Electronic supplementary information

Improvement of $n$-butanol Guerbet condensation: a reaction integration of $n$-butanol Guerbet condensation and 1,1-dibutoxybutane hydrolysis

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1. Catalyst preparation

Ni-Co/HAP (Ni=12.0 wt% and Co=2.4 wt%) catalyst was prepared by the stepwise impregnation method. A nickel nitrate aqueous solution was prepared by dissolving 2.98 g Ni(NO₃)₂·6H₂O (99.9%, Alfa Company) in 100 mL deionized water. A cobalt nitrate aqueous solution was prepared by dissolving 0.5 g Co(NO₃)₂·6H₂O (99.9%, Alfa Company) in 100 mL deionized water. 5 g HAP (Acros Company, USA) was dispersed in the nickel nitrate aqueous solution and mixed thoroughly. Then the mixture was transferred into a rotatory evaporator to remove water. The resulting powder was dried at 120 °C and calcined at 400 °C for 4 h in the air to obtain NiO/HAP. After that, 5 g NiO/HAP was dispersed in the cobalt nitrate aqueous solution and mixed thoroughly. The mixture was transferred into a rotatory evaporator to remove water. The resulting powder was dried at 120 °C and calcined at 400 °C for 4 h in the air. Finally, Ni-Co/HAP catalyst was obtained after reduced at 500 °C for 4 h by a gas mixture with 80% H₂ in N₂.

TiO₂ was prepared by the sol-gel method and the specific preparation method has been described in the previous paper 0. HY (Si/Al=5.2) (analytical grade, Nankai University Catalyst Factory, China) was used after calcinated at 550 °C for 3 h.

2. Catalyst characterization

The crystalline phases of the catalyst samples were confirmed by powder X-ray diffraction (XRD) analysis on a Rigaku D/MAX-2500 X-ray diffractometer with Cu-Kα radiation. The metal loadings of the catalysts were verified by ICP analysis using a PerkinElmer Optima 7300V instrument.
3. Thermodynamic analysis of $n$-butanol Guerbet condensation reaction and its reaction integration with 1,1-dibutoxybutane hydrolysis

![Graphs showing K and $\Delta G$ for different reactions](image)

**Fig. S1.** $K$ and $\Delta G$ of the different reaction at different temperatures
(a) $K$ of reaction (1); (b) $\Delta G$ of reaction (1); (c) $K$ of reaction (2); (d) $\Delta G$ of reaction (2); (e) $K$ of reaction (3); (f) $\Delta G$ of reaction (3)
4. Stability of catalyst for reaction integration of \( n \)-butanol Guerbet condensation and 1,1-dibutoxybutane hydrolysis

Fig. S2. Reusability of Ni-Co/HAP catalyst
Reaction conditions: \( \text{Ni-Co/HAP} = 15 \text{wt.\%}, \text{TiO}_2 = 0.15 \text{\%, } n(\text{BO}): n(1,1\text{-dibutoxybutane}) = 20:1, 230 \ ^\circ\text{C}, \ 12 \text{ h.} \)

Table S1  ICP analysis results of Ni and Co contents in Ni-Co/HAP catalyst before and after reaction

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<th>Ni content / wt.%</th>
<th>Co content /wt.%</th>
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<tr>
<td>Recovered twice</td>
<td>12.2</td>
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<td>Recovered five times</td>
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Fig. S3. XRD pattern (a) and partial enlargement (b) of fresh and recovered Ni-Co/HAP catalyst

5. Elimination of external and internal diffusion influence

Fig. S4. Effect of stirring speed on n-butanol conversion  
Fig. S5. Effect of particle size on n-butanol conversion

6. Derivation process of reaction kinetics equation

6.1 n-Butanol Guerbet condensation

\[ r_1 = k_1 C_A^{m_1} \]  
\[ r_1 = k_1 C_A^{m_1} \]  
\[ r_1 = k_1 C_A^{m_1} \]

The reaction rate of each component can be expressed as follows:

\[ -r_A = -\frac{dC_A}{dt} = r_1 = k_1 C_A^{m_1} \]
\[ r_B = \frac{dC_B}{dt} = r_1 - r_2 = k_1 C_A^{m_1} - k_2 C_B^{m_2} \]  
(S5)

\[ r_C = \frac{dC_C}{dt} = r_2 - r_3 = k_2 C_B^{m_2} - k_3 C_C^{m_3} C_H^{m_4} \]  
(S6)

\[ r_D = \frac{dC_D}{dt} = r_3 = k_3 C_C^{m_3} C_H^{m_4} \]  
(S7)

Where,

\[ C_w = C_C + C_D \]  
(S8)

\[ C_{H_2} = C_B + C_D + 0.5 C_C \]  
(S9)

6.2 Reaction integration of \( n \)-butanol Guerbet condensation and 1,1-dibutoxybutane hydrolysis

\[ r_1 = k_1 C_A^{m_1} \]  
(S10)

\[ r_2 = k_2 C_B^{m_2} \]  
(S11)

\[ r_3 = k_3 C_C^{m_3} C_H^{m_4} \]  
(S12)

\[ r_4 = k_4 C_E^{m_5} C_w^{m_6} \]  
(S13)

The reaction rate of each component can be expressed as follows:

\[ -r_A = - \frac{dC_A}{dt} = r_1 - r_4 = k_1 C_A^{m_1} - k_4 C_E^{m_5} C_w^{m_6} \]  
(S14)

\[ r_B = \frac{dC_B}{dt} = r_1 - r_2 + r_4 = k_1 C_A^{m_1} - k_2 C_B^{m_2} + k_4 C_E^{m_5} C_w^{m_6} \]  
(S15)

\[ r_C = \frac{dC_C}{dt} = r_2 - r_3 = k_2 C_B^{m_2} - k_3 C_C^{m_3} C_H^{m_4} \]  
(S16)

\[ r_D = \frac{dC_D}{dt} = r_3 = k_3 C_C^{m_3} C_H^{m_4} \]  
(S17)

\[ -r_E = - \frac{dC_E}{dt} = r_4 = k_4 C_E^{m_5} C_w^{m_6} \]  
(S18)

Where,

\[ C_w = C_C + C_D + C_E - C_{E0} \]  
(S19)

\[ C_{H_2} = C_B + C_D + 0.5 C_C \]  
(S20)

7. Kinetic experiments
The reaction temperature in the kinetic experiments was controlled at 210 °C, 220 °C and 230 °C. Under the conditions of a stirring speed of 600 r/min, a catalyst weight percentage of 15 wt.%, and a catalyst particle size of 0.2 to 0.15 mm, the concentration changes of each component versus reaction time at different temperatures were examined. In n-butanol Guerbet condensation and its reaction integration with DBB hydrolysis, the concentrations of each component versus reaction time at different temperatures are shown in Figures S6 and S7. Figure S6 shows that n-butanol concentration gradually decreased while the concentration of n-butyraldehyde and 2-ethyl-2-hexenal increased first and then slightly decreased, and the 2EHO concentration increased monotonously with the prolonging of reaction time. The concentration change trend of each component at different temperatures was basically the same.

![Concentration vs reaction time at different temperatures](image)

**Fig. S6.** Concentrations of each component in the n-butanol Guerbet condensation reaction at different reaction temperature versus reaction time

(a) 210 °C; (b) 220 °C; (c) 230 °C

In the reaction integration of n-butanol Guerbet condensation and DBB hydrolysis,
the concentrations of n-butanol, n-butyraldehyde, 2-ethyl-2-hexenal, 2EHO and DBB changed with reaction time at different temperatures are shown in Figure S7. As can be seen, the concentration of DBB decreased monotonously until it approached to 0 at the end of the reaction. The variation trend of the concentrations of other components at different temperatures were consistent with those in the n-butanol Guerbet condensation.

![Graphs showing concentration changes](image)

Fig. S7. Concentrations of each component in the reaction integration of n-butanol Guerbet condensation and DBB hydrolysis at different reaction temperature versus reaction time

(a) 210 °C; (b) 220 °C; (c) 230 °C

8. Kinetic models

8.1 n-Butanol Guerbet condensation

The kinetic equations for n-butanol Guerbet condensation catalyzed by Ni-Co/HAP and TiO₂ are as follows.

\[-r_A = 2.38 \times 10^5 \exp\left(-\frac{68.50 \times 10^3}{RT}\right)C_A^{0.82}\]
\[ r_b = 2.38 \times 10^5 \exp\left(\frac{-68.50 \times 10^3}{RT}\right)c_A^{0.82} - 2.55 \times 10^5 \exp\left(\frac{-53.74 \times 10^3}{RT}\right)c_B^{1.95} \]

\[ r_c = 2.55 \times 10^5 \exp\left(\frac{-53.74 \times 10^3}{RT}\right)c_B^{1.95} - 1.28 \times 10^4 \exp\left(\frac{-38.24 \times 10^3}{RT}\right)c_C^{1.12}c_H_2^{0.84} \]

\[ r_D = 1.28 \times 10^4 \exp\left(\frac{-38.24 \times 10^3}{RT}\right)c_C^{1.12}c_H_2^{0.84} \]

8.2 Reaction integration of \textit{n}-butanol Guerbet condensation and 1,1-dibutoxybutane hydrolysis

The kinetic equations for reaction integration of \textit{n}-butanol Guerbet condensation and 1,1-dibutoxybutane hydrolysis catalyzed by Ni-Co/HAP and TiO2 are as follows.

\[ -r_A = 1.97 \times 10^4 \exp\left(\frac{-57.94}{RT}\right)c_A^{1.01} - 7.10 \times 10^3 \exp\left(\frac{-39.67}{RT}\right)c_E^{1.17}c_w^{0.83} \]

\[ r_B = 1.97 \times 10^4 \exp\left(\frac{-57.94}{RT}\right)c_A^{1.01} - 7.20 \times 10^4 \exp\left(\frac{-47.63}{RT}\right)c_B^{1.98} + 7.10 \times 10^3 \exp\left(\frac{-39.67}{RT}\right)c_E^{1.17}c_w^{0.83} \]

\[ r_C = 7.20 \times 10^4 \exp\left(\frac{-47.63}{RT}\right)c_B^{1.98} - 1.49 \times 10^4 \exp\left(\frac{-38.37}{RT}\right)c_C^{1.02}c_H_2^{0.93} \]

\[ r_D = 1.49 \times 10^4 \exp\left(\frac{-38.37}{RT}\right)c_C^{1.02}c_H_2^{0.93} \]

\[ -r_E = -7.10 \times 10^3 \exp\left(\frac{-39.67}{RT}\right)c_E^{1.17}c_w^{0.83} \]
9. Test of kinetic models

9.1 *n*-butanol Guerbet condensation

\[ T = 210 \, ^\circ \text{C} \]

Fig. S8. Comparison of experimentally measured concentrations with those predicted by kinetic models at 210 °C
(a) Concentration of *n*-butanol; (b) concentration of *n*-butyraldehyde; (c) concentration of 2-ethyl-2-hexenal; (d) concentration of 2EHO
T=220 °C

Fig. S9. Comparison of experimentally measured concentrations with those predicted by kinetic models at 220 °C
(a) Concentration of n-butanol; (b) concentration of n-butyraldehyde; (c) concentration of 2-ethyl-2-hexenal; (d) concentration of 2EHO
Fig. S10. Comparison of experimentally measured concentrations with those predicted by kinetic models at 230 °C
(a) Concentration of n-butanol; (b) concentration of n-butyraldehyde; (c) concentration of 2-ethyl-2-hexenal; (d) concentration of 2EHO
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<th>Free variation No.</th>
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<th>Residual squares sum</th>
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I: Rate equation \((r_A)\); II: Rate equation \((r_B)\); III: Rate equation \((r_C)\); IV: Rate equation \((r_D)\).
9.2 Reaction integration of $n$-butanol Guerbet condensation and 1,1-dibutoxybutane hydrolysis

$T= 210 \, ^\circ\text{C}$

Fig. S11. Comparison of experimentally measured concentrations with those predicted by kinetic models at $210 \, ^\circ\text{C}$
(a) Concentration of $n$-butanol; (b) concentration of $n$-butyraldehyde; (c) concentration of 2-ethyl-2-hexenal; (d) concentration of 2EHO; (e) concentration of DBB
$T = 220 \, ^\circ\text{C}$

Fig. S12. Comparison of experimentally measured concentrations with those predicted by kinetic models at 220 °C

(a) Concentration of $n$-butanol; (b) concentration of $n$-butyraldehyde; (c) concentration of 2-ethyl-2-hexenal; (d) concentration of 2EHO; (e) concentration of DBB
T= 230 ℃

Fig. S13 Comparison of experimentally measured concentrations with those predicted by kinetic models at 230 ℃

(a) Concentration of n-butanol; (b) concentration of n-butyraldehyde; (c) concentration of 2-ethyl-2-hexenal; (d) concentration of 2EHO; (e) concentration of DBB
<table>
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<th>Model</th>
<th>Reaction temperature /℃</th>
<th>Experiment No.</th>
<th>Free variation No.</th>
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I: Rate equation \((r_A)\); II: Rate equation \((r_B)\); III: Rate equation \((r_C)\); IV: Rate equation \((r_D)\); V: Rate equation \((r_E)\).

References