Supplementary Information

One-step synthesis of 2-cyclopentylcyclopentanone from cyclopentanone catalyzed by NiO-Co_3O_4/TiO_2: reaction pathway

Rui Zhang [a], Danhui Li [a], Peng Zhao[b], Lili Zhao* [a] and Hualiang An* [c]

a. College of Science and Technology, Hebei Agricultural University, Huanghua 061100, China.

b. School of Chemistry & Material Science, Langfang Normal University, Langfang, 065000, China.

c. Hebei Provincial Key Lab of Green Chemical Technology and Efficient Energy Saving, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, China.

*Corresponding author. E-mail: lilizhaohebut@163.com.(Lili Zhao); anhl@hebut.edu.cn.(Hualiang An).

S1 Effect of reaction condition

S1.1 Catalyst amount

The impact of catalyst amount on the one-step synthesis of CPCPO from CPO is shown in Table S1. As the catalyst amount increased, the conversion and yield of CPO first increased and then decreased. The amount of catalyst was 7.5 wt.%, the active center of CPO self-condensation was less, and the CPO conversion was 79.3%. With the increase of the catalyst amount, the number of hydrogenation active components increased, leading to an initial increased and then decreased in the selectivity of CPL. However, when catalyst amount exceeded 10 wt.%, increasing the catalyst amount would lead to poor hydrogenation performance and lower CPO conversion. When the catalyst amount was 10 wt.%, the catalytic performance was the best, the conversion of CPO was 86.4%, and the selectivity of CPCPO was 79%. Therefore, 10 wt.% was selected as the appropriate catalyst amount.

Table S1 The influence of catalyst amount on the one-step synthesis of CPCPO from CPO

Catalyst amount/wt.%	X_{CPO}/%	S_{CPCPO}/%	S_{CPL}/%	S_{CPCPL}/%	S_{CPECPO}/%	S_{C15}/%	Y_{CPCPO}/%
7.5	79.3	80.3	3.4	0.2	2.0	9.7	63.7
10	86.4	79.0	8.8	1.5	0	8.6	68.3
12.5	80.9	82.0	3.8	0.3	0.6	9.7	66.3

Reaction conditions: T=200 °C，P_{H2}=3 MPa，t=6 h.

X: conversion; S: selectivity; Y: yield.

S1.2 Reaction temperature

The results of the impact of reaction temperature on the one-step synthesis of CPCPO from CPO are shown in Table S2. As the reaction temperature increased, the conversion of CPO increased, while the selectivity of the target product decreased and the amount of the byproduct C15 increased accordingly. This indicates that an increase in temperature favored deeper condensation of the condensation products. Specifically, CPO underwent self-condensation to produce CPECPO, and at higher temperatures, CPECPO underwent aldol condensation to form the trimer. At the reaction temperature of 200 °C, the selectivity of CPCPO was 86.4%, the conversion of CPO was 79.0%, and the yield of CPCPO was 68.3%. Therefore, 200 °C was chosen as the appropriate reaction temperature.

Table S2 The influence of reaction temperature on the one-step synthesis of CPCPO from CPO

Reaction temperature/°C	X_{CPO}/%	S_{CPCPO}/%	S_{CPL}/%	S_{CPCPL}/%	S_{CPECPO}/%	S_{C15}/%	Y_{CPCPO}/%
190	80.6	82.4	7.8	0.9	0.6	7.3	66.4
200	86.4	79.0	8.8	1.5	0	8.6	68.3
210	87.4	77.4	3.4	0.6	4.2	12.4	67.6

Reaction conditions: a weight percentage of catalyst=10 %，P_{H2}=3 MPa，t=6 h.

X: conversion; S: selectivity; Y: yield.

S1.3 Reaction pressure

The influence of reaction pressure on the one-step synthesis of CPCPO from CPO was shown in Table S3. With the increase of pressure, the conversion of CPO also increased, the selectivity of CPCPO showed a trend of increasing first and then decreasing, and the selectivity of by-product CPL and CPCPL gradually increased. This indicated that the increase of reaction pressure promoted the direct hydrogenation of CPO and the hydrogenation of product CPCPO, while the self-condensation reaction of CPO was inhibited, which also led to the decrease of CPCPO selectivity. When the reaction pressure was 3 MPa, the selectivity of CPCPO was 86.4%, the conversion of CPO was 79.0%, and the yield of CPCPO was 68.3%. Therefore, 3 MPa was chosen as the appropriate reaction pressure.

Table S3 The influence of reaction pressure on the one-step synthesis of CPCPO from CPO

Reaction pressure/MPa	X_{CPO}/%	S_{CPCPO}/%	S_{CPL}/%	S_{CPCPL}/%	S_{CPECPO}/%	S_{C15}/%	Y_{CPCPO}/%
2	84.1	42.5	1.4	0	47.7	5.8	35.7
3	86.4	79.0	8.8	1.5	0	8.6	68.3
4	93.9	67.2	18.7	4.3	0.2	7.5	63.1

Reaction conditions: a weight percentage of catalyst=10 %，T=200 °C，t=6 h.

X: conversion; S: selectivity; Y: yield.

S2 Particle size of catalyst

To investigate the influence of internal diffusion resistance, NiO-Co_3O_4/TiO_2 was sieved into four particle size fractions for a catalyst particle size experiment, with the results presented in Table S4. It can be observed that the catalyst with different particle sizes has a relatively small impact on the selectivity of CPCPO and the conversion of CPO. This indicated that there was no internal diffusion effect within these four particle size ranges. Therefore, a catalyst with a particle size of 150-180 μm was selected for subsequent experiments.

Table S4 Effect of particle size of $NiO\text{-}Co_3O_4/TiO_2$ on the one-step synthesis of CPCPO from CPO

Entry	Particle size of catalyst/μm	X_{CPO}/%	S_{CPCPO}/%
1	150-180	86.4	79.0
2	180-250	86.2	78.7
3	250-425	85.8	79.0
4	425-850	86.1	78.8

Reaction conditions: a weight percentage of catalyst=10 %，T=200 ℃，P_{H2}=3 MPa，t=6 h.

X: conversion; S: selectivity.

S3 Cyclopentanone self-condensation catalyzed by acetic acid or ammonia

Table S5 Acetic acid or ammonia water catalyzed CPO self-condensation reaction

Additive	X_{CPO}/%	S_{CPECPO}/%
Acetic acid	4.6	79.0
Ammonia water	6.2	77.3

Reaction conditions: T=200 ℃， t=6 h, m (additive) =0.096g.