Supporting Materials for:

Ti/ZnO–M_xO_y composite (M=Al, Cr, Fe, Ce): synthesis, characterization and application as a highly efficient photocatalyst for hexachlorobenzene degradation

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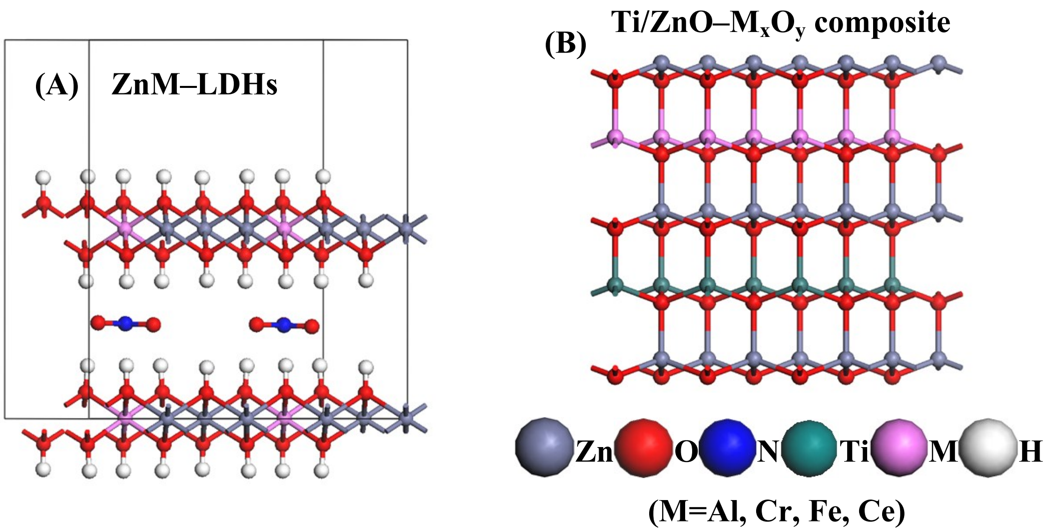

Figure S1 The cluster models and structural schematic diagram for ZnM–LDHs (A) and Ti/ZnO–M_xO_y composite (B).

Cluster Model of LDHs and Composite

According to the references [S1], to study the structural properties of ZnM–LDHs, the formulation of $[Zn_3M(OH)_8]^+$ was used as the cluster model. The periodical model of $Zn_6M_2(OH)_{16}(NO_3^-)_2$ was established in hexagonal (2H) stacking sequence, containing $Zn_3M(OH)_8^+$ as host layer and NO_3^- as guest anion, that was the host–guest interaction model with NO_3^- in the position of hcp–M. And the host–guest calculation model of ZnM–LDHs was shown in Scheme 2A. Moreover, for the purpose of reflecting the objective composition of Ti/ZnO–M_xO_y composite best, we make some optimization for the calculation parameter and models. The designated mole ratios of M_xO_y and TiO_2 were used to replace the adjacent ZnO (see Scheme 2B).

Computational Model: Geometry optimization and property analysis were performed in the framework of density functional theory (DFT), using the LDA–CA–PZ and Ultrasoft Psedupotential [S2] for atom and electron calculation, energy quality is set as medium, energy cutoff is 340.0 eV, SCF tolerance is fixed at 2×10^{-6} $eV\cdot atom^{-1}$, and k–point set of Brillouin zone is 4×4×1. Pulay Mixing Scheme is used for the calculation of ground state energy, and the electronic configuration of Zn^{2+}, M^{3+}, Ti^{4+} is calculated in the high–spin state. Total charge of every model is set as 0. All the above–mentioned parameters were tested and found to be enough to ensure the energy and stress well converged. The calculations have been completed with the CASTEP code of the software Materials Studio 5.5.

(S1) Yan, H., Lu, J., Wei, M., Ma, J., Li, H., He, J., Evans, D. G., Duan, X. Theoretical Study of the Hexahydrated Metal Cations for the Understanding of Their Template Effects in the Construction of Layered Double Hydroxides. *J. Mol. Struc–Theochem.* **2008**, 866, 34–45.

(S2) Yan, H., Wei, M., Ma, J., Li, F., Evans, D. G., Duan, X. Theoretical Study on the Structural Properties and Relative Stability of M(II)−Al Layered Double Hydroxides Based on a Cluster Model. *J. Phys. Chem. A* **2009**, 113, 6133–6141.

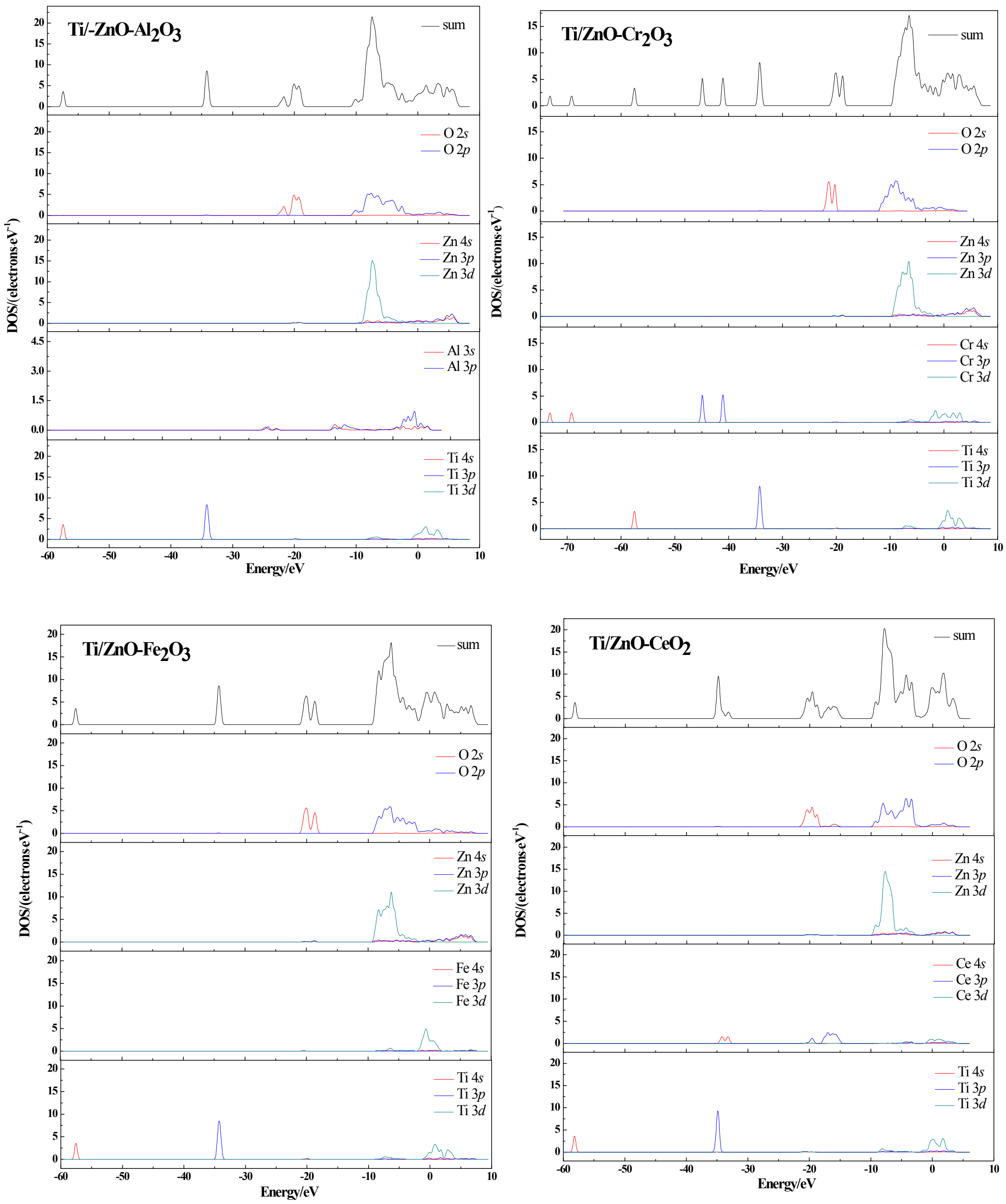

Figure S2 The electronic density of states of all elements for Ti/ZnO–M_xO_y composite (M=Al, Cr, Fe, Ce).

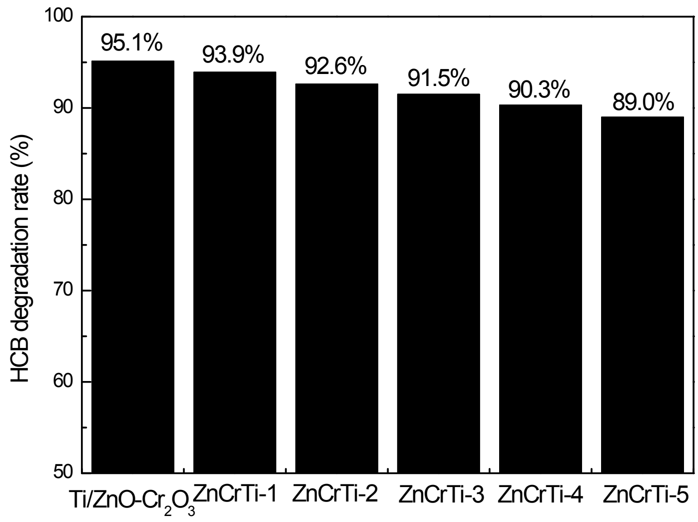

Figure S3 The comparison of HCB decomposition between original Ti/ZnO–Cr_2O_3 composite and thermally regenerated materials from used material. Note: ZnCrTi–1, ZnCrTi–2, ZnCrTi–3, ZnCrTi–4 and ZnCrTi–5 are the products after the first–, second–, third–, fourth– and fifth–cycle thermal regenerations of Ti/ZnO–Cr_2O_3, respectively.

Regeneration of used composites

In this work, to determine the reutilization of those Ti/ZnO–Cr_2O_3 composite for HCB removal from aqueous solutions, the materials after photo–reaction were regenerated using a thermal recycle method like this [S3]: after completing equilibrium degradation experiments described in Section 2.4, the suspension was filtered and washed twice both by water and ethanol for complete cleaning of the catalyst, then the catalyst was dried at 65 °C for 12 h, calcined in the tube furnace at 500 °C for 5 h under N_2 atmosphere and re–dispersed in HCB solution with known concentrations. This procedure was repeated three times and the amount of HCB after each dispersion–regeneration cycle was determined.

(S3) M.D. Romero, J.A. Calles, M.A. Ocana, J.M. Gomez, Epoxidation of cyclohexene over basic mixed oxides derived from hydrotalcite materials: Activating agent, solvent and catalyst reutilization, *Micropor. Mesopor. Mat.* **2008**, 111, 243–

Additional Materials Characterization

HPLC–MS and GC–MS analysis were tested by Agilent 1100 series (HPLC), Bruker Daltonics Esquire 3000 plus (MS) and Varian CP–3800/Sature2200 (GC/MS).

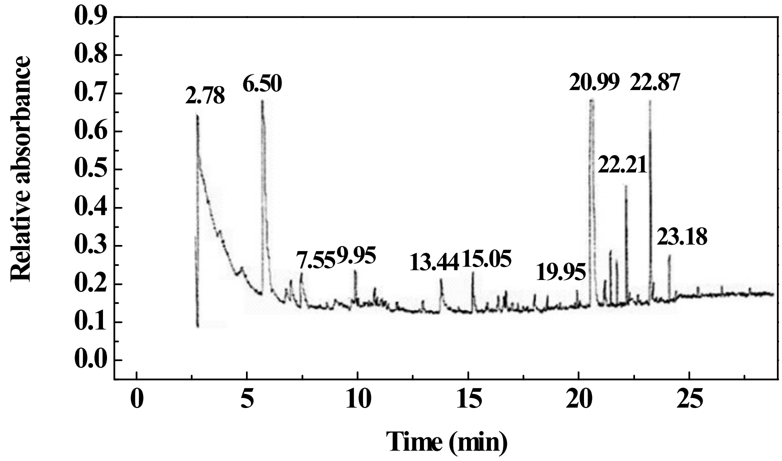

Figure S4 The GC curves for photo–degradation process of HCB by Ti/ZnO–Cr_2O_3 composite after 60 min irradiation.

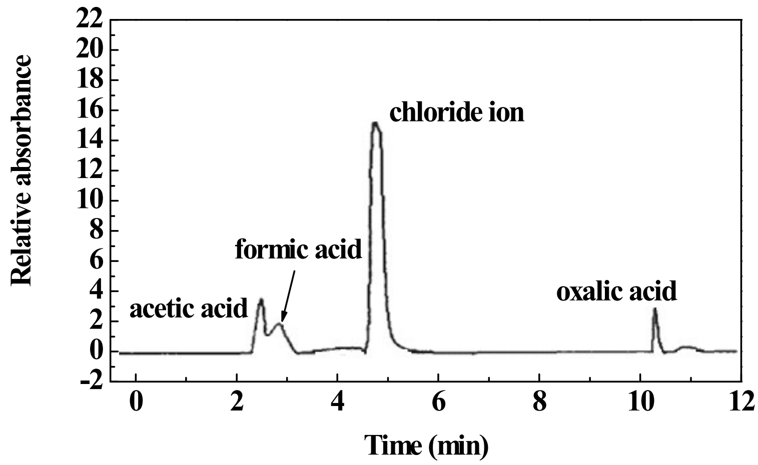

Figure S5 The HPLC curves for photo–degradation process of HCB by Ti/ZnO–Cr_2O_3 composite after 180 min irradiation.

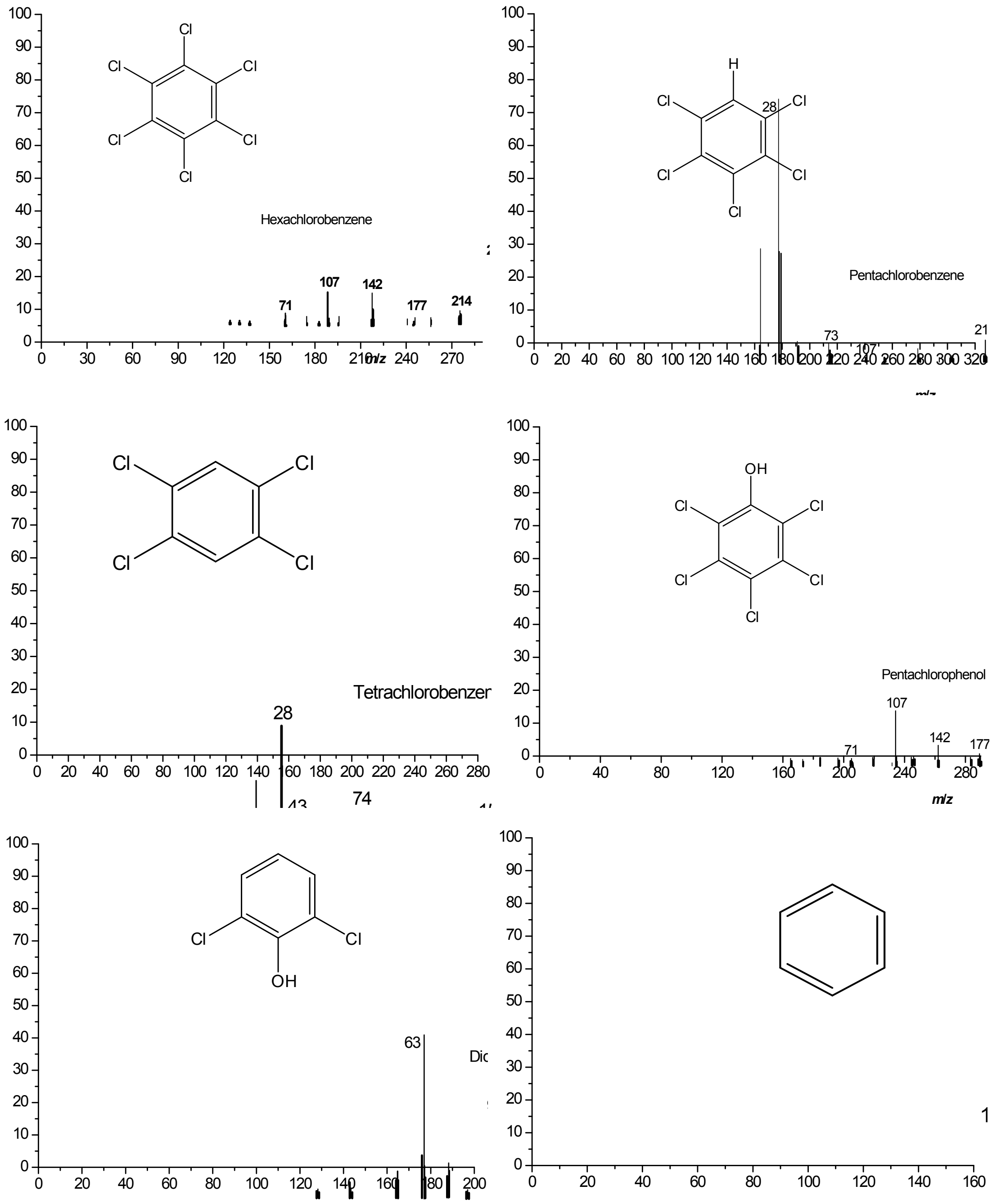

Figure S6 Mass images of intermediates from GC–MS.

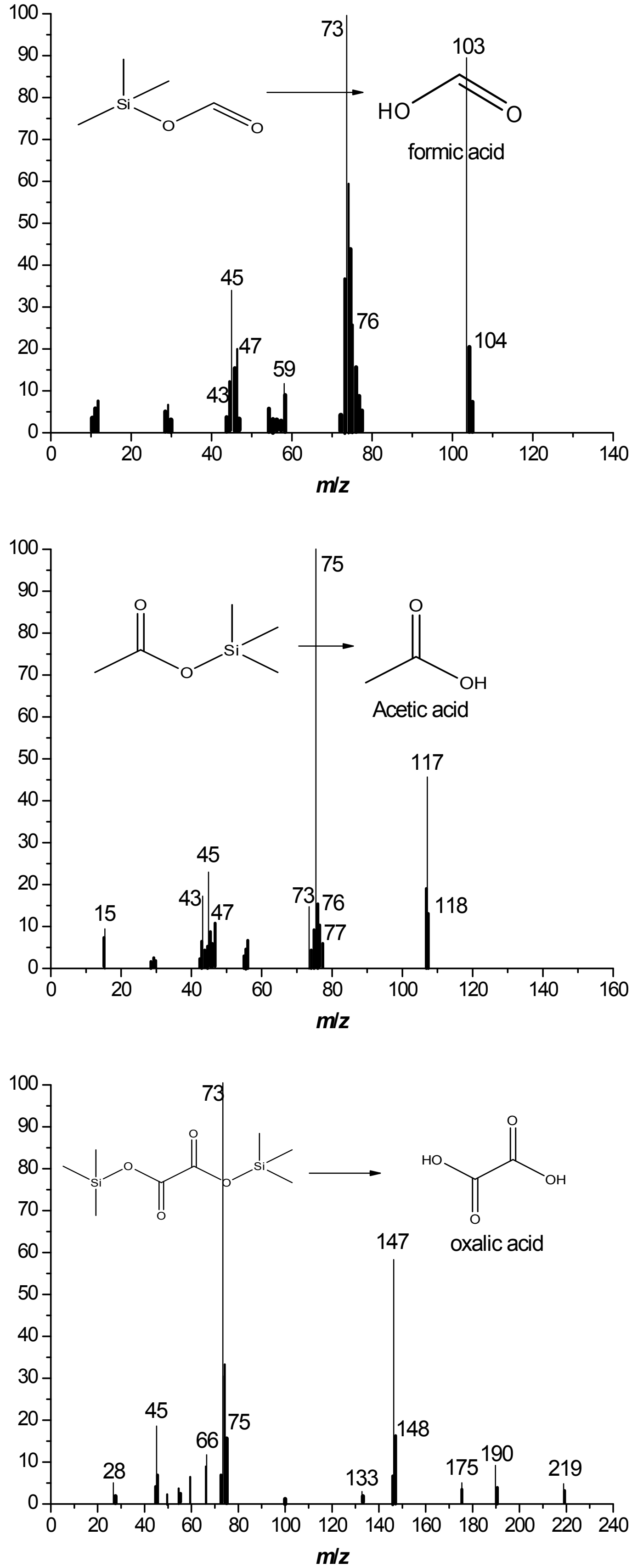

Figure S7 Mass images of intermediates from HPLC–MS.