Supporting Information

CO₂ Oxidative Dehydrogenation of Propane to Olefin over Cr-M (M = Zr, La, Fe) Based Zeolite Catalyst

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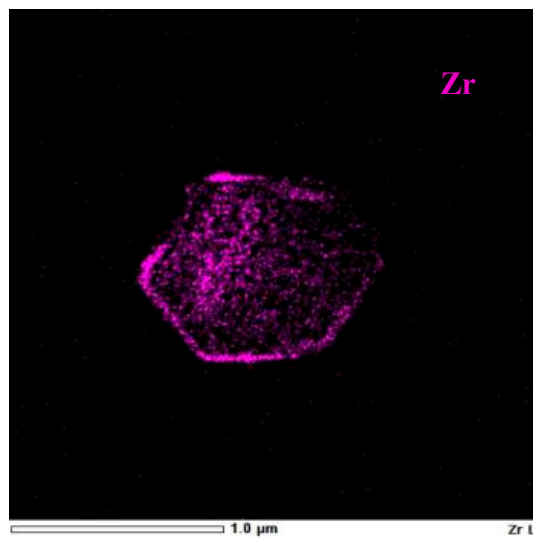
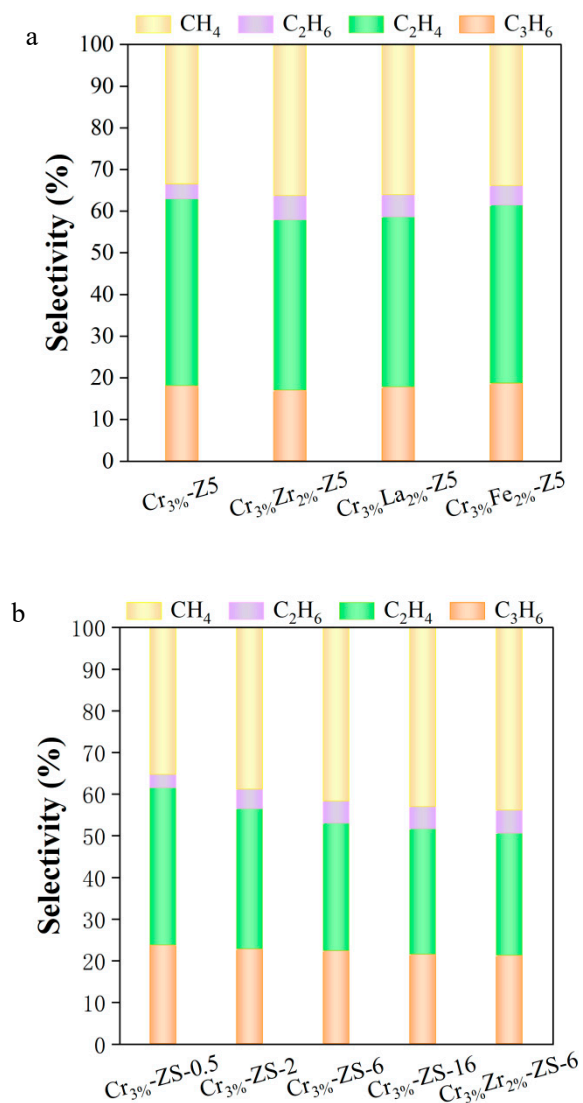* Correspondence: liuning@bjut.edu.cn

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Constructed models and computational Method
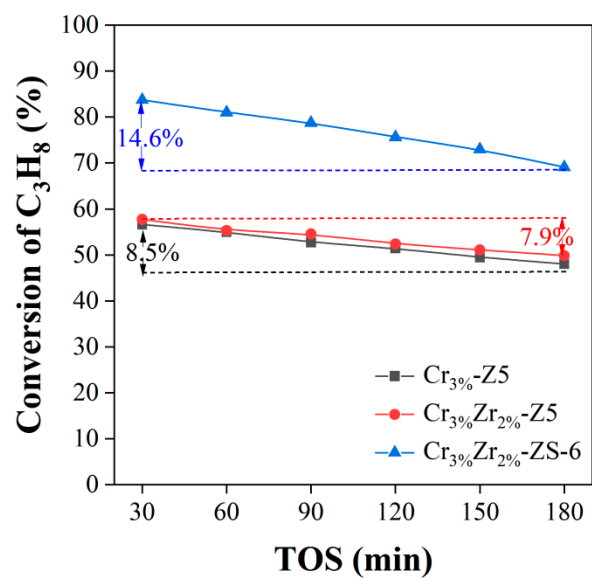
The [110] plane of CrO_3 p (2×2) and [111] plane of ZrO_2 (2×2) were constructed for the CO_2 and C_3H_8 adsorption simulations. The optimized models were depicted in Table S1. Periodic density-functional theory (DFT) calculations were performed using the Vienna Nonlinear Simulation Package (VASP. 6.3.2) [1].Van der Waals interactions were described by using empirical corrections in the Grimme scheme (DFT-D2). The energy convergence threshold was set to 10^{-5} eV, and the geometric convergence criterion was set to 0.02 eV $\mathring{A}^{-1}$. The K-points were set to $2 \times 1 \times 1$ according to the Monkhorst-Pack method.

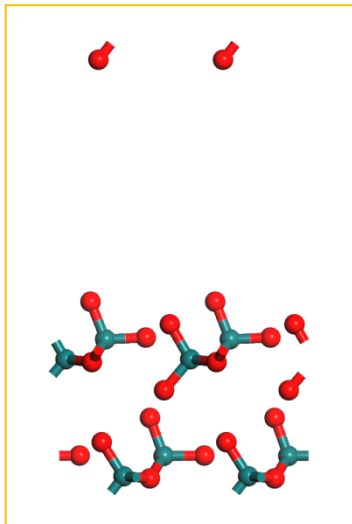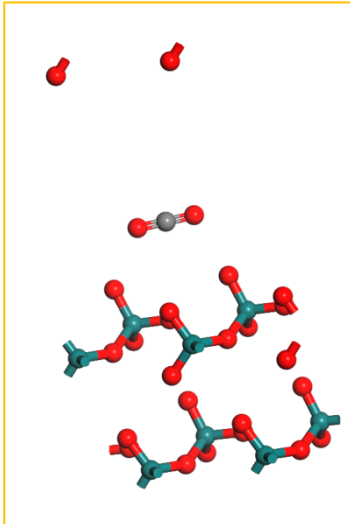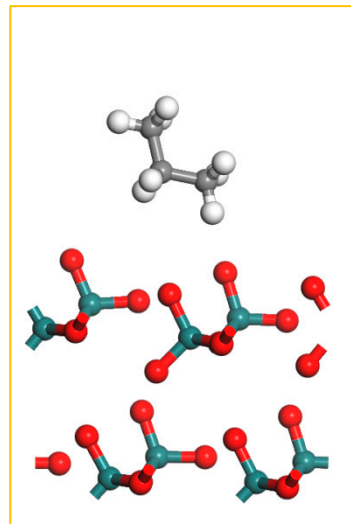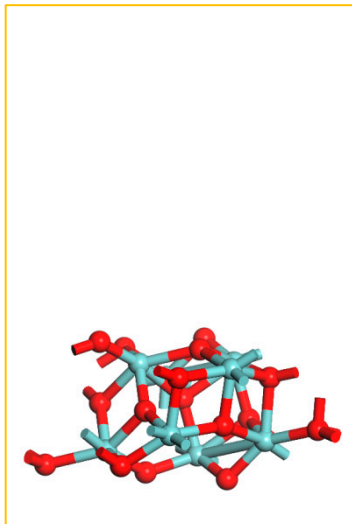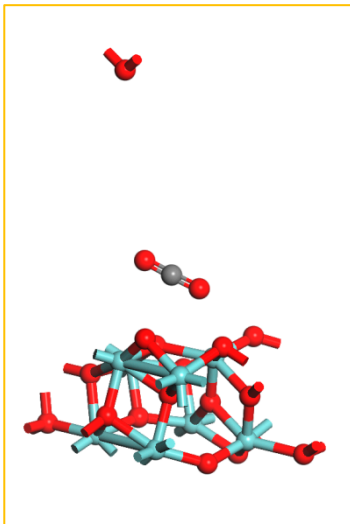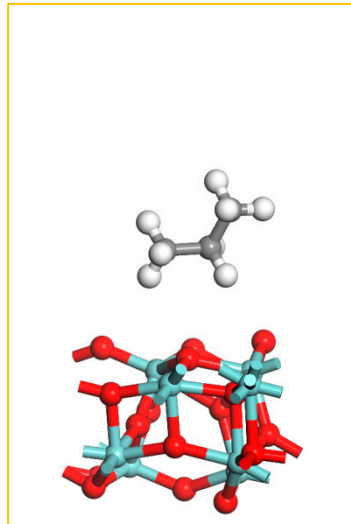**Figure S1.** EDS-Mapping image of Zr in catalyst Cr$_{3\%}$Zr$_{2\%}$-Z5.

Figure S2. Selectivity of the synthesized samples of (a) Cr3%-Z5, Cr3%M2%-Z5 (M=La, Zr, Fe) and (b) Cr3%-ZS-n (n= 0.5, 2, 6, 16) as well as Cr3%Zr2%-ZS-6 (mass ratio of 6).

Figure S3. Conversion of propane with catalysts Cr3%-Z5, Cr3%Zr2%-Z5 and Cr3%Zr2%-ZS-6 (reaction time: 180 min).

Table S1. Model diagram of CO_2 and C_3H_8 adsorption over CrO_3 [110] and ZrO_2

[111]

[110] CrO_3 slab	CrO_3+CO_2	CrO_3+C_3H_8
[111] ZrO_2 slab	ZrO_2+CO_2	ZrO_2+C_3H_8

Table S2. Adsorption energy of CO_2 and C_3H_8 over CrO_3 [110] and ZrO_2 [111]

Model	Energy (eV)	Adsorption Energy (eV)
[110] CrO_3	-205.78	—
CrO_3+CO_2	-228.85	-0.09
CrO_3+C_3H_8	-262.85	-0.06
[111] ZrO_2	-221.78	—
ZrO_2+CO_2	-244.90	-0.14
ZrO_2+C_3H_8	-278.82	-0.03

NOTE: The adsorption energies of CO_2 and C_3H_8 on molecular sieve supports with surface-loaded metals ZrO_2 and CrO_3 were calculated by DFT. The adsorption models of CO_2 and C_3H_8 on ZrO_2 and CrO_3, respectively, were established (Table S1). Table S2 shows the adsorption energies of each model, and it can be concluded that: the adsorption energy of ZrO_2 for CO_2 is larger, while that of CrO_3 for C_3H_8 is larger.

Reference

1. Kresse, G.; Furthmuller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B.* **1996**, *54*, 11169-11186.