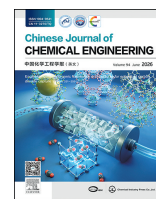




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Full Length Article

Mechanism and kinetics study on fixed-bed dehydrogenation of liquid organic hydrogen carriers over Pt-based catalyst

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ABSTRACT

Liquid organic hydrogen carriers (LOHCs) enable long-distance hydrogen transport, and the continuous-flow dehydrogenation kinetic is crucial for the rational design of dehydrogenation system. This work investigates the dehydrogenation reaction pathway, apparent kinetic modeling and impact of products on fixed-bed dehydrogenation of LOHCs over Pt/Al₂O₃, using perhydro-benzyltoluene (H12-BT) as a model. Experiment results indicate that the initial dehydrogenation of H12-BT predominantly occurs on the mono-substituted side ring (82%), yielding the dehydrogenated intermediate (H6-BT (SR)). The developed kinetic model reveals a zero-order dependence on H12-BT partial pressure, whereas first-order dependence on H6-BT partial pressure. The activation energy of the first step is slightly higher than that of the second step. Critically, predicted concentration trajectories for all species closely track experimental data points throughout the reaction progress, with a mean relative error of 9.02%. This work elucidates reaction mechanisms and provides essential kinetics for the LOHCs system scale-up.

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1. Introduction

Propelled by the global energy transition, hydrogen has emerged as the quintessential clean-energy vector owing to its exceptional gravimetric energy density and inherent carbon neutrality [1–5]. However, large-scale implementation requires integrated solutions to storage and distribution challenges that extend beyond technological barriers to encompass stringent economic and safety constraints [6,7]. Liquid organic hydrogen carriers (LOHCs) store energy within chemical bonds through reversible hydrogenation [8–11]. This mechanism facilitates safe hydrogen storage/transport under ambient conditions – the core rationale for IEA's formal endorsement of LOHCs as efficient long-

distance hydrogen carriers [12–14]. Their high hydrogen density (>6.0% (mass)), safety profile, and petroleum infrastructure compatibility further position LOHCs as ideal candidates for seasonal energy storage and cross-regional renewable energy distribution [15–18]. Specifically, the benzyltoluene (H0-BT) system (comprising H0-BT and its fully hydrogenated analogue H12-BT) exhibits a competitive hydrogen capacity (ca. 6.2% (mass)), low toxicity, wide liquid temperature range, and exceptional cycling stability, thereby promising hydrogen carrier as a typical LOHC [19–22].

The dehydrogenation of H12-BT is a crucial step in the dehydrogenation of LOHC technology [22]. Currently, platinum (Pt)-based catalysts are widely used in the dehydrogenation of H12-BT due to their excellent selectivity and activity [23–28]. Mahayni *et al.* [29] found that Pt particle size is crucial for the structure-sensitive dehydrogenation of LOHCs, with an optimal size to maximize low-temperature performance. Sun *et al.* [30]

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boosted LOHC dehydrogenation by tuning the Pt d-band center, revealing the electronic effect and offering a strategy for advanced catalyst design. Additionally, Pt/Al₂O₃ catalysts, distinguished by their outstanding catalytic performance, superior thermal stability, and high specific surface area [31–33], have become a major research focus. On *et al.* [34] revealed that S-modified Pt/θ-Al₂O₃ boosts reaction rate and stability by controlling intermediate re-adsorption, offering new insights for H12-BT dehydrogenation. As reported by Shi *et al.* [35], the acidic sites on the surface of Pt/Al₂O₃ catalysts can help reduce side reactions and enhance the desorption of intermediates in dehydrogenation processes. Despite intensive research on catalyst development and production process [36], there is a significant lack of experimental evidence in the kinetic investigations of H12-BT dehydrogenation. Wang *et al.* [37] used catalytic distillation to study the kinetics of the dehydrogenation reaction of H12-BT in a batch reactor. In kinetic investigations, continuous-flow reactors surpass their batch counterparts [38] by providing operability and stability [39], elevated productivity, facile modeling [40], facile tuning of process parameters [41], inherent safety [42], and suitability for multi-phase reactions [43].

Kinetic studies are crucial for elucidating catalytic reaction mechanisms, optimizing reaction parameters, and developing efficient catalysts [21,44]. However, the vaporization of H12-BT at 270 °C makes it difficult to investigate the dehydrogenation kinetics of H12-BT at high temperatures using a batch reactor [19], and the isomer selectivity of the dehydrogenation intermediate (H6-BT) has not yet been investigated, leading to an unclear dehydrogenation reaction pathway [45]. Based on the above considerations, this work systematically investigates the dehydrogenation reaction pathway, kinetic model, and the influence of H12-BT products over the Pt/Al₂O₃ catalyst in a continuous-flow fixed-bed reactor, specifically aiming to develop a kinetic model that accurately represents the dehydrogenation properties of H12-BT. The established kinetic framework provides theoretical foundations for reactor design and process optimization, while offering new insights into the development of high-performance catalytic systems.

2. Experiments

2.1. Materials

H0-BT (99% (mass)) was purchased from Liaoning Zhenghe Chemical Co., Ltd. Since the commercial H12-BT was not accessible, H12-BT with a purity of 99% (mass) was obtained by hydrogenation of H0-BT using NiO-Al₂O₃ catalyst (Fig. S1, Supplementary Material). For more detailed information on the H12-BT preparation process and purity analysis, can be found in Supplementary Material. High purity hydrogen gas (H₂, 99.999%) and nitrogen gas (N₂, 99.999%) were sourced from Air Liquide Tianjin Co., Ltd. Aluminum oxide (γ-Al₂O₃, particle size 10 nm) was obtained from Shanghai Macklin Bio-Chem Technology Co., Ltd. Chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, 99.95%, Pt ≥ 38% (mass)) was provided by Beijing Innochem Technology Co., Ltd. Silicon dioxide (SiO₂, 180–420 μm) was obtained from Tianjin Jiangnan Chemical Technology Co., Ltd.

2.2. Catalyst preparation

The 2.65% (mass) Pt/Al₂O₃ catalyst was prepared using the incipient wetness impregnation method [46]. The impregnated sample was kept under ambient conditions for 24 h, followed by drying at 60 °C for 10 h. Subsequently, the catalyst was calcined at

450 °C for 4 h with a heating rate of 5 °C·min^{−1}. Next step, the catalyst powder was pelletized and sieved to obtain the desired catalyst particle size.

2.3. Catalyst characterizations

The fundamental physicochemical properties of Pt/Al₂O₃ catalyst were characterized by inductively coupled plasma (ICP), field emission transmission electron microscopy (TEM), N₂ adsorption-desorption isotherms, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance (NMR) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) (Detailed test conditions are shown in Supplementary Material), and the comprehensive characterization results are provided in Figs. S2–S7 and Table S1.

2.4. Catalytic dehydrogenation of H12-BT

The dehydrogenation of H12-BT over Pt/Al₂O₃ was conducted in a fixed-bed stainless-steel reactor (inner diameter: 6 mm; Fig. S8 and Supplementary Material). The catalyst particles were uniformly mixed with an equal mass of silicon dioxide (SiO₂; identical particle size) to eliminate radial concentration and thermal gradients. Then the catalysts were placed in a fixed-bed reactor for *in-situ* reduction with hydrogen gas (60 ml·min^{−1}) at 350 °C for 3 h. Mass flow controllers were employed to precisely regulate the gas flow rates, while the raw materials were introduced into the system through a syringe pump. The reactants are vaporized at the reaction temperature (280–320 °C), suggesting this is a gas-solid reaction. Therefore, partial pressure rather than concentration was adopted as the kinetic descriptor. The products condense downstream while maintaining constant molar percentages before and after condensation, allowing the condensed products to be collected for analysis.

For the kinetics study, the extent of H12-BT dehydrogenation was evaluated by varying the residence time (τ) (The formula is given in Eq. (S1) from 100 to 399 g_{cat}·min·mol^{−1}, while other parameters were kept constant (reaction conditions: $m_{\text{cat}} = 0.1\text{ g}$ (250–420 μm), $P_{\text{total}} = 0.2\text{ MPa}$ (20 kPa H12-BT, N₂ balanced), $T = 280\text{ °C}$). The formula for the feed flow rate of N₂ is given in Eqs. (S2)–(S4). To probe product inhibition effects during dehydrogenation, H₂ and H0-BT partial pressures were systematically varied from 8.47 to 25.11 kPa and 0.57–1.82 kPa, respectively. H₂ and H0-BT formation rates were monitored under otherwise constant reaction conditions.

A small amount of liquid product was collected for quantitative analysis using the GC-FID (Shimadzu GC-2014, SK-5 capillary column, 30 m × 0.25 mm × 0.25 μm). The components were qualitatively analyzed using GC-MS (Agilent Technologies 6890 N, HP-5 capillary column, 30 m × 0.25 mm × 0.25 μm). The quantitative analysis of the liquid products was performed by area normalization [37], and the molar content of each substance, partial pressure, and the degree of dehydrogenation (DoD, % (mol)) were calculated as shown in Eqs. (1)–(4):

$$m_i = \frac{A_i}{A_{\text{total}}} \quad (1)$$

$$x_i = \frac{\frac{m_i}{M_i}}{\sum \frac{m_i}{M_i}} \quad (2)$$

$$P_i = P_{\text{H12-BT},0} \cdot x_i \quad (3)$$

$$\text{DoD} = (0.5x_{\text{H6-BT}} + x_{\text{H0-BT}}) \times 100\% \quad (4)$$

Where i represent H0-BT, H6-BT, and H12-BT, respectively; A_i , $A_{\text{total}} = \sum A_i$, m_i , M_i , x_i , P_i denotes individual peak area, total peak area, mass fraction, molar mass, mole fraction, and partial pressure, respectively.

To determine the product inhibition exponents m and n in the reaction kinetic model, constrained nonlinear least squares method was employed for parameter fitting. Parameter optimization was performed using MATLAB for constrained optimization.

3. Results and Discussion

3.1. Dehydrogenation reaction pathway

GC-MS and GC were used to analyze the dehydrogenation products of H12-BT. Fig. 1 presents a representative chromatogram obtained under the specified reaction conditions, revealing three primary substances—H0-BT, H6-BT, and H12-BT (GC-MS information in Fig. S9)—and trace amounts of light and heavy by-products (Specific by-products are analyzed in Section 3.2.1). Due to the close boiling points of H6-BT and H12-BT, their chromatographic peaks exhibit partial yet minor overlap, exerting a negligible effect on the experimental results. H12-BT dehydrogenation proceeds in two consecutive stages: first to H6-BT, then to H0-BT, as reported [24,37]. Moreover, the first-rank Delplot analysis (Fig. S10) further confirms that H6-BT is a primary product (rank 1), and H0-BT is a non-primary product (rank ≥ 2) [47,48]. However, GC-MS identification relies solely on relative molecular mass and therefore lacks the resolving power to distinguish H6-BT isomers. The questions of whether the first dehydrogenation of H12-BT preferentially yields the di-substituted main-ring (MR) or the mono-substituted side-ring (SR) isomer and whether the conformation of H6-BT is related to the extent of the reaction are both poorly investigated, mandating a mechanistic elucidation of the initial pathway.

Five products of differing DoD, together with the reference compounds H12-BT and H0-BT, were isolated. Quantitative GC analysis (Fig. S11) furnished the molar distributions of H12-BT, H6-BT, and H0-BT. Detailed characterization was performed using ^1H NMR to further investigate the isomers of H6-BT. Leveraging the differential shielding experienced by the $-\text{CH}_2-$ protons of H6-BT and the CH_3- protons of H6-BT (MR) relative to their reference counterparts, we identify the constitutional isomers of H6-BT (Detailed ^1H NMR assignments are provided in Figs. S6–S7). As

Table 1

^1H NMR results of liquid-phase products with varying degrees of reaction.

DoD/(mol)	H6-BT/(mol)	H6-BT (MR)/%	H6-BT (SR)/%
12	14	18	82
19	18	17	83
23	26	19	81
28	32	18	82
42	28	19	81

Note: Two samples, 100% H0-BT and 100% H12-BT, are not included.

presented in Table 1, both H6-BT (MR) and H6-BT (SR) are formed in the reaction, but with a notable difference in their selectivity. While the DoD of the five products (12% to 42%) exhibits significant differences, the selectivity ratios of H6-BT (MR) and H6-BT (SR) are nearly identical. Collectively, the initial step in the dehydrogenation of H12-BT produces H6-BT, with the sterically favored H6-BT (SR) isomer predominating at 82%. Jo *et al.* [32] demonstrated that tailoring Pt dispersion to optimize the surface structure of the catalyst significantly enhances the selectivity for H12-BT. On *et al.* [34] employed model compounds as surrogates for the different aliphatic segments of H12-BT in competitive adsorption studies, which revealed that rings with less steric hindrance (lacking methyl groups) exhibit a stronger adsorption tendency. Furthermore, their *in-situ* DRIFTS characterization of four H6-BT fragment molecules indicated that modifying the electronic structure of Pt/ Al_2O_3 alters the selectivity towards H6-BT isomers, thereby steering the dehydrogenation pathway [49]. In conclusion, the superior selectivity towards H6-BT (SR) arises from the combined effects of steric hindrance and the surface structure of the catalyst. This distribution further refines the mechanistic understanding of H12-BT dehydrogenation pathway (Fig. 2). The observed preference for side-ring reactivity finds further evidence in the studies of Kim *et al.* [50] and On *et al.* [34], as documented in monobenzytoluene systems.

3.2. Kinetic study

3.2.1. Influence of inert media and byproducts

A blank trial was performed to isolate the contribution of the inert packing. The stainless-steel reactor was charged exclusively with SiO_2 at $\tau = 399 \text{ g}_{\text{cat}} \cdot \text{min} \cdot \text{mol}^{-1}$. H12-BT conversion and product selectivity were assessed at 280 °C, 300 °C, and 320 °C (Table S2). Conversion remained below 1% throughout, confirming that all observed products originate from the catalytic dehydrogenation of H12-BT.

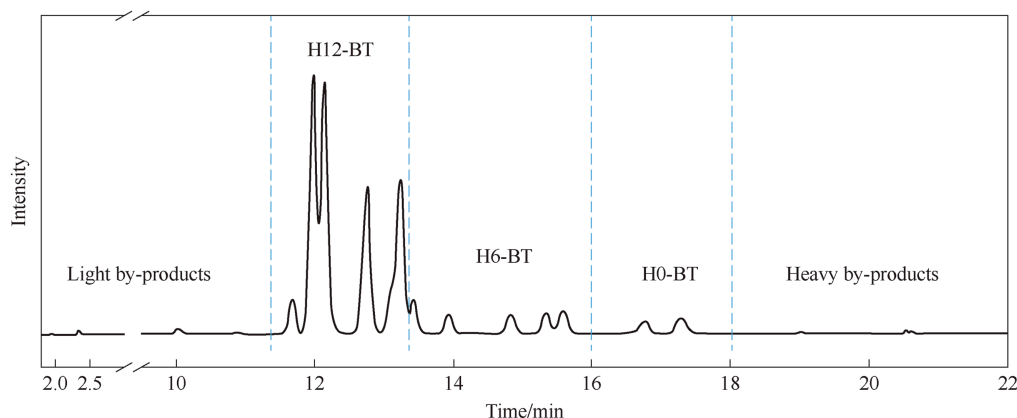


Fig. 1. Chromatogram of H12-BT dehydrogenation product. Reaction conditions: $\tau = 399 \text{ g} \cdot \text{min} \cdot \text{mol}^{-1}$, $m_{\text{cat}} = 0.1 \text{ g}$ (250–420 μm), $P_{\text{total}} = 0.2 \text{ MPa}$ (20 kPa H12-BT, N_2 balanced), $T = 310 \text{ }^\circ\text{C}$.

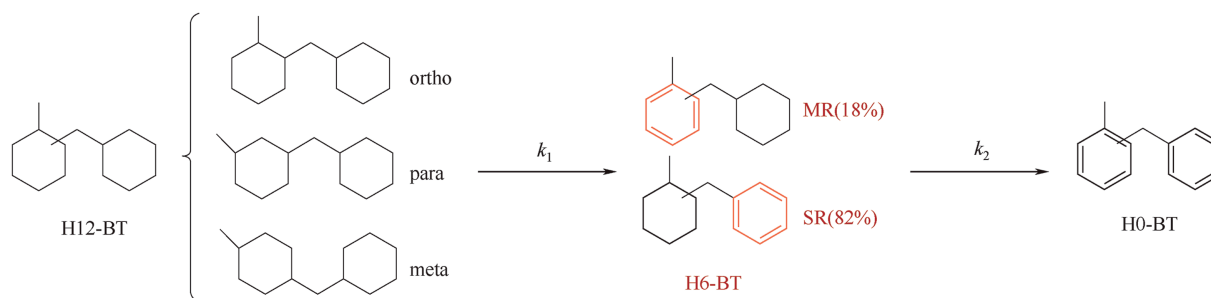


Fig. 2. Dehydrogenation pathway of H12-BT incorporating H6-BT isomerism.

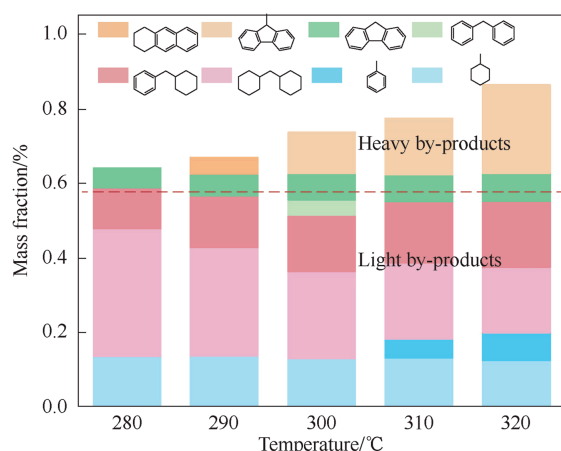


Fig. 3. Distribution of by-products at 280–320 °C. Reaction conditions: $\tau = 399 \text{ g}_{\text{cat}} \cdot \text{min} \cdot \text{mol}^{-1}$, $m_{\text{cat}} = 0.1 \text{ g}$ (250–420 μm), $P_{\text{total}} = 0.2 \text{ MPa}$ (20 kPa H12-BT, N_2 balanced).

The temperature dependence of by-product evolution was mapped across 280–320 °C (Fig. 3). Analysis of temperature effects (Table 2) reveals a marked positive correlation between total by-product formation and increasing temperature. Light by-products consistently dominate over heavy components, with their cumulative concentration (0.55 to 0.65% (mass)) showing negligible temperature dependence. In contrast, heavy by-products (0.05% to 0.31% (mass)) exhibit substantial temperature-induced amplification, though light constituents persistently prevail in abundance. Notably, individual by-products demonstrate non-monotonic temperature relationships (GC-MS information in Fig. S12). As shown in Fig. 3, fluorene and methylcyclohexane maintain near-constant concentrations regardless of temperature elevation. Conversely, the dicyclohexylmethane displays a distinct negative correlation with temperature, while cyclohexylphenylmethane shows a pronounced positive correlation. Toluene and methylfluorene concentrations increase measurably with heating and become detectable only at elevated temperatures. Although total

Table 2
Light by-products, heavy by-products, and BT mass fraction.

Temperature/°C	Light by-products/% (mass)	Heavy by-products/% (mass)	BT/% (mass)
280	0.59	0.05	99.36
290	0.65	0.10	99.25
300	0.60	0.18	99.22
310	0.58	0.22	99.19
320	0.55	0.31	99.14

Note: Reaction conditions: $\tau = 399 \text{ g} \cdot \text{min} \cdot \text{mol}^{-1}$, $m_{\text{cat}} = 0.1 \text{ g}$ (250–420 μm), $P_{\text{total}} = 0.2 \text{ MPa}$ (20 kPa H12-BT, N_2 balanced).

by-products increase from 0.64% (mass) to 0.86% (mass) with temperature rise, the total amount is still below 1% (mass). Owing to their negligible concentration, these impurities exert an imperceptible influence on dehydrogenation kinetics. However, repeated hydrogenation–dehydrogenation cycles may lead to the progressive accumulation of by-products under practical operating conditions.

3.2.2. Exclusion of internal and external diffusion

Reducing catalyst particle size effectively mitigates internal diffusion limitations [47,48]. As illustrated in Fig. 4(a), H12-BT conversion exhibits invariance at particle sizes $\leq 420 \mu\text{m}$ (including 250–420 μm and finer fractions), thus demarcating internal diffusion-controlled and diffusion-independent regimes. Internal diffusion effects become negligible when employing catalysts with particles $\leq 420 \mu\text{m}$.

From a mass transfer perspective, enhanced fluid turbulence mitigates external diffusion limitations [51,52]. Fig. 4(b) demonstrates progressive decline in H12-BT conversion with increasing τ . At $\tau \leq 399 \text{ g}_{\text{cat}} \cdot \text{min} \cdot \text{mol}^{-1}$, conversion remains invariant when using either 0.1 g or 0.2 g catalyst at equivalent τ . The left region of Fig. 4(b) corresponds to negligible external diffusion effects, while the right region indicates diffusion-controlled operation. Thus, kinetic investigations employed $\tau \leq 399 \text{ g}_{\text{cat}} \cdot \text{min} \cdot \text{mol}^{-1}$ and catalyst particles sized 250 to 420 μm .

3.2.3. Apparent kinetic model

Kinetic experiments were conducted under low H12-BT conversion regimes to simplify reaction pathways, enhance data accuracy, and improve process control [53,54]. This approach effectively mitigates product inhibition effects while rendering reverse reactions negligible, thereby yielding more accurate apparent kinetics. Power-law formalism provides a concise representation of the relationship between reaction rates and reactant concentrations in consecutive dehydrogenation systems, making it a conventional approach for modeling apparent kinetics. However, this methodology exhibits inherent limitations. Current research confirms its applicability in kinetic studies of organic liquid hydrogen carriers [37,55,56]. Thus, the apparent consumption rate of H12-BT and formation rates of H6-BT/H0-BT are described by Eqs. (5)–(7), respectively.

$$r_1 = -\frac{dP_{\text{H12-BT}}}{d\tau} = k_1 \cdot P_{\text{H12-BT}}^\alpha \quad (5)$$

$$r_2 = \frac{dP_{\text{H6-BT}}}{d\tau} = k_1 \cdot P_{\text{H12-BT}}^\alpha - k_2(\text{H6-BT}) \cdot P_{\text{H6-BT}}^\beta \quad (6)$$

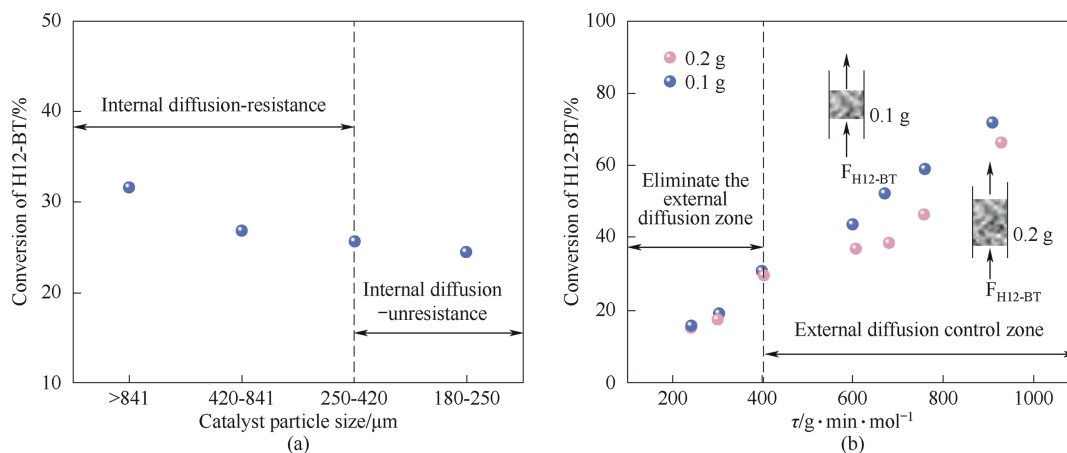


Fig. 4. (a) Elimination of internal diffusion; (b) Elimination of external diffusion. Reaction conditions: $P_{\text{total}} = 0.2$ MPa (20 kPa H12-BT, N_2 balanced), $T = 280$ °C.

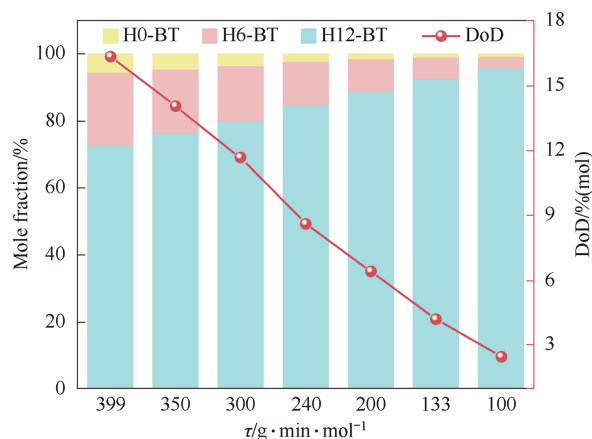


Fig. 5. Composition and DoD of the products at different τ at 280 °C. Reaction conditions: $m_{\text{cat}} = 0.1$ g (250–420 μm), $P_{\text{total}} = 0.2$ MPa (20 kPa H12-BT, N_2 balanced).

$$r_3 = -\frac{dP_{\text{H0-BT}}}{d\tau} = k_2(\text{H0-BT}) \cdot P_{\text{H6-BT}}^{\beta} \quad (7)$$

Where r_1 , r_2 , and r_3 denote the dehydrogenation rate of H12-BT $\rightarrow$ H6-BT, the net formation rate of H6-BT, and the formation rate of H0-BT, respectively. All rates are expressed in $\text{kPa} \cdot \text{mol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{min}^{-1}$. The elementary rate constants for the two consecutive dehydrogenation steps are k_1 , $k_2(\text{H6-BT})$, and $k_2(\text{H0-BT})$, while α and β represent the reaction orders concerning H12-BT and H6-BT.

During the experimental procedure, the temperature, pressure, and partial pressure of H12-BT were strictly maintained at constant levels, while the reaction extent of H12-BT within the fixed-bed reactor was adjusted by changing the feed quantity. Kinetic data were acquired at low H12-BT conversions (<30%) across varied τ . Fig. 5 demonstrates progressive declines in DoD of H12-BT and in mole fractions of H6-BT/H0-BT with decreasing τ at 280 °C. Reduced reactant-catalyst contact time at shorter τ directly suppresses H12-BT conversion. The inability to perform continuous sampling in fixed-bed reactors precludes the determination of non-integer reaction orders *via* differential methods. Due to inherent fixed-bed reactor characteristics, gasification of H12-BT during dehydrogenation, and challenges in isolating pure H6-BT, the kinetic model was calibrated using postulated reaction orders [56–58].

$$P_{\text{H12-BT}} = P_{\text{H12-BT},0} - k_1 \cdot \tau \quad (8)$$

$$P_{\text{H6-BT}} = (k_1 - k_2(\text{H6-BT})) \cdot \tau \quad (9)$$

$$P_{\text{H0-BT}} = k_2(\text{H0-BT}) \cdot \tau \quad (10)$$

The dehydrogenation kinetics of H12-BT were modeled *via* integral analysis across varied reaction orders. For $\alpha = 0$, $\beta = 0$, temporal integration yields Eqs.(8)–(10). Constrained to fixed orders ($\alpha = 0$, $\beta = 1$), analytical solutions of integral rate equations (Eqs. (11)–(13)) were derived through temporal integration of differential equations. Kinetic fitting (Fig. 6(b)) indicates the highest effective desorption rate constant for H12-BT ($k_1 = 0.01306$ $\text{kPa} \cdot \text{mol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{min}^{-1}$), while the $k_2(\text{H6-BT}) = 0.00121$ $\text{mol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{min}^{-1}$ and $k_2(\text{H0-BT}) = 0.00126$ $\text{mol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{min}^{-1}$. Notably, the model reveals significant dependence on H6-BT partial pressure but independence from H12-BT. All fitted curves exhibit excellent agreement ($R^2 > 0.95$).

$$P_{\text{H12-BT}} = P_{\text{H12-BT},0} - k_1 \cdot \tau \quad (11)$$

$$P_{\text{H6-BT}} = \frac{k_1}{k_2} - \frac{k_1}{k_2 \cdot e^{k_2 \cdot \tau}} \quad (12)$$

$$P_{\text{H0-BT}} = k_1 \cdot \tau - \frac{k_1}{k_2} + \frac{k_1}{k_2 \cdot e^{k_2 \cdot \tau}} \quad (13)$$

Under reaction orders $\alpha = 0$, $\beta = 2$, Eqs. (14)–(16) provide integrated rate solutions. Corresponding experimental data fits appear in Fig. 6(c). For $\alpha = 1$, $\beta = 0$, temporal integration yields Eqs.(17)–(19) (Fig. 6(d)). When $\alpha = 1$, $\beta = 1$, Eqs.(20)–(22) describe the integrated kinetics (Fig. 6(e)). Finally, setting $\alpha = 2$, $\beta = 0$ generates Eqs. (23)–(25), with data fits illustrated in Fig. 6(f).

$$P_{\text{H12-BT}} = P_{\text{H12-BT},0} - k_1 \cdot \tau \quad (14)$$

$$P_{\text{H6-BT}} = \frac{\sqrt{k_1} \cdot e^{2\sqrt{k_1}\sqrt{k_2}\tau} - \sqrt{k_1}}{\sqrt{k_2} \left(e^{2\sqrt{k_1}\sqrt{k_2}\tau} + 1 \right)} \quad (15)$$

$$P_{\text{H0-BT}} = k_1 \cdot \tau - \frac{\sqrt{k_1} \cdot e^{2\sqrt{k_1}\sqrt{k_2}\tau} - \sqrt{k_1}}{\sqrt{k_2} \left(e^{2\sqrt{k_1}\sqrt{k_2}\tau} + 1 \right)} \quad (16)$$

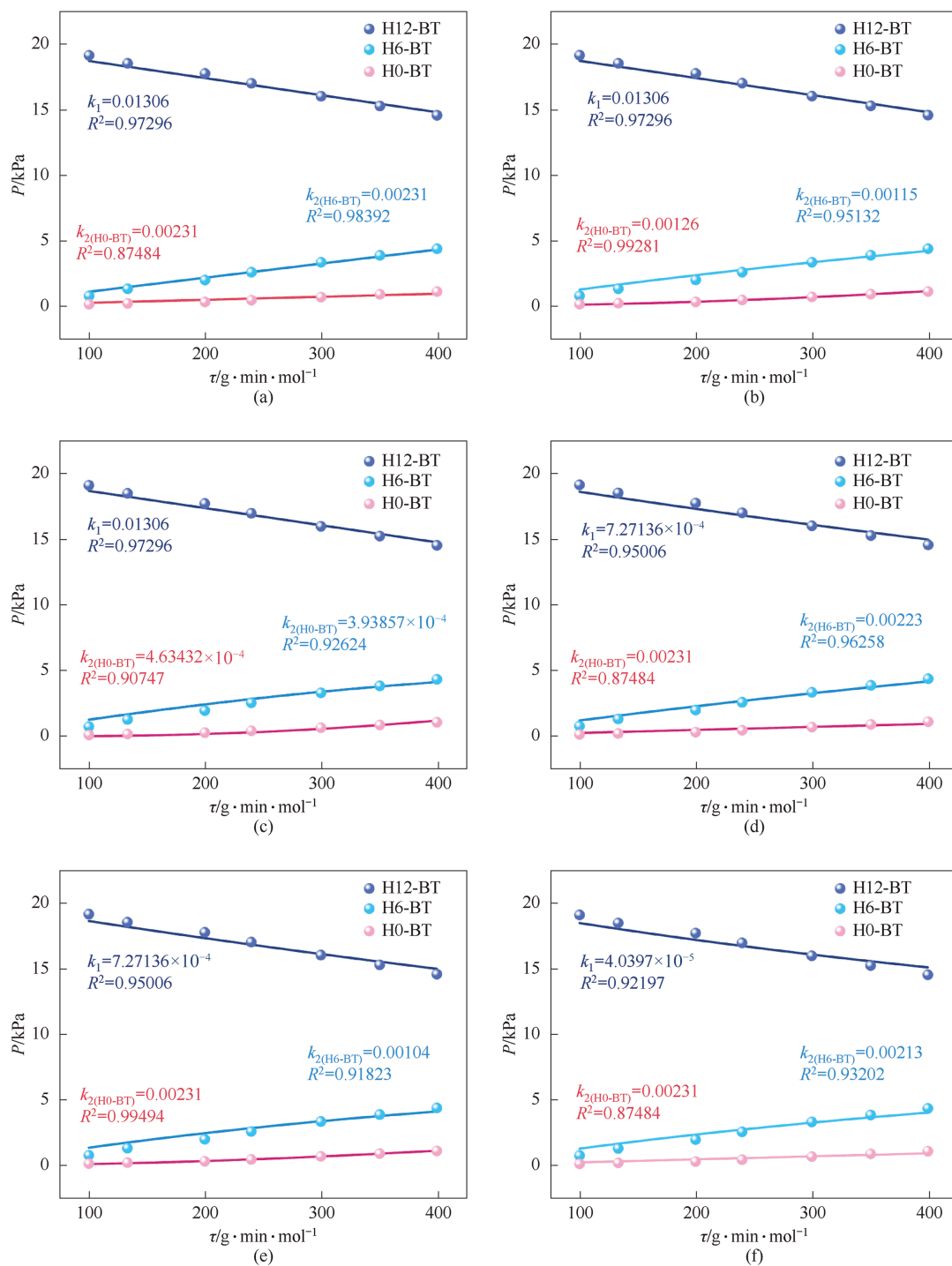


Fig. 6. Results of different models fit at 280 °C (a) $\alpha = 0, \beta = 0$; (b) $\alpha = 0, \beta = 1$; (c) $\alpha = 0, \beta = 2$; (d) $\alpha = 1, \beta = 0$; (e) $\alpha = 1, \beta = 1$; (f) $\alpha = 2, \beta = 0$.

$$P_{H12-BT} = \frac{P_{H12-BT,0}}{e^{k_1 \cdot \tau}} \quad (17)$$

$$P_{H6-BT} = -\frac{P_{H12-BT,0}}{e^{k_1 \cdot \tau}} - k_2 \cdot \tau + P_{H12-BT,0} \quad (18)$$

$$P_{H0-BT} = k_2 \cdot \tau \quad (19)$$

$$P_{H12-BT} = \frac{P_{H12-BT,0}}{e^{k_1 \cdot \tau}} \quad (20)$$

$$P_{H6-BT} = \frac{P_{H12-BT,0} \cdot k_1}{k_1 - k_2} (e^{-k_2 \cdot \tau} - e^{-k_1 \cdot \tau}) \quad (21)$$

$$P_{\text{H0-BT}} = P_{\text{H12-BT},0} \left(1 + \frac{k_2 \cdot e^{-k_1 \cdot \tau} - k_1 \cdot e^{-k_2 \cdot \tau}}{k_1 - k_2} \right) \quad (22)$$

$$P_{\text{H12-BT}} = \frac{P_{\text{H12-BT},0}}{k_1 \cdot \tau \cdot P_{\text{H12-BT},0} + 1} \quad (23)$$

$$P_{\text{H6-BT}} = P_{\text{H12-BT},0} - k_2 \cdot \tau - \frac{P_{\text{H12-BT},0}}{k_1 \cdot \tau \cdot P_{\text{H12-BT},0} + 1} \quad (24)$$

$$P_{\text{H0-BT}} = k_2 \cdot \tau \quad (25)$$

Due to the non-elementary functional forms arising from integrating rate equations at alternative reaction orders and

Table 3

Rate constants and R^2 of H12-BT dehydrogenation for different kinetic models at 280 °C.

Model	α	β	k_1	R^2	$k_{2(\text{H6-BT})}$	R^2	$k_{2(\text{H0-BT})}$	R^2
a	0	0	0.01306	0.97296	0.00231	0.98392	0.00231	0.87484
b	0	1	0.01306	0.97296	0.00121	0.95132	0.00126	0.99281
c	0	2	0.01306	0.97296	3.94×10^{-4}	0.92624	4.63×10^{-4}	0.90747
d	1	0	7.27×10^{-4}	0.95006	0.00223	0.96258	0.00231	0.87484
e	1	1	7.27×10^{-4}	0.95006	0.00104	0.91823	0.00123	0.99494
f	2	0	4.04×10^{-5}	0.92197	0.00213	0.93202	0.00231	0.87484

considering the declining R^2 values with increasing reaction order (Fig. 6), only six models were fitted. Table 3 presents the fitting outcomes for H12-BT dehydrogenation kinetics at 280 °C. Among these, model b ($\alpha = 0, \beta = 1$) demonstrates superior accuracy, with $R^2 > 0.95$ for H12-BT, H6-BT, and H0-BT functions, confirming excellent model-experiment correlation. The rate constant for the second dehydrogenation step can be determined from both H6-BT and H0-BT equations. A minor discrepancy exists between $k_{2(\text{H6-BT})}$ and $k_{2(\text{H0-BT})}$ values (Table 3), attributable to peak co-elution interference between H12-BT and H6-BT; Error propagation from H6-BT's dual role as product (first step) and reactant (second step). Consequently, $k_{2(\text{H0-BT})}$ was adopted for subsequent activation energy calculations.

Fig. 7 depicts H12-BT dehydrogenation at 290–320 °C. Experimental data confirm pronounced temperature sensitivity: at $\tau = 399 \text{ g}_{\text{cat}} \cdot \text{min} \cdot \text{mol}^{-1}$, the DoD increases from 22.9% to 43.0% when temperature rises from 290 °C to 320 °C. The process follows Arrhenius kinetics, showing a strong positive correlation between apparent rate constants and temperature. Elevated temperatures significantly enhance BT system performance, enabling rapid hydrogen storage via LOHC technology. At all temperatures, reduced τ decreases DoD (Fig. 7), indicating diminished reactant-catalyst contact that suppresses conversion rates.

Fitting results of six kinetic models across 290–320 °C are presented in Figs. S13–S16, with corresponding rate constants and R^2 values tabulated in Tables S3–S6. Kinetic trends at these temperatures parallel those at 280 °C: zero-order kinetics for H12-BT

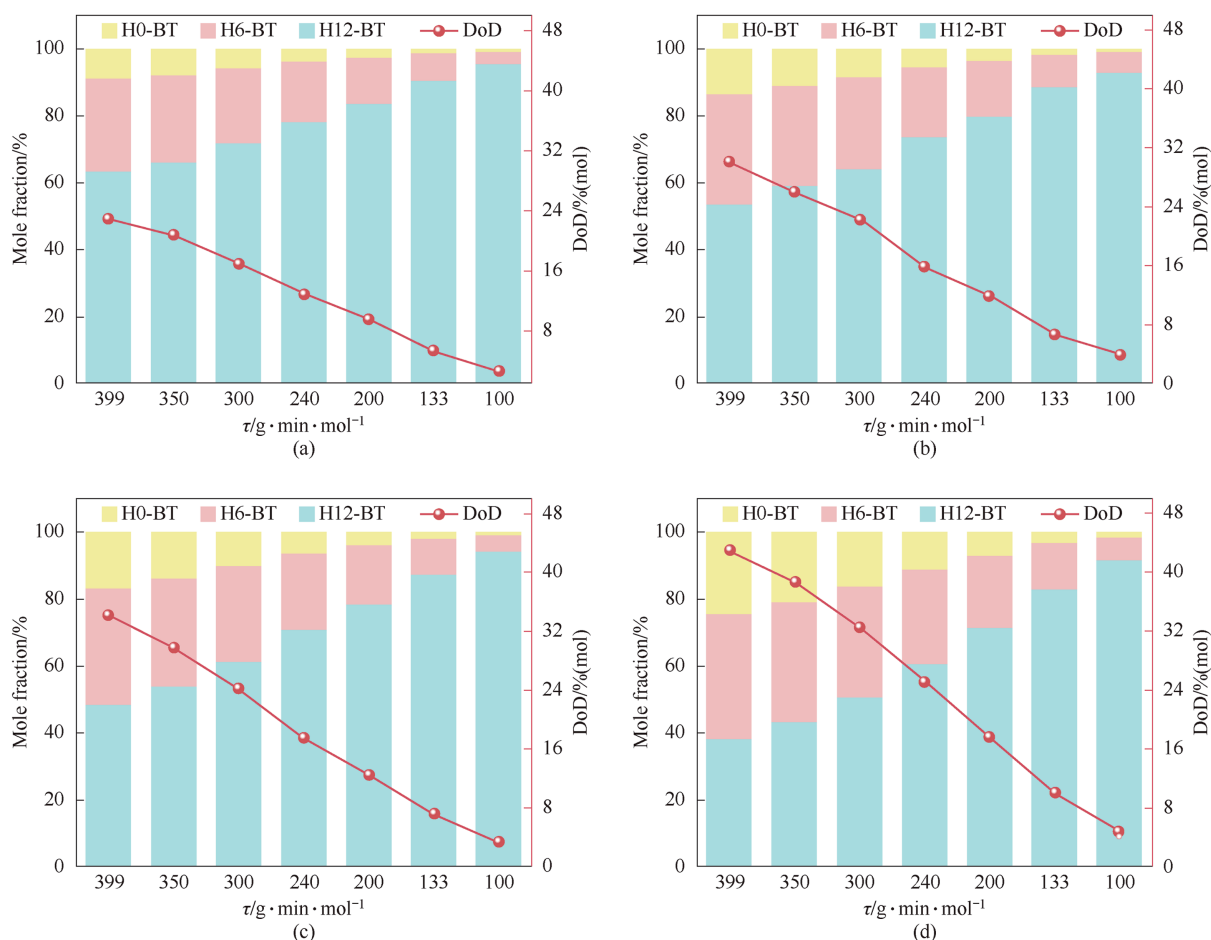


Fig. 7. Substance composition and dehydrogenation degree of H0-BT, H6-BT, and H12-BT at different τ from 290 °C to 320 °C. (a) 290 °C; (b) 300 °C; (c) 310 °C; (d) 320 °C. Reaction conditions: $m_{\text{cat}} = 0.1 \text{ g}$ (250–420 μm), $P_{\text{total}} = 0.2 \text{ MPa}$ (20 kPa H12-BT, N_2 balanced).

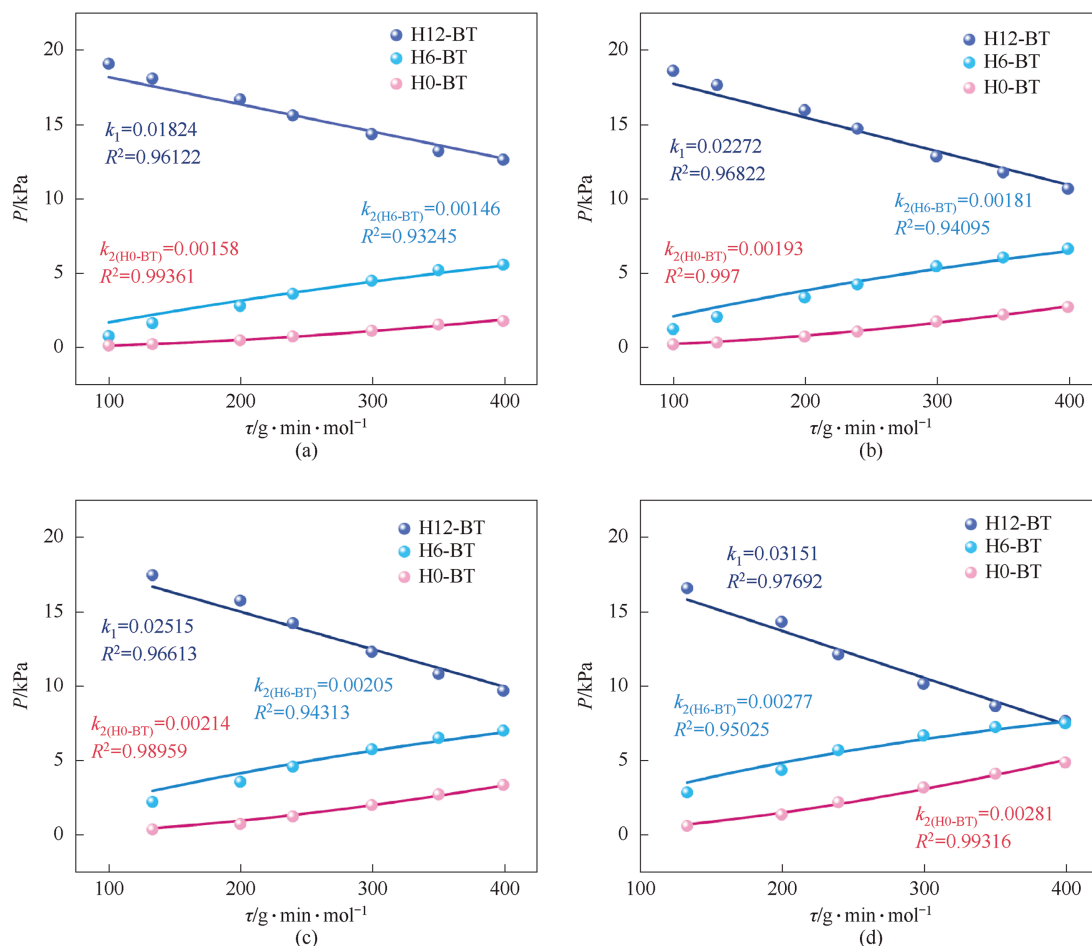


Fig. 8. Results of kinetic experiments at 290 °C–320 °C using model fitting with $\alpha = 0$, $\beta = 1$ (a) 290 °C; (b) 300 °C; (c) 310 °C; (d) 320 °C.

→ H6-BT dehydrogenation provide optimal accuracy. Among $\alpha = 0$ models, model b ($\beta = 1$) exhibits superior fitting for H6-BT/H0-BT data. Fig. 8 shows the best-fit models for 290–320 °C. Consistency across five temperatures confirms $\alpha = 0$ for H12-BT and $\beta = 1$ for H6-BT as the optimal reaction orders. The zero-order dependence on H12-BT indicates that the catalyst surface is saturated under the reaction conditions [59,60].

In summary, the whole reaction process of H12-BT dehydrogenation can be written as Eqs.(26)–(28):

$$r_1 = -\frac{dP_{\text{H12-BT}}}{d\tau} = k_1 \quad (26)$$

$$r_2 = -\frac{dP_{\text{H6-BT}}}{d\tau} = k_1 - k_2 \cdot P_{\text{H6-BT}} \quad (27)$$

$$r_3 = -\frac{dP_{\text{H0-BT}}}{d\tau} = k_2 \cdot P_{\text{H6-BT}} \quad (28)$$

3.2.4. Activation energy

In consecutive dehydrogenation kinetics, determining activation energies is critical as it elucidates the temperature dependence of reaction rates and provides theoretical guidance for catalyst design and process optimization. Through the analysis of kinetic data at five distinct temperatures, we determined the optimal kinetic model for the dehydrogenation of H12-BT ($\alpha = 0$, $\beta = 1$). Subsequently, thermodynamic analysis was conducted to determine the sensitivity of the reaction rate to temperature changes. Table 4 provides the rate constant for the two-step dehydrogenation of H12-BT. The Arrhenius equation (Eq. (29)) in kinetics systematically examines the correlation between the rate constant (k) and the activation energy (E_a).

Table 4

Rate constants for $\alpha = 0$, $\beta = 1$ kinetic model fits at 280–320 °C.

Temperature/°C	$k_1/kPa \cdot \text{mol} \cdot g_{\text{cat}}^{-1} \cdot \text{min}^{-1}$	R^2	$k_{2(\text{H0-BT})}/\text{mol} \cdot g_{\text{cat}}^{-1} \cdot \text{min}^{-1}$	R^2
280	0.01306	0.97296	0.00126	0.99281
290	0.01824	0.96122	0.00158	0.99361
300	0.02272	0.96822	0.00193	0.997
310	0.02515	0.96613	0.00214	0.98959
320	0.03151	0.97692	0.00281	0.99316
A	3327.58		103.54	
$E_a/kJ \cdot \text{mol}^{-1}$	56.96		52.86	

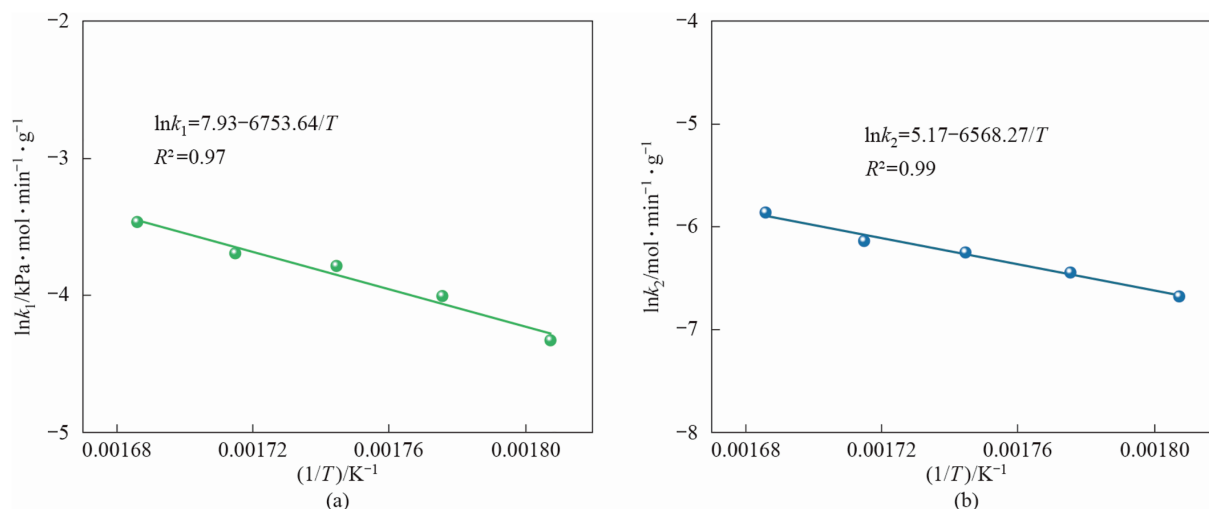


Fig. 9. Arrhenius plots for the first (a) and second (b) dehydrogenation steps of H12-BT.

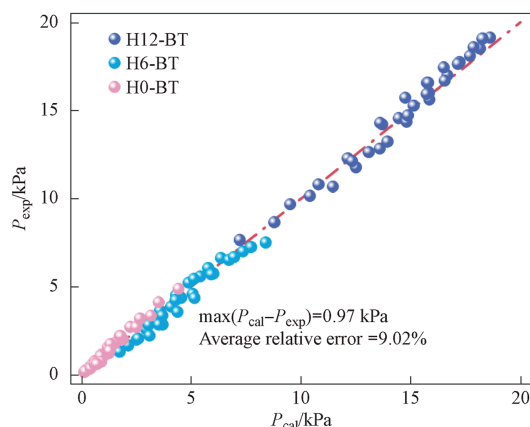


Fig. 10. Experimental and model calculated values of H12-BT dehydrogenation reaction.

$$k = A \cdot e^{-\frac{E_a}{R \cdot T}} \quad (29)$$

where A is the pre-exponential factor, independent of temperature, and has the same order of magnitude as the k ; E_a is the activation energy, $\text{J} \cdot \text{mol}^{-1}$; R is the gas constant, $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; and T is the reaction temperature, K.

Fig. 9 presents the Arrhenius plots for the two-step dehydrogenation of H12-BT. The activation energies are $56.96 \text{ kJ} \cdot \text{mol}^{-1}$ (E_{a1} , H12-BT $\rightarrow$ H6-BT) and $52.86 \text{ kJ} \cdot \text{mol}^{-1}$ (E_{a2} , H6-BT $\rightarrow$ H0-BT), indicating similar energy barriers with marginally higher requirements for the initial step. Contrary to the exponential inverse k - E_a correlation dictated by the Arrhenius equation, k_1 significantly exceeds $k_{2(\text{H0-BT})}$ in Table 4. This apparent anomaly stems from the dominant pre-exponential factor of the first step ($A_1 = 3327.58 \text{ kPa} \cdot \text{mol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{min}^{-1}$), which counteracts its elevated activation energy, yielding a net higher rate constant versus the second step ($A_2 = 103.54 \text{ mol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{min}^{-1}$). Pre-exponential factors reflect molecular collision frequencies and steric orientation probabilities [61]. The physical origin of the pre-exponential factor A is directly associated with the microscopic characteristics of the reaction system near the transition state. The differences in molecular configuration [62,63],

adsorption geometry [64], and surface coverage [65,66] between the two dehydrogenation reactants, H12-BT and H6-BT, lead to the disparity between A_1 and A_2 through their influence on the reaction rate and kinetic parameters of the system.

Model validation was performed by comparing experimental and simulated dehydrogenation data for H12-BT. Theoretical partial pressures (P_{cal}) derived from activation energy correlations (Eqs. (30)–(32)) were quantitatively compared against experimental values (P_{exp}). Fig. 10 demonstrates excellent agreement between model predictions and empirical data. The maximum absolute deviation is 0.97 kPa, and the Mean relative error is maintained at 9.02%. The model exhibits exceptional robustness in characterizing H12-BT dehydrogenation kinetics, maintaining errors significantly below literature benchmarks [37,55,67]. Partial pressures of H0-BT, H6-BT, and H12-BT show uniform distribution across concentration gradients. Critically, predicted concentration trajectories for all species closely track experimental datapoints throughout reaction progress (Fig. 10), confirming model reliability in complex reaction systems.

$$P_{\text{H12-BT}} = P_{\text{H12-BT},0} - 2779.43 \cdot \left(e^{-\frac{56950}{R \cdot T}} \right) \cdot \tau \quad (30)$$

$$P_{\text{H6-BT}} = 32.14 \cdot e^{-\frac{3730}{R \cdot T}} \left(1 - e^{-103.54 \cdot \left(e^{-\frac{52860}{R \cdot T}} \right) \cdot \tau} \right) \quad (31)$$

$$P_{\text{H0-BT}} = 2779.43 \cdot e^{-\frac{56950}{R \cdot T}} \cdot \tau - 32.14 \cdot e^{-\frac{3730}{R \cdot T}} \cdot \left[1 - e^{-103.54 \cdot \left(e^{-\frac{52860}{R \cdot T}} \right) \cdot \tau} \right] \quad (32)$$

3.3. The impact of products on the hydrogen production rate

Product inhibition effects were quantified by systematically varying H0-BT and H_2 partial pressures (N_2 -balanced) using a

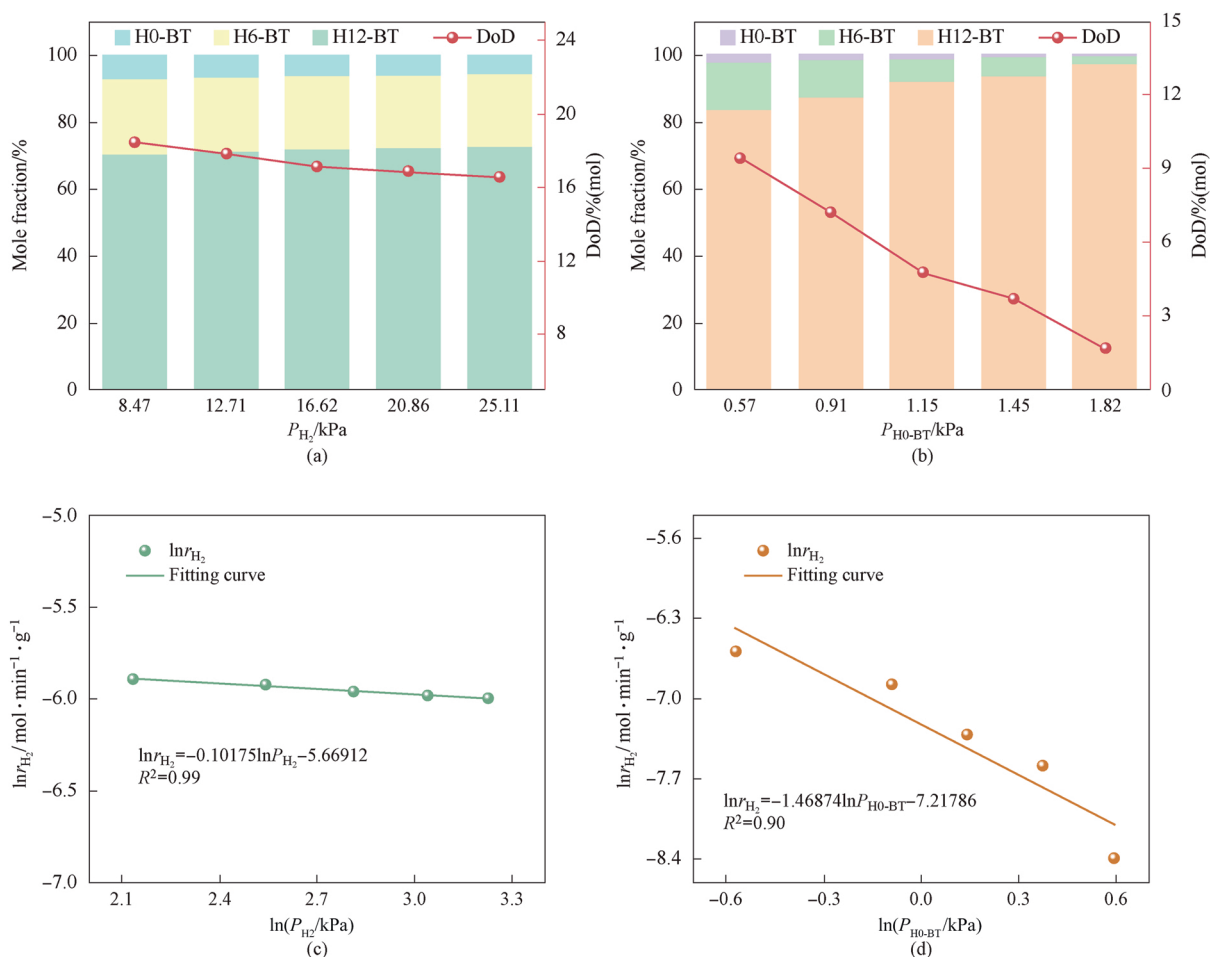


Fig. 11. Effect of H_2 (a), $H0-BT$ (b) partial pressure variation on hydrogen production rate; (c), (d) Reaction order fitting results. Reaction conditions: $m_{cat} = 0.1g$ (250–420 μm), $P_{total} = 0.2$ MPa (20 kPa $H12-BT$, N_2 balanced), $T = 280$ °C.

controlled-variable approach. As shown in Fig. 11(a) and (b), H_2 production rates exhibit significant inhibition with increasing P_{H_2} and P_{H0-BT} . Kinetic modeling via Eqs. (33) and (34) revealed reaction orders of -0.10 for H_2 ($R^2 = 0.99$) and -1.47 for $H0-BT$ ($R^2 = 0.90$), with fitted curves shown in Fig. 11(c), (d). Kinetic analysis indicates that the minor negative reaction order (-0.10) for H_2 partial pressure suggests minimal inhibitory effects of gaseous hydrogen on dehydrogenation reactions. The significant negative reaction order (-1.47) for $H0-BT$ points to a pronounced inhibitory mechanism.

$$r_{H_2} = \frac{F_{H12-BT,0}}{m_{cat}} \times DoD \times 6 = k \cdot P_{H_2}^{n_1} \quad (33)$$

$$r_{H_2} = \frac{F_{H12-BT,0}}{m_{cat}} \times DoD \times 6 = k \cdot P_{H0-BT}^{n_2} \quad (34)$$

The kinetic model was refined by incorporating reverse reaction parameters to account for product inhibition. As the first dehydrogenation step showed low conversion with excess reactants, its reverse reaction was excluded. The revised rate equations (Eqs. (6)–(8), in Supplementary Material) maintain the original form for the first step ($\alpha = 0$, $\beta = 1$, k_1 unchanged), while adopting the previously fitted $k_{2(H6-BT)}$ as k_2 for the second step.

Nonlinear regression of the third-step rate equation (Eq. (11), in Supplementary Material) determined the reaction orders ($m = 0.80$ for $H0-BT$, $n = 0.10$ for H_2) and the activation energy (54.61 $kJ \cdot mol^{-1}$) for the second step. The excellent fit aligns with the original model, and the higher reaction order of $H0-BT$ confirms its stronger product inhibition, consistent with experimental observations.

In-situ DRIFTS analysis was performed to investigate the adsorption of $H12-BT$ and $H0-BT$ [34]. For $H12-BT$, the intensities of its C–H stretching vibrations (cyclic C–H: $2930/2859$ cm^{-1}) [68,69] gradually decreased with increasing temperature. In contrast, the desorption of $H0-BT$ was monitored via the characteristic aromatic C=C stretching bands at 1475 and 1600 cm^{-1} [70]. As shown in Fig. S17, the results demonstrate that the adsorption stability of $H0-BT$ on the catalyst surface is significantly stronger than that of $H12-BT$. This indicates that the product and $H12-BT$ undergo competitive adsorption on the catalyst surface. $H0-BT$ exhibits stronger adsorption capability, occupying more active sites and thereby reducing the adsorption and activation of $H12-BT$, which leads to a decline in the dehydrogenation reaction rate. The desorption rate of H_2 is likely rapid, resulting in low surface coverage on the catalyst. Consequently, even with increased H_2 partial pressure, its impact on the reaction rate remains negligible.

During kinetic experiments, the catalyst bed was intentionally kept short in length; the feed was highly diluted by N₂ carrier gas; both reacted H12-BT and products were rapidly swept out of the reaction zone; reactions were conducted at low conversion levels. These conditions collectively ensured that product inhibition effects were negligible in the observed kinetics. Thus, the established model authentically and accurately reflects the intrinsic reaction behavior. To overcome H0-BT inhibition in pilot-scale applications, functional catalysts can be combined in a layered fixed-bed for multi-step dehydrogenation to maintain selectivity and performance. Additionally, optimizing the H12-BT dehydrogenation catalyst via selective sulfur poisoning can enhance H0-BT desorption.

4. Conclusions

This study examined the dehydrogenation pathways and kinetics of H12-BT over Pt/Al₂O₃ using H6-BT as an intermediate. Results demonstrate that during the initial reaction stage, H6-BT (SR) exhibits higher selectivity (82%) than H6-BT (MR). An apparent kinetic model for H12-BT dehydrogenation was developed in a continuous reactor, revealing a slightly higher activation energy barrier for the initial dehydrogenation step. The model demonstrates exceptional accuracy, with experimental and predicted values showing excellent agreement (average relative error: 9.02%). Product inhibition analysis further indicated competitive adsorption between H0-BT and H12-BT on the active sites, which exponentially suppressed the hydrogen formation rate. The experimental datasets and process parameters derived from this bench-scale continuous dehydrogenation model provide critical reference values for pilot-scale process scale-up.

CRedit Authorship Contribution Statement

Rumeng Lan: Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. Chao Sun: Writing – review & editing, Methodology, Investigation, Formal analysis. Jin Yang: Writing – review & editing, Supervision, Project administration, Formal analysis. Kang Xue: Writing – review & editing, Validation, Supervision, Software. Xiaolei Guo: Writing – review & editing, Visualization, Software. Zhenfeng Huang: Writing – review & editing, Resources, Project administration. Ruijie Gao: Writing – review & editing, Visualization, Project administration. Xiangwen Zhang: Writing – review & editing, Supervision, Funding acquisition. Jijun Zou: Writing – review & editing, Resources, Funding acquisition. Lun Pan: Writing – review & editing, Supervision, Methodology, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2025.12.027>.

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