Supporting Information

Hydrodechlorination under O_2 Promote Catalytic Oxidation of CVOCs over Pt/TiO$_2$ Catalyst at Low-temperature

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Summary: 18 Pages, 1 Table, and 12 Figures

MATERIAL AND METHODS

Catalyst Preparation

Pt/TiO$_2$ catalyst wit Pt content of 0.5 wt.% was prepared by a wet impregnation method. Typically, 100 mL solution with H$_2$PtCl$_6$ concentration of 10 g·L^{-1} was firstly prepared. 4.2 mL H$_2$PtCl$_6$ solution was added into 30 mL ultrapure water, then 4.0 g TiO$_2$ (Anatase, T299213-500g, Aladdin) was added into the solution. The solution was dried at 80 °C under magnetic stirring. After that, the obtained sample was calcined at 450 °C for 3 h in a muffle furnace and then calcined in the presence of 5.0% H$_2$/Ar at 450 °C for another 3 h.

Activity Measurement

Activity of Pt/TiO$_2$ catalyst in the oxidation of vinyl chloride was measured in a fixed-bed reactor with a quartz tube of inner diameter as 8 mm. In order to avoid the thermal effect, 0.8 g catalyst (40-60 mush) was mixed with 0.8 g quartz sand (40-60 mush). The mixed gas (800 mL/min) contained 500 ppm vinyl chloride, 20% O$_2$, 1000 ppm H$_2$ (when used), and balanced with N$_2$ (space velocity of 60,000 mL·g^{-1}·h^{-1}). An IGS FT-IR analyzer (Thermo Scientific, USA) was used to detect the concentration of vinyl chloride, HCl, and CO$_2$ in the mixed gas. The conversion of vinyl chloride (x_{VC}), yield of CO$_2$ (Y_{CO2}) and HCl (Y_{HCl}) were calculated by the following equations.

$$x_{VC} = \frac{C_{VC,in} - C_{VC,out}}{C_{VC,in}}$$

$$Y_{HCl} = \frac{C_{HCl}}{C_{VC,in}}$$

$$Y_{CO2} = \frac{C_{CO2}}{C_{VC,in} \times 2}$$

where $C_{VC,in}$ is the concentration of vinyl chloride in the inlet the reactor; $C_{VC,out}$, C_{HCl} and

C_{CO2} are the concentration of vinyl chloride, HCl and CO_2 in the outlet of the reactor.

The turnover frequency (TOF) of the catalyst at 225 °C was calculated by the following formula:

$$TOF = \eta_{VC} F_{VC} \frac{M_{Pt}}{m_{cat} X_{Pt} D_{Pt}}$$

Where η_{VC} was VC conversion (%) at 225 °C, F_{VC} was the VC flow rate ($mol \cdot s^{-1}$), m_{cat} was the weight of catalyst (g), M_{Pt} was the relative atomic mass of Pt ($g \cdot mol^{-1}$), X_{Pt} was the Pt mass fraction in the catalyst (%) and DPt was the dispersion of Pt on the catalyst (%).

Characterizations

N_2 adsorption-desorption isotherm was recorded at -196 °C on a NOVA 2000e surface area and pore size analyzer (Quantachrome, USA) and the specific surface area of the catalyst was calculated by Brunauer-Emmett-Teller (BET) method. XRD was collected on an X'Pert Pro XRD diffractometer (Panalytical, Netherlands) with Cu Kα radiation. XPS was measured on an ESCALAB 250 spectrometer with Al Kα radiation (Thermofisher, USA). Raman spectroscopy was recorded on a Renishaw inVia Qontor Raman spectrometer (Renishaw, UK) at 532 nm.

Temperature-programmed surface reaction-Mass spectrum (TPSR-MS) was carried out on a Quantachrome ChemBET-3000 TPR-TPD chemisorption analyzer (Quantachrome, USA) with an online MS (OmniStar GSD 320, Pfeiffer, Germany) as detector. 0.05 g catalyst was pretreated under 10.0% H_2/Ar at 400 °C for 1 h and then the temperature was cooled to room temperature. After that, mixed gas was inlet for 30 min and the temperature increased to 400 °C with 10 °C/min.

Deuterium gas (D_2, 99.999%, SUZHOU CHANGYOU GAS, China) was used in isotope experiment.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) were performed on a Tensor 37 FTIR (Bruker, German) with a mercury-cadmium-telluride (MCT) detector. The sample was pretreated under N_2 at 400 °C for 1 h. Then the temperature was cooled to 150 or 250 °C for 15 min and the background spectra were recorded at corresponding temperature. Finally, switching to the target gas and then the spectrum was recorded at 100 scans, 4 cm^{-1}.

DFT Calculations

Density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional were performed on Vienna Ab initio Simulation Package (VASP). Projected augmented wave (PAW) potentials was chosen to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. The DFT-D3 empirical correction method was employed to describe van der Waals interactions. Geometry optimizations were performed with the force convergency smaller than 0.05 eV/Å. Gamma Scheme k-points of 1 × 1 × 1 was applied for all the calculations. The atoms at bottom were fixed in all the calculations. DFT + U approach was introduced to Ti treat the highly localized 3*d* states, using parameters of U–J = 4.0 eV. Spin-polarization effect was also considered. A model of Pt-cluster with 4 Pt atoms supported on anatase (101) was built.[1,2]

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Supplementary Table

Table S1 Activity of reported typical catalysts for vinyl chloride oxidation.

Catalyst	Space velocity (mL·g^{-1}·h^{-1})	Conversion temperature* (°C)	Refs.
Ru-Ce$_{0.5}$Zr$_{0.5}$O$_2$	60,000	T_{90} = 262, T_{50} = 220	S1
Ru/Co$_3$O$_4$	50,000	T_{90} = 278, T_{50} = 250	S2
Ru/Sn-MFI	30,000	T_{90} = 306, T_{50} = 264	S3
Pt/WO$_3$-CeO$_2$	15,000	T_{90} = 254, T_{50} = 210	S4
Pt/CeO$_2$	15,000	T_{90} = 280, T_{50} = 230	S5
Pt/Al$_2$O$_3$	80,000	T_{90} = 307, T_{50} = 231	S6
Pt/Al$_2$O$_3$	80,000	T_{90} = 307, T_{50} = 231	S6
Pt/TiO$_2$	60,000	T_{90} = 309, T_{50} = 268	This work
Pt/TiO$_2$ (1000 ppm H$_2$)	60,000	T_{90} = 198, T_{50} = 164	This work

*T_{50} and T_{90} represented temperatures corresponding to the toluene conversion of 50% and 90%.

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S5. Qifeng Zhang, Jiyuan Liu, Chen Wang, Yanglong Guo, Wangcheng Zhan, Li Wang, Xueqing Gong, Yun Guo. Chemosphere, 2022, 307, 135861.

S6. Min-Hao Yuan, Chia-Chi Chang, Ching-Yuan Chang, Wei-Chu Liao, Je-Lueng Shie, Yi-Hung Chen, Dar-Ren Ji & Chao-Hsiung Wu. Journal of Environmental Science and Health, Part A 2015, 50, 1187-1193.
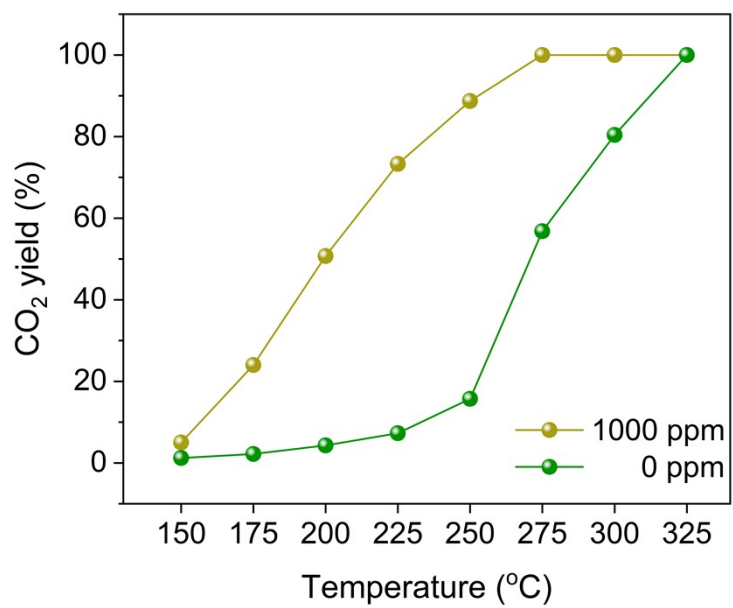
Supplementary Figures

Figure S1. CO_2 yield on Pt/TiO_2 catalyst in the absence and presence of H_2.
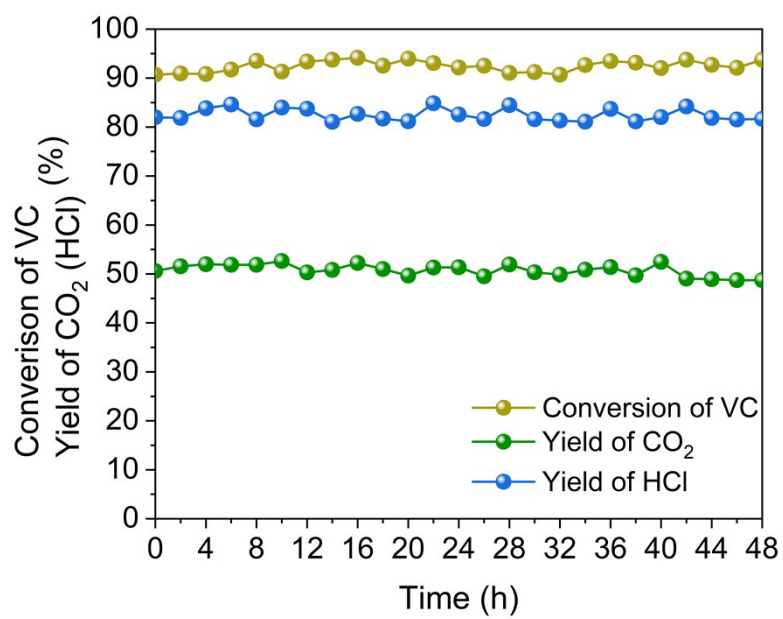
Figure S2. Stability of Pt/TiO$_2$ catalyst in oxidation of VC with H$_2$.
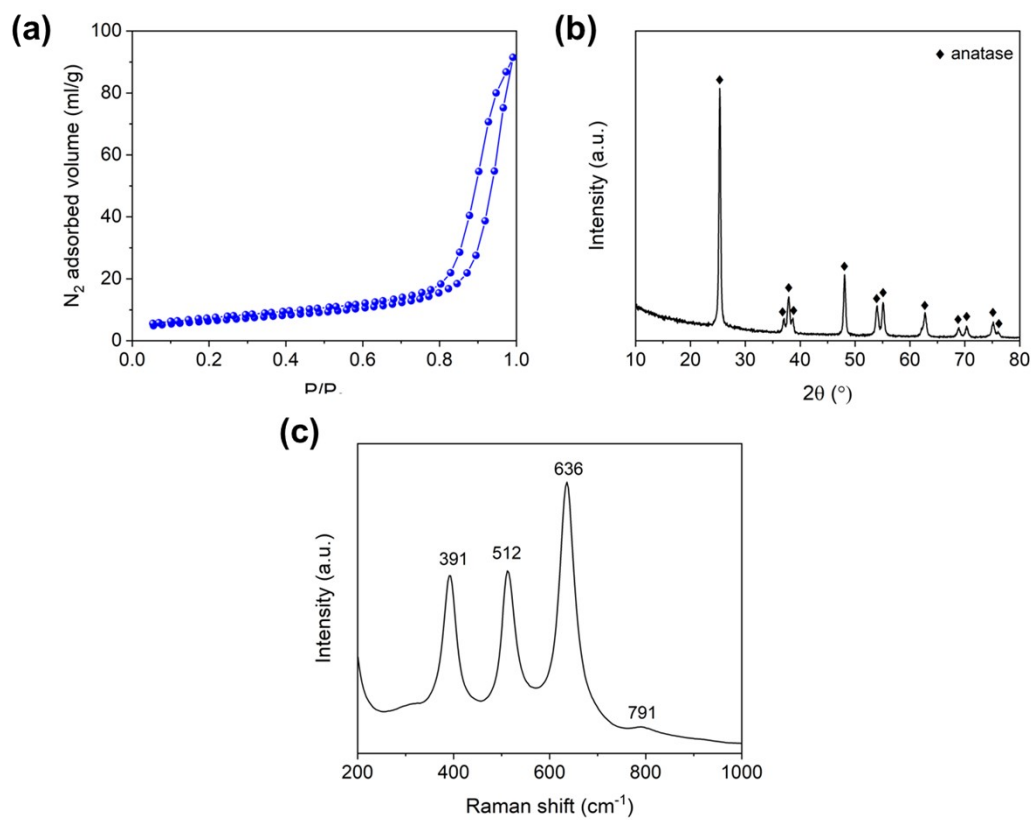
Figure S3. (a) N_2 adsorption-desorption isotherm, (b) XRD and (c) Raman result of the catalyst.
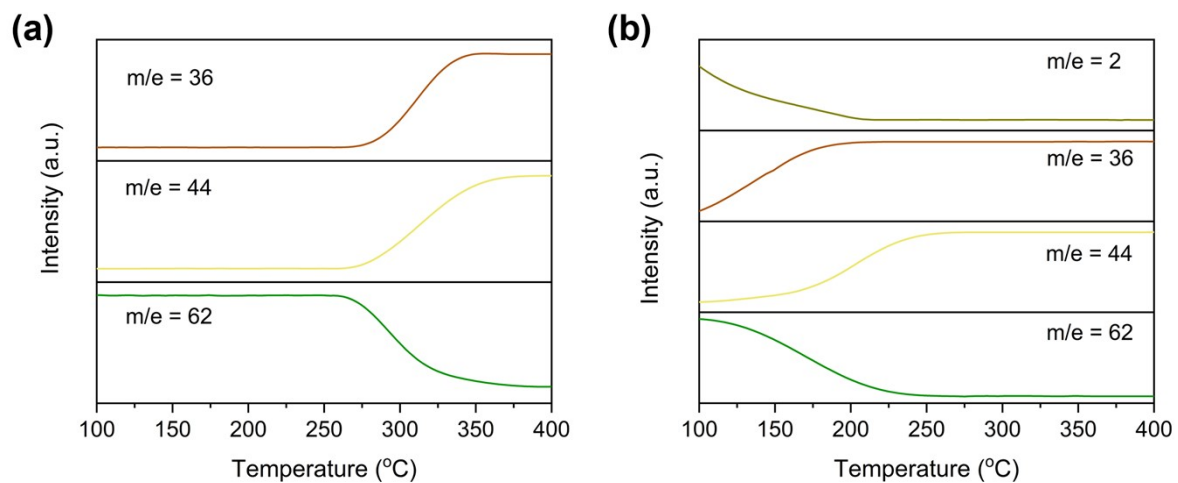
Figure S4. TPSR-MS result of (a) O_2 + VC and (b) O_2+VC+H_2 over Pt/TiO$_2$ catalyst.
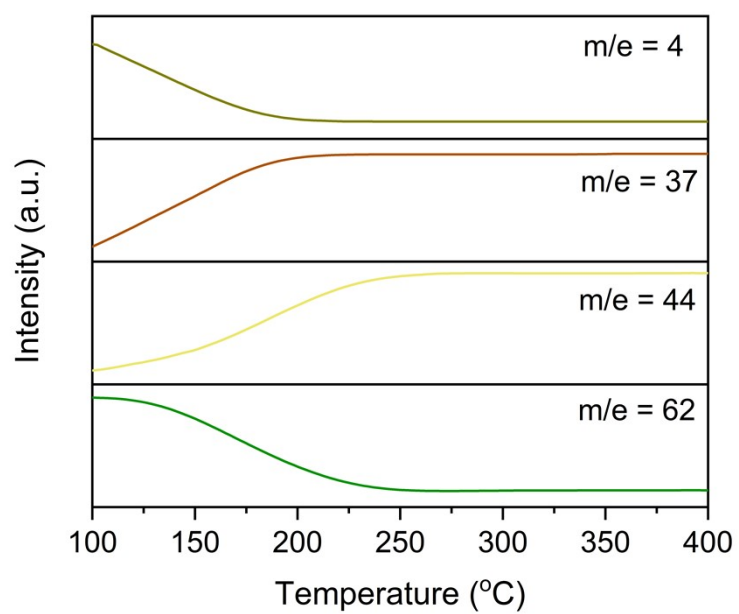
Figure S5. TPSR-MS result of O_2+VC+D_2 over Pt/TiO$_2$ catalyst.
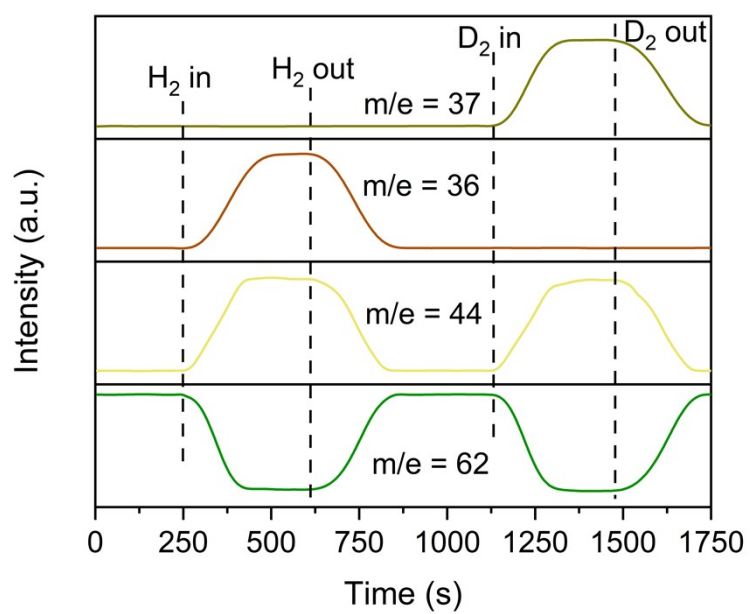
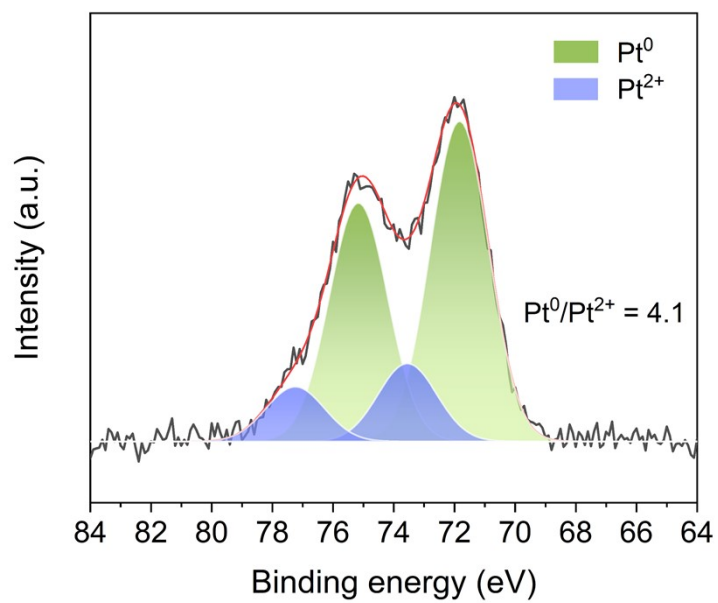**Figure S6.** The effect of H_2 and D_2 on the oxidation of VC over Pt/TiO$_2$ catalyst.

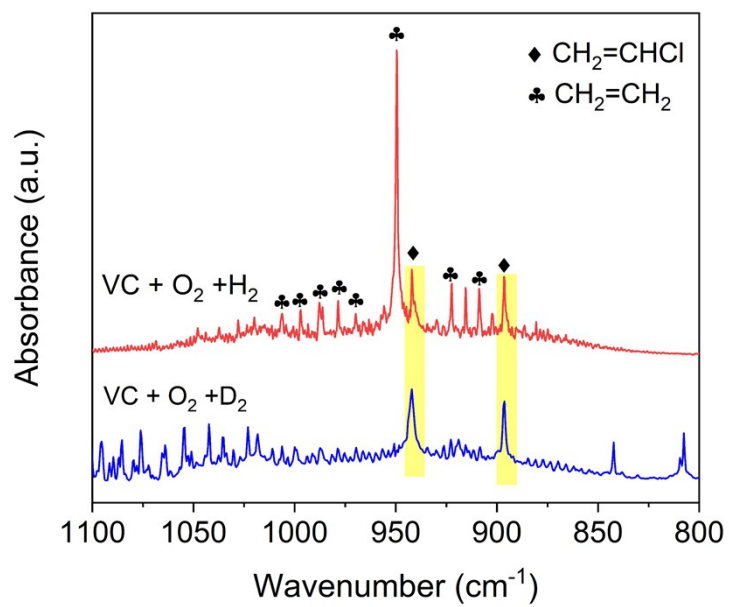**Figure S7.** XPS result of Pt 4f of Pt/TiO$_2$ catalyst.

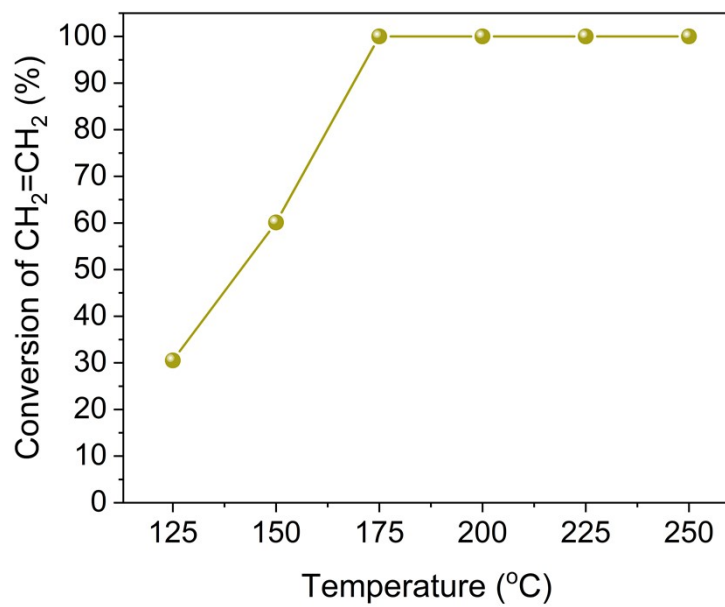**Figure S8.** FT-IR spectra of mixture gas from reactor outlet at 200 °C.

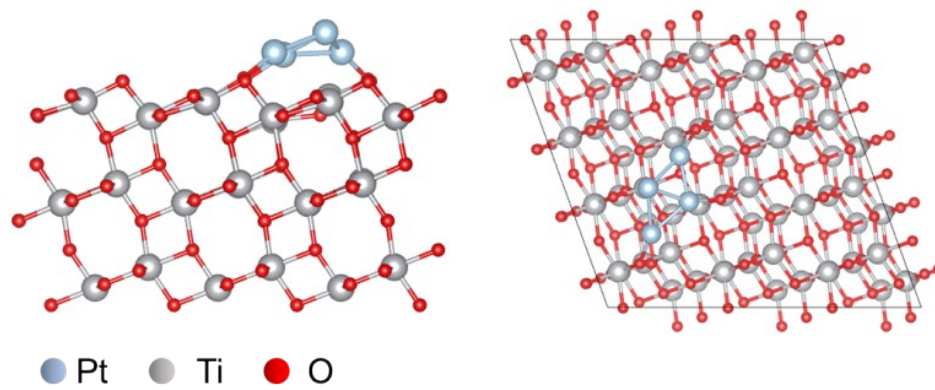**Figure S9.** Conversion of $CH_2=CH_2$ on Pt/TiO_2 catalyst.
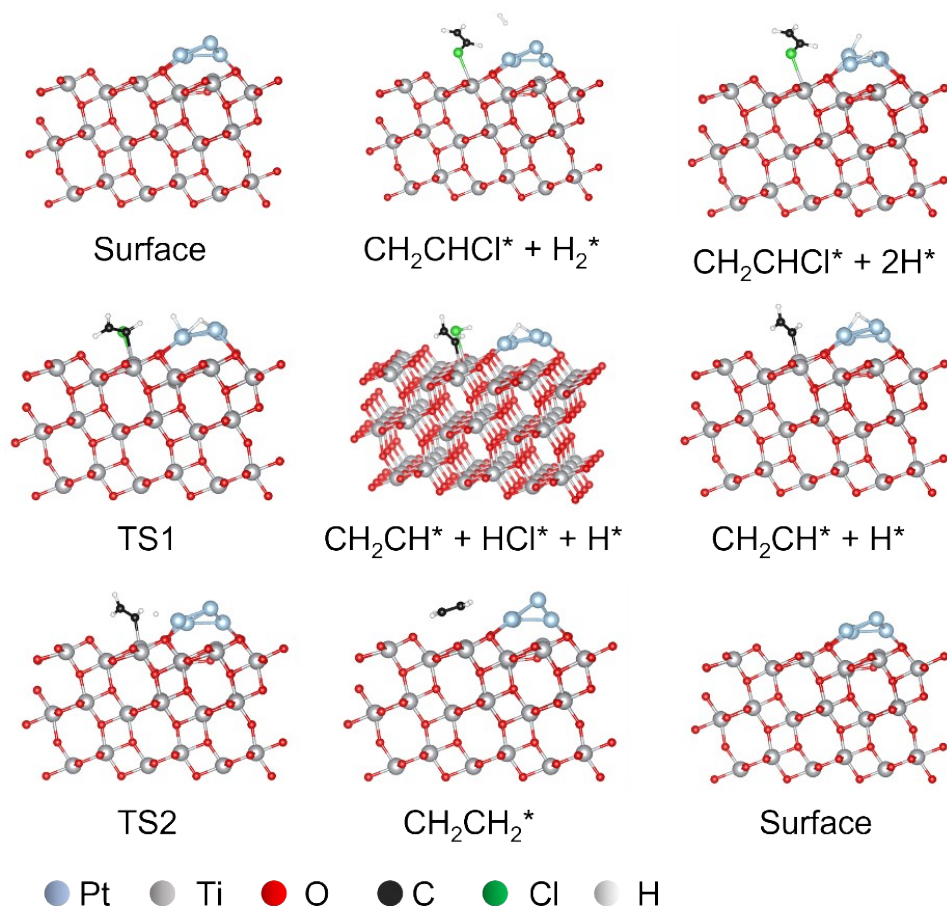
Figure S10. Model of Pt/TiO$_2$ catalyst calculated.

Figure S11. The optimized structures of intermediates and transition states in hydrogenation of CH_2CHCl on Pt/TiO_2 surface.
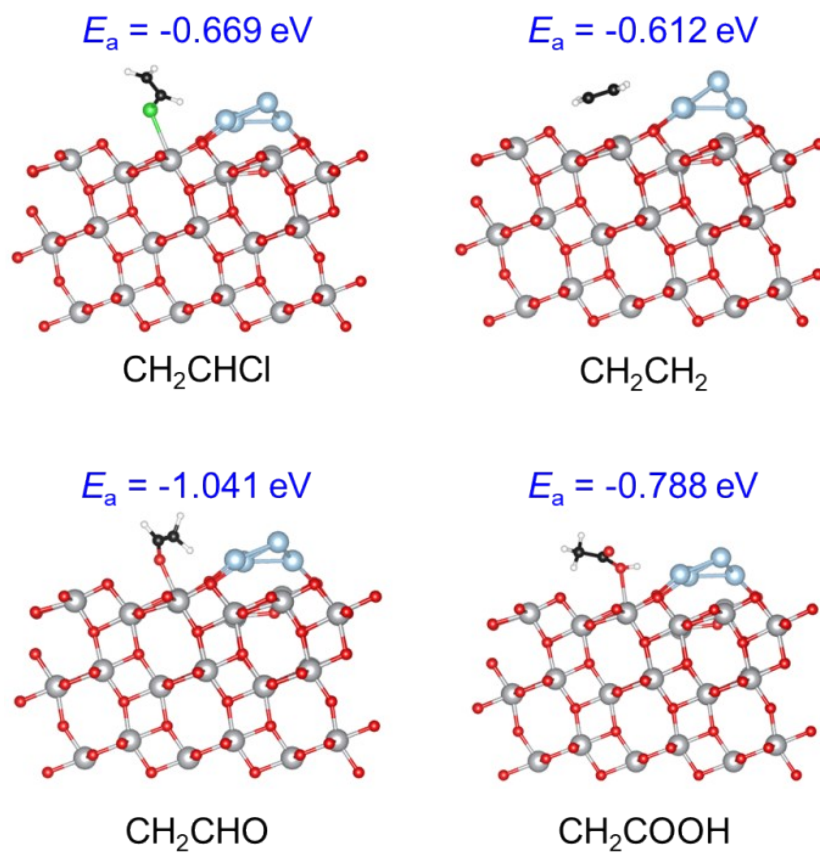
E_a = -0.669 eV E_a = -0.612 eV

CH_2CHCl CH_2CH_2

E_a = -1.041 eV E_a = -0.788 eV

CH_2CHO CH_2COOH

Figure S12. The adsorption energy of CH_2CHCl, CH_2CH_2, CH_2CHO and CH_2COOH on Pt/TiO_2 surface.

Discussion of potential competing pathways in oxidation of C_2H_4.

As shown in Fig. S8 and Fig. 4b, $CH_2=CH_2$ was formed by hydrodechlorination of VC under O_2 on Pt/TiO_2 catalyst. The partial oxidation of $CH_2=CH_2$ might occur in the presence of O_2 over the catalyst and formed ethylene oxide (C_2H_4O), acetaldehyde CH_3CHO), acetic acid (CH_3COOH). FT-IR spectra of mixture gas from reactor outlet at 200 °C were shown in Fig. 2 and S8. As the figure showed, besides HCl, CO_2, CH_2CH_2 and CH_2CHCl, no bands assigned to other products (C_2H_4O, CH_3CHO, CH_3COOH, etc.) could be found, thus CH_2CH_2 should be completely oxidized to CO_2 over Pt/TiO_2 catalyst. In addition, catalysts should have a large influence on the oxidation of CH_2CH_2. On Ag-based catalyst, CH_2CH_2 was partially oxidized to C_2H_4O.[1] However, for Pt-based catalysts, previous works indicated that CO_2 was easy to form by oxidation of CH_2CH_2.[2]

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