Supporting Information

Room Temperature Activation of C-H Bond in the Ethane

Dehydrogenation over a Cu/TiO₂ Catalyst

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1. Experimental

1.1 Materials

The commercial P25 (Degussa) and the Cu(NO₃)₂·3H₂O (99%) are used as TiO₂ and Cu precursor. NaBH₄ (98%) and any other reagents were purchased from Kelong Chemical Co., Ltd., China. Ar (\geq 99.999%) and C₂H₆ (\geq 99.99%) was supplied by Southwest chemical design institute of China. All of the chemicals above were used without any purification.

1.2 Sample preparations

TiO₂-supported cooper catalysts were synthetized by a facile impregnationreduction method. Typically, commercial TiO₂ was dispersed in distilled water. An appropriate amount of Cu(NO₃)₂·3H₂O solution (0.5 mgCu/ml) were added to above TiO₂ suspension solution according to the mass fraction of Cu, varying from 0.2 to 2%. After sonicating for 20 min, excessive NaBH₄ solution was added dropwise to the suspension under vigorous stirring. The mixture was aged overnight and the prepared catalysts were washed and separated by centrifugation with deionized water and absolute ethyl alcohol for several times. The final Cu/TiO₂ catalyst obtained after vacuum dried at 333 K for 10 h. Other metal supported TiO₂ was synthetized by replacing Cu(NO₃)₂·3H₂O with HAuCl₄·xH₂O, H₂PtCl₆·6H₂O, Co(NO₃)₂·3H₂O and Fe(NO₃₎₂·9H₂O.

1.3 Photocatalytic ethane dehydrogenation

The photocatalytic reaction was carried out in a 100 ml autoclave equipped with

a visual quartz window on the top of the reactor. The reactant gas of Ar and C_2H_6 were in a ratio of 9:1 controlled by flow meters. Before reaction, 25 mg of catalyst was spread evenly on a sample stage and the initial air in the reactor was completely replaced by the reactant gas. After that, the reactant gas was introduced to the reactor until the pressure get to 0.2 Mpa and the constant temperature water bath outside the reactor was set to 293 K. The photocatalytic reaction started with the UV lamp (CEL-HXF300, Ceaulight, Beijing) on.

After irradiation for a certain time, the product was analysed by an online gas chromatography (Micro GC 490, Agilent Technologies Inc.,), equipped with two thermal conductivity detectors (TCD). The two TCDs are connected to a PoraPLOT U(PPU) column (inner diameter, 0.25 mm, length, 10 m, film thickness, 8 μm) and a CP-Molesieve 5Å(MS5A) column (the same specification as PoraPLOU U column), respectively.

1.4 Calculation of ethane conversion and ethylene selectivity

According to the carbon deposition detection and GC results, there was no carbon produced and methane. CH_4 , C_2H_4 and H_2 the only products observed. So, all the ethane was converted to CH_4 , C_2H_4 and H_2 . Herein,

Mole of ethane consumed= $0.5 \times Mole$ of methane + Mole of ethylene

 $\frac{\text{Mole of ethane consumed}}{\text{Conversion of ethane}=} \times 100\%$

Selectivity of ethylene= $\frac{\text{Mole of ethylene produced}}{\text{Mole of ethane consumed}} \times 100\%$

1.5 Characterization

The Raman spectrum (Raman, DXR Microscope, Thermo Fisher) was used to measure the chemical bonds. The crystal structure of the samples and the particle size of the Cu species were measured by X-ray diffraction (XRD, Dandong DX2700) with Cu K α radiation (λ =51.5406Å) in the 2 θ range from 10° to 90°. The morphologies of samples were observed by high resolution transmission electron microscopy (HRTEM, FEI Tecnai G20) and element mapping. The chemical compositions of the samples were measured by X-ray photoelectron spectrocopy (XPS, Thermo Escalab 250Xi) and Auger electron spectroscopy (XAES) equipped with an Al K α irradiation source (h ν =1486.7 eV). Cu⁺ spices were detected by *in situ* DRIFT spectra of CO absorption. The optical properties of the samples were measured by UV-vis DRS (PE Lambda 750s).

1.6 Density functional theory (DFT) Calculation

DFT calculations were performed using the "Vienna *ab initio* simulation package" (VASP5.4) and a generalized gradient correlation function. A plane-wave basis set with a cut-off energy at 400 eV and the projector-augmented wave method framework was used. The Gaussian smearing width was set to 0.2 eV. The Brillouin zone was sampled with a $3 \times 3 \times 1$ Monkhorst Pack grid. All atoms were converged to 0.01 eV Å⁻¹. Anatase was selected as the model of P25, and the 2×2 supercell include TiO₂ with 48 oxygen atoms, and 24 titanium atoms. The supercells of TiO₂ were relaxed. For subsequent C₂H₄ and C₂H₆ adsorption/activation calculation, the 2 \times 2 supercell of TiO₂ was further used, respectively. Then, electronic localization function, charge difference density and density of states between catalyst surface and adsorbed molecules were carefully investigated by a VASP code.

1.7 *In situ* diffuse reflectance FTIR spectroscopy (DRIFTS) investigation of photocatalytic ethane dehydrogenation reaction

In situ infrared spectra were investigated by a FT-IR spectrometer (Thermo NICOLET iS50 FT-IR) equipped with a visual reaction cell (Harrick). The catalyst was filled in the reaction chamber. Prior to the reactant gas absorption, the sample was degassed by Ar for 30 min at 110 °C. The background spectrum was collected after the temperature lowered to room temperature. The reactant gas (50 ml/min of C_2H_6 , 50 ml/min of Ar) was then introduced into the reaction chamber. After adsorption for 10 min, close the inlet and outlet valves and turn on the UV-light source (CEL-HXF300, Ceaulight, B. During 10 min of adsorption and 90 min of irradiation, the FTIR spectra were recorded automatically every two minutes.)



Figure S1. The stability test of 1%-Cu/TiO₂ with 5 times recycle experiment



Figure S2. The Raman spectra of x%-Cu/TiO₂(x=0, 0.2, 0.5, 1, 1.5, 2)



Figure S3. The particle size distribution over the 2%-Cu/TiO_2 catalyst



Figure S4. TEM images of EDS mapping for Cu, Ti and O



Figure S5. O 1s XPS spectra of x%-Cu/TiO₂ (x=0.2, 1, 2) samples



Figure S6. Cu/TiO₂ models



Figure S7. the electronic location function (ELF) results of Cu species on TiO_2



Figure S8. The DOS result of TiO_2, Cu_{4S}/TiO_2, Cu_{4C}/TiO_2 and Cu_{16C}/TiO_2



Figure S9. Ethane optimized absorption on different model



Figure S10. Ethylene optimized absorption on different model



Figure S11. Spin-trapping ESR spectra under UV light irradiation for 10 min: (a) e^{-} , (b) \cdot OH, (c) solid state for h^+ of x%-Cu/TiO₂.



Figure S12. The UV-Vis DRS results of x%-Cu/TiO₂

Catalyst	Production (μ mol/g _{cat})			Conversion (%)	C ₂ H ₄ Selectivity (%)
	H_2	CH_4	C_2H_4		
Au/TiO ₂	26.01	42.19	15.36	0.08	15.40
Pt/TiO ₂	116.42	44.46	2.51	0.37	2.74
Cu/TiO ₂	587.60	16.56	533.46	1.70	98.41
Co/TiO ₂	17.51	2.32	4.69	0.06	50.30
Fe/TiO ₂	6.67	5.18	4.47	0.02	30.14
Equilibrium ^b				8.77×10 ⁻⁷	

Table S1. Photocatalytic activities of different metals loaded on TiO₂^a

a Reaction condition: Ar: $C_2H_6 = 9:1$, 25 mg of catalyst, a 1 h irradiation time, 0.2 MPa, and 293 K.

b The equilibrium data of ethane dehydrogenation were simulated by Aspen Plus.