REVIEW

Progress in Processes and Catalysts for Dehydrogenation of Cyclohexanol to Cyclohexanone

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Abstract

The dehydrogenation of cyclohexanol to cyclohexanone is a crucial industrial process in the production of caprolactam and adipic acid, both of which serve as important precursors in nylon textiles. This endothermic reaction is constrained by thermodynamic equilibrium and involves a complex reaction network, leading to a heightened focus on catalysts and process design. Copper-based catalysts have been extensively studied and exhibit exceptional low-temperature catalytic performance in cyclohexanol dehydrogenation, with some being commercially used in the industry. This paper specifically concentrates on research advancement concerning active species, reaction mechanisms, factors influencing product selectivity, and the deactivation behaviors of copper-based catalysts. Moreover, a brief introduction to the new processes that break thermodynamic equilibrium via reaction coupling and their corresponding catalysts is summarized here as well. These reviews may offer guidance and potential avenues for further investigations into catalysts and processes for cyclohexanol dehydrogenation.

Keywords Cyclohexanol · Dehydrogenation · Cyclohexanone · Copper-based catalyst · Reaction coupling processes

Introduction

Cyclohexanone is a vital intermediate in the production of ε-caprolactam and adipic acid, which serve as the main raw materials for nylon 6 (PA6) and nylon 66 (PA66), respectively. Besides polyamide fibers, cyclohexanone is utilized in the manufacturing of pharmaceuticals and fine chemicals [1–3], as shown in Fig. 1a. Currently, the global nylon market predominantly comprises PA6 and PA66, accounting for about 86% of total consumption [4]. The production of ε-caprolactam and adipic acid constitutes 80% of the total consumption of cyclohexanone [5]. In 2022, the worldwide cyclohexanone market was valued at US$8.34 billion. By 2023, it is projected to rise to US$8.72 billion, with an expected compound annual growth rate of 4.5% [6], as illustrated in Fig. 1b. Efficient production of high-purity cyclohexanone is paramount to meet the demands of the rapidly expanding industry.

Cyclohexanol dehydrogenation is a crucial industrial process in the production of cyclohexanone. However, its reaction network is complex, as illustrated in Fig. 2; the entire network encompasses several steps, including aromatization of cyclohexanol to phenol, dehydration of cyclohexanol to cyclohexene, and condensation of cyclohexanone to cyclohexylidencyclohexanone, in addition to dehydrogenation of cyclohexanol to cyclohexanone [7]. The heterogeneous catalytic gas-phase cyclohexanol dehydrogenation at atmospheric pressure is an endothermic reaction ($\Delta H = 65$ kJ/mol) and is limited by thermodynamic equilibrium [8]. The equilibrium conversion of cyclohexanol dehydrogenation at various temperatures is listed in Table 1 [9]. Increasing the reaction temperature serves to promote forward reaction and can enhance the conversion of cyclohexanol. However, simultaneously, it will intensify the side reactions of dehydration and aromatization, resulting in a higher demand for the design of suitable catalysts

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Fig. 1 **a** Main applications of the cyclohexanone. **b** Global cyclohexanone market. The data are from Ref. [6]
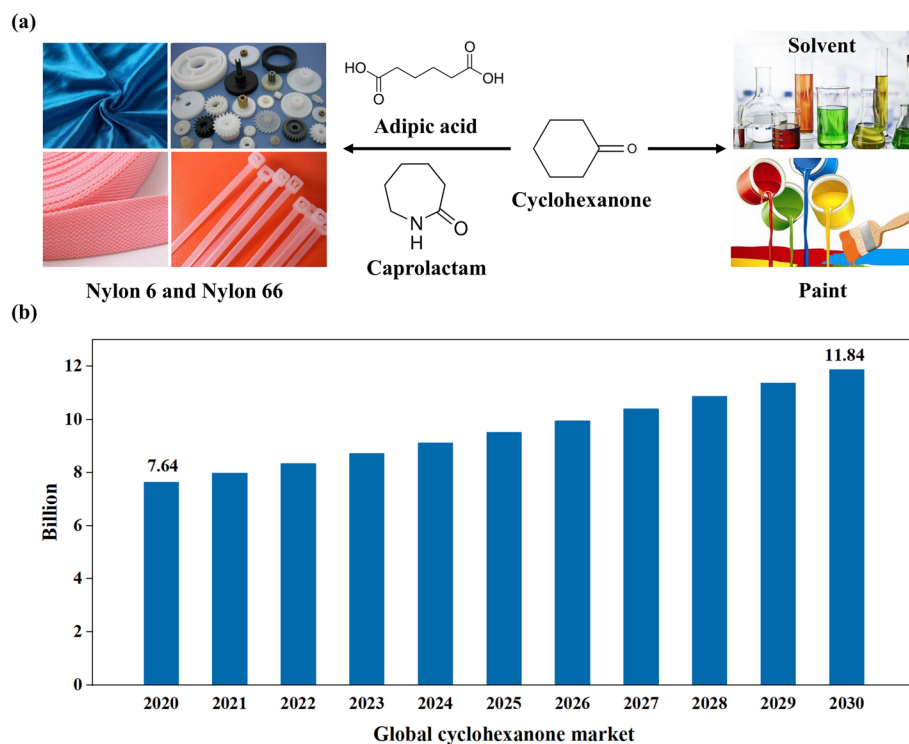

Fig. 2 Reaction network of the cyclohexanol dehydrogenation. Reproduced with permission from Ref. [7]. Copyright 2000, Elsevier
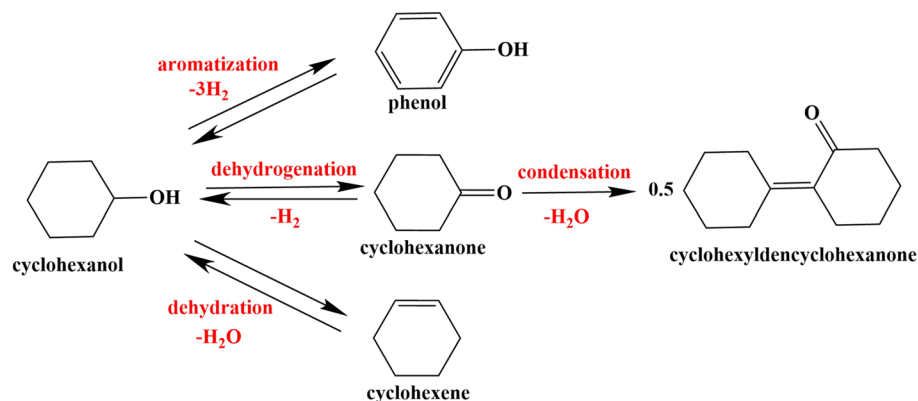

Table 1 Equilibrium conversion of the cyclohexanol dehydrogenation at different temperatures [9]

Reaction temperature (°C)	Equilibrium conversion (%)
220	48
250	68
280	76
300	89
350	95

and processes to achieve both high activity and selectivity for cyclohexanol dehydrogenation.

Previous works primarily utilized the ZnO/CaO catalyst for cyclohexanol dehydrogenation [10, 11]. The conversion of cyclohexanol via a ZnO/CaO catalyst was high (approximately 70%–80%), and the selectivity of cyclohexanone was < 98% at reaction temperatures ranging from 350 °C to 400 °C. However, the active component ZnO grains tended to grow at high temperatures, leading to a decrease in catalytic performance and a consequent reduction in the lifespan of the ZnO/CaO catalyst. Recently, copper-based catalysts have gained widespread attention due to their excellent low-temperature catalytic performance in the dehydrogenation of cyclohexanol to cyclohexanone [12–15]. The conversion of cyclohexanol could approach equilibrium values, with the selectivity of cyclohexanone usually exceeding 99% at reaction temperatures between 200 °C and 300 °C. In comparison with the ZnO/CaO catalyst, copper-based catalysts exhibit a higher reaction rate and require less catalyst

loading when processing the same amount of cyclohexanol, resulting in correspondingly smaller equipment size. Moreover, copper sources are cheap and readily available, and the lower reaction temperatures conserve energy in terms of a reduced heating load, making copper-based catalysts a popular choice in the industry.

Researchers have made continuous efforts to synthesize high-performance copper-based catalysts for the dehydrogenation of cyclohexanol to cyclohexanone and to investigate their structure–performance relationship. In this paper, we summarized the discussions on active species, factors influencing product selectivity, and the strategy for improving catalyst stability. Additionally, we propose novel processes that couple with the dehydrogenation of cyclohexanol to break the thermodynamic equilibrium conversion of cyclohexanol and utilize the generated hydrogen, along with investigations on corresponding catalysts. The study concludes with a brief discussion regarding the challenges associated with cyclohexanol dehydrogenation.

Copper-Based Catalysts for the Cyclohexanol Dehydrogenation

Discussion on the Active Species

The catalytic performance of Cu-based catalysts in cyclohexanol dehydrogenation is summarized in Table 2. As demonstrated, persistent research efforts have led to an excellent catalytic performance in copper-based catalysts. Although much debate surrounds the identification of active species for cyclohexanol dehydrogenation over copper-based catalysts, the topic remains controversial.

Some researchers believe that Cu^+ species act as active sites for the aromatization of cyclohexanol to phenol, whereas Cu^0 sites serve as active sites for the dehydrogenation of cyclohexanol to cyclohexanone [12, 16–19]. The catalyst activity increased linearly with an increasing amount of reversibly adsorbed CO in the Cu–ZnO–Al$_2$O$_3$ catalyst, leading to the conclusion that metallic copper species served as the primary active sites for cyclohexanol dehydrogenation [12]. Ji et al. [20] compared Cu/SiO$_2$ and Cu–ZnO/SiO$_2$ catalysts, suggesting that following reduction, the former contained only Cu^0 species, whereas both Cu^0 and Cu^+ species were present on the surface of the reduced Cu–ZnO/SiO$_2$ catalyst. They demonstrated that the conversion of cyclohexanol was 83% using the Cu/SiO$_2$ catalyst at 300 °C, with selectivities of 93.4% for cyclohexanone and 0.6% for phenol. In contrast, the conversion was 92.0% over Cu–ZnO/SiO$_2$, with selectivities of 78.6% for cyclohexanone and 14.2% for phenol. This suggests that Cu^+ species facilitated the phenol generation, whereas Cu^0 was the primary active site for the cyclohexanol dehydrogenation to cyclohexanone.

The promoted Cu–MgO catalysts also provided evidence for the role of Cu^0 species. With the introduction of Cr$_2$O$_3$, the proportion of Cu^0 increased, and the catalytic performance was considerably enhanced [18]. The conversion of cyclohexanol over the Cu–MgO–Cr$_2$O$_3$ catalyst reached 64.3%, and the selectivity of cyclohexanone exceeded 99% at 250 °C. However, another type of active site was proposed in Cu–MgO catalysts. It has been demonstrated that the basic sites of MgO in close proximity to Cu^0 sites played a critical role in facilitating the dehydrogenation of alcohols [17, 18]. The basic sites could act as nucleophiles to abstract the proton from the O–H group of cyclohexanol, forming a

Table 2 Catalytic performance of cyclohexanol dehydrogenation over Cu-based catalysts

Catalyst	Cu loading (%)	T (°C)	LHSV[a] (h^{-1})	Conversion (%)	Selectivity (%)	Refs.
Cu/Al$_2$O$_3$	55.7	250	5	81.5	79.6	[1]
Cu–Al$_2$O$_3$–ZnO	50	250	15.9	42	99	[12]
Cu/TiO$_2$–ZrO$_2$	10.8	250	3.8	33	77	[13]
Cu/MgO–SBA15	15	275	0.78	89	93	[14]
Cu/MgO	16	250	0.96	64	100	[16]
Cu/MgO	16	250	5	65.3	98	[17]
Cu–MgO–Cr$_2$O$_3$	22	270	0.8	68	99	[18]
CuO/ZnO/C	33	250	2.89	35	97	[19]
Cu–ZnO/SiO$_2$	23	300	6.39	91	85	[20]
CuO–ZnO–MgO	34.6	260	2.34	55	99.2	[21]
Cu–Cr–Mg–Al	59.6	330	2.2	86.1	95	[22]
Cu/Al$_2$O$_3$–ZrO$_2$	5	250	n/a	50	100	[23]
Cu/ZrO$_2$	2.7	250	11.55	54	100	[24]
CuFe$_2$O$_4$	n/a	300	1.14	68	84	[25]
CuO–Nb$_2$O$_5$	10	250	7.8	22	72	[26]

[a] liquid hourly space velocity

n/a: not available

negatively charged alkoxide intermediate. Following C_α–H elimination, this intermediate produced cyclohexanone, which eventually desorbed from the catalyst surface along with the H_2 molecule [14, 17, 27]. The reaction mechanism of cyclohexanol dehydrogenation over Cu–MgO catalysts is illustrated in Fig. 3.

However, some researchers have proposed that Cu^+ species exhibit higher activity in cyclohexanol dehydrogenation compared to Cu^0 species [1, 7, 21, 22, 28]. Fridman et al. [7] investigated the influence of copper oxidation states on catalytic activity. The reduced Cu–Mg catalyst contained only Cu^0 species on the surface, while both Cu^0 and Cu^+ species coexisted on the surface of the reduced Cu–Zn–Al catalyst. Cu–Zn–Al demonstrated a cyclohexanone formation

but a much slower rate of phenol formation compared to the Cu–Mg catalyst, indicating that Cu^0 species catalyzed both dehydrogenation and aromatization reactions, while Cu^+ sites catalyzed only cyclohexanol dehydrogenation to cyclohexanone. The adsorption behavior of cyclohexanol on Cu^0 and Cu^+ species was also studied using in situ FTIR [29]. As shown in Fig. 4, it is demonstrated that cyclohexanol adsorbed molecularly onto Cu^+ at room temperature, forming cyclohexanol alcoholate, which was considered the intermediate for cyclohexanone formation. However, for Cu^0 species, dissociative adsorption was observed only at temperatures of 50 °C or higher. Cyclohexanol adsorption on Cu^0 was accompanied by the formation of both cyclohexanol alcoholate and phenolate species, which explained the low product selectivity.

The studies involving modulated Cu^+/Cu^0 ratios of catalysts supported the aforementioned opinions. Cyclohexanol conversion improved proportionally with the increasing ratio of Cu^+/Cu^0, while the selectivity of cyclohexanone remained relatively stable at around 80% over a series of Cu/Al_2O_3 catalysts [1]. Adding certain reducible metal oxides, such as ZnO, Cr_2O_3, and La_2O_3, as promoters to the copper-based catalysts can also modulate the Cu^+/Cu^0 ratio and enhance the catalytic performance in cyclohexanol dehydrogenation [18, 20, 30, 31]. La_2O_3 species promoted the dispersion of copper species, increased the Cu^+/Cu^0 ratio, and stabilized the Cu^+ species of Cu–ZnO–Cr_2O_3 catalyst during the reduction and reaction processes, resulting in 15% and 11.5% increase in cyclohexanol conversion and cyclohexanone selectivity, respectively [30].

Sancheti et al. [21] also supported the notion of Cu^+ species as active sites. They utilized an unreduced CuZnMg
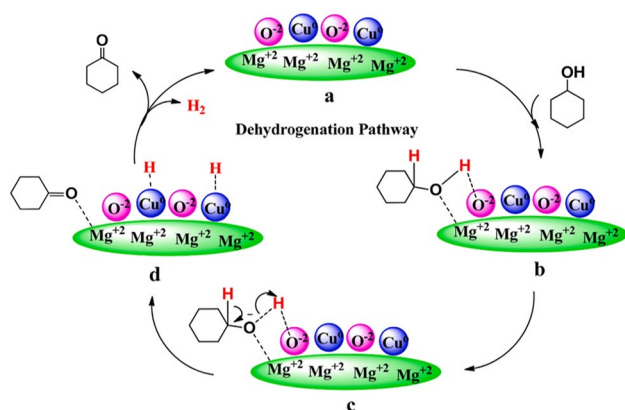

Fig. 3 Reaction mechanism of cyclohexanol dehydrogenation over Cu–MgO catalysts. Reproduced with permission from Ref. [17]. Copyright 2023, Elsevier
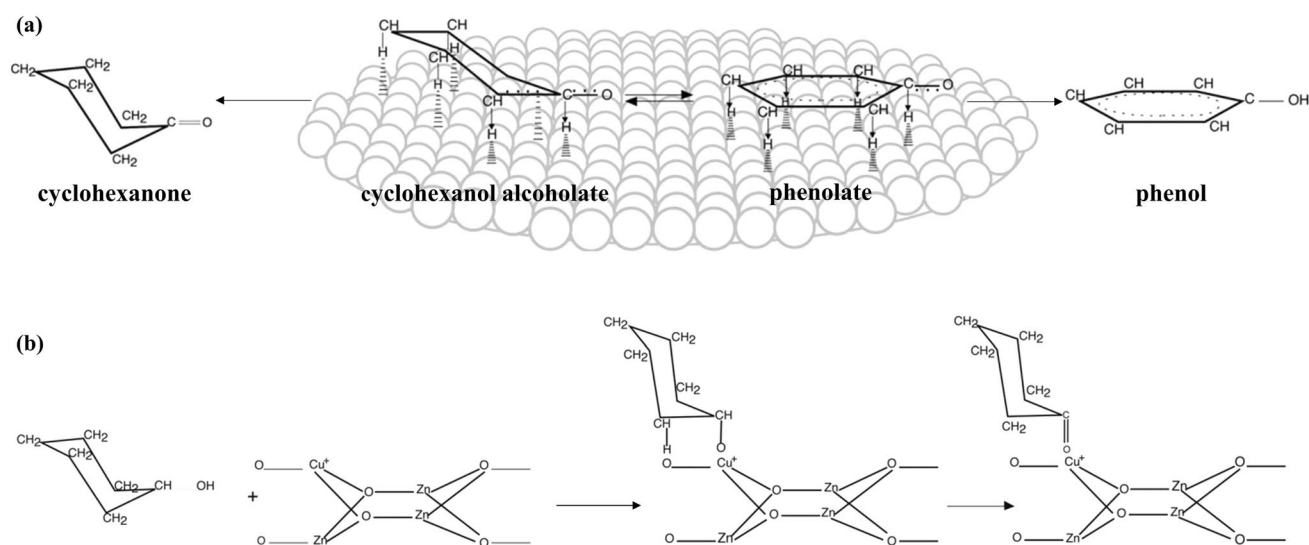

Fig. 4 Schematic of cyclohexanol adsorption on the surface of **a** Cu^0 and **b** Cu^+. Reproduced with permission from Ref. [29]. Copyright 2004, Elsevier

catalyst and achieved 55.0% cyclohexanol conversion and 99.2% cyclohexanone selectivity at 260 °C. By examining the catalyst's characterizations before and after the reaction, it was discovered that some Cu^{2+} species were reduced to a lower valence during the reaction, forming the Cu^+/Cu^{2+} redox couple [32, 33]. Figure 5 presents the plausible reaction mechanism of cyclohexanol dehydrogenation over such a structure: (i) cyclohexanol was adsorbed on copper oxide, and the hydroxyl group interacted with lattice oxygen and Cu^+; (ii) this interaction led to the dissociated chemisorption of the hydroxyl group, where the oxygen formed a bond with Cu^+ and hydrogen was abstracted as a proton by lattice oxygen; (iii) α–H was transferred to Cu^{2+} species to produce cyclohexanone; (iv) Cu^+–O bond was broken, cyclohexanone desorbed, and free hydrogen was generated [21].

Recent experimental studies and DFT (Density Functional Theory) calculations have suggested the existence of a synergistic effect between Cu^0 and Cu^+ species; this effect plays a crucial role in alcohol dehydrogenation [34, 35]. It was discovered that C–O bonds in alcohols preferentially adsorbed onto Cu^+ sites, whereas Cu^0 facilitated the transfer of H atoms over the CuAl-mixed metal oxide (CuAl–MMO) catalyst during the 2-propanol dehydrogenation. The corresponding reaction mechanism unfolded as follows: 2-propanol adsorbed on Cu^+ sites; the O–H and C–H bonds broke, and the H atoms transferred to Cu^0 sites, forming metal hydride; finally, the product desorbed. The cleavage of the O–H bond in 2-propanol was determined to be the rate-determining step in the dehydrogenation process.

Thus far, no consensus has been reached on the precise roles of Cu^0 and Cu^+ species in cyclohexanol dehydrogenation. This may be attributed to the fact that most of the published reports date back to the beginning of the twentieth century when in situ or *operando* experiments on catalyst structure and reactions were not well developed. Additionally, the chemical states of copper species can easily change during the reaction and exposure to air. However, due to the importance of this reaction within the industry, further investigation into the behavior of active species and their reaction mechanisms is imperative to provide guidance for catalyst development. For example, the preparation of copper-based catalysts with varying surface Cu^0 and Cu^+ distribution while maintaining consistent textural properties and particle sizes. Moreover, it has been reported that the composition of reducing agents during activation and the composition of the feed stream during the reaction can lead to instantaneously gas-induced dynamic transitions over commercial Cu/ZnO catalysts. In situ time-resolved XAFS (X-Ray Absorption Fine Structure) spectra, *operando* synchrotron X-ray powder diffraction, modulated-excitation infrared spectroscopy, and quasi in situ X-ray photoelectron spectra for the catalyst collected at different stages with time on stream provide excellent opportunities for monitoring the dynamic behaviors of both geometric structure and electronic environment of copper sites [36–40]. By examining the morphology and surface chemistry via in situ or *operando* experiments and combining theoretical DFT calculations, it is possible to gain valuable insights into the catalytic behaviors of active sites and the structure–performance relationship of the catalysts.

Fig. 5 Plausible mechanism of selective dehydrogenation of cyclohexanol to cyclohexanone. Reproduced with permission from Ref. [21]. Copyright 2021, Elsevier
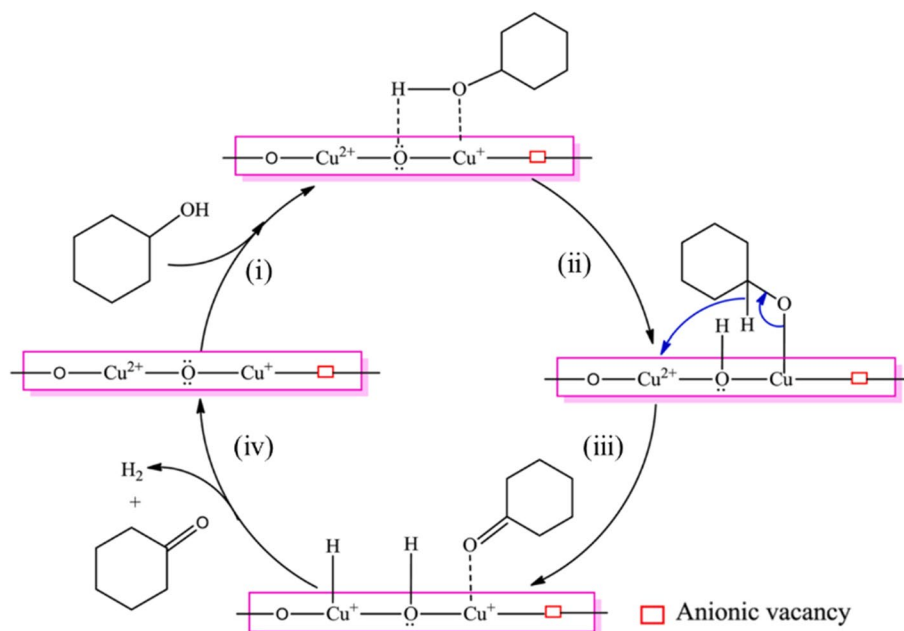
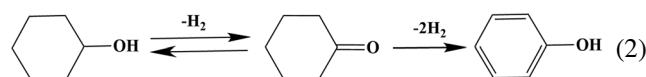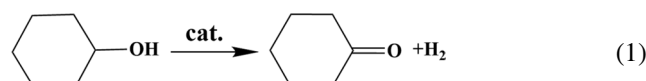## Factors Influencing the Product Selectivity

The reaction network of cyclohexanol dehydrogenation is complex, as illustrated in Fig. 2. There are numerous side reactions, such as the aromatization of cyclohexanol to phenol, dehydration of cyclohexanol to cyclohexene, and condensation of cyclohexanone to cyclohexyliden-cyclohexanone. Therefore, the factors influencing product selectivity are among the essential aspects to be investigated.

The primary byproducts are cyclohexene and phenol. It is generally believed that the dehydration reaction is catalyzed by the surface acid sites of the catalyst. Doping copper-based catalysts with alkali metals, alkaline earth metals, or transition metals can neutralize some acidic sites, thereby reducing the formation of cyclohexene. It was discovered that the intensity of strong acid sites decreased when Mn was added to the Cu–Si catalyst, resulting in a significant decrease in cyclohexene selectivity from 14.6% to 1.2% [41]. Chary et al. [42] suggested that cyclohexene might be generated on medium–strong acid sites. As the copper loading increased, the amount of medium–strong acid sites decreased and then increased, with the selectivity of cyclohexene changing synchronously.

It has also been reported that cyclohexanol can undergo dehydration reactions not only at acidic sites but also at basic sites [43]. The yield of cyclohexene linearly increased with the growing amount of both total acidity and total basicity, and a correlation commonly observed in a series of metal phosphates, metal oxides, and sulfates [43] as well as the Cu/Al$_2$O$_3$–ZrO$_2$ catalysts [23].

The product distribution is also influenced by the different structures of copper when combined with a secondary component. It has been found that when the catalyst precursor contains Cu$_x$Co$_{3-x}$O$_4$ spinel species, the copper and cobalt could transfer to CoCu alloy after reduction, which can prevent the formation of phenol. The authors attributed this to the fact that precursors containing Cu$_x$Co$_{3-x}$O$_4$ spinel species exhibit the highest H$_2$ chemisorption and inhibit the formation of multipoint adsorbed complexes on the surface, which serve as intermediates for phenol generation [44].

There is some debate regarding the pathway of phenol formation. Some studies suggest that phenol can be formed directly from cyclohexanol (direct route, Eq. 1) [7, 20], while others propose that phenol could be produced simultaneously from cyclohexanol and cyclohexanone (consecutive route, Eq. 2) [45]. Romero et al. [45] conducted a kinetics study of these two possible reaction routes for phenol generation over the copper–zinc oxide catalyst. Their finding demonstrated that the phenol generation rate aligned well with the consecutive route kinetic model, indicating that phenol was produced from cyclohexanone.

$$\text{OH} \xrightarrow{\text{cat.}} \text{O} + \text{H}_2 \qquad (1)$$

$$\text{OH} \underset{}{\overset{-\text{H}_2}{\rightleftharpoons}} \text{O} \xrightarrow{-2\text{H}_2} \text{OH} \qquad (2)$$

Stability of the Copper-Based Catalysts

Simón et al. [19] examined the deactivation behaviors of commercial copper–chromite and copper–zinc oxide catalysts used in cyclohexanol dehydrogenation. After a 350 h reaction at a high liquid hourly space velocity (LHSV) and 250 °C, a 50% reduction in activity was observed. Based on their characterizations, it was suggested that coke deposits on copper species and copper sintering were the main causes of deactivation. Notably, coke deposition on the copper–zinc oxide was severer, resulting in the blockage of pores.

A kinetic model was further developed for the commercial copper–zinc oxide catalyst, taking into account deactivation and considering the influence of hydrogen and cyclohexanone in the feed stream [2]. A coke deposit of about 7 wt% was demonstrated, increasing with higher cyclohexanone content and decreasing as hydrogen concentration increased. It was observed that the soft coke consisted of high-molecular weight aliphatic oligomers. Combined with the kinetic study and catalyst characterizations, it was suggested that H$_2$ likely inhibited coke formation due to a reduction in the concentration of coke precursors.

Cr$_2$O$_3$ can be employed as a structural additive to the Cu–Mg–Al catalyst, promoting copper dispersion and enhancing the catalyst's stability [46]. Additionally, with the inclusion of a ZnO promoter, the Cu–ZnO–MgO catalyst displayed remarkable thermal and structural stability during the dehydrogenation of cyclohexanol. Cyclohexanol conversions remained constant in the range of 51%–55%, and the selectivity of cyclohexanone was nearly 99% even after 125 h at 260 °C (Fig. 6). The spent catalyst could be easily regenerated by calcining at 500 °C in an air flow inside the reactor and reused for at least four cycles, demonstrating the robust and stable structure of the catalyst [21].

Adjusting the preparation methods or preparation conditions can also enhance the dispersion of active copper species and increase resistance to copper sintering. Jeon et al. [47] optimized the precipitation pH values during the preparation of Cu/SiO$_2$ catalysts to reduce surface acid sites, effectively suppressing side reactions and oligomer deposits that deactivated the active species. This led to superior catalytic performance and stability compared to commercial Cu–MgO and Cu–ZnO catalysts. It has also been reported that the Cu/SiO$_2$ catalyst prepared by using the ammonia evaporation method exhibited
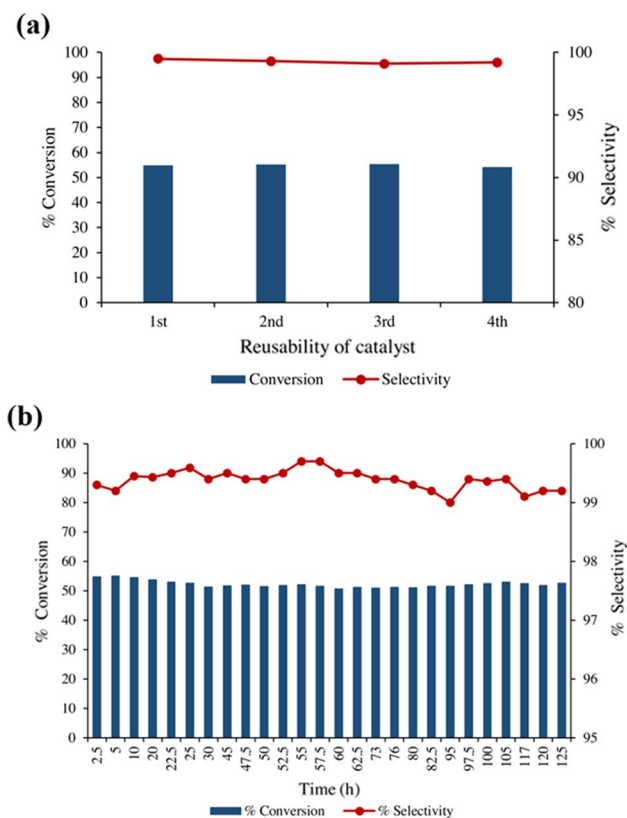
Oxidative Dehydrogenation of Cyclohexanol

In order to utilize the hydrogen generated during the reaction, a gaseous oxidant was introduced into the feed stream, converting the direct dehydrogenation process into an oxidative dehydrogenation process [49]. This approach not only overcomes the thermodynamic equilibrium limitation but also offers the advantage of using environmentally friendly, cost-effective oxidants, such as oxygen, which can inhibit the formation of oligomer deposits and consequently improve catalyst stability. Given these benefits, the oxidative dehydrogenation of cyclohexanol has garnered significant interest in recent years.

Cyclohexanol can undergo both dehydrogenation and oxidative dehydrogenation reactions over CuO–ZnO catalysts when oxygen or air is added to the feed, as demonstrated in Eq. 3) [49]. The catalyst remains stable at a low mole ratio of oxygen to cyclohexanol at 240 °C. As the mole ratio of oxygen to cyclohexanol increases, the conversion of cyclohexanol also rises, and the selectivity of cyclohexanone consistently remains above 99%. Furthermore, due to the endothermic nature of cyclohexanol's direct dehydrogenation, the LHSV of cyclohexanol is typically limited to a range of 0.5–2.0 h^{-1} constrained by the low external heat supply in a practical reactor. However, for the oxidative dehydrogenation process, the thermal effect can be modulated by adding oxidants to the feed stream, benefiting from the coupling with the exothermic reaction of converting hydrogen to water. In this scenario, the processing capacity of the reactor can be improved.

In addition to copper-based catalysts, other catalyst systems have also been developed for the oxidative dehydrogenation of the cyclohexanol process. The titanosilicate molecular sieve with an open 12-membered-ring channel system (ETS-10) and considerable basicity was employed for the oxidative dehydrogenation of cyclohexanol [56]. Utilizing O$_2$ as the oxidant, ETS-10 achieved 100% selectivity to cyclohexanone and 75% cyclohexanol conversion at reaction temperatures below 200 °C. However, noticeable deactivation of the catalyst could be observed during a period of 120 min. The deactivation was accelerated with increased basicity or decreased oxygen/cyclohexanol ratio, as the formation of cyclohexanone oligomers blocked partial microporous structures. This was further evidenced by the complete regeneration of the catalyst after calcination. Cobalt oxides encapsulated in SBA15 were also used in this process and exhibited a 42% cyclohexanol conversion at room temperature, using tert-butyl hydrogen peroxide as the oxidant in a batch reactor [57]. Due to the confined and uniformly dispersed cobalt species, the catalyst was able to be used up to four times without any significant change in its catalytic activity.

Gold has been reported to exhibit a strong activation capability on the C$_\alpha$–H bond of alcohols. Recently, Hensen and

Fig. 6 **a** Catalyst reusability study and **b** stability test for the dehydrogenation of cyclohexanol over ZnO modified Cu–MgO catalysts. Reproduced with permission from Ref [21]. Copyright 2021, Elsevier

outstanding stability during the ethanol dehydrogenation reaction. The ethanol conversion was over 90% with a selectivity of 99% to acetaldehyde throughout the 500 h time on stream at 280 °C [48]. This excellent performance can be attributed to the strong interaction between copper and SiO$_2$, resulting from the formation of an intermediate copper phyllosilicate phase.

New Processes for the Cyclohexanol Dehydrogenation

The dehydrogenation of cyclohexanol faces challenges due to thermodynamic equilibrium limitations and the formation of oligomers from condensation reactions, which can cover active species. Furthermore, the hydrogen released during the reaction is not effectively utilized [8]. To tackle these challenges, researchers have proposed alternative processes for cyclohexanol dehydrogenation, such as the oxidative dehydrogenation process using various oxidants [49–54] and reaction coupling processes involving different hydrogenation reactions [17, 18, 41, 55].

coworkers [50] applied a series of highly dispersed gold nanoparticles supported on Cu-doped spinel oxides catalysts in the oxidative dehydrogenation of cyclohexanol, using O_2 as the oxidant. The conversion of cyclohexanol and the selectivity of cyclohexanone were achieved at 70% and 92%, respectively, at 260 °C using the Au/MgCuCr$_2$O$_4$ catalyst. The catalyst exhibited excellent stability over 100 h of reaction (Fig. 7a). During the reaction, the 3 nm Au nanoparticles barely changed due to the strong metal-support interaction. The study proposed a synergistic catalysis of Au/MgCuCr$_2$O$_4$ catalyst for the oxidative dehydrogenation of cyclohexanol; this involved the basic Mg–O sites facilitating alcohol deprotonation, the gold nanoparticles selectively cleaving the C–H bond, and the Cu–O sites removing H atoms in the form of water.

Hensen [51] further investigated the active sites of the Au/MgCuCr$_2$O$_4$ catalysts and revealed their reaction mechanism by modulating the Cu contents. A conversion of 99.1% and a cyclohexanone selectivity of 90.2% were achieved over the stable Au/Mg$_{0.25}$Cu$_{0.75}$Cr$_2$O$_4$ catalyst at 300 °C. During the reaction, it was demonstrated that the surface Cu^{2+} species were reduced and migrated to the metallic gold nanoparticles, forming Au–Cu alloy species. This migration of Cu resulted in the creation of defects (oxygen vacancies) on the support. Based on these findings, a possible reaction mechanism is shown in Fig. 8. Oxygen vacancies could activate molecular O_2 to form active oxygen species, although it cannot be ruled out that the Cu species in the Au–Cu alloy may also promote oxygen activation. These active oxygen species were involved in the activation of O–H bonds in cyclohexanol, while gold played a role in activating C$_\alpha$–H bond.

ZnCr$_2$O$_4$ was also used as a support to disperse and stabilize gold due to its strong interaction. In conjunction with various characterizations, it was demonstrated that gold supported on a high-temperature (≥ 700 °C) calcined ZnCr$_2$O$_4$ support exhibited superior selectivity, with a cyclohexanone yield of 91% at 300 °C, and remained stable during a 90 h reaction (Fig. 7b) [58]. The near-complete removal of Lewis acid sites via high-temperature calcination reduced side reactions and inhibited the deposition of cyclohexene oligomers that deactivated the active species surface.

Ordered mesoporous silica with extra-large spherical cages (EP-FDU-12) was also used to obtain highly stable and dispersed gold species, achieving exceptional performance and superior stability (> 550 h) in the oxidative dehydrogenation of cyclohexanol (Fig. 7c) [59]. Following the reaction, no considerable growth of Au particles was observed, and the formation of carbon deposits on the AuNPs/EP-FDU-12 catalyst was minimal. This suggests that the large and opened three-dimensional mesoporous networks facilitated the diffusion of products, thus suppressing coke formation.

However, in certain oxidative dehydrogenation processes, the usage of O_2 (strong oxidant) resulted in the production of numerous unwanted byproducts [60, 61]. Over the past two decades, CO and CO_2 have garnered considerable interest as soft oxidants in oxidative dehydrogenation, facilitating the suppression of total oxidation [60, 62, 63]. Kumar et al. [30] conducted the cyclohexanol dehydrogenation reaction in the presence of CO and revealed that methanol was produced along with cyclohexanone, as demonstrated in Eqs. 4 and 5. A 90% conversion and 67.8% selectivity of cyclohexanone

Fig. 7 **a** Stability test of Au/MgCuCr$_2$O$_4$ in the gas-phase oxidative dehydrogenation of cyclohexanol. Reproduced with permission from Ref. [50]. Copyright 2018, Elsevier. **b** Catalytic stability of Au/ZnCr$_2$O$_4$ in the gas-phase cyclohexanol oxidation. Reproduced with permission from Ref. [58]. Copyright 2019, American Chemical Society. **c** Time-on-stream activity plot for the cyclohexanol oxidation on AuNPs/EP-FDU-12 catalyst. Reproduced with permission from Ref. [59]. Copyright 2017, Elsevier
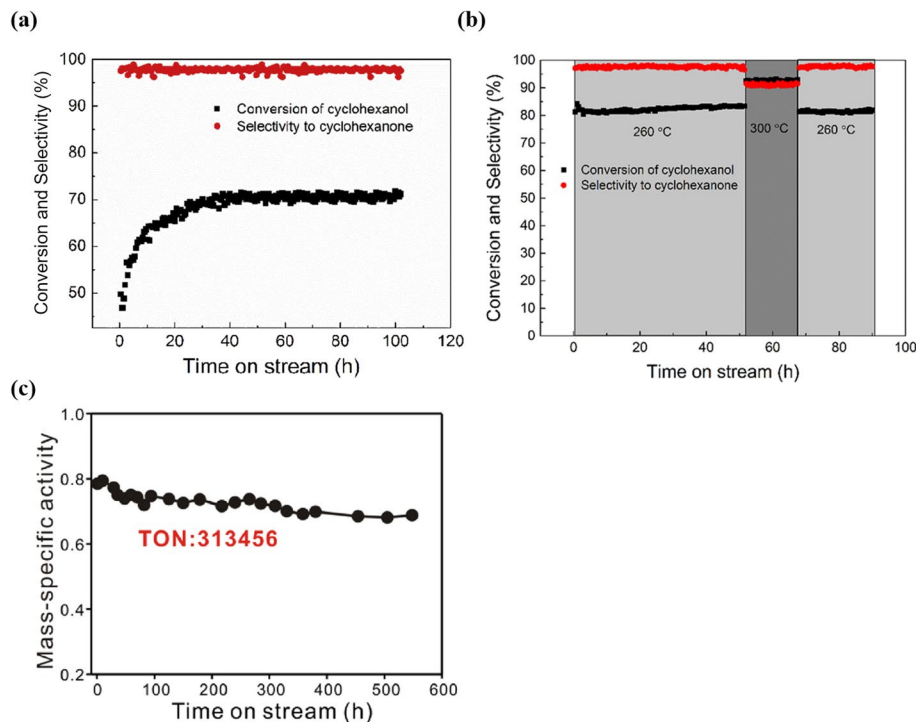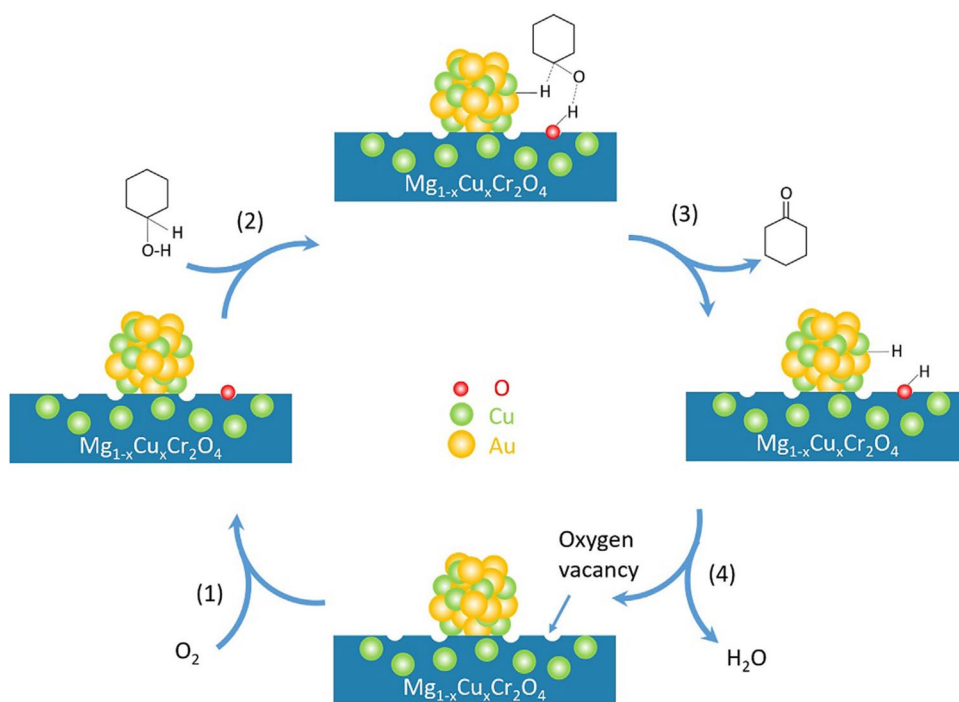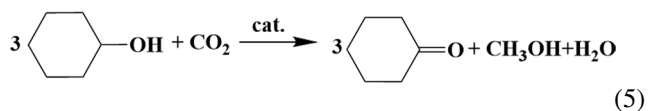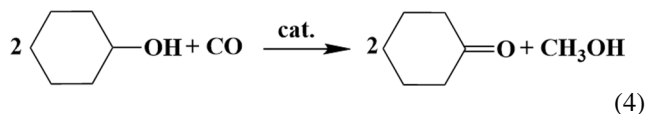
were achieved at 250 °C using the Cu–ZnO catalyst. The equations for oxidative dehydrogenation processes using different oxidants are shown below, and the catalytic performance is summarized in Table 3.

$$\text{—OH} + 0.5O_2 \xrightarrow{\text{cat.}} \text{=O} + H_2O \quad (3)$$

$$2\,\text{—OH} + CO \xrightarrow{\text{cat.}} 2\,\text{=O} + CH_3OH \quad (4)$$

$$3\,\text{—OH} + CO_2 \xrightarrow{\text{cat.}} 3\,\text{=O} + CH_3OH + H_2O \quad (5)$$
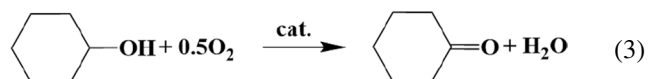
Reaction Coupling Processes with Hydrogenation Reactions

To optimize the utilization of hydrogen generated during cyclohexanol dehydrogenation, certain reaction coupling processes have been developed. These processes involve using unsaturated organic compounds alongside cyclohexanol as reactants in the feed. The heat released by the hydrogenation reaction can then be harnessed for cyclohexanol dehydrogenation. This approach facilitates easy temperature control and optimal hydrogen mass balance, eliminating the need for an external supply of H_2 and ultimately leading to reduced operational costs and energy savings [41, 65, 66].

The coupling of furfural hydrogenation and cyclohexanol dehydrogenation in vapor-phase conditions over Cu–MgO catalysts is a highly efficient and environmentally friendly process for synthesizing furfuryl alcohol and cyclohexanone,
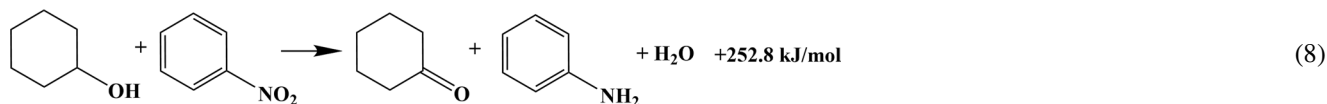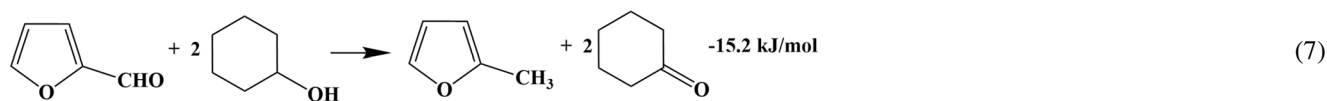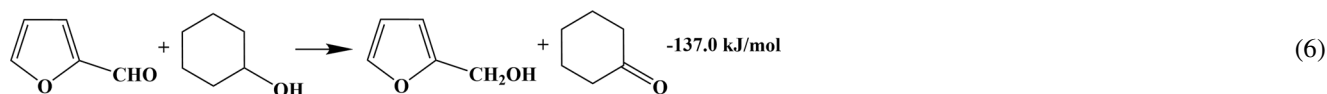
Table 3 Catalytic performance of oxidative dehydrogenation of cyclohexanol to cyclohexanone over different catalyst systems

Catalyst	T (°C)	Conversion (%)	Selectivity (%)	Oxidant	A molar ratio of oxidant to cyclohexanol	Refs.
Cu/ZnO	240	73.7	99.0	O_2	0.14	[8]
Cu–ZnO	250	90	67.8	CO	0.28	[30]
$Au/MgCuCr_2O_4$	300	71	98	O_2	6	[50]
$Au/Mg_{0.75}Cu_{0.25}Cr_2O_4$	300	99.1	90.2	O_2	6	[51]
ETS-10	200	42.2	100	O_2	89	[56]
$Au/ZnCr_2O_4$	300	93	91	O_2	6	[58]
AuNPs/EP-FDU-12	250	48	98	O_2	2.51	[64]

as demonstrated in Eq. 6 [18, 67]. Compared to independent reactions, the yield of furfuryl alcohol and cyclohexanone in the coupled reaction was improved by 18% and 7%, respectively, at 200 °C. It has also been proposed that the introduction of chromium could enhance Cu dispersion and stabilize Cu^+ species during reduction, resulting in exceptional catalytic performance.

Utilizing Cu–Zn–Al, 2-methylfuran, instead of furfuryl alcohol, was obtained alongside cyclohexanone, as shown in Eq. 7 [65]. The catalytic performances of both reactions improved, and no noticeable deactivation was observed during the 250 h reaction. The enhancement of 2-methylfuran selectivity in the coupling process could be attributed to the presence of activated hydrogen species on the catalyst surface resulting from dehydrogenation. Furthermore, the Cu–Mn–Si catalyst was introduced, exhibiting excellent catalytic performance in this coupling reaction [41]. The enhanced Cu dispersion, the presence of medium–strong acid sites due to manganese addition, and the interface between Cu and MnO contributed to the superior catalytic performance. The conversion of cyclohexanol and furfural was 66.8% and 99.1%, respectively, with selectivity for both cyclohexanone and 2-methylfuran exceeding 91% at 279 °C.

Direct catalytic coupling of nitrobenzene hydrogenation and cyclohexanol dehydrogenation (Eq. 8) was investigated using a Cu/MgO–SBA15 catalyst [14]. Although the catalyst exhibited excellent thermal stability, a rapid condensation reaction between cyclohexanone and aniline occurred. Competitive adsorption between the two reactants was observed, which negatively affected the selective reaction's efficiency.

and the occurrence of various side reactions may increase, leading to additional energy requirements during subsequent separation processes, reduced product quality, and potential impacts on downstream polymer synthesis.

Conclusion and Outlook

Cyclohexanol dehydrogenation to cyclohexanone is a vital industrial process used in the production of nylon materials, which hold a substantial share in the global commercial market. However, its reaction network is complex and limited by thermodynamic equilibrium. Considerable advancements have been made in copper-based catalysts for cyclohexanol dehydrogenation, leading to the realization of their applications in several industrial processes. Nonetheless, challenges persist in identifying active sites, understanding reaction mechanisms, and improving product selectivity and catalyst stability. This review provides a comprehensive summary of the active species, factors influencing product selectivity, and studies on deactivation. It suggests that more detailed and careful mechanistic investigations involving in situ or *operando* characterizations, isotopic tracer technology, and computational studies could provide insights and new possibilities in cyclohexanol dehydrogenation and guide the development of industrial catalysts. Furthermore, this review introduces new processes of oxidative dehydrogenation and reaction coupling processes with hydrogenation reactions. These novel processes offer several advantages, such as breaking the equilibrium conversion, ensuring high energy effi-

-137.0 kJ/mol (6)

-15.2 kJ/mol (7)

+252.8 kJ/mol (8)

Considerable progress has been made in researching new processes for cyclohexanol dehydrogenation. These advancements offer benefits such as high cyclohexanol conversion, improved energy efficiency, optimal hydrogen utilization, and enhanced environmental sustainability. However, challenges still remain in these new processes. For instance, cyclohexanol may become over-oxidized,

ciency, achieving optimal hydrogen utilization, and promoting environmental sustainability. However, the cost of separation and the occurrence of side reactions should be considered, as they may pose challenges to downstream product utilization in industrial applications.

Declarations

Conflict of interest Xinbin Ma is an editorial board member for *Transactions of Tianjin University* and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.

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