Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Vacancy-rich $Ti_3C_2O_x$ (MXene)-anchored Co nanocluster catalyst enhances the selective hydrogenation of cinnamaldehyde

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Test methods of in-situ DRIFTS

For the pretreatment of samples, all catalysts are pretreated at 300 °C with argon before testing to clean the adsorbed pollutant. After that, the background is recorded under 30 mL·min^{-1} argon flowing and 50 °C. And the dilute CAL solution was bubbled and blown into the in-situ cell by 30 mL·min^{-1} argon flowing until adsorption saturation, then record the adsorbed CAL spectra after remove the physical adsorbed CAL. The spectra of CAL hydrogenation need to record the background at 120 °C and treat the sample adsorbed CAL under 120 °C and 30 mL·min^{-1} H_2, and the spectra are recorded per 10 min.

Computational method

The spin-polarized Density function theory (DFT) calculation was used to reveal the surface structure of catalysts and the potential adsorption configuration of CAL over the catalysts. All calculations were performed by Vienna Ab-initio Simulation Package (VASP) with the projector augmented wave (PAW) method[1, 2], in a combination with the DFT-D3 correction[3]. The cell structure of $Ti_3C_2O_2$ was referring to the previous research, and the $Ti_3C_2O_2$(001) and TCOs(001) was modelled as a 4×4 supercell with a 30 Å thickness of the vacuum. Further, based on the potential positions for anchoring Co atoms over the $Ti_3C_2O_2$(001) (Scheme 1), a several structures of Co/$Ti_3C_2O_2$ and Co/TCOs were built. The energy cutoff was 500 eV after structural optimization, and a Gamma k-point was set as 3×3×1 grid to sample for Brillouin zone. The Gaussian smearing method was employed with a width of 0.1 eV. The geometry relaxation was terminated when the forces on all the atoms were converged to smaller than 0.05 eV/Å. The adsorption energy (E_{ads}) was defined as equation: $E_{ads}=E_{adsorbate+surface}-E_{adsorbate}-E_{surface}$. The transfer amount of charges were obtained by the Bader approach[4]. Transition state searches were performed at the same theoretical level with the CI-NEB method. All the models are the most stable structure obtained through optimization and screening.

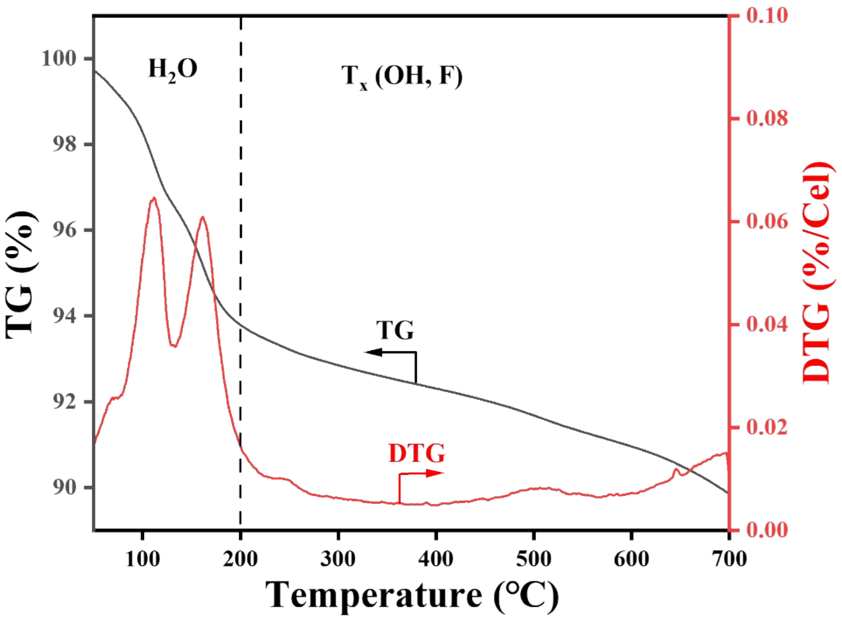

Fig. S1 The TG and DTG curves of $Ti_3C_2T_x$ under argon atmosphere.

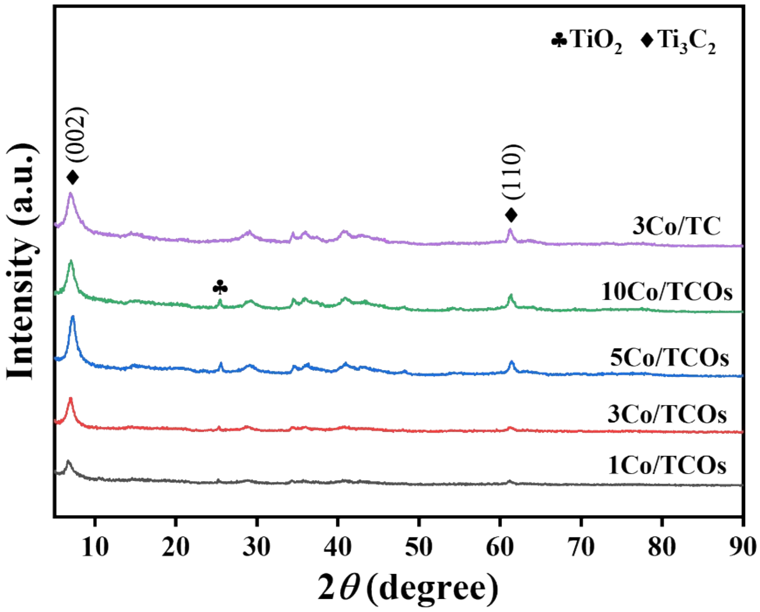

Fig. S2 XRD patterns of *x*Co/TCOs samples.

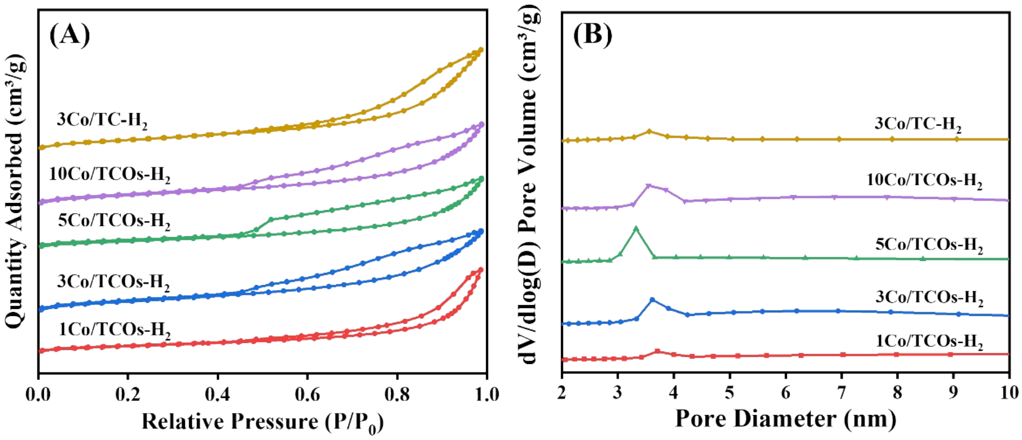

Fig. S3 (A) N_2 adsorption-desorption isotherms and (B) pore size distribution of catalysts.

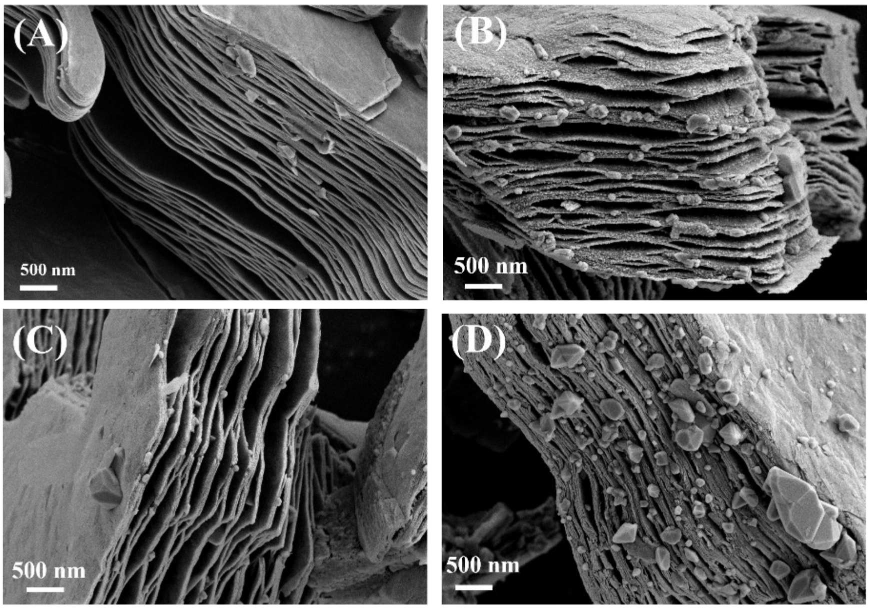

Fig. S4 SEM images of (A) TC, (B) TCOs, (C) TCOs-H_2, and (D) spent 3Co/TCOs-H_2.

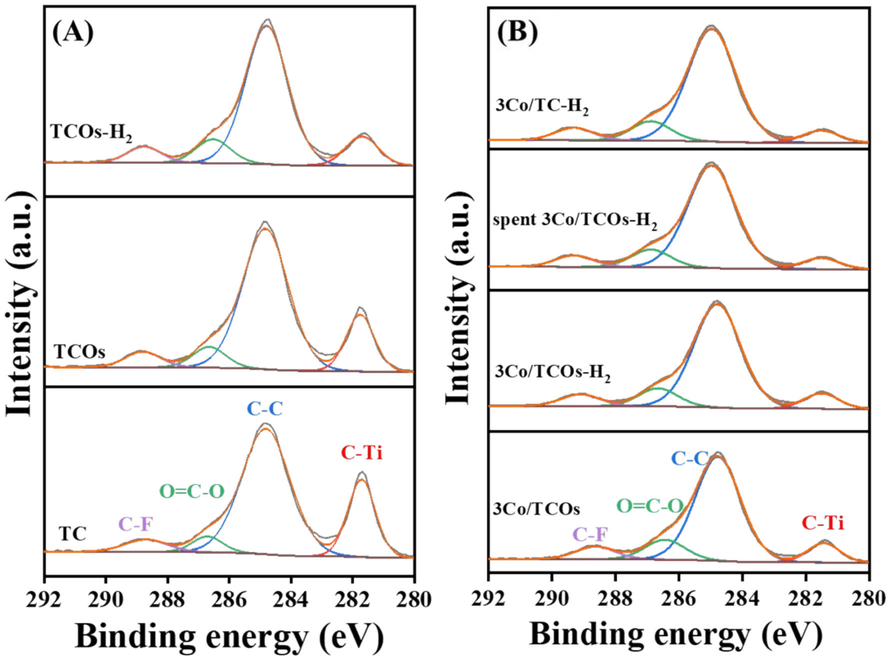

Fig. S5 C 1*s* XPS spectra of various (A) supports and (B) catalysts.

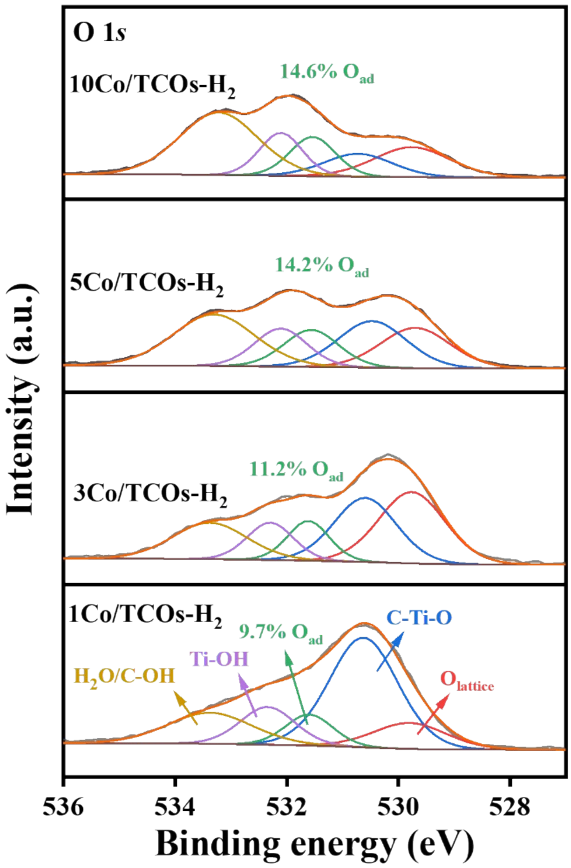

Fig. S6 O 1*s* XPS spectra of *y*Co/TCOs-H_2 catalysts (*y*=1, 3, 5, 10).

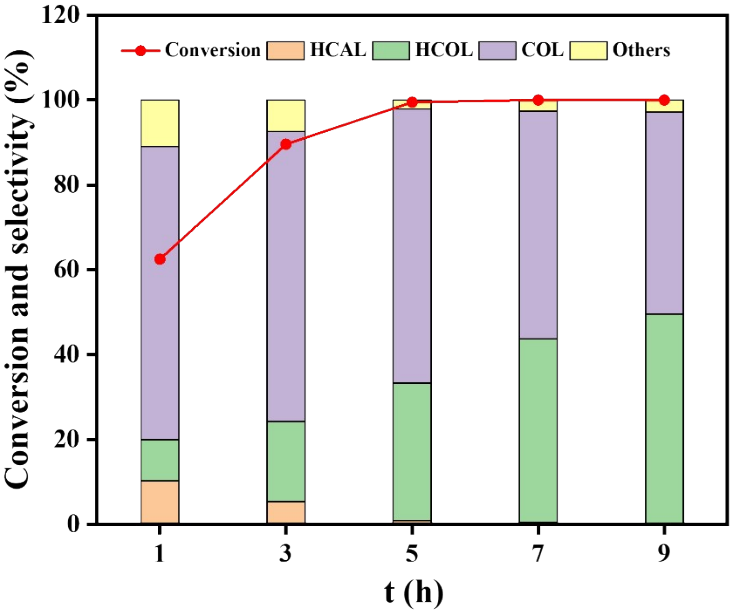

Fig. S7 Hydrogenation activities of 5Co/TCOs-H_2 catalyst.

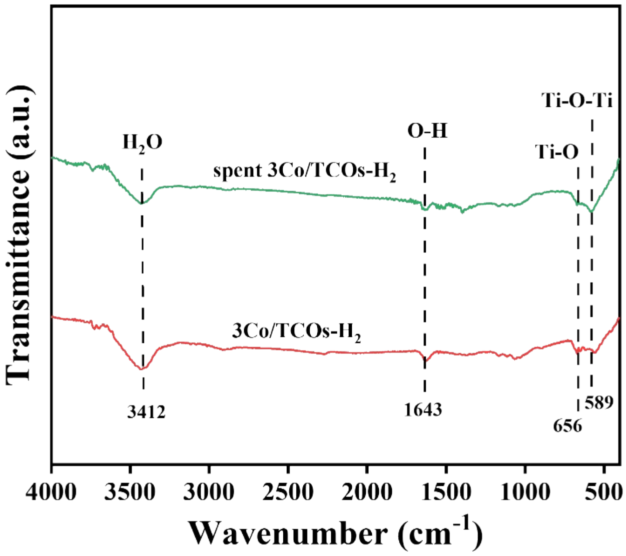

Fig. S8 The FT-IR spectra of 3Co/TCOs-H$_2$ and spent 3Co/TCOs-H$_2$ catalyst.

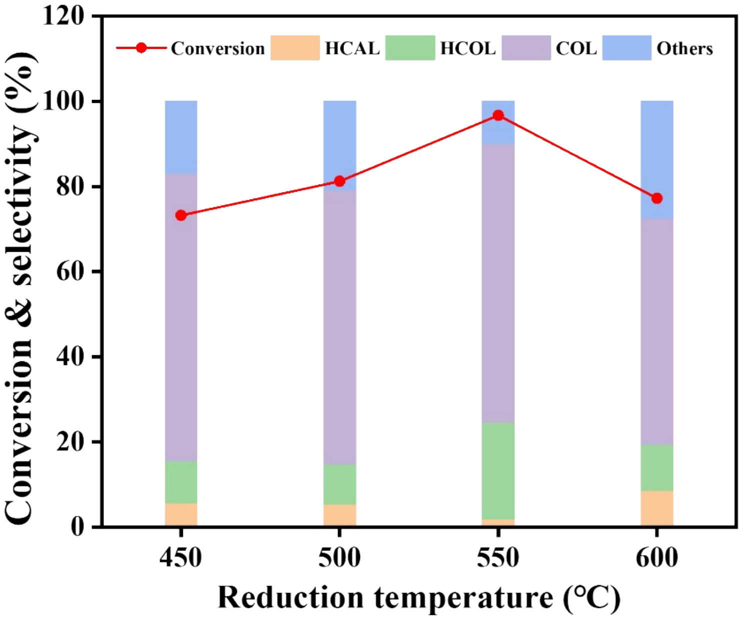

Fig. S9 Hydrogenation activities of 3Co/TCOs-H_2 catalyst at different reduction temperatures.

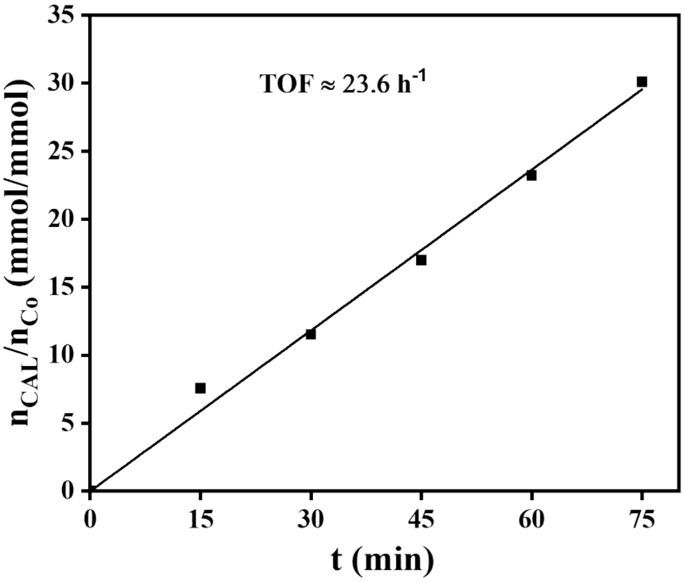

Fig. S10 The selective hydrogenation of CAL over 3Co/TCOs-H_2 catalyst.

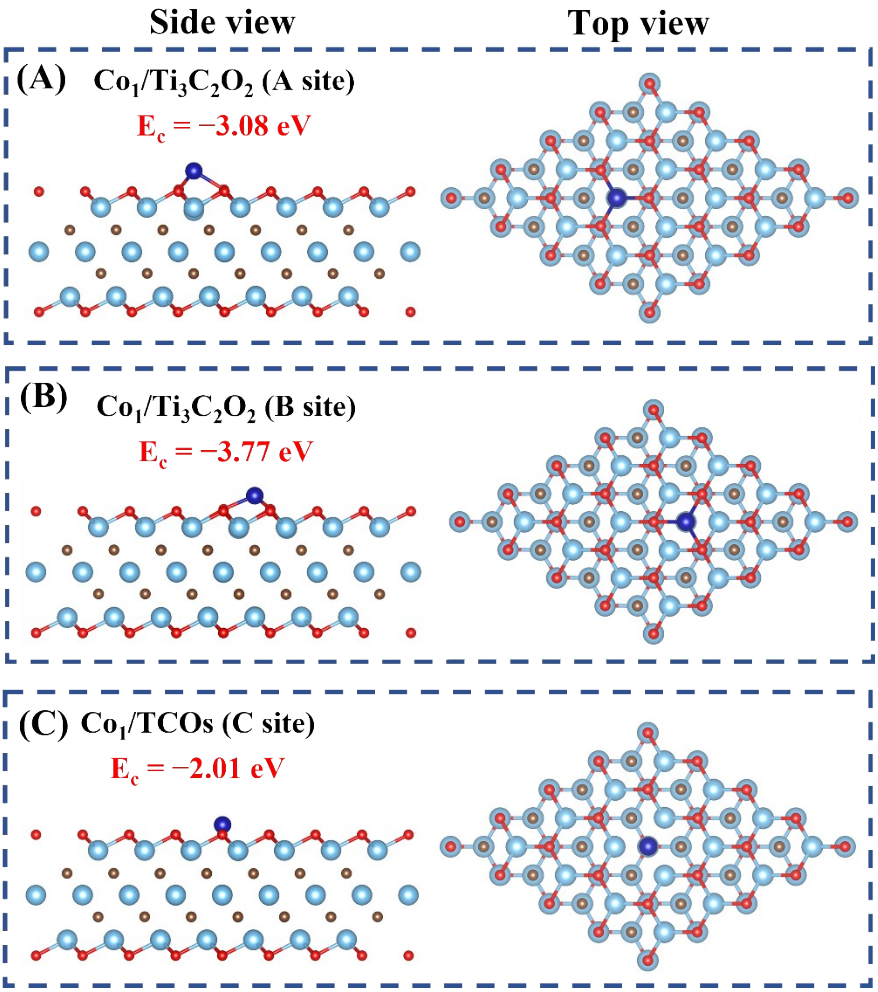

Fig. S11 The side and top view of optimized structures and corresponding combination energy (E_c) of single Co atom anchored on (A) A site, (B) B site, and (C) C site.

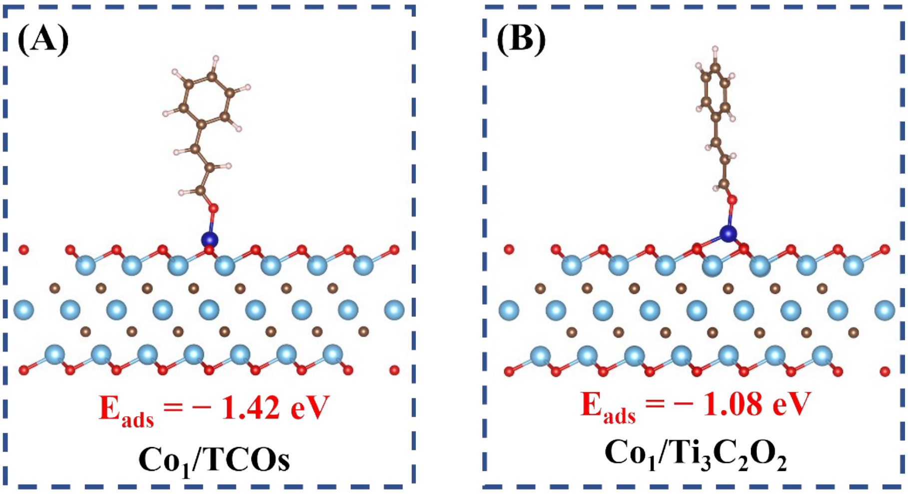

Fig. S12 The optimized configurations and adsorption energy of CAL over (A) $Co_1/TCOs$ and (B) $Co_1/Ti_3C_2O_2$.

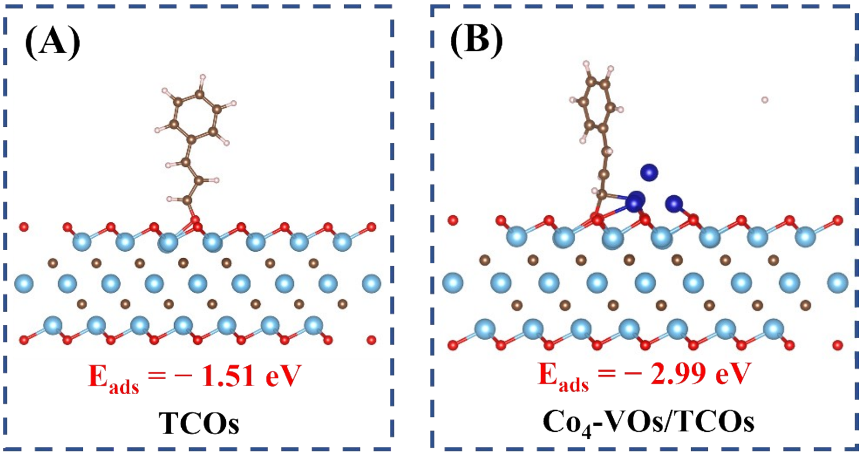

Fig. S13 The optimized configurations and adsorption energy of CAL over (A) TCOs and (B) Co_4-VOs/TCOs.

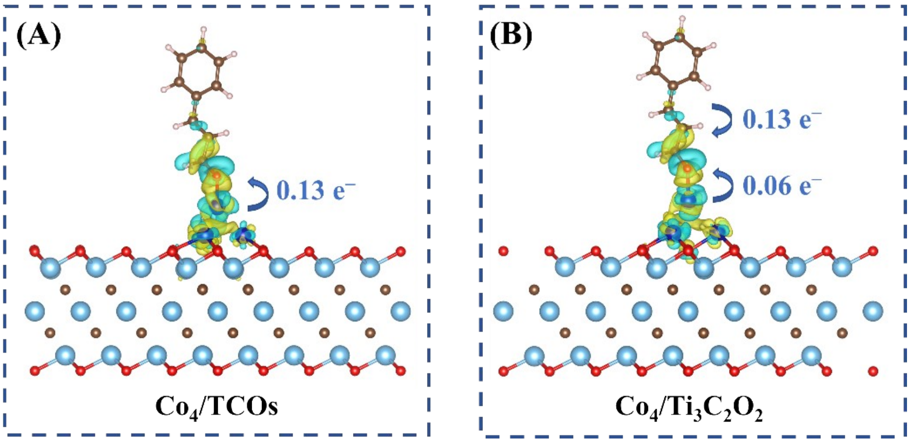

Fig. S14 Differential charge density of CAL adsorbed on (A) Co$_4$/TCOs and (B) Co$_4$/Ti$_3$C$_2$O$_2$.

Table S1 The Co amount of Co/TCOs-H_2 catalysts calculated by ICP results.

Catalyst	Co content（wt%）
1Co/TCOs-H_2	0.92
3Co/TCOs-H_2	2.84
5Co/TCOs-H_2	4.15
10Co/TCOs-H_2	8.18
spent 3Co/TCOs-H_2	2.82

Table S2 The structural properties of *y*Co/TCOs-H_2 catalysts calculated by BET methods.

Catalyst	S_{BET} ($m^2 \cdot g^{-1}$)	V_p ($cm^3 \cdot g^{-1}$)	D_{pore} (nm)
1Co/TCOs-H_2	39.57	0.08	6.59
3Co/TCOs-H_2	67.51	0.12	6.01
5Co/TCOs-H_2	63.67	0.09	4.91
10Co/TCOs-H_2	62.34	0.11	5.57
3Co/TC-H_2	64.20	0.13	7.12

Table S3 H_2 chemisorption and metal dispersion degree of several samples.

Samples	H_2 uptake (μmol·g^{-1})	Co dispersion (%)
3Co/TC-H_2	3.56	0.75
3Co/TCOs-H_2	22.86	4.49
Spent 3Co/TCOs-H_2	5.92	1.24

Table S4 Constitution of surface O species and F/O calculated from XPS results.

Sample	Proportion of O species (%)					
	$O_{lattice}$	C−Ti−O	O_{ad}	Ti−OH	C−OH/H_2O	F/O
TC	20.4	17.1	N/A	41.7	20.8	1.08
TCOs	35.3	26.1	11.7	10.6	16.3	0.60
TCOs-H_2	31.0	26.3	13.7	8.4	14.9	0.96
3Co/TCOs	49.7	15.3	13.8	9.4	11.8	0.13
3Co/TCOs-H_2	31.8	27.1	11.2	11.8	18.1	0.18
3Co/TC-H_2	32.3	40.3	8.4	10.9	8.1	0.18
1Co/TCOs-H_2	12.1	48.3	9.7	13.0	16.9	0.18
5Co/TCOs-H_2	19.8	22.4	14.2	14.2	29.5	0.16
10Co/TCOs-H_2	18.2	12.6	14.6	15.0	39.5	0.15

Table S5 Constitution of Co species calculated by XPS results.

Sample	Proportion of Co species (%)		
	Co^{3+}	Co^{2+}	Co^0
3Co/TCOs	61.7	38.3	-
3Co/TCOs-H_2	44.8	40.8	14.3
Spent 3Co/TCOs-H_2	50.5	30.8	18.7
3Co/TC-H_2	25.8	54.9	19.2

Table S6 Hydrogenation properties of reactivated 3Co/TCOs-H_2 catalyst.

Recycle	Conversion (%)	Selectivity (%)			
		HCAL	HCOL	COL	Others
Fresh catalyst	96.9	2.2	20.8	69.5	7.5
	67.9	10.3	7.1	72.1	10.5
Reactivated cycle 1	95.4	3.9	19.2	68.3	8.6
	78.8	8.5	7.8	71.2	12.5
Reactivated cycle 2	92.8	4.0	18.6	70.6	6.8
	62.5	10.3	9.7	69.1	10.9
Reactivated cycle 3	91.6	5.4	18.9	68.3	7.4

Reaction conditions: 1.0 g of CAL; 30 mL of isopropanol; 0.2 g of catalyst; reaction temperature of 120 °C; H_2 pressure of 1.0 MPa; and reaction time of 5 h.

Table S7 Hydrogenation properties of 3Co/TCOs-H_2 catalyst with different solvents.

Solvent	Conversion (%)	Selectivity (%)			
		HCAL	HCOL	COL	Others
Water	32.8	22.9	10.0	67.1	0.0
Methanol	97.3	0.7	12.6	25.8	60.9
Ethanol	90.0	1.5	5.7	23.9	68.9
Isopropanol	96.7	1.9	22.7	65.5	9.9
cyclohexanol	66.1	9.0	13.8	64.7	12.5

Reaction conditions: 1.0 g of CAL; 30 mL of isopropanol; 0.2 g of catalyst; reaction temperature of 120 °C; H_2 pressure of 1.0 MPa; and reaction time of 5 h.

Table S8 The bader charge quantity of Co atoms and unsaturated bond of CAL for several samples.

Catalysts	Charge quantity					
	Co1	Co2	Co3	Co4 (top)	C=O	C=C
$Co_4/Ti_3C_2O_2$	8.27	8.33	8.28	9.05	–	–
$Co_4/Ti_3C_2O_2$-CAL	8.28	8.34	8.30	8.80	10.42	8.01
Co_4/TCOs	8.63	8.61	8.63	8.96	–	–
Co_4/TCOs-CAL	8.64	8.64	8.63	8.75	10.37	8.14
CAL	–	–	–	–	10.23	8.14

Reference

1. P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953-17979.

2. J. Hafner, *J. Comput. Chem.*, 2008, **29**, 2044-2078.

3. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.

4. G. Henkelman, A. Arnaldsson and H. Jónsson, *Computational Materials Science*, 2006, **36**, 354-360.