Supplementary Material

High-Stability Ce-TiO_2 Catalyst for the Self-Condensation of Cyclopentanone

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S1 Experimental section

S1.1 Evaluation of catalytic activity

The conversion of CPO, yield and selectivity of CPECPO were calculated using the internal standard method, and cyclohexanol was selected as the internal standard. The relative mass correction factors of CPO and CPECPO were determined to be 1.1029 and 1.2179, respectively.

Conversion of CPO (%) = (moles of CPO in the feedstock – moles of CPO in the products) / (moles of CPO in the feedstock) ×100%

Selectivity of CPECPO (%) = (Carbon moles of products) / (Carbon moles of reagents consumed) ×100%

Yield of CPECPO (%) = Conversion of CPO × Selectivity of CPECPO

S2 Characterization of Catalyst

X-ray diffraction was detected by a Rigaku D/max-2500 X-ray diffractometer (Rigaku Co., Ltd., Japan) under the following operating conditions: Cu rotating anode target, scanning range: 10~90°, scanning rate: 8 °/min. The chemical state of the elements on the catalyst surface was analyzed using the K-Alpha type photoelectron spectrometer produced by Thermo Scientific in the United States. The excitation source was monochromatic A1-Ka (1486.6 eV), the light spot was 400 μm, the voltage was 12 kV, the scanning step size was 1 eV, and the energy range was 150 eV. The precise binding energy (±0.1 eV) was equivalent to the position determination of the external C 1s at 284.8 eV. Using the Fourier Transform Infrared Spectrometer IRAffinity-1S from Japan's SHIMADZU company, the functional groups contained in Ce-TiO_2 before and after the reaction were determined. The resolution was set at 4 cm^{-1}, the scanning rate was 0.2 cm^{-1}/s, and the wavenumber range was 400 cm^{-1} to 4000 cm^{-1}. The sample was prepared by potassium bromide pressing, and then the reaction solution was added for measurement. The catalyst samples were tested and analyzed using the TGA 2 produced by Mettler Toledo of Switzerland. The operation steps were as follows: The samples were dried under vacuum at 100 ℃ for 12 hours, then placed in an air atmosphere, and heated at a rate of 10 ℃/min from room temperature to 800 ℃, and the thermogravimetric curve was recorded. The catalyst samples were measured for their specific surface area and pore structure using the ASAP2020M+C type analyzer (from Micromeritics, USA). The surface morphology and elemental composition of the catalyst samples were tested using SEM technology. Electron microscope: Zeiss Gemini Sigma 500 field emission; Energy spectrum: Bruker 60 dual-probe energy spectrometer. Resolution: 0.8 nm @ 1 kV. Magnification:

100 x ~ 300,000 x; Acceleration voltage: 1 kV ~ 20 kV. The samples were weighed, adhered to the sample stage using conductive glue, and then subjected to gold spraying for testing.

The catalysts were tested for NH_3-TPD and CO_2-TPD using an AutoChem Ⅱ-2920 chemisorbentimeter (Micromeritics, USA). The CO_2-TPD test, for example, was performed as follows: the test sample was loaded into a U-shaped quartz tube and heated to 500 °C at a rate of 10 °C/min under helium purge for 60 min at a constant temperature to remove surface impurities. After cooling to 105 °C, CO_2 was adsorbed to saturation (30 min), followed by helium blowing for 60 min to remove physically adsorbed CO_2. After the baseline was stabilized, it was heated to 500 °C again. The amount of CO_2 resolved was recorded by a thermal conductivity detector (TCD). The NH_3-TPD test was similar.

S3 NH_3-TPD and CO_2-TPD profiles

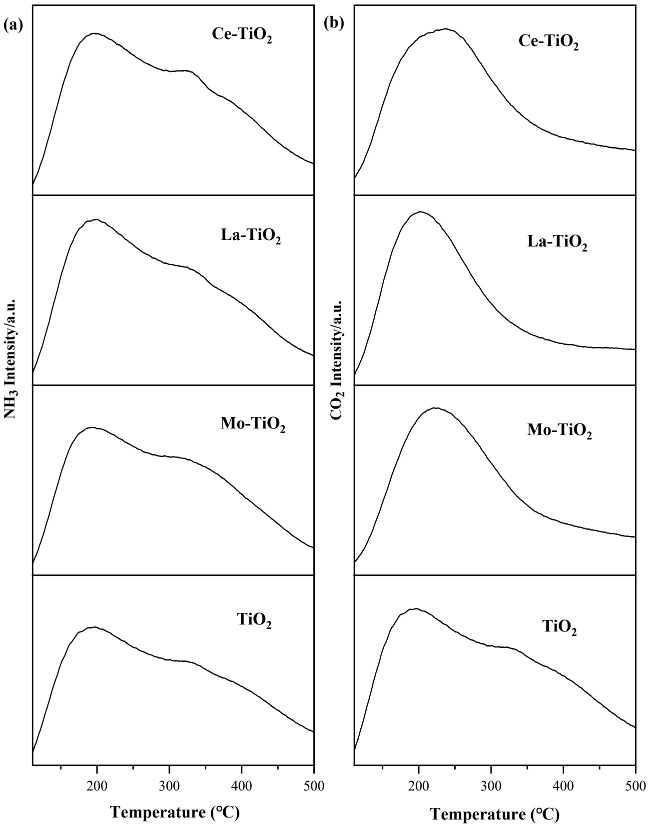

Fig. S1 NH_3-TPD (a) and CO_2-TPD (b) curves of TiO_2 modified by different modifiers

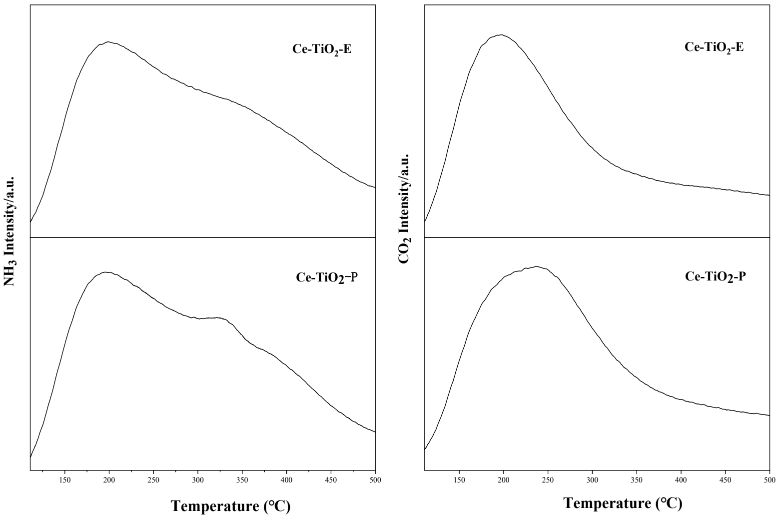

Fig. S2 NH_3-TPD(a) and CO_2-TPD(b) curves of Ce-TiO_2 with preparation methods

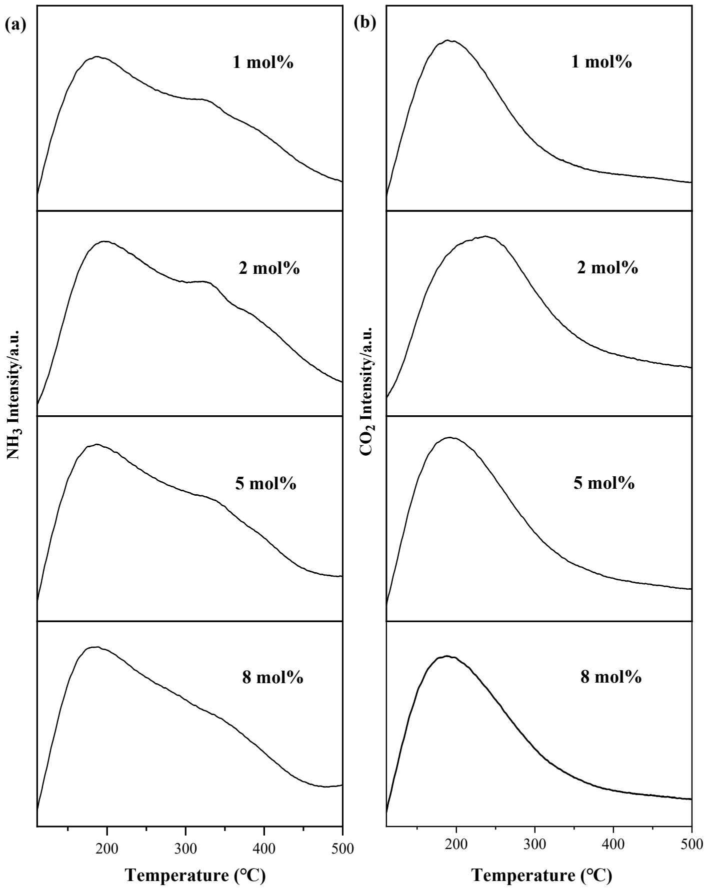

Fig. S3 NH_3-TPD(a) and CO_2-TPD(b) curves of Ce-TiO_2 with different Ce content

S4 Effect of reaction conditions

S4.1 Effect of catalyst amount

The effect of catalyst amount on cyclopentanone self-condensation was investigated and the results are shown in Table S1. The catalyst amount/cyclopentanone = 10 wt.%, 12.5 wt.%, 15 wt.%, and 17.5 wt.%. It can be seen that as the catalyst amount increases, the conversion of cyclopentanone improves. However, the yield of CPECPO shows a trend of increasing first and then decreasing, and its selectivity gradually decreases. This can be attributed to the increase in catalyst amount allowing cyclopentanone to come into contact with more active sites on the catalyst surface, thereby promoting the conversion of cyclopentanone.[1] However, when the catalyst amount is excessive, 2,5-dicyclopentylidenecyclopentane-1-one, and polymers will be generated in the reaction, resulting in a decrease in the selectivity of CPECPO. When the mass ratio of the catalyst to cyclopentanone reaches 12.5 %, the conversion of cyclopentanone and the yield of CPECPO reach the highest values of 86.0% and 82.2 %, respectively. After that, further increasing the catalyst amount leads to a stable conversion and yield of cyclopentanone and CPECPO. Therefore, the catalyst amount of 12.5 wt.% is determined.

Table S1 Effect of catalyst amount on cyclopentanone self-condensation reaction

Catalyst amount / wt.%	X_{CPO} / %	Y_{CPECPO} / %	S_{CPECPO} / %
10	83.1	79.3	95.5
12.5	86.0	82.2	95.6
15	86.8	81.8	94.2
17.5	87.0	81.6	93.8

*Reaction conditions: T=170 ℃, t=2 h, solvent-free reaction.

*CPO: cyclopentanone; CPECPO: 2-cyclopentylidenecyclopentanone; X: conversion, Y: yield; S: selectivity.

S4.2 Effect of reaction temperature

Table S2 presents the reaction results of Ce-TiO_2 catalyzing the self-condensation of cyclopentanone at different reaction temperatures. The results show that when the reaction temperature increases from 150 ℃ to 180 ℃, the conversion of cyclopentanone increases. This indicates that the increase in reaction temperature helps to improve the mass transfer efficiency of cyclopentanone and enhances the interaction between cyclopentanone and the catalyst, thereby promoting the conversion of cyclopentanone.[1-3] At a temperature of 170 ℃, the conversion of cyclopentanone reaches 86.0 %, and the yield of CPECPO reaches the highest of 82.2 %. After exceeding 170 ℃, the yield and selectivity of CPECPO significantly decrease. The yield of CPECPO initially increases and then decreases, and the reason for the continuous decrease in selectivity is that the excessively high temperature causes side reactions to occur, generating 2,5-dicyclopentylidenecyclopentane-1-one, which leads to a decrease in the selectivity and yield of CPECPO.[1] In conclusion, the reaction temperature is set at 170 ℃.

Table S2 Effect of reaction temperature on cyclopentanone self-condensation

Reaction temperature / ℃	X_{CPO} / %	Y_{CPECPO} / %	S_{CPECPO} / %
150	68.2	66.1	96.9
160	73.1	70.6	96.6
170	86.0	82.2	95.6
180	88.5	72.8	82.3

*Reaction conditions: catalyst amount=12.5 wt.%, *t*=2 h, solvent-free reaction.

*CPO: cyclopentanone; CPECPO: 2-cyclopentylidenecyclopentanone; *X*: conversion; *Y*: yield; *S*: selectivity.

S4.3 Effect of reaction time

Table S3 shows the results of the Ce-TiO_2 catalyzed self-condensation of cyclopentanone under different reaction times. It can be seen that as the reaction time increases from 1 hour to 3 hours, the conversion rate of cyclopentanone increases, while the selectivity of CPECPO slightly decreases. When the reaction lasts for 2 hours, the maximum conversion of cyclopentanone reaches 86.0 %, and the yield and selectivity of CPECPO reach 82.2 % and 95.6 % respectively. When the reaction time exceeds 2 hours, the yield of CPECPO remains basically stable, its selectivity slightly decreases, although the conversion of cyclopentanone increases, the increase is relatively small. Therefore, the reaction time is set at 2 hours.

Table S3 Effect of reaction time on cyclopentanone self-condensation

Reaction time / h	X_{CPO} / %	Y_{CPECPO} / %	S_{CPECPO} / %
1	74.9	72.1	96.2
2	86.0	82.2	95.6
3	87.5	82.0	93.7

*Reaction conditions: catalyst amount =12.5 wt.%, *T*=170 ℃, solvent-free reaction.

*CPO: cyclopentanone; CPECPO: 2-cyclopentylidenecyclopentanone; *X*: conversion; *Y*: yield; *S*: selectivity.

S5 Reusability of Ce-TiO$_2$ Catalyst

Table S4 Compared the catalytic performance of this study with previously published results

Catalyst	T /°C	t /h	X_{CPO} /%	Y_{CPECPO} /%	Ref.
ZrO_2	130	3	18.4	18.4	4
La_2O_3	140	4	86.0	70.0	2
CaO	180	2	92.1	92.1	5
Mg-Al-O/HBC	170	9	95	-	6
Mg-Al-O	170	9	-	69.3	7
Mg_2Al-LDO(NO_3^-)	140	6	85.9	84.9	8
SO_3H-APG	150	4	85.53	59.05	9
TiO_2-ZrO_2	140	6	92	75.6	10
EAOAc	80	6	88.5	68.5	11
MgO-ZrO_2	130	4.5	88.2	84.6	12
Ce-Zr-O	170	9	93.71	41.12	13
TiO_2-SnO_2	150	6	92.5	79.2	14
Ce-TiO_2	170	2	86.0	82.2	this study

*CPO: cyclopentanone; CPECPO: 2-cyclopentylidenecyclopentanone; *X*: conversion; *Y*: yield

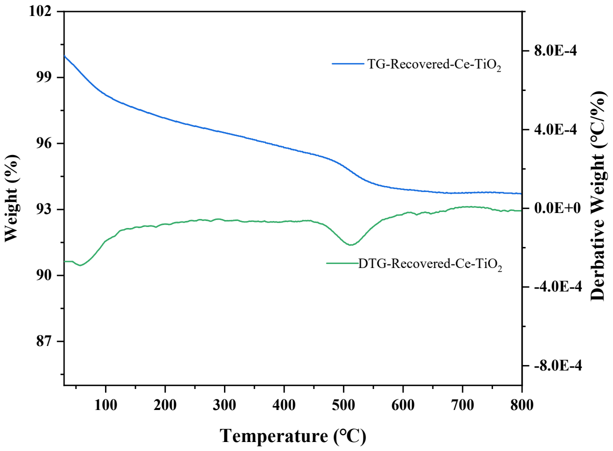

Fig. S4 TG and DTG of recovered Ce-TiO$_2$

Table S5 Textural parameters of fresh and recovered Ce-TiO_2 catalysts

Catalyst	Specific surface area/$m^2 \cdot g^{-1}$	Pore volume/$cm^3 \cdot g^{-1}$	Pore size/nm
Fresh Ce-TiO_2	232.76	0.32	5.96
Recovered Ce-TiO_2	227.60	0.30	6.18

Table S6 Acid properties of fresh and recovered Ce-TiO_2 catalysts

Catalyst	Desorption amount of NH_3				
	Peak top temperature/°C	Weak acid amount/ μmol·g^{-1}	Peak top temperature/°C	Medium acid amount/ μmol·g^{-1}	Total acid amount/ μmol·g^{-1}
Fresh Ce-TiO_2	195.8	425.9	325.3	536.1	962.0
Recovered Ce-TiO_2	228.0	481.4	360.7	453.6	935.0

Table S7 Base properties of fresh and recovered Ce-TiO_2 catalysts

Catalyst	Desorption amount of CO_2				
	Peak top temperature/°C	Weak base amount/ μmol·g^{-1}	Peak top temperature/°C	Medium base amount/ μmol·g^{-1}	Total base amount/ μmol·g^{-1}
Fresh Ce-TiO_2	188.0	112.5	265.5	267.5	380.0
Recovered Ce-TiO_2	204.4	168.6	314.5	231.4	400.0

S6 Elimination of the influence of internal and external diffusion

Table S8 Effect of stirring speed on the catalytic performance of Ce-TiO_2 catalyst

Stirring speed/rpm	X_{CPO}/%	Y_{CPECPO}/%	S_{CPECPO}/%
460	46.5	44.2	95.0
560	47.2	45.1	95.6
660	47.0	44.7	95.2
760	47.1	44.8	95.1

*Reaction conditions: T=110 ℃, t=3 h, a catalyst amount=12.5 wt.%.

*CPO: cyclopentanone; CPECPO: 2-cyclopentylidenecyclopentanone; X: conversion; Y: yield; S: selectivity.

Table S9 Effect of Ce-TiO_2 catalyst partical size on its catalytic performance

Mesh	Partical size/μm	X_{CPO}/%	Y_{CPECPO}/%	S_{CPECPO}/%
40-60	425-250	47.2	44.9	95.1
60-80	250-180	47.0	44.8	95.3
80-100	180-150	47.3	44.9	95.0
> 100	< 150	47.2	45.1	95.6

*Reaction conditions: T=110 ℃, t=3 h, a catalyst amount=12.5 wt.%.

*CPO: cyclopentanone; CPECPO: 2-cyclopentylidenecyclopentanone; X: conversion; Y: yield; S: selectivity.

S7 Validation of hypothetical response levels

Substituting m=2 and n=2 into eqn

$$\frac{dx_A}{dt} = k_+ C_{A0}^{m-1}\left(1 - x_A\right)^m - k_- C_{A0}^{n-1}\left(\frac{x_A}{2}\right)^n \#1$$

, we get

Integrating the rate equation:

$$\frac{dx_A}{dt} = k_+ C_{A0}\left(1 - x_A\right)^2 - k_- C_{A0}\left(\frac{x_A}{2}\right)^2 \#2$$

$$\frac{1}{2\sqrt{a^2 - a}}\ln\frac{\left(x_A - a\right) - \sqrt{a^2 - a}}{\left(\left(x_A - a\right) + \sqrt{a^2 - a}\right)} = \frac{C_{A0}}{a}t + C$$

Among them: $a = \frac{k_+}{\left(k_+ - \frac{k_-}{4}\right)}$

Substituting the experimental data x_A and time t into the above equation, so that $b = \frac{\left(x_A - a\right) - \sqrt{a^2 - a}}{\left(\left(x_A - a\right) + \sqrt{a^2 - a}\right)}$, then

$$\frac{1}{2\sqrt{a^2 - a}}\ln b = \frac{C_{A0}}{a}t + C$$

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(denoted as lnb) is plotted as a straight line against t (in the case of 383 K, as shown in **Fig. S5)**, indicating that the original hypothesis of a second-order reversible reaction is correct.

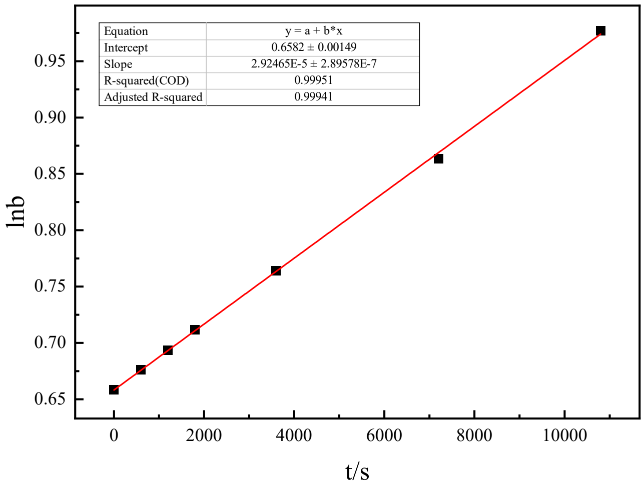

Fig. S5 lnb versus reaction time at 383K

Wan et al. investigated the activation energies of TiO_2-ZrO_2 catalyzed cyclopentanone self-condensation reaction before and after calcination,[15] and the results showed that the activation energy of uncalcined TiO_2-ZrO_2 was 63.5 kJ/mol, and that of calcined TiO_2-ZrO_2 was 40.5 kJ/mol. In comparison to this, the activation energy of the Ce-TiO_2-catalyzed cyclopentanone self-condensation reaction in this paper has a slightly higher activation energy, indicating that the reaction has a higher energy barrier and therefore requires a higher reaction temperature.

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