

Supporting Information

Praseodymium-doped Cr₂O₃ prepared by in situ pyrolysis of MIL-101(Cr) for highly efficient catalytic oxidation of 1,2-dichloroethane

Pengfei Zhu, Zhaoxia Hu and Shouwen Chen*

School of Biological and Environmental Engineering, Nanjing University of Science & Technology, Nanjing 210094, China

Keywords: Catalytic oxidation; 1,2-dichloroethane; Praseodymium; In situ pyrolysis; Synergistic effect.

Catalyst Characterization Methods:

The powder X-ray diffraction patterns (XRD) of the samples were collected by a BRUKER D8ADVANCE powder diffractometer with Cu K α radiation ($\lambda=1.54178$ Å) at 40 kV and 40 mA. The patterns were recorded from 5 to 90° at a 10°/min scan speed. Images of scanning electron microscopy (SEM) were obtained using a FEI Quanta 250FEG electron microscope with an acceleration voltage of 3 to 15 kV. The elemental distribution of the samples was detected using Oxford X-Max energy dispersive spectroscopy (EDS). The BET surface area (SBET) and pore volume (V_{pore}) of the catalysts were determined at 77 K on a Micromeritics ASAP 2020 automatic specific surface analyzer after pretreatment at 200 °C for 2 h under vacuum.

The specific surface area was acquired using the Brunauer-Emmett-Teller equation, and the pore size distribution was measured by the Barrett-Joyner-Halenda (BJH) method. The XPS measurements were carried out on a Thermo ESCALAB 250XI spectrometer equipped with AlK α radiation (1486.6 eV) as the excitation source.

Temperature-programmed reduction by hydrogen (H₂-TPR) was carried out on a conventional apparatus equipped with a thermal conductivity detector (TCD). In each test, the sample (50 mg) was first pretreated at 400 °C for 1 h under a N₂ flow (30 mL/min) and then cooled to room temperature. The test was performed by heating the samples in a 5% H₂/Ar (N₂) flow (30 mL/min) at a heating rate of 5 °C/min from 50 to 800 °C. The amount of H₂ consumption was calibrated by the complete reduction of a standard 50 mg CuO sample. Temperature-programmed desorption of NH₃ (NH₃-TPD) was measured on the same apparatus as H₂-TPR. Before analysis, each sample (100 mg) was pretreated at 400 °C for 1 h with N₂, cooled to 50 °C, saturated with a NH₃ flow (20 mL/min) for 1 h, and then flushed with a N₂ flow (30 mL/min) at the same temperature for 0.5 h to remove the physically adsorbed NH₃. The desorption was performed by heating the samples in a N₂ flow (30 mL/min) from 50 to 800 °C at a heating rate of 5 °C/min. The thermal behavior of MIL-101(Cr) in an air environment was evaluated using a Discovery TGA5500 thermogravimetric analysis (TGA) system with a temperature ramp rate of 5 K/min.

The powder X-ray diffraction patterns (XRD) of samples were recorded on a BRUKER D8ADVANCE powder diffractometer using Cu K α radiation ($\lambda=1.54178$ Å) at 40 kV and 40 mA. The patterns were measured from 5 to 90° at a scanning rate of 10 °/min. Images of scanning electron microscopy (SEM) were obtained via a FEI Quanta 250FEG electron microscope. The elemental distribution of sample was detected using energy dispersive spectroscopy (EDS). The nitrogen adsorption-desorption isotherms were determined at 77 K on a Micromeritics ASAP2020 automatic specific surface analyzer with pretreatment at 200 °C under vacuum for 2 h. The specific surface area was acquired by the Brunauer-Emmett-Teller method, and the pore size distribution was calculated from the desorption branch according to the Barrett-Joyner-Halenda method. The XPS measurements were carried out on a Thermo ESCALAB 250XI spectrometer with AlK α radiation (1486.6 eV) as the excitation source.

Temperature-programmed reduction by hydrogen (H₂-TPR) was carried out in a conventional apparatus equipped with a TCD. The samples (100 mg) were first pretreated for 2 h at 400 °C with a N₂ flow (60 mL/min) before cooled to room temperature. The test was performed by heating the samples in a 5% H₂/N₂ flow (60 mL/min) at a heating rate of 5 °C/min from 50 to 900 °C. The temperature-programmed desorption of NH₃ (NH₃-TPD) was measured on the same apparatus as H₂-TPR. Before measurement, each sample (100 mg) was pretreated at 400 °C for 2 h with N₂, cooled to 50 °C, saturated with 5% NH₃ in Ar. The test was performed by heating the samples in a Ar flow (60 mL/min) at a heating rate of 5 °C/min from 50 to

900 °C. The effluent was quantified by a TCD detector.

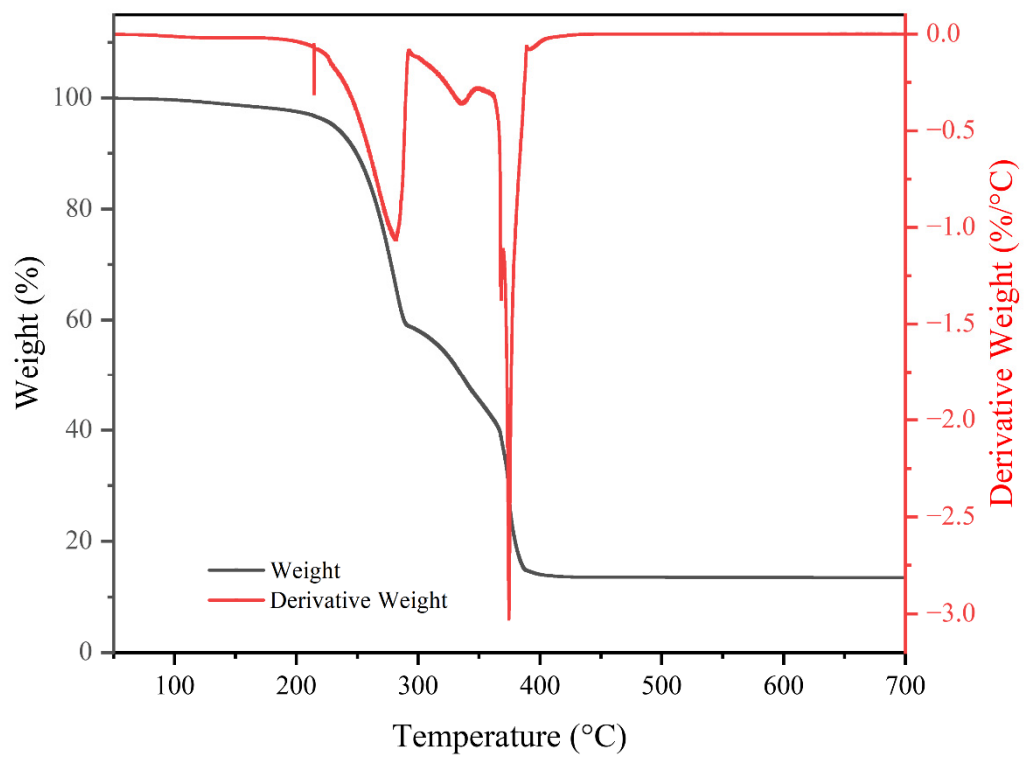


Figure S1. TGA analysis of MIL-101(Cr).

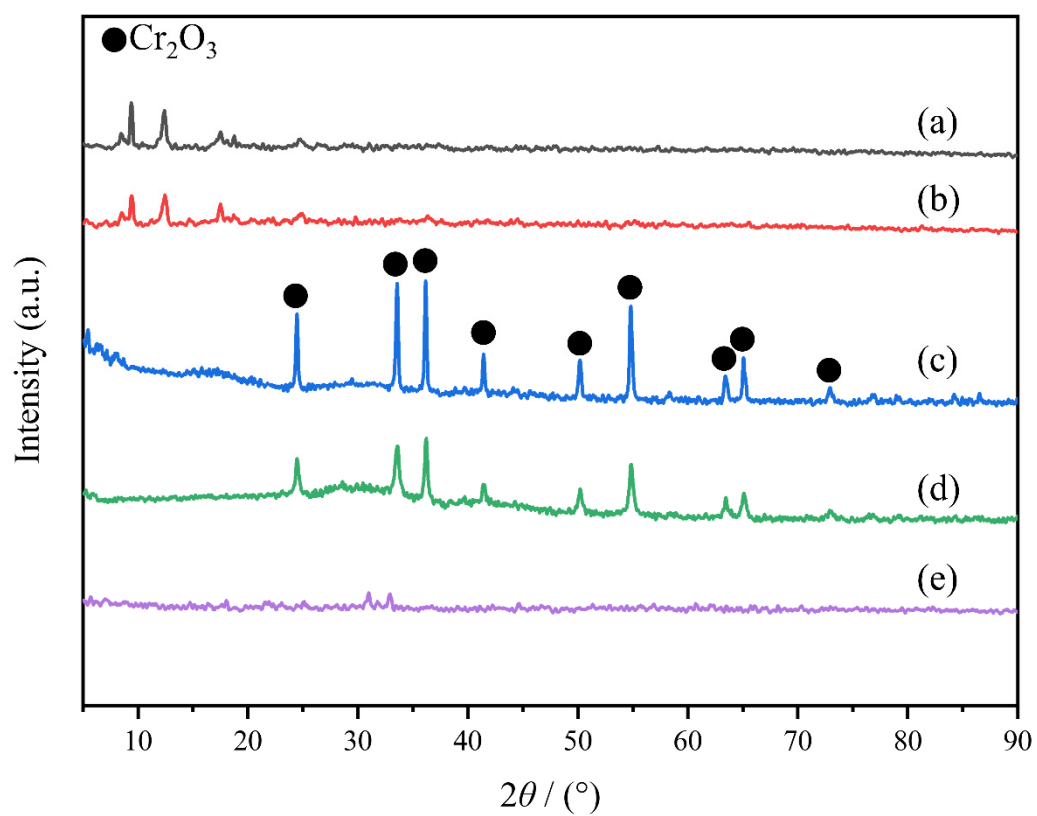


Figure S2. XRD patterns of samples: (a) MOF-Cr; (b) MOF-30PrCr; (c) M-Cr; (d) M-30PrCr; (e) P-30PrCr.

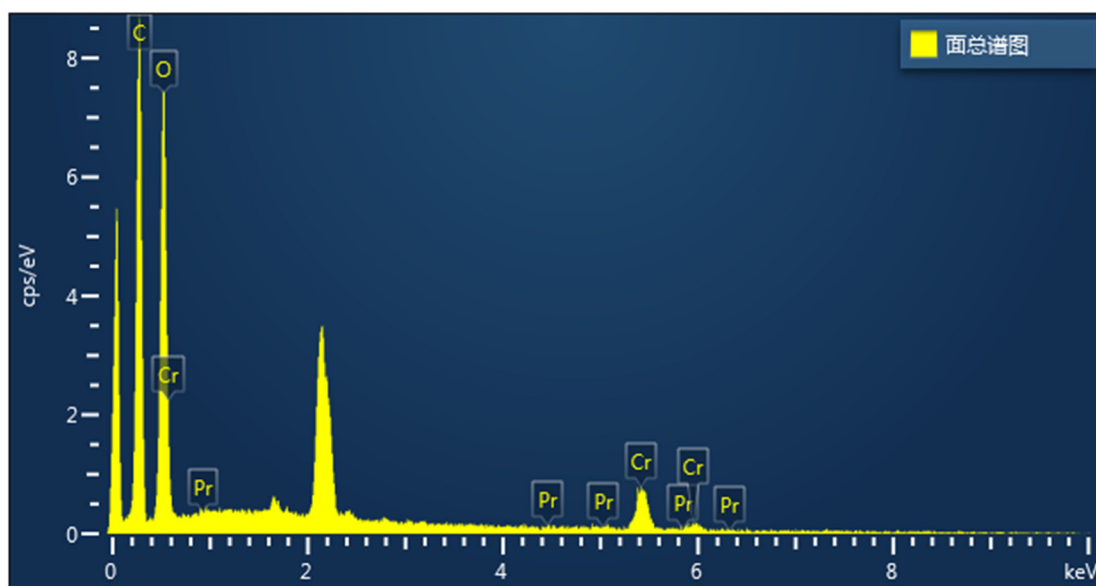


Figure S3. The EDS characterization result for M-30PrCr (total graph).

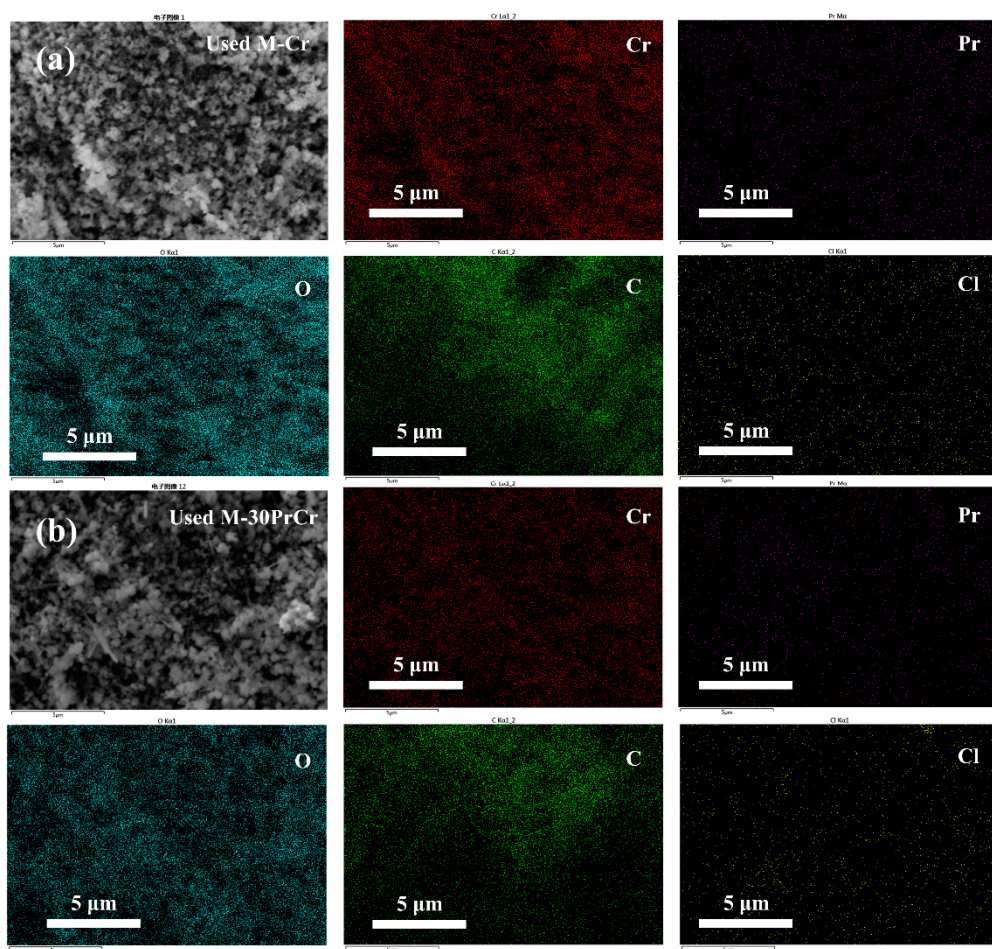


Figure S4. SEM images and EDS mapping results of used catalysts : (a) used M-Cr, (b) used M-30PrCr.

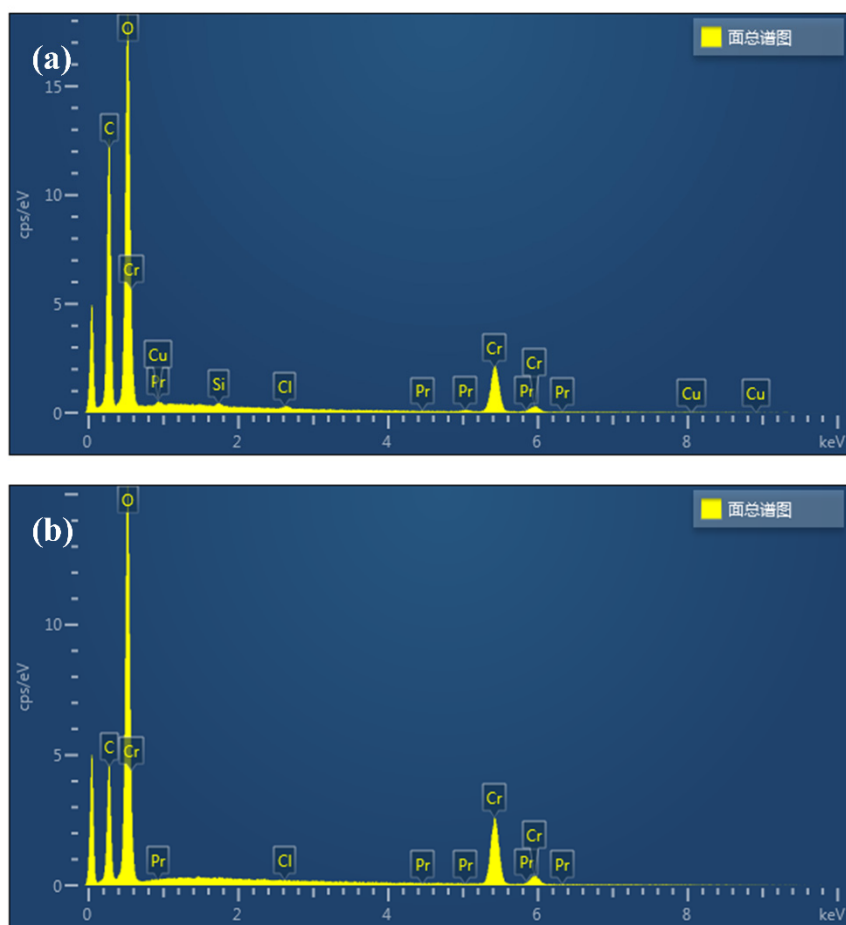


Figure S5. The EDS characterization result for (a) used M-Cr and (b) used M-30PrCr (total graph).

Table S1

Surface element distribution of used catalysts.

Sample	C wt% ^a	Cl wt%	Cr wt%	O wt%
Used M-Cr	21.41	0.73	48.89	24.06
Used m-30PrCr	5.13	0.28	65.49	26.72

^a The distribution of surface elements on used catalysts is scanned and analyzed by EDS in randomly selected regions.

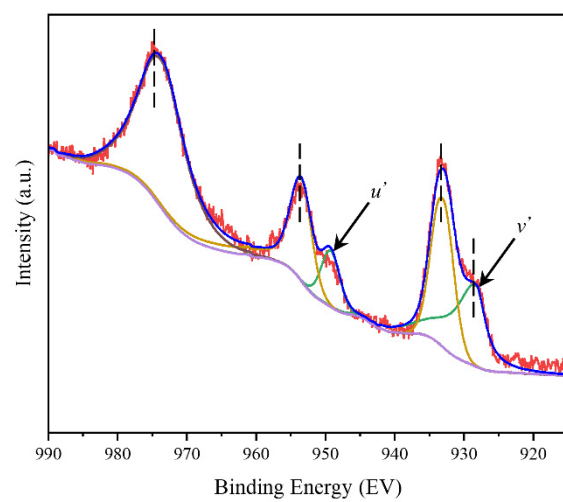


Figure S6. The XPS Pr 3d spectra for P-30PrCr.