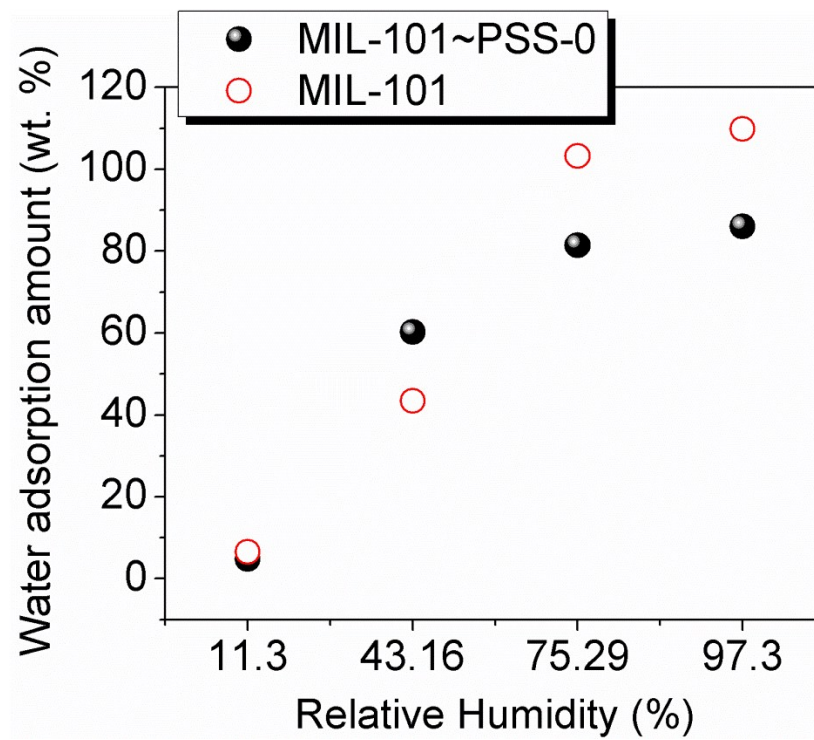
**Figure S8.** XRD patterns of MIL-101 and MIL-101~PSS-X after esterification.



**Figure S9.** FTIR spectra for MIL-101 and MIL-101~PSS-X after esterification.



**Figure S10.** (a) relative conversion efficiency (normalized to that of 3 g/mol of reactant) and (b) recyclability (for the first 1h) of MIL-101~PSS-0 catalyst with different ratio to reactant.



**Figure S11.** Moisture uptake of MIL-101 and MIL-101~PSS-0 under different relative humidity.