Supporting Information

Metal–Organic Framework Based upon the Synergy of a Brønsted Acid Framework and Lewis Acid Centers as a Highly Efficient Heterogeneous Catalyst for Fixed-Bed Reactions

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Experimental Details

Materials

All reagents were purchased in high purity grade from Fisher Scientific, Sigma-Aldrich, Alfa and used without further purification. Solvents were purified according to standard methods and stored in the presence of molecular sieves. The gibbsite [γ-Al$(OH)_3$] (research grade, synthetic) was obtained from Ward's Natural Science (Rochester, NY), and was found to contain Al carbonate as an impurity. The γ-Al_2O_3 was >99% pure and was obtained from Alfa Aesar (Ward Hill, MA). The corundum (α-Al_2O_3) (99% pure), AlPO4 (>99% pure) and Al phenol sulfonate (purity unknown) were obtained from Sigma-Aldrich (Milwaukee, WI).

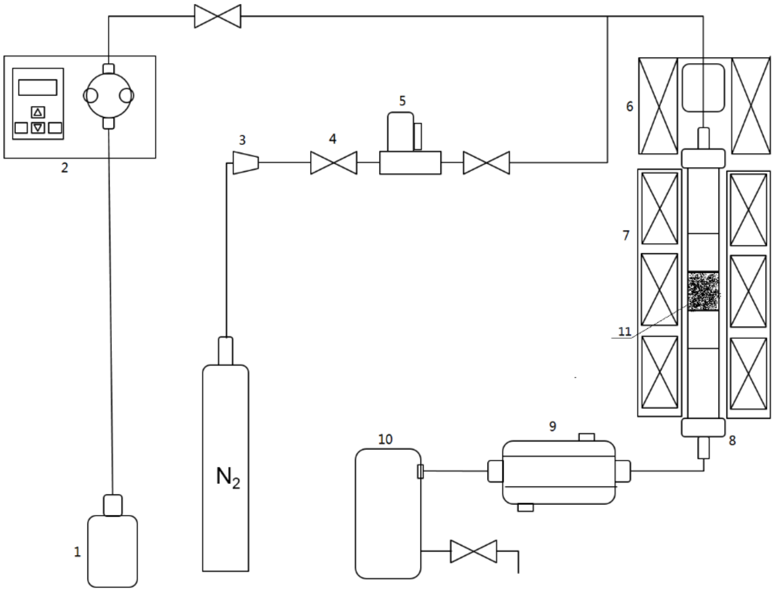
Methods

Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instrument TGA Q50. SEM analysis was performed on a JEOS JSM 6700. The Bright Field STEM images were collected by a JEM 2100F transmission electron microscope at 200kV. The EDS Mapping analysis was acquired by an EDAX GENESIS XM2 System. X-ray powder diffraction (XPD) data were recorded on a Bruker D8 Advance X-ray diffractometer. Elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. Inductively coupled plasma (ICP) analysis was performed on a Perkin–Elmer Optima 3300DV spectrometer. XPS measurements were performed on an ESCALAB 250 X-ray photoelectron spectroscopy, using Mg Kα X-ray as the excitation source. Gas sorption isotherms were measured on the Micrometrics ASAP 2020 Surface Area and Porosity Analyzer.

Detailed procedures for catalytic experiments

The reactions for benzylation of aromatics with benzyl alcohol (BA) were carried out in a fixed-bed reactor home-made by stainless steel tube with 10 mm inner diameter and 530 mm length. The reactor was heated by a high temperature furnace with three-section automatic controller. The CAD sketches and photos of the device were displayed in Scheme S1 and Figure S1. 50.0 mg catalyst mixed with 1.0 g quartz sand (20~40 mesh) was filled into the reactor between quartz wool plugs. Before reaction, all catalysts were in-situ activated by calcination at 550 ^{o}C for 5 h in air. Then, the temperature of the reaction system was decreased to the desired reaction temperature. Meanwhile, N_2 with a flow rate of 10 ml/min was introduced into the system to replace air. The mixture of aromatics and benzoyl alcohol (their molar ratio is 80) was fed by a HPLC pump (Series 1, Lab Alliance) with a liquid rate of 0.06 ml/min. The reactions were carried out under atmosphere pressure. Liquid samples were withdrawn at regular intervals from the storage silo. The products were analyzed by gas chromatography on an Agilent 7890A GC with an FID detector using a 30 m packed HP5 column and identified by GC-MS (5975C-7890A) analysis. Since aromatic reactant was in excess, conversion was calculated based on BA. The selectivity to the product was expressed as the amount of particular product divided by the amount of total products and multiplied by 100. The yield of the product is the conversion multiplied by selectivity. The product amount y (mg) during a period time was calculated based on the following equation:

$y = M \times \int_{t1}^{t2} f(t)\,dt$ M stand for the theoretical product amount produced at unit time (mg/min), $f(t)$ stand for the curve of reaction yield (assuming the yield between two monitor points are linear), t stand for the reaction time.



Scheme 1. CAD sketches of the home-made fixed-bed reactor.

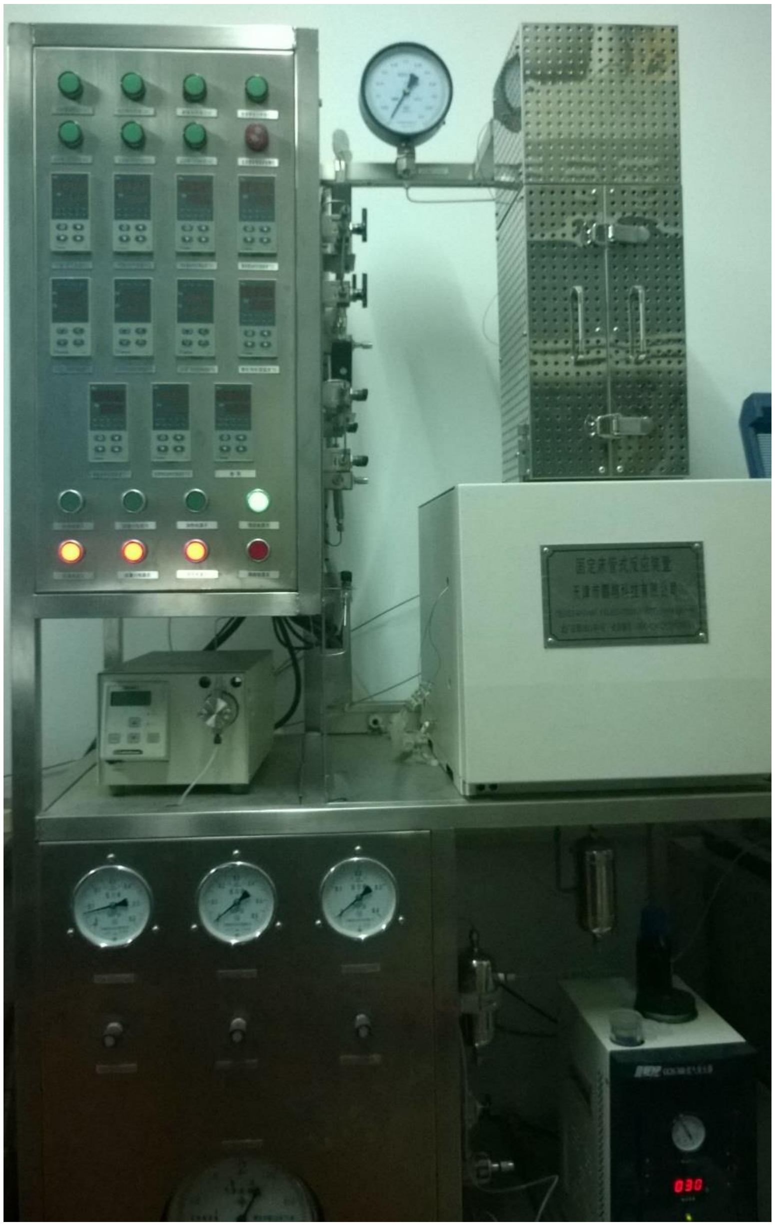


Figure S1. Photo of the home-made fixed-bed reactor.

Synthesis of MIL-101-Cr

MIL-101-Cr was synthesized according to the procedure reported by the literature.[1]

Synthesis of HMOR

HMOR was synthesized according to the procedure reported by the literature.[2]

Synthesis of H-Beta

H-Beta was synthesized according to the procedure reported by the literature.[3]

Synthesis of HKUST-1

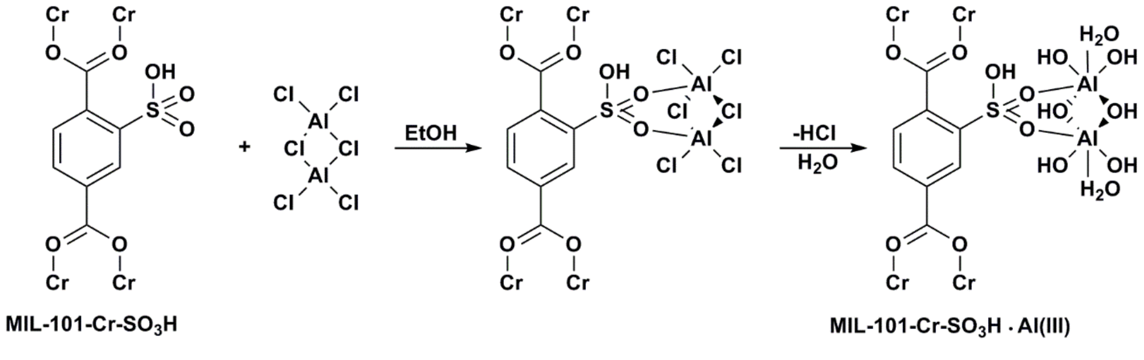
HKUST-1 was synthesized according to the procedure reported by the literature.[4]

Synthesis of MIL-100-Fe

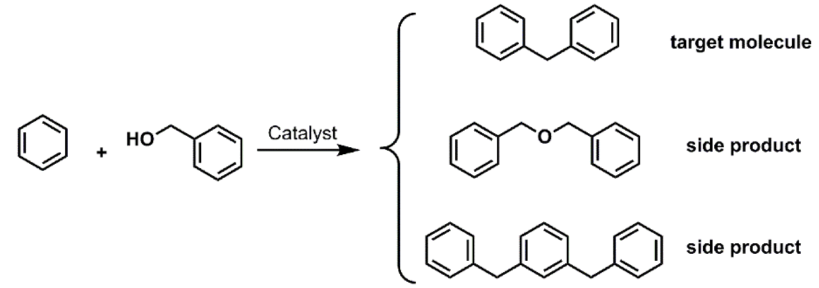
MIL-100-Fe was synthesized according to the procedure reported by the literature.[5]

Synthesis of PW@MIL-101-Cr

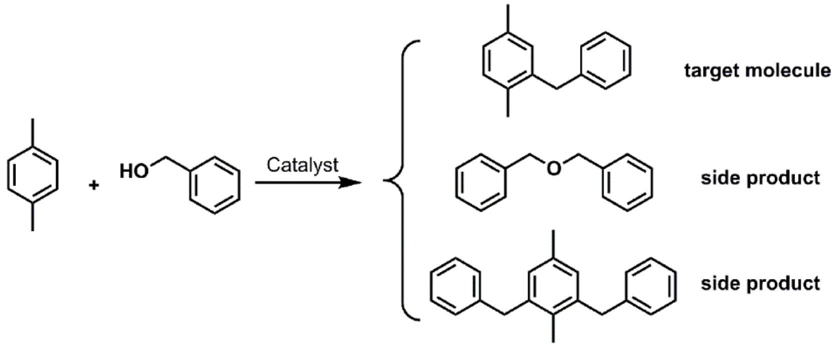
PW@MIL-101-Cr was synthesized according to the procedure reported by the literature.[6]



Scheme S2. The proposed synthesis process and local structure of MIL-101-Cr-$SO_3H{\cdot}Al(III)$.



Scheme S3. The benzylation reaction of benzene.



Scheme S4. The benzylation reaction of p-xylene.

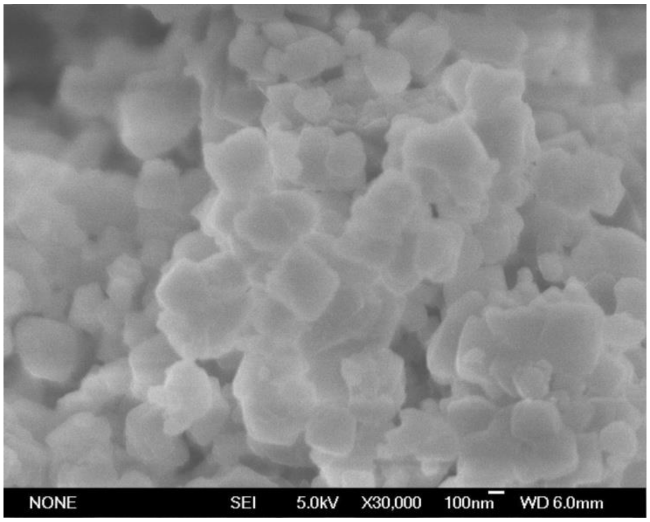


Figure S2. The SEM picture of MIL-101-Cr-SO_3H·Al(III).

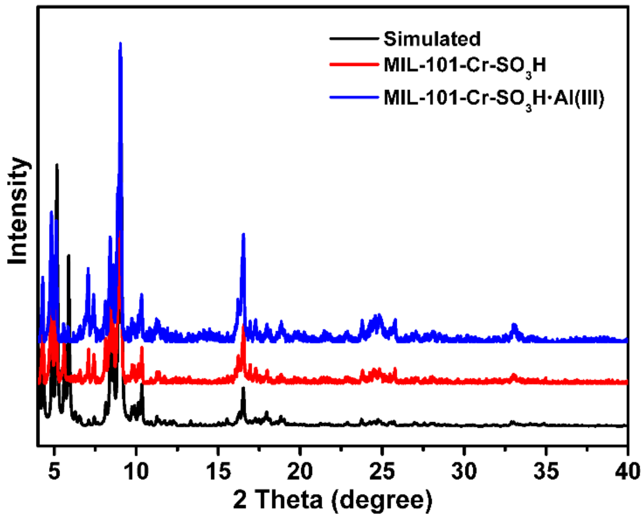


Figure S3. PXRD patterns of simulated MIL-101-Cr (black), MIL-101-Cr-SO_3H (red) and MIL-101-Cr-SO_3H·Al(III) (blue).

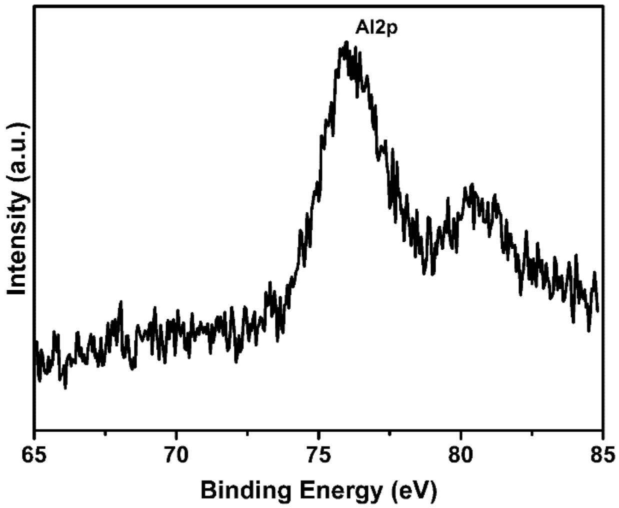


Figure S4. XPS spectra of MIL-101-Cr-SO_3H·Al(III).

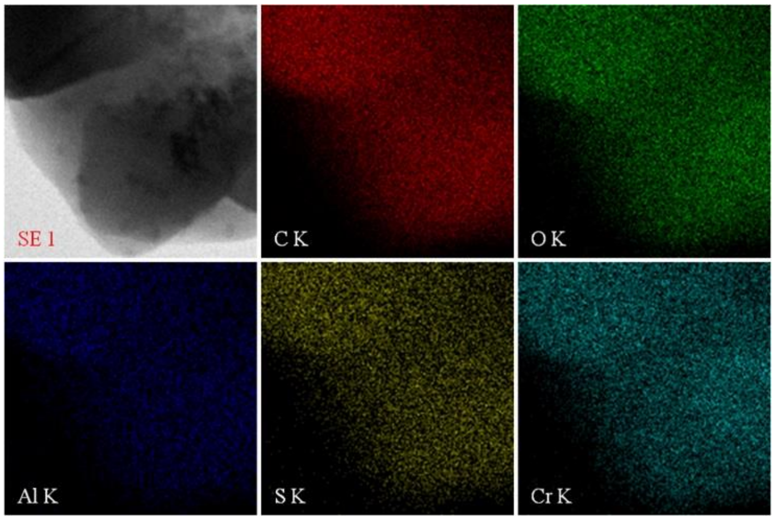


Figure S5. TEM-EDS analysis for MIL-101-Cr-$SO_3H\cdot$Al(III).

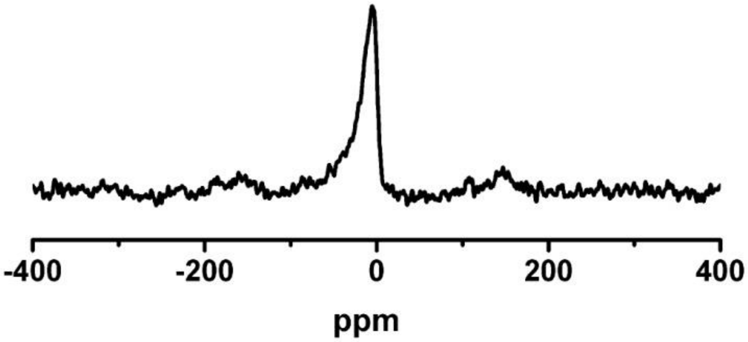


Figure S6. ^{27}Al NMR for MIL-101-Cr-$SO_3H\cdot$Al(III).

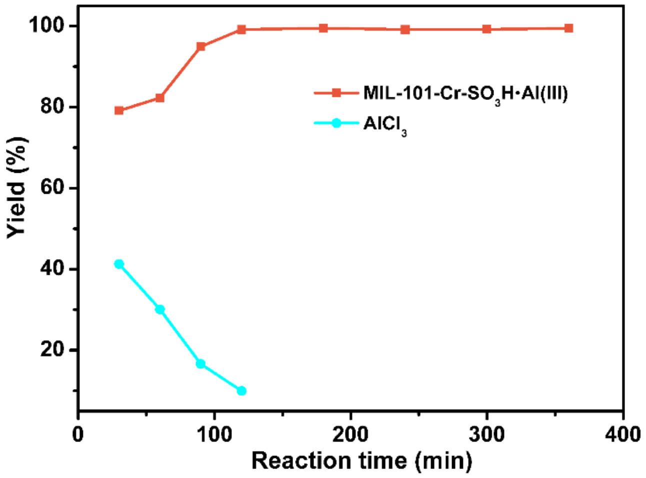


Figure S7. The yield of BTMB catalyzed by MIL-101-Cr-SO_3H·Al(III) and $AlCl_3$ at different interval time.

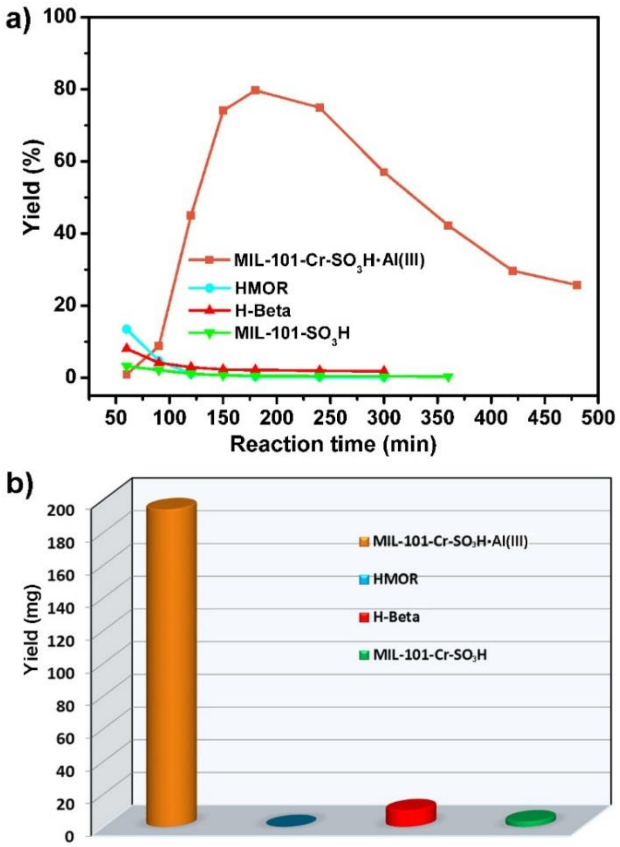


Figure S8. a) The yield of diphenylmethane (DPM) catalyzed by different catalysts at different interval time; b) The product amount of DPM yielded by different catalysts during the same reaction time period from 60 min to 300 min.

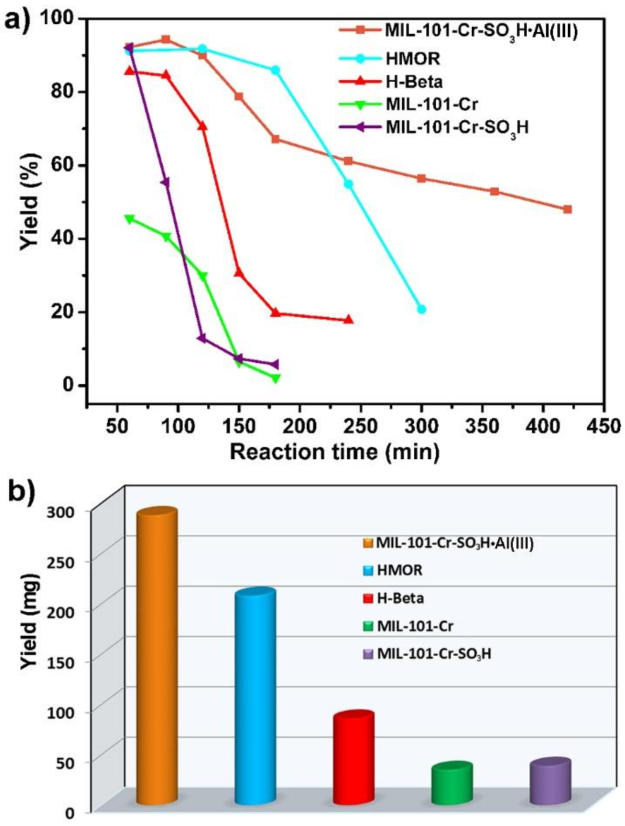


Figure S9. a) The yield of 2-benzyl-1,4-dimethylbenzene (BDMB) catalyzed by different catalysts at different interval time; b) The product amount of BDMB yielded by different catalysts from 60 min to the time point of yield lower than 20%.

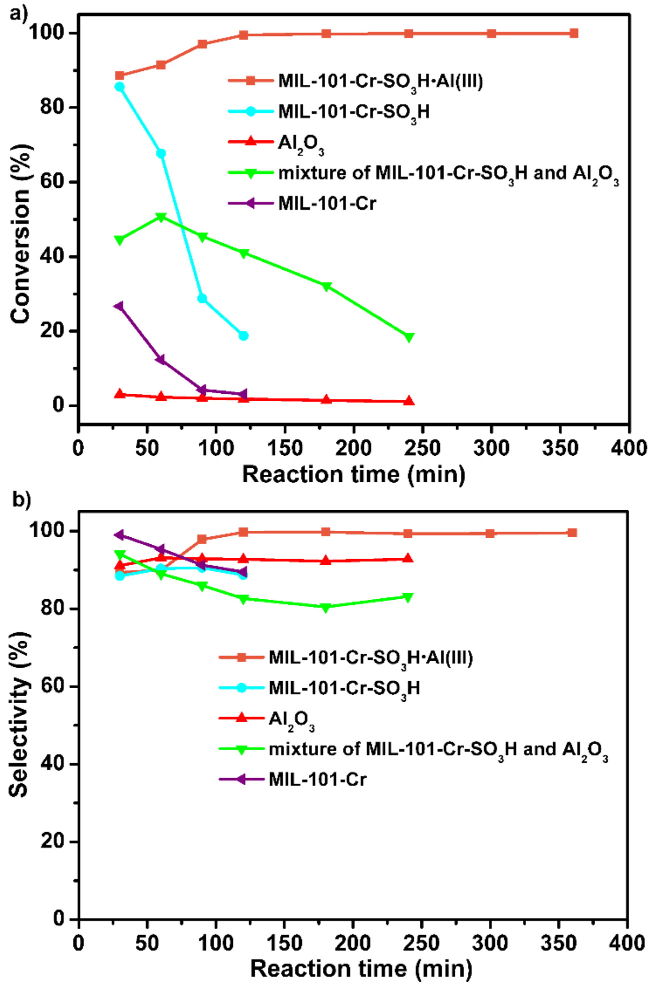


Figure S10. a) The conversion and selectivity of benzyl alcohol catalyzed by different catalysts at different interval time; b) The selectivity of BTMB catalyzed by different catalysts at different interval time.

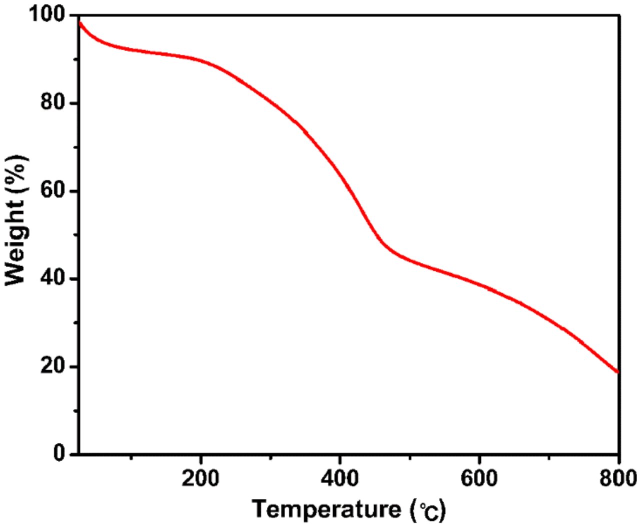


Figure S11. The TGA plot of MIL-101-Cr-$SO_3H\cdot$Al(III).

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