# Carbon-Based, Metal-Free Catalysts for Chemical Productions

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## 10.1 Introduction

All kinds of chemicals play a very important role in the progress of mankind evolvement. An efficient and low-cost catalyst can significantly increase the yield of chemicals. Metal catalysts have demonstrated their high performance in the synthesis of chemicals. However, the limited reserves of metal, especially precious metals, will increase the prime cost of chemical productions. It is urgent to search low-cost and efficient metal-substituted catalysts. Recently, carbon-based, metal-free catalysts for chemical productions have attracted an increasing interest in the fundamental study and possible applications [1-5]. Many kinds of carbon, particularly nanostructural carbons such as active carbon, fullerene, carbon nanotubes (CNTs), graphene, diamond, and C<sub>3</sub>N<sub>4</sub>, have been studied as the potential catalysts for chemicals due to their rich structural and electronic properties and low cost [2, 6, 7]. Although they show great potential, pure carbon is usually inert in chemistry. It needs to tune the structural and electronic properties to enhance the catalytic activity of carbon via physical or chemical modification [1]. In particular, it has been demonstrated that many perturbations to the carbon structure, e.g. dislocations, vacancies, edges, heteroatoms, and functional groups, readily modify the density of states in carbon and promote their catalytic properties [1, 3, 5].

Currently, the chemicals using carbon-based, metal-free catalysts almost involve all kinds of oxidation and hydrogenation, which can be driven by thermal, electrical, and solar energies. In this chapter, we will briefly overview the recent advances in carbon-based, metal-free catalysts for chemical productions via concentrating on the active sites, reaction process, and chemicals. The new opportunities in catalysis brought by carbon materials, the various routes to tune the electronic states of carbon materials, and the corresponding active sites are analyzed. The oxidation and reduction, and typically the  $H_2O_2$  synthesis and the vinyl chloride monomer (VCM) synthesis using metal-free carbon catalysts, are fully discussed. We will also go beyond the fundamental properties of such structures and discuss the perspective of using such materials for future applications in catalysis.

## 10.2 Active Sites of Carbon-Based, Metal-Free Catalysts

The big family with multivariate structures renders carbon many potential applications in catalysis. The different structural and electronic properties of carbon family lead to different active centers for the production of chemicals. One typical representation is graphene because it is a basic construction unit of several other allotropes such as zero-dimensional (0D) fullerene, 1D CNTs, and 3D graphite [8] (Figure 10.1). For pure graphene, it is inert in chemistry because of the low density of states around the Fermi level, whereas it is reported that it is active at the defects and edges, e.g. the zigzag edge can efficiently activate the oxygen molecule in electrocatalysis [9]. One possible route is to reduce the lateral size in order to increase the active edges. But for the in-plane atoms of graphene, the chemical activity is very low. In order to trigger the activity, different heteroatoms such as O, N, B, S, P, and their corresponding functional groups have been introduced to enhance the activity of the in-plane structure [1, 5, 10]. These heteroatoms and functional groups can be directly used as the active sites such as B site in B-doped graphene [11, 12] and some oxygen groups due to the their base and alkaline [2, 3], or can affect the electronic structure of the nearby carbon atoms and enhance the activity of carbon atoms [10, 13]. In addition, the heteroatoms and functional groups can also modify the electronic structure of



**Figure 10.1** Schematic showing catalytic active sites in graphene due to the edges, defects, heteroatoms, and groups. Source: Su and Loh 2013 [3]. Reproduced with permission from American Chemical Society.

the graphene edges and tune the activity of the edges. Similarly, the catalytic activity of other carbon allotropes can be optimized by tuning their structural and electronic properties.

#### 10.3 Oxidation Reactions

Oxidation is a kind of important reaction to produce chemicals using oxidants such as oxygen and hydrogen peroxide. The oxidation by carbon-based catalysts starts from their capacity for activation of oxygen. It is demonstrated that the molecular oxygen can be efficiently reduced over the disordered carbon such as the vacancy, the heteroatom-doped carbon, and the edges of graphitic layers, which can be applied in fuel cells and metal–air batteries [5, 9, 10]. As oxygen can be reduced over the carbon-based materials, it is reasonable that the carbon-based materials can be used as catalysts for chemicals via selective oxidation. It is reported that the carbon-based materials such as active carbon, fullerene, CNTs, graphene, diamond and carbon nitride with modest defects, heteroatoms, or oxygen-containing functional groups can efficiently catalyze the oxidative reactions for value-added chemicals [2, 3, 14]. Currently, two systems are widely investigated, i.e. one is high-temperature reaction in gas phase and another is low-temperature reaction in liquid phase.

For high-temperature reaction in gas phase, the O<sub>2</sub> is usually used as the oxidant. Although it is reported that the metal-free carbon can electrocatalyze the reduction of oxygen molecules at room temperature, the direct activation of oxygen at low temperature without any other energy input is difficult because the cleavage of bond of O-O is unfavorable on carbon materials. The reaction using  $O_2$  as the oxidation usually needs higher temperature, i.e. over 100 °C [2]. It is found that the defects, heteroatoms, or some groups such as  $PO_x$  group can induce the catalytic activity directly as the active sites [9, 15] or triggering the activity around carbon atoms [10]. The typical reactions are the oxidative dehydrogenation of alkanes to chemicals such as butane to butylene [15] and ethylbenzene to styrene [16]. The oxidative dehydrogenation of alkanes has gotten great progress by designing different structural nanocarbons during the past few years. However, one drawback is that the carbon easily burns at high temperature, limiting the industrial application. It needs to develop high-efficient and stable carbon catalysts for high-temperature reaction in O2 atmosphere.

For low-temperature reaction in liquid phase, the selective oxidation of benzene, cyclohexane, aliphatic and benzylic alcohols, phenyl alkane, and phenyl olefins has been investigated by metal-free, carbon-based materials [3, 17, 18] (Table 10.1). Because the activation is difficult at low temperature, using more active oxidants such as  $HNO_3$ ,  $H_2O_2$ , *tert*-butyl hydroperoxide (TBHP), and NaClO is a good choice to reduce the reaction temperature on carbon materials [19–22]. Usually, the inorganic small molecules such as light alkanes and olefin

Conversion Conversion Alcohol Product (%) Alkvne Product (%) OH  $\cap$ Ο >98 >98 HC OH 96 52 OH 26 41 >98 26 OН 18 27

**Table 10.1** Conversion of benzylic and aliphatic alcohols to their respective ketones or aldehyde products and conversion of aryl and aliphatic alkynes to their respective methyl ketone products by graphene oxide catalysts.

Source: Dreyer et al. 2010 [18]. Reproduced with permission from John Wiley & Sons.

cannot be directly activated on carbon materials because of their adsorption is difficult. The typical low-temperature reaction in liquid phase usually involves the bigger molecules, especially molecules including benzene and cyclohexane groups because the  $\pi$ - $\pi$  interactions between the molecules and the carbon surface will promote the adsorption of the molecules. For example, around 17% yield of phenol from the oxidation of benzene over chemically converted graphene was obtained by Ma and coworkers, who used H<sub>2</sub>O<sub>2</sub> as the oxidant [23]. The  $\pi$ - $\pi$  interactions of benzene and graphene are considered to facilitate the adsorption of benzene on the graphene surface. The structural and electronic differences of carbon materials compared with metal materials may change the selectivity in some reactions. Take the selective oxidation of cyclohexane as an example. The cyclohexane can be oxidized to cyclohexanone, cyclohexanol, and adipic acid by typical metal catalysts in the industry [24]. It is reported that Au nanoparticles supported on zeolite Socony Mobil-5 (ZSM-5) zeolite has a 15% conversion of cyclohexane with a 92% selectivity for cyclohexanone and cyclohexanol under 1 MPa O<sub>2</sub> [24], but it is a great challenge to directly get adipic acid with a high selectivity using metal catalysts. Peng and coworkers used N-doped CNTs as the catalyst for the oxidation of cyclohexane and obtained an adipic acid selectivity of 60% at a high conversion of 45% [25]. This high yield of adipic acid is remarkable because the conventional metal catalysts could not efficiently convert cyclohexane to adipic acid.

### 10.4 Reduction Reactions

Compared with the oxidation reactions, the hydrogenation reactions on carbon materials are few because activation of  $H_2$  is more difficult compared with  $O_2$ . There are only several examples to use metal-free carbon as the catalyst for reduction in the presence of  $H_2$  [26, 27]. For example, it is reported that graphene and reduced graphene oxide (RGO) could catalyze the hydrogenation with H<sub>2</sub> [27]. The neutral fullerenes and fullerene anions were also reported to be as the catalysts for the reduction of nitroarenes with  $H_2$  as the reductant [26]. However, the active sites and the activation mechanism for these reduction reactions are still under debate. The more efficient way is to use a strong reductant such as hydrazine [28] and sodium borohydride. Cho and coworkers has tried to use graphite as the catalyst and hydrazine as the reductant to reduce nitrobenzene to the corresponding aniline [28]. Recently, Gao et al. found that graphene-based materials could further improve this catalytic efficiency with a yield up to 97.4% even at room temperature [29]. The graphite or graphene catalyst could promote the adsorption of the reactants as well as the electron transfer between nitrobenzene and hydrazine [29, 30].

Alternatively, the researchers have tried to utilize the H from H<sub>2</sub>O for reduction using an electrochemical method. This is motivated from  $H_2$  production by electrolyzing water, but it actually needs to utilize the intermediate, i.e. adsorbed hydrogen atom as the reductant and avoid the H<sub>2</sub> generation during water splitting. The typical reaction is the electrochemical reduction of  $CO_2$  for value-added chemicals such as methanol and ethylene. It was found that the metal-free nanostructural carbon such as graphene with heteroatom doping or nanofibers can be used as an efficient catalyst. For example, carbon nanofibers in ionic liquids reduce  $CO_2$  to CO at lower overpotentials with higher efficiency than silver [31]. The B-doped graphene could reduce  $CO_2$  to formic acid/formate [32]. Very recently, it was reported that the N-doped graphene quantum dots (NGQDs) could catalyze the electrochemical reduction of carbon dioxide into multi-carbon hydrocarbons with a high faradaic efficiency up to 90% [33] (Figure 10.2). The product distribution can be controlled via using the graphene quantum dots (GQDs) and NGQDs, as well as changing the reaction potential. The optimized selectivity for ethylene and ethanol conversions using NGQDs catalyst could reach 45%.

# 10.5 H<sub>2</sub>O<sub>2</sub> Synthesis

 $H_2O_2$  is an important chemical, which is usually used as an oxidizer, bleaching agent, and disinfectant. The current synthesis route in industry is from  $H_2$  and  $O_2$  by a metal catalyst via anthraquinone process. The economics of the process depend heavily on effective recycling of the expensive quinone and extraction solvents and of the hydrogenation catalyst. However, direct synthesis is difficult to achieve, as the reaction of hydrogen with oxygen thermodynamically favors production of water. Great efforts for direct synthesis have been devoted, most



**Figure 10.2** Electrocatalytic activity and product distribution of carbon nanostructures toward CO<sub>2</sub> reduction at various applied cathodic potential for N-doped graphene quantum dots (NGQDs) (a) and graphene quantum dots (GQDs) (b). Source: Wu et al. 2016 [33]. Reproduced with permission from Springer Nature.

of which are based around finely dispersed metal catalysts. None of these has yet reached a point where they can be used for industrial-scale synthesis [34, 35]. One possible route is to use electrochemical method via choosing the proper reaction overpotential [35–37]. It is reported that oxygen reduction reaction (ORR) proceeds with a two-electron transfer process over some carbon-based, metal-free catalysts [36], although it is an unwanted side reaction in ordinary

 $\rm H_2-O_2$  fuel cells, which ideally needs four-electron transfer process. The target product is  $\rm HO_2^-$  in alkaline media (Reaction (10.1)) and  $\rm H_2O_2$  in acid media (Reaction (10.2)), respectively. It should avoid a further oxidation of the product via additional two-electron transfer, as shown in Reactions (10.2) and (10.4). The key is to explore the ideal catalyst. Metal catalysts such as precious Pt- and Fe-based catalysts widely used in fuel cells usually proceed with a four-electron transfer process [38, 39].

Alkaline media:

$$O_2 + H_2O + 2e^- = HO_2^- + OH^-$$
 (10.1)

$$HO_2^{-} + H_2O + 2e^{-} = 3OH^{-}$$
(10.2)

Acid media:

$$O_2 + 2H^+ + 2e^- = H_2O_2$$
(10.3)

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O$$
(10.4)

It was reported that some carbon-based materials can catalyze oxygen via a two-electron process [36], which provides the possibility to produce hydrogen peroxide. Intensive investigations for electrochemical synthesis of hydrogen peroxides started in 1970s, and it attracted particular interest in recent years [36]. Graphite electrodes with trickle bed, fixed bed, or packed bed strategies have been tried to synthesize peroxides via a two-electron reduction of  $O_2$  [35, 36]. In addition, it was found that different carbons such as glassy carbon and carbon black can also be used as electrocatalysts for hydrogen peroxides. It has been previously proposed that  $O_2$  reduction occurs on the quinonyl (Q) of carbon electrodes via mediation of semiquinone radical anion (Q<sup>•-</sup>) in alkaline solution [40, 41]. In this reaction process, the semiquinone radical anion (Q<sup>•-</sup>) can be formed on active site Q via one-electron transfer. In the following chemical step, semiquinone reacts with molecular oxygen yielding superoxide anion ( $O_2^{•-}$ ):

$$Q + e^- \to Q^{\bullet -} \tag{10.5}$$

$$\mathbf{Q}^{\bullet-} + \mathbf{O}_2 \to \mathbf{O}_2^{\bullet-} + \mathbf{Q} \tag{10.6}$$

$$O_2^{\bullet-} + H_2O + e^- \to HO_2^- + OH^-$$
 (10.7)

Reaction (10.6) is considered the rate-determining step in the overall reduction of oxygen. The superoxide radical anion formed either disproportionates or is further reduced, both of which yield  $HO_2^-$  in alkaline solution. In all, quinonyl on carbon electrodes can effectively catalyze the two-electron reduction of oxygen to peroxide anion. Direct preparation on plate or bulk carbon electrodes usually offers a low efficiency because of the low active sites and low solubility of oxygen in aqueous solution. The maximum possible current density is no more than  $1 \text{ mA cm}^{-2}$  (equivalent to  $\leq 20 \text{ µmol cm}^{-2} \text{ h}^{-1}$ ) [35]. One promising route is to use the three-dimensional cathodes such as beds of carbon particles and reticulated vitreous carbon [42], and oxygen diffusion cathodes [42, 43] to increase the active sites and the oxygen diffusion. It is reported that the peroxide can be up to 0.8 M via the optimization of carbon electrode [36, 44]. Nevertheless, it is hard to further increase the production of peroxide because it can be further reduced to H<sub>2</sub>O

via additional two-electron transfer. One possible route is to use the flow reaction mode in order to quickly separate the  $H_2O_2$  during the electrochemical synthesis process [45]. Alternatively, one can also directly utilize the generated  $H_2O_2$  to oxidize the molecules to valued chemicals at the anode or directly degrade the organic contaminant for water treatment via a Fenton process [34, 35, 46].

### 10.6 Vinyl Chloride Monomer Synthesis

Polyvinyl chloride (PVC) polymerized from VCM is one of the mostly used engineering plastics in the world, which provides cornerstone for the modern industry. Calcium carbide method (as shown in Figure 10.3) is the first industrialized process to produce VCM and is still dominant in countries rich in coal, such as China and India. However, HgCl<sub>2</sub> is used as the catalyst in acetylene hydrochlorination reaction, which poses great threat to both environment and human health. As stipulated by "Minamata Convention on Mercury," Hg will be globally prohibited in 2020; this exerts intense pressure on coal-based VCM synthesis process and provokes extensive efforts to develop mercury-free catalysts [47].

Systematical studies carried out by Hutchings showed that  $AuCl_3$  could be a potentially alternative catalyst with activity close to  $HgCl_2$ . With the development over the years, the lifetime of  $Au^{3+}$  has been improved significantly [48–50]. At the same time, wide efforts have also been devoted to exploring mercury-free and even metal-free catalysts. Pan, Bao, and coworkers reported that N doping could endow carbon materials' catalytic activity for acetylene hydrochlorination without adding any metal. The acetylene conversion reached 77% and vinyl chloride selectivity was above 98% at gas hourly space velocity (GHSV) of 32 h<sup>-1</sup> and a temperature of 200 °C. The catalyst was rather stable and no obvious deactivation was observed during a 100 h test. For comparison, the undoped carbon materials such as carbon black and CNTs showed a negligible activity, suggesting the promoting effects of the doped nitrogen heteroatoms [51]. Although the activity is still low for real applications, this already opens up an alternative approach for the design of metal-free catalysts for acetylene hydrochlorination.

However, it remains challenging to elucidate the catalytic roles of doped heteroatoms because the nitrogen species are frequently present in three different structures, i.e. pyridinic-N, pyrrolic-N, and quaternary-N whether they are introduced by bottom-up or top-down synthesis methods. These different types of nitrogen species exhibit different electronic structures, which may play different roles in catalysis. Therefore, many studies were devoted to investigation of the reaction mechanism by constructing model catalysts and employing density functional theory (DFT) calculations. However, the conclusions are still disputable. Li et al. [52] found that pyrrolic-N could induce localized electronic states below Fermi level on the carbon sites, which benefits the adsorption of acetylene. The catalytic activity increases with the increase in exposed pyrrolic-N content. Kinetic study shows that the reaction follows the Eley–Rideal mechanism with chemically adsorbed acetylene on pyrrolic-N-bonded carbon



Figure 10.3 A scheme for coal-based process to produce PVC.

structures reacting with gas-phase HCl. The temperature-programmed desorption (TPD) experiments presented by Zhang et al. [53] also supported the above conclusion. Those authors demonstrated that there is a positive correlation between the content of pyrrolic-N species and the desorption amount of HCl and  $C_2H_2$ . It was shown that the activity follows the sequence of pyrrolic-N>graphitic-N>pyridinic-N [53]. Zhou et al. [54] reported that N-doped carbon nanotubes (NCNTs) could increase the nucleophilicity of CNTs and enhance the interactions between the HOMO (highest occupied molecular orbital) of NCNT and the low-lying lowest unoccupied molecular orbital (LUMO) of acetylene. This consequently promotes the addition reaction between C<sub>2</sub>H<sub>2</sub> and HCl forming C<sub>2</sub>H<sub>3</sub>Cl. Furthermore, those authors proposed that quaternary-N is catalytically more active and there is a good linear relationship between the activity and quaternary-N content. In comparison, Li et al. [55] stressed the importance of pyridinic-N species when they studied the activated-carbon-supported  $g-C_3N_4$  as a catalyst. They observed that pyridinic nitrogen is responsible to activate hydrogen chloride while acetylene is chemically adsorbed on the carbon atom of g-C<sub>3</sub>N<sub>4</sub>, forming CHCl=CH-C<sub>3</sub>N<sub>4</sub>H unit as the intermediate [55]. In order to expose the doped nitrogen sites as many as possible, ZIF-8 with a super large surface area (>2000 m<sup>2</sup> g<sup>-1</sup>) was used as a precursor to produce N-doped porous carbon materials in NH<sub>3</sub> atmosphere [56]. The resulting catalyst shows a quite high activity with acetylene conversion reaching 92%, although the conversion decreases slightly during a 200-h test at 30 h<sup>-1</sup> and 200 °C. Theoretical calculations and experimental results showed that C atoms adjacent to the pyridinic-N are the active sites and coke covered on the pyridinic-N is the main reason for the catalyst deactivation [56]. However, direct evidence is still lacking to precisely define the active center, mainly because of lack of appropriate characterization techniques for in situ studies under acetylene hydrochlorination conditions and the complexity of the practical N-doped carbon materials.

Meanwhile, efforts are directed to further improve the catalytic performance. For instance, Dai et al. [57] showed that B,N-co-doped graphene significantly improved the acetylene conversion (about 95%) compared to the carbon catalyst doped by either just B or just N. It was attributed to the promoted HCl adsorption. However, the stability was poor because the acetylene conversion decreased from 95% to 62% within only 4 h. Thermogravimetric analysis (TGA) detected coked carbon formed on the catalyst during the reaction, which blocked the pores

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and covered the active sites leading to fast deactivation. The authors tried to remove the coke with  $H_2$  at 600 °C, which recovered the activity partially and the conversion increased to 82% [57]. Li et al. [58] reported that the deactivation of nitrogen-doped, carbon-based catalyst was likely caused by the carbon-like deposition in another study. It was demonstrated that regeneration with  $NH_3$  at 700 °C may be an effective approach to remove the coke and fully recover the activity. In-situ mass spectrometer revealed that coked carbon was reacted away by  $NH_3$ . Meanwhile, the treatment in  $NH_3$  atmosphere could efficiently prevent the leaching of the doped nitrogen atoms as  $NH_3$  decomposes to nitrogen species at the regeneration temperature.

Despite of wide efforts, the activity of carbon-based catalysts remains to be improved for commercial applications. Furthermore, carbon-based materials are usually easy to crush and hard to shape due to the low mechanical strength. This could also accelerate deactivation. To this point, shaped SiC could provide a possible solution by serving as a substrate of functional carbon-based catalysts because of its properties such as high mechanical strength, good heat conductivity, and chemically stable in acid [52].

#### 10.7 Perspectives

The synthesis of chemicals by metal-free carbon has attracted an increasing attention during the past decades. The low cost of carbon materials and the novel structural and electronic properties render them a promising potential in the applications. All kinds of routes have been used to tune the structural and electronic properties of carbon materials in order to improve their catalytic performance. In general, the design of carbon-based catalysts and their catalytic performance have a great improvement during the past few decades. However, there are still several challenges for the chemicals by metal-free carbon to be solved.

1) Although great efforts by researchers have been devoted to exploring the nature of the carbon catalyst, it is still far from clear. The first reason is that the current preparation technology of carbon catalysts is far from controllable. The obtained carbon usually includes all kinds of defects. Although it can be further doped with heteroatoms or modified by different groups, the defects still remain. It is difficult to get rid of the defect effect on the catalytic performance. In addition, many carbon materials actually include trace metals because the current preparation technology usually uses the metal as the catalysts. Typically, the RGO is from the reduction of graphene oxide (GO), where the KMnO<sub>4</sub> is usually used during the preparation process of GO. The trace of Mn is difficult to be removed because some could be doped or completely encapsulated by graphene during the reduction process. In addition, the 3D transition metals such as Fe and Co are usually used to grow CNTs. The metal nanoparticles can be encapsulated within the carbon walls, which are hardly removed even using strong acid. Although it usually seems that there are no metals in the carbon according to the X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDX), it can be tested by inductively coupled plasma (ICP). The encapsulated metals with graphene or carbon wall may provide the activity through electron transfer to trigger the activity on the graphene surface [59, 60]. Therefore, it is hard to say that the catalytic activity only starts from the metal-free carbon. It is better to use completely pure carbon, which should be obtained from direct carbonization of high-purity carbon-containing molecules without using any metal catalysts, for the fundamental study of metal-free carbon catalysts. Therefore, the really active sties of carbon catalysts for chemicals are still on debate, which need more accurate preparation and characterizations.

- 2) The second challenge is that the performance of the current metal-free carbon catalysts for chemicals is still worse than the metal catalysts. Although the metal-free carbon has shown the potential in some reactions, the reaction usually needs more active oxidants and reductants in order to increase the activity. However, the strong oxidants and reductants will accelerate the corrosion of the carbon, e.g. be oxidized into  $CO_2$  and reduced into  $CH_4$ , which will result in significant decay in the activity. One possible route is to reduce the reaction temperature, but it meanwhile reduces the reaction activity. Instead, adding a very small amount of metals will significantly increase the activity, e.g. adding around 1% Fe into N-doped carbon will significantly increase the ORR activity [39, 61]. In addition, using graphene-encapsulating metals can also enhance the activity of graphene via electronic modulation by the metals [1, 59]. For the fundamental study, metal-free catalysts are needed, but for the real applications, the composites of carbon and metals may be needed in order to increase the activity and stability.
- 3) The third challenge is how to assemble carbon materials into a real catalyst. Although the free-standing carbon materials can be used as an efficient catalyst for chemicals in fundamental study, it is unsuitable for the industrial application. It needs to develop efficient forming methods for metal-free carbon materials in order to optimize their mass transfer, heat conduction, and mechanical strength. The possible routes include direct assembling of the metal-free carbon materials and forming with other materials as composites or substrates, e.g. highly stable SiO<sub>2</sub>, and SiC.

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