Electronic Supplementary Information (ESI)

Effect of Ni/Co mass ratio and NiO-Co_3O_4 loading on catalytic performance of NiO-Co_3O_4/Nb_2O_5-TiO_2 for direct synthesis of 2-propylheptanol from *n*-valeraldehyde

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S1. XPS spectra of NiO-Co_3O_4/Nb_2O_5-TiO_2 with different Ni/Co mass ratios before and after reaction

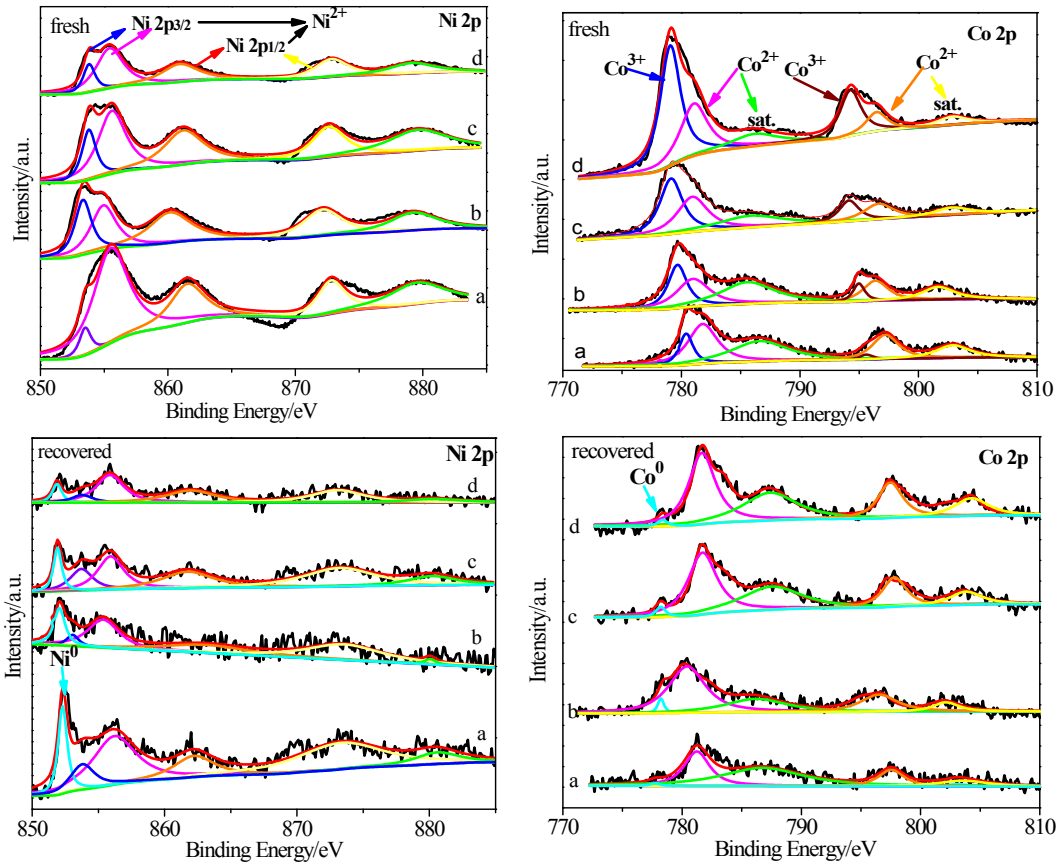

Fig. S1 Ni 2p and Co 2p XPS spectra of NiO-Co_3O_4/Nb_2O_5-TiO_2 with different Ni/Co mass ratios before and after reaction. a: Ni/Co=10; b: Ni/Co=8/3; c: Ni/Co=6/5; d: Ni/Co=4/7.

S2. Catalytic performance of NiO-Co_3O_4/Nb_2O_5-TiO_2

The NiO-Co_3O_4/Nb_2O_5-TiO_2 catalyst with a Ni/Co mass ratio of 8/3 and a NiO-Co_3O_4 loading of 14 wt.% was used to study the effect of reaction conditions.

The effect of catalyst amount was investigated and the result is listed in Table S1. With an increase of catalyst amount, *n*-valeraldehyde could be converted completely until the catalyst weight percentage reached 20 %. The selectivity of 2-PH increased firstly, reached its highest value at a catalyst weight percentage of 15 %, decreased and finally dropped to zero at a catalyst weight percentage of 20 %. The selectivity of *n*-pentanol decreased firstly, reached its lowest value at a catalyst weight percentage of 15 %, and then increased. When the catalyst weight

percentage was 10 %, the selectivity of *n*-pentanol, 2-propylheptanal and 2-PH was almost 1/3 due to less active sites. 2-PH was not formed and 2-propyl-2-heptenal and 2-propylheptanal were the main products at catalyst amount of 20 %, possibly owing to incomplete reduction of NiO.

Table S1 Effect of catalyst amount on direct synthesis of 2-PH from *n*-valeraldehyde

Catalyst amount/%	X_V/%	S_{PO}/%	$S_{2\text{-PHEA}}$/%	$S_{2\text{-PHA}}$/%	$S_{2\text{-PH}}$/%
10	100	30.7	0	34.9	31.9
12.5	100	28.1	0	0	69.6
15	100	18.2	0	0	81.4
17.5	100	25.1	0	0	73.0
20	92.5	10.6	30.6	50.4	0

Reaction conditions: *T*=200 ℃, *P*=3 MPa, *t*=6 h.
V: *n*-valeraldehyde; PO: *n*-pentanol; 2-PHEA: 2-propyl-2-heptenal; 2-PHA: 2-propylheptanal;
2-PH: 2-propylheptanol. *X*: conversion; *S*: selectivity.

The effect of reaction pressure on direct synthesis of 2-PH from *n*-valeraldehyde was investigated and the result was listed in Table S2. *n*-Valeraldehyde was not completely reduced and 2-PH was not formed at a reaction pressure of 2 MPa. The main products were 2-propylheptanal and 2-propyl-2-heptenal instead. When reaction pressure was higher than 3 MPa, *n*-valeraldehyde was reduced completely while the selectivity of 2-PH reached its optimum at reaction pressure of 3 MPa and then decreased. The selectivity of *n*-pentanol increased significantly with a decrease of 2-PH selectivity at a reaction pressure of 4 MPa.

Table S2 Effect of reaction pressure on direct synthesis of 2-PH from *n*-valeraldehyde

Reaction pressure/MPa	X_V/%	S_{PO}/%	$S_{2\text{-PHEA}}$/%	$S_{2\text{-PHA}}$/%	$S_{2\text{-PH}}$/%
2	94.7	8.2	32.8	52.8	0
3	100	18.2	0	0	81.4
4	100	33.1	0	0	59.4

Reaction conditions: a weight percentage of catalyst =15 %, *T*=200 ℃, *t*=6 h.
V: *n*-valeraldehyde; PO: *n*-pentanol; 2-PHEA: 2-propyl-2-heptenal; 2-PHA: 2-propylheptanal;
2-PH: 2-propylheptanol. *X*: conversion; *S*: selectivity.

The effect of reaction temperature on direct synthesis of 2-PH from *n*-valeraldehyde was investigated. As can be seen from Table S3, conversion of *n*-valeraldehyde was 100 % at a reaction temperature ranging from 180 °C to 210 °C. With an increase of reaction temperature,

selectivity of 2-PH increased first and then decreased while that of *n*-pentanol changed just the opposite. *n*-Valeraldehyde self-condensation is controlled by kinetics at a lower reaction temperature and the increase of reaction temperature is conducive to increasing the reaction rate. However, the reaction is controlled by thermodynamics at a higher reaction temperature and the increase of reaction temperature is not conducive to the reaction.[S1] In addition, total selectivity of both *n*-pentanol and 2-PH decreased at reaction temperature of 210 ℃, possibly due to esterification of *n*-pentanol or 2-PH with by-product *n*-pentanoic acid which was confirmed by gas chromatography-mass spectrometry (GC-MS) analysis results. This indicated that a higher reaction temperature promoted the occurrence of side-reactions such as esterification. Selectivity of 2-PH was the highest (81.4 %) and that of *n*-pentanol was the lowest (18.2 %) at a reaction temperature of 200 ℃.

Table S3 Effect of reaction temperature on direct synthesis of 2-PH from *n*-valeraldehyde

Reaction temperature/℃	X_V/%	S_{PO}/%	$S_{2\text{-PHA}}$/%	$S_{2\text{-PH}}$/%
180	100	28.0	27.3	43.6
190	100	27.6	0	71.1
200	100	18.2	0	81.4
210	100	25.0	0	66.1

Reaction conditions: a weight percentage of catalyst =15 %, *P*=3 MPa, *t*=6 h.
V: *n*-valeraldehyde; PO: *n*-pentanol; 2-PHA: 2-propylheptanal; 2-PH: 2-propylheptanol.
X: conversion; *S*: selectivity.

The effect of reaction time on direct synthesis of 2-PH from *n*-valeraldehyde was investigated and the results are shown in Table S4. 2-Propylheptanal was formed at a reaction time less than 5 h, indicating that C=O bond of 2-propylheptanal was not completely hydrogenated. The main product was 2-PH at reaction time of 5 h, indicating that the product was completely hydrogenated. However, selectivity of *n*-pentanol decreased slightly while selectivity of 2-PH remained basically unchanged at reaction time of 7 h, possibly due to the reaction of *n*-pentanol

with by-product *n*-pentanoic acid to amyl valerate.

Table S4 Effect of reaction time on direct synthesis of 2-PH from *n*-valeraldehyde

Reaction time/h	X_V/%	S_{PO}/%	$S_{2\text{-PHA}}$/%	$S_{2\text{-PH}}$/%
4	100	19.1	15.2	65.1
5	100	19.0	0	80.4
6	100	18.2	0	81.4
7	100	15.0	0	79.2

Reaction conditions: a weight percentage of catalyst =15 %, *P*=3 MPa, *T*=200 ℃.

V: *n*-valeraldehyde; PO: *n*-pentanol; 2-PHA: 2-propylheptanal; 2-PH: 2-propylheptanol.

X: conversion; *S*: selectivity.

Reference

S1 L. Zhao, H. An, X. Zhao and Y. Wang, *Ind. Eng. Chem. Res.*, 2016, **55**, 12326-12333.