Electronic Supplementary Information (ESI)

Experimental Section

Materials. Chromium (III) nitrate nonahydrate (Sigma-Aldrich, 99%), hydrofluoric acid (Duksan, 48%), 1,4-benzene dicarboxylic acid (Sigma-Aldrich, 98%), tetralin (Sigma, 99%), trimethylacetaldehyde (Aldrich, 96%), and *tert*-butyl hydroperoxide (Sigma, 5-6 M solution in decane) were obtained commercially and used without further purification.

Catalyst preparation. MIL-101 was hydrothermally prepared from Chromium (III) nitrate nonahydrate, hydrofluoric acid, and 1,4-benzene dicarboxylic acid by the method reported in the literature.[1] The green solid product obtained after hydrothermal reaction was filtered through 100 μm sieves to remove crystalline terephthalic acid and then through 25 μm filter paper for separation of dissolved terephthalic acid. The obtained sample was treated with ethanol at 100 °C for 20 h with stirring. The product was filtered off while hot, washed with hot ethanol, and dried overnight at 150 °C. Chemical washing of the catalyst was further carried out by treating the ethanol-washed catalyst with 0.3M ammonium fluoride solution. In a typical procedure, 0.50 g of dry catalyst was added to ammonium fluoride solution (200 ml). The mixture was stirred for 12 h at 100 °C and filtered off, and then activated via the same procedure as that employed for ethanol-washed catalyst. The water-saturated sample was prepared by placing the dried catalyst (100 mg) in 5 ml of de-ionized water and then allowed to stand at room temperature for 24 h. The sample was dried at room temperature overnight.

Catalyst characterization. X-ray powder diffraction patterns were recorded on a Rigaku Miniflex diffractometer using CuK$_\alpha$ (λ=1.54Å) at 0.5 $^\circ$ min^{-1}. SEM micrographs were taken on a Hitachi S-4200. Thermogravimetric analyses were carried out on a TGA (Scinco S-1000) system under a flow of N_2 and a heating rate of 5 ^oC/min. Nitrogen adsorption/desorption isotherms were measured on a Micromeritics ASAP 2000 surface analyzer at -196 ^oC. Prior to the measurement, the sample was degassed at 150 ^oC for 12 h. The UV-Visible diffuse reflectance spectra were obtained on a Varian CARY 3E double-beam spectrophotometer using MgO as a reference at ambient temperature. Metal contents were determined using inductively coupled plasma-MASS spectrometry (ICP-MS, Perkin-Elmer élan 6100).

Catalytic Reaction. Catalytic reactions using *t*-BuOOH as an oxidant were carried out using a Chemistation PPS-2510 fitted with a condenser (Eyela). In a typical reaction, a mixture of 8 mmol tetralin, 5 ml chlorobenzene (solvent), and 50 mg of catalyst was placed into a Chemistation glass reactor and heated to a desired temperature. The oxidant (*t*-BuOOH, 16 mmol) was then added through a septum to the reactant mixture and stirred at 600 rpm.

Oxidation of tetralin was also carried out using O_2 at atmospheric pressure in a three-necked round flask equipped with a condenser. In a typical run, 2 mmol of tetralin, 4 mmol trimethylacetaldehyde, 10 ml solvent, and 10 mg of catalyst were stirred while bubbling O_2 at atmospheric pressure and kept at the desired reaction temperature. After completion of the reaction, the catalyst was filtered off.

Hot filtering experiments were carried out by separating the catalyst quickly from the reaction mixture after 30 minutes reaction time, maintaining the reaction temperature at 80 °C. The filtrate mixture was then stirred at 80 °C for an additional duration of up to 450 min.

The selectivity and conversion were measured using a GC (7890A GC System, 7683B series injector, Agilent Technologies, USA) fitted with a high performance HP-5 capillary column (30 m, 0.32 mm, 0.25 μm) and a FID.

References

1. G. Férey, C. Mellot-Draznieks, C. Serrer, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040.

Figures

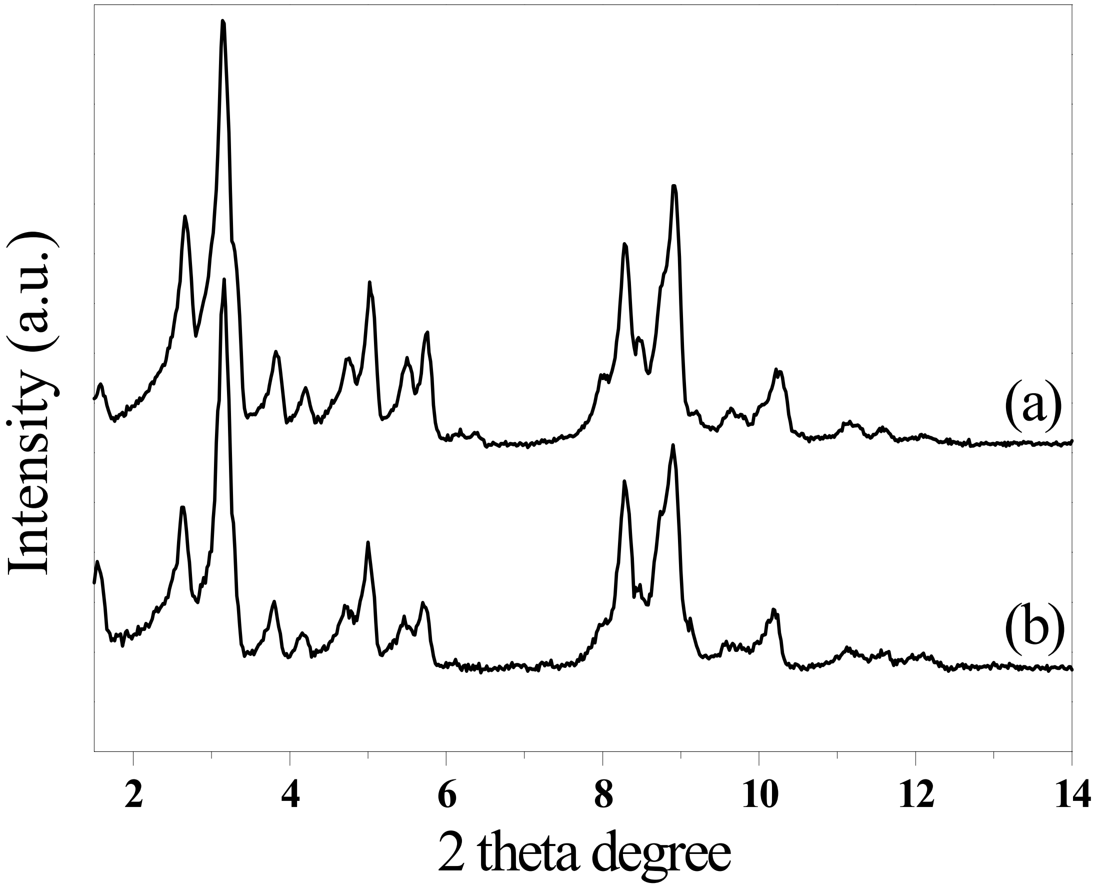

Fig. S1 X-ray powder diffraction patterns: (a) fresh MIL-101 catalyst and (b) reused catalyst after fifth cycle.

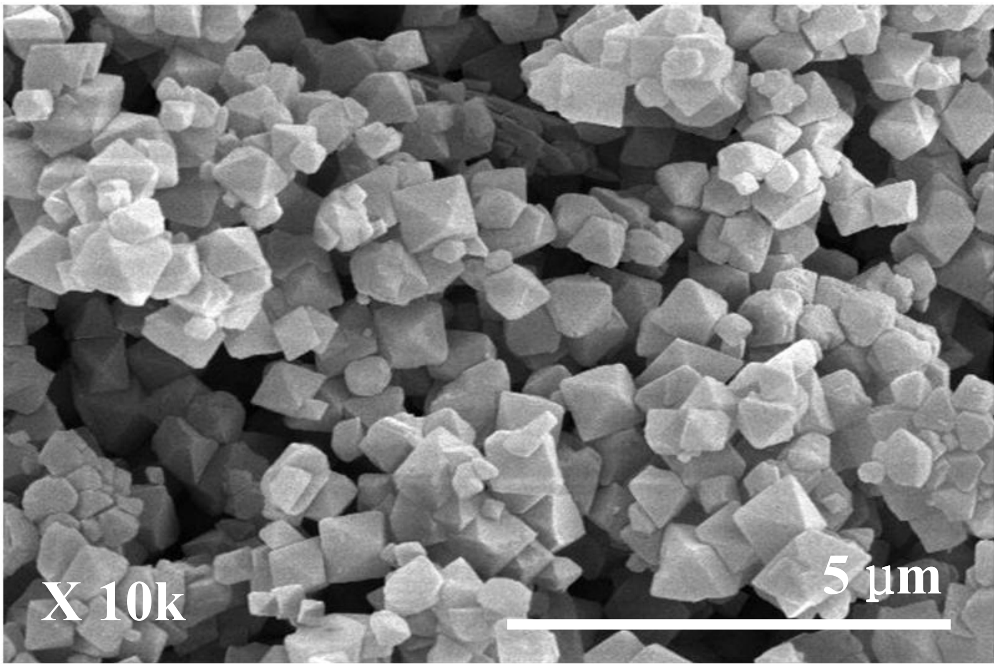

Fig. S2 Scanning electron micrograph of MIL-101.

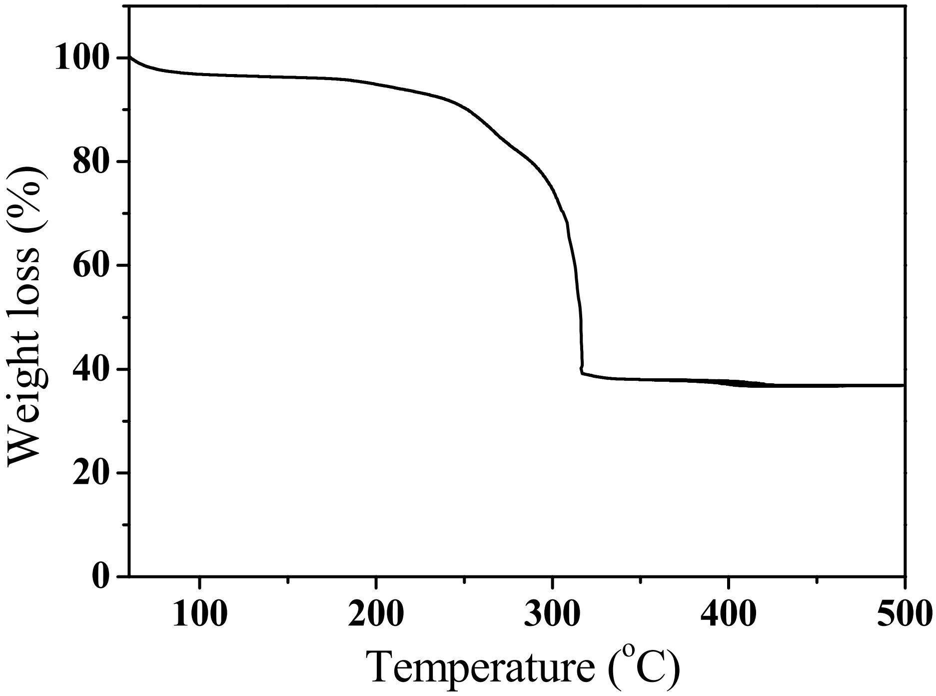

Fig. S3 Thermogravimetric analysis of MIL-101.

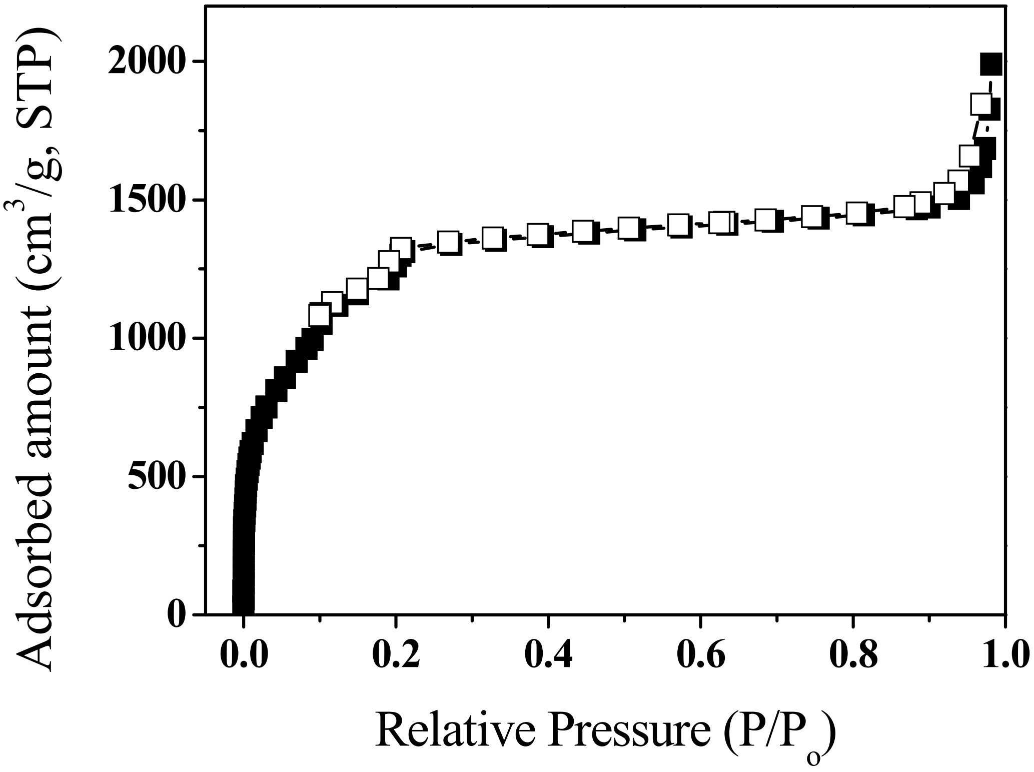

Fig. S4 N_2 adsorption (■)-desorption (□) isotherms at -196 °C.

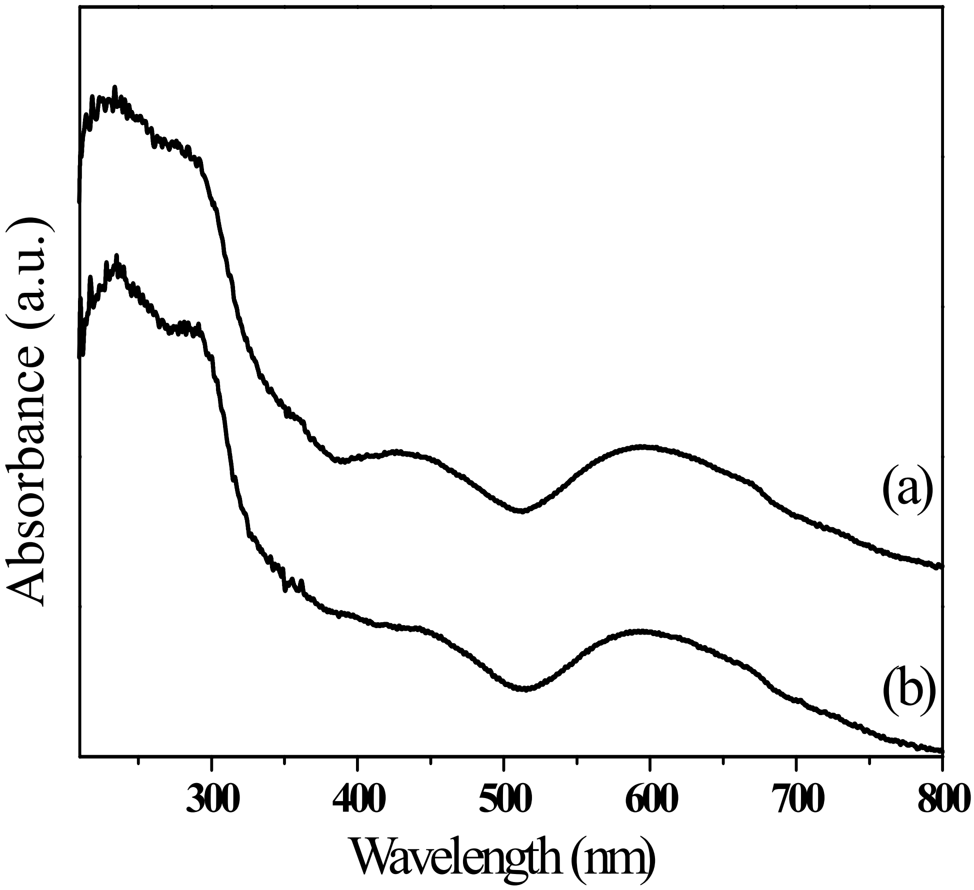

Fig. S5 UV-Visible diffuse reflectance spectra: (a) fresh MIL-101catalyst and (b) reused catalyst after fifth cycle.

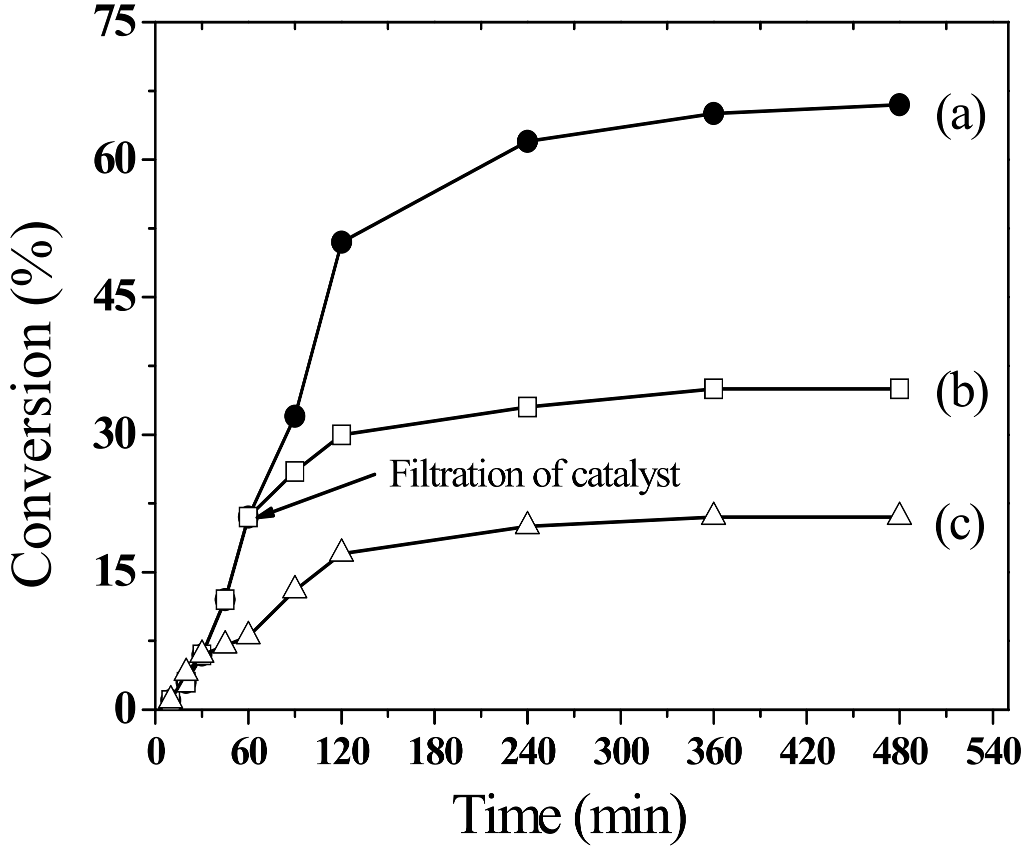

Fig. S6 Tetralin oxidation using trimethylacetaldehyde and O_2 at 80 °C: (a) fresh MIL-101 catalyst, (b) filtered catalyst after 60 min reaction time, and (c) without MIL-101 (in the presence of O_2 and trimethylacetaldehyde).