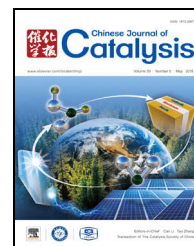


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Review

Recent advances on controllable and selective catalytic oxidation of cyclohexene

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Cyclohex-2-en-1-one

ABSTRACT

Because of multiple potential reaction sites and variable oxidation depths, oxidation of cyclohexene can lead to a mixture of products with different oxidation states and functional groups, such as 7-oxabicyclo[4.1.0]heptane, *trans/cis*-cyclohexane-1,2-diol, cyclohex-2-en-1-ol, cyclohex-2-en-1-one, and even adipic acid. These products are broadly and abundantly used intermediates in the chemical industry; therefore, controllable oxidation reactions for cyclohexene that can selectively afford the targeted products are synthetically valuable for applications in both the academy and industry, thus becoming the aim of synthetic and catalytic chemists in the field. Many reports on selective oxidation of cyclohexene have recently appeared in the literature because of its significance. This short review summarizes the recent advances on this subject, and the contents are mainly classified based on the chosen oxidants. We hope that this review can provide a useful guide for controllable and selective catalytic oxidation of cyclohexene for interested readers from both the academy and industry.

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1. Introduction

Cyclohexene (**1**) is a cheap, abundant, and easily accessible raw material in industry that is mostly produced through selective hydrogenation of benzene [1–3]. Though simple in its chemical structure, there are two potential oxidation sites in cyclohexene, and the usual oxidation reactions generally lead to a mixture of products with different oxidation states and functional groups (Scheme 1): oxidation of the C=C bond (site *a*) can lead to 7-oxabicyclo[4.1.0]heptane (**2**), *trans/cis*-cyclohexane-1,2-diol (**3**), or adipic acid (**4**); oxidation at the allylic C–H position (site *b*) may produce cyclohex-2-en-1-ol (**5**) or cyclo-

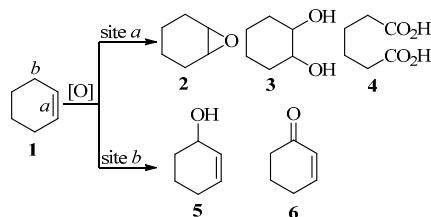
hex-2-en-1-one (**6**). Since these products (**2**–**6**) are useful industrial intermediates that have been widely employed in organic synthesis, medicinal chemistry, pesticide chemistry, materials science, *etc.* [4–7], selective oxidation of cyclohexene to produce one of these chemicals is synthetically valuable for applications in both the academy and industry. Hence, this subject has attracted the interest of synthetic and industrial chemists. In recent years, many reports have appeared for selective catalytic oxidation of cyclohexene. During our own research on green catalysis and synthesis [8–17], we have also been engaged in this area [15–17]. We found that reviews on this subject were rare [18]. Therefore, this short review sum-

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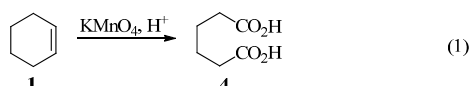


Scheme 1. Reaction paths of cyclohexene oxidation.

marizes the recent advances in this area; the contents are mainly classified based on the chosen oxidants. We hope that this review can provide a useful guide for controllable and selective catalytic oxidation of cyclohexene for interested readers from both the academy and industry.

2. Oxidation using a chemical oxidant

As an olefin, cyclohexene **1** can be oxidized by stoichiometric KMnO_4 under strong acid conditions to produce adipic acid **4** (Eq. (1)). This reaction is well documented in textbooks [19]. Although the reaction provides adipic acid **4**, a useful industrial intermediate, in a very high yield, the reaction could not be applied to large-scale production because a large amount of manganese solid waste is generated.



Analogously, other reactions using chemical oxidants that lead to solid waste are less applicable to industrial production, but they have been reported in recent years as an example of alkene oxidation to evaluate the catalyst activity. For example, in 2017, Kim *et al.* [20,21] designed and prepared nickel complexes **7** and **8** (Fig. 1), which were efficient catalysts in alkene oxidation reactions. Catalyzed by $\text{Ni}(\text{dpaq})\text{Cl}$ (**7**), cyclohexene could be oxidized by *m*-chloroperoxybenzoic acid (*m*-CPBA) to give epoxide **2** in 40% yield, while generating allylic oxidation byproducts **5** and **6** (Eq. (2)) [20]. Dinuclear Ni complex **8** was an even better catalyst, affording **2** in an enhanced yield of 65%, and the generation of allylic oxidation byproducts **5** and **6** was further restrained (Eq. (2)) [21]. Similarly, the oxidation reactions of cyclohexene by *m*-CPBA were also employed to evaluate the catalytic activities of cobalt complexes by the same group [22,23].

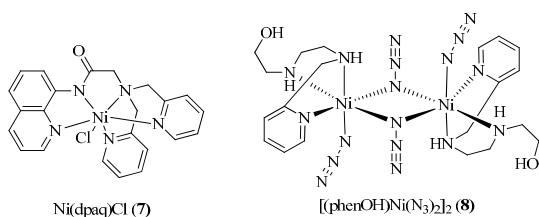
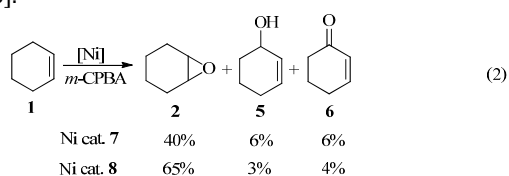
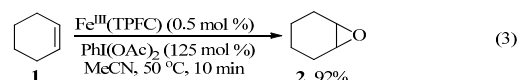


Fig. 1. Chemical structures of the Ni complexes.

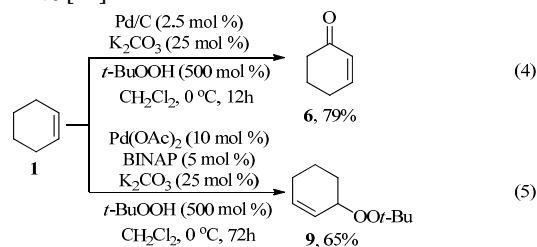
Hypervalent iodine compounds are also popular oxidants in organic reactions, including the epoxidation of cyclohexene. For example, in the presence of the iron tris(pentafluorophenyl)corrole complex $[\text{Fe}^{\text{III}}(\text{TPFC})]$, cyclohexene was oxidized by a slight excess of (diacetoxy)iodobenzene to produce epoxide **2** at an excellent yield (Eq. (3)). The reaction was impressively fast and it finished within 10 min under mild conditions [24]. Besides Fe [24,25], the oxidation reaction of cyclohexene by hypervalent iodine reagents was catalyzed by complexes of other transition metals, such as Cu and Mn, and was reported as an example for substrate extension of the alkene oxidation reactions [26,27].



3. Oxidation using *t*-BuOOH

t-BuOOH is cleaner than other chemical oxidants (*e.g.*, metal salts/oxides, MCBPA, or $\text{PhI}(\text{OAc})_2$) because the reduction by-product of this reagent is *t*-BuOH, a small organic molecule without hazardous elements (*e.g.*, Cl, Br, and S) that can be easily removed by distillation and recycled or eliminated by incineration. Therefore, oxidation methods with *t*-BuOOH as the oxidant are more acceptable for industrial production, regardless of cost. There have been many examples of cyclohexene oxidation using *t*-BuOOH as the oxidant.

In 2002, Corey *et al.* [28] reported Pd-catalyzed selective allylic oxidation reactions of cyclohexene with *t*-BuOOH, in which the reaction selectivities were controlled by the catalyst system: The Pd/C-catalyzed reaction afforded cyclohex-2-en-1-one **6** in a 79% yield (Eq. (4)); interestingly, with the $\text{Pd}(\text{OAc})_2$ catalyst and BINAP ligand, allylic *tert*-butylperoxy ether **9** was obtained as the major product (Eq. (5)). The reactions have been successfully applied on a series of cyclic, chained, aromatic, or aliphatic alkene substrates and should occur via a *t*-BuOO-free radical-mediated mechanism under basic conditions [28]. Copper-catalyzed allylic oxidation of cyclohexene by *t*-BuOOH was also investigated, and CuCl_2/L -proline was shown to be a good catalyst system in water, affording the full conversion of cyclohexene and a very high cyclohex-2-en-1-one **6** selectivity at 92% [29].



Besides the conventionally employed metal catalyst/ligand systems, a series of novel metal complex catalysts or ligands has been developed to achieve controllable and selective catalytic oxidation reactions with *t*-BuOOH (Fig. 2). Table 1 summarizes several typical examples. In 2004, Doyle *et al.* [30] reported a dirhodium caprolactamate catalyst **10** (Fig. 2), which was efficient for allylic oxidation of cyclic alkenes and could

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