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Metal-Free Carbon Catalysts for Oxidative Dehydrogenation Reactions

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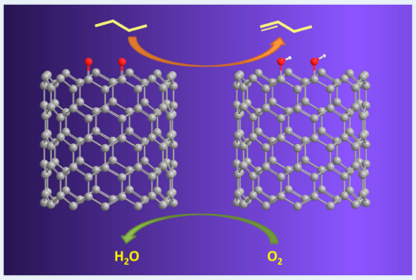

ABSTRACT: Catalysis over carbon, especially nanocarbon, is an attractive topic in material science and chemical engineering fields due to its significant advantages compared with conventional metal or metal oxide catalysts. This paper summarizes the recent developments, basic concepts, and commonly accepted understandings on the nature of carbon catalysis in oxidative dehydrogenation reactions, including: introduction and comparison of various reaction systems; identity and quantity of active sites on carbon catalysts; mechanism for the reactions; and structure−selectivity relations for modified carbon catalysts. These fruitful conclusive achievements are the basis for in-depth comprehension of carbon-catalyzed oxidative dehydrogenation process at the molecular level, and many other efforts, such as detailed kinetic study, precisely controllable synthetic technique for nanocarbon catalysts, are still needed to further push carbon catalysis fields to practical applications.

KEYWORDS: *nanocarbon, oxidative dehydrogenation, heterogeneous catalysis, metal-free catalysis, carbon catalysis*

1. INTRODUCTION

In catalytic chemical industry, carbon has been used as a support for other active materials to improve their dispersion or stability.[1] In the 1960s, it was reported that carbon deposition sites on iron oxide catalysts are the real active sites for oxidative dehydrogenation (ODH) of ethylbenzene, and for the first time, researchers working in the field of catalysis realized that carbon is also catalytically active under certain reaction conditions.[2] However, the catalytic activity and stability of amorphous carbon are normally poor because of both their low surface area and thermal stability, which seriously limits the development of related fields. Over the past decade, many extended versions of carbon materials, such as carbon nanotubes (CNTs), graphene, and ordered mesoporous carbon, among others, have been discovered or synthesized successfully, accompanying the great progress made in nanotechnology and advanced material synthetic or characteristic methods. The applications of carbon, especially nanoscaled carbon, as catalysts (active phase) have attracted considerable interest in catalysis and material science.[3] Carbon materials normally exhibit significant advantages in activity, stability, and regenerability over traditional metal or metal oxide catalysts due to their easily tunable surface chemical properties (acidity/basicity, electron density, etc.) and easy recovery features.[4] Carbon materials have been proven to be potential alternatives to conventional catalysts to meet the requirements of sustainable chemistry.[5]

Dehydrogenation of hydrocarbon is one of the most important reactions in petrochemical industry. Traditional direct dehydrogenation technology is normally under the catalysis of iron catalysts with potassium as promoters.[6] The direct dehydrogenation reaction is an endothermic and thermodynamically limited process,[6] and excess steam is always needed to reduce coke formation and prevent the deactivation of the catalysts, which results in low energy efficiency for the reaction system. ODH is a promising alternative process, which is exothermic (for example, $\Delta G = -116$ kJ/mol for ethylbenzene ODH reactions) and could effectively improve the energy efficiency of the system. The ODH reaction is the one that has been first discovered and thoroughly investigated in the carbon catalysis field. Different from the previously reported literature review,[7,8] this Perspective will first provide a brief account of typical carbon catalytic systems for ODH reactions and then provide a short discussion on their advantages and disadvantages. The main body of the paper will focus on summarizing the current understanding of several basic questions for the nature of carbon catalysis. We try to extract some basic concepts and regularities in carbon catalysis with this Perspective, including identity and quantity of active sites, mechanism, and structure−function relations.

2. TYPICAL CARBON-CATALYZED ODH SYSTEMS

ODH reactions under the catalysis of carbon materials could be divided into two categories according to the differences in the nature of reactants, namely, ODH of aryl hydrocarbons and light alkanes. Table 1 lists the typical ODH reaction systems under the catalysis of carbonaceous materials. Numerous carbon materials have shown comparable or even higher activity than traditional metal or metal oxide catalysts in ODH reactions, and each of them exhibits its unique properties.

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Table 1. Typical ODH Reaction Systems Catalyzed by Carbonaceous Materials

reaction systems	catalysts	optimum yield (%)	ref
ethylbenzene to styrene	CNTs	~70	12
	CNFs	~50	19−21
	mesoporous carbon	41	11, 42
	nanodiamond	38	17
	OLCs	62	14, 17
	active carbon	56	9, 27
	carbon foam	23	10
	phenanthrenequinone	84	29
ethane to ethene	CNTs	6	15
propane to propene	CNTs	4.5	16, 43
	doped CNTs	16.7	39
butane to butene	modified CNTs	9.5	25
	nanodiamond	1	44
	single-wall CNTs	0.5	44
isobutane to isobutene	graphene oxide	3	18
	active carbon	10	45, 46
butene to butdiene	CNTs	28	47
2-butanol to 2-butanone	amorphous carbon		48
ethanol to acetaldehyde	CNTs	8.5	49
9, 10-dihydroanthracene to anthracene	CNTs	99	50

Amorphous carbons, such as active carbon[9] and carbon foams,[10] normally exhibit a relatively high initial activity in ODH reactions (an initial alkene yield over 50%, as shown in Table 1), and the main advantage of these materials is the mature preparation technology. The deactivation of the amorphous carbon catalysts is unavoidable, and several efforts to stabilize the promising initial activities failed because of the rapid coke formation on these materials.[9] Mesoporous carbon exhibits a higher degree of order than amorphous carbons and which shows a higher resistance against oxidation and coking during catalysis.[11] The optimum styrene yield reaches 41% for mesoporous carbon catalysts in ethylbenzene (EB) ODH reactions. However, deactivation of mesoporous carbon also happens during ODH process, because olefins, as the main product of hydrocarbon ODH reactions, are easy to polymerize in the micro- or mesopores causing unwanted deposition of disordered carbon.[9,12]

Nanocarbon materials with high crystallinity could be fabricated free of micro- or mesopores, and which should result in much more stable activity than amorphous or mesoporous carbons. In 2001, Prof. Robert Schlögl and his co-workers reported that muti-wall CNTs and carbon nanofibers (CNFs) are active and selective catalysts in EB ODH reactions, and the styrene yield is over 50%.[13] In particular, these nanocarbon catalysts did not show any detectable deactivation for 32 days in a scale-up ODH stability test (100 g of CNT catalysts), indicating their potential applications.[14] These findings open a new era for carbon catalysis, and many nanocarbon materials with various topologies and chemical structures have been tested in hydrocarbon ODH reactions. CNTs normally possess hydroxyl, carboxylic, and ketonic groups on their surface defects after oxidation treatment. The oxidized CNTs (o-CNTs) exhibit a relatively high and stable ODH catalytic activity for various alkanes.[12,15,16] Similar with o-CNTs, onion-like carbon (OLC) is also composed of sp^2 hybridized graphene sheets at out layers and sometimes a sp^3 hybridized core depending on the treatment temperature. OLC has a much smaller size and higher surface area than CNTs, and together with its highly curved graphene out layers, it shows a very high activity in ODH reactions (the optimum styrene yield reaches 62%).[14,17] Graphene oxide (GO) is a few layers of flat graphene sheets modified by oxygen, which contains a mixture of sp^2 and sp^3 hybridized carbon atoms. It normally has epoxy and hydroxyl groups at basal planes and other types of oxygen groups at graphene edges. It is reported to be very active in ODH of isobutane.[18] Platelet CNFs possess large fraction of graphene edge sites, and they are expected to show higher activity than CNTs or GO materials in ODH reactions.[19−21] It should be noted that graphene edges are also the spots where carbon deposition easily happens. The balance between activity and stability of the catalysts should also be considered. In summary, various nanocarbon catalysts have shown their unique properties in ODH reactions due to their differences in chemical structures and topologies, and a proper choice of carbon catalyst is significantly important to achieve ODH reaction systems with high performance. Despite the differences in physical chemical structures and distinct catalytic performances, nanocarbon catalysts also exhibit some similarities in ODH reactions (e.g., the active sites, catalytic mechanism, and structure−function relations, etc.). We will focus on the discussion and summary of these regularity results for carbon catalysis in ODH systems in the following sections.

3. ACTIVE SITES

Carbon materials normally possess complex surface chemical compositions and structures, which makes it difficult to identify and quantify the active sites for catalytic reactions. It has been proved both theoretically[22] and experimentally[23] that there is a very large energy barrier for chemical adsorption of alkane or oxygen molecules on the perfect graphene surface. On the other hand, the energy for chemical adsorption of oxygen on defects or edge sites is considerably low (around 7 kcal mol^{-1}), indicating that these sites may be responsible for oxygen activation.[24] The oxygen functionalities on defect sites, especially the ones with higher electronegativity (ketone or lactone groups), are possible active sites for hydrocarbon activation.[25] Temperature-programmed desorption (TPD) is a powerful technique to characterize the oxygen functionalities on nanocarbon surface. The identity and quantity of oxygen functionalities could be determined through the release of CO_2 (for carboxyl, carboxylic anhydride, or lactone groups) and CO (hydroxyl or carbonyl groups) at different temperature.[26] Correlation between the surface concentration of oxygen functionalities on carbon catalysts and EB ODH conversion rates indicates that the ODH catalytic activity of carbon catalysts is linearly dependent on their surface concentration of ketonic carbonyl groups.[27] However, the most important issue missing in the above research is the evaluation on the dynamic change of the oxygen functionalities on carbon catalysts under reaction conditions. For example, it has been reported that most of the hydroxyl, carboxylic acid, and anhydride groups on CNT surface would convert to ketonic or quinoidic carbonyl groups which has a higher thermal stability.[26] Moreover, the defect sites on CNT surface will be oxidized during ODH reactions, which could also affect the oxygen content on CNT catalysts.[26] It should be emphasized that the correlation between oxygen content on fresh catalysts and the activity at steady state, which has commonly appeared in the literature, is not accurate enough and should be avoided.

Microcalorimetric analysis (MCA) is a useful technique that could directly provide the information on the interactions between catalysts and reactants. MCA under reaction conditions could provide an overview of the identity and quantity of the ODH active sites on carbon catalysts through measuring adsorption heat and the amount of adsorbed molecules on the catalysts.[28] Measurements of differential adsorption heats of propane and propene allows the classification of four different adsorption sites on CNT catalysts, including carbonyl, carboxylic anhydride, lactone/hydroxyl groups, and basal planes of graphitic carbons.[28] Among them, ketonic or quinoidic carbonyl groups exhibit the highest adsorption heat and amount for both propane and propene molecules, indicating the importance of these oxygen functionalities for ODH reactions.[28] Another effective technique to in situ monitor carbon catalysts is near-ambient XPS.[25] Based on the deconvolution of O 1s XPS at 375 °C in the presence of butane and O_2, two contributions from ketonic (C═O) and hydroxyl (C−OH) groups are distinguishable. A sharp decrease of the relative ratio between ketonic and hydroxyl groups ($I_{(C=O)}/I_{(C-OH)}$) could be observed after switching off the oxygen, suggesting that ketonic groups are critical ingredient of the active sites for ODH reactions.[25] The major advantage of MCA or near-ambient XPS characterization method is that the measurements could be performed under the chemical environment similar to reaction conditions. The technique allows the in situ monitoring and understanding of the chemical composition of the working catalyst surface. However, accurate identification and quantification of active sites are still difficult to achieve through above methods.

Aimed at that, a chemical titration method is proposed to quantify the surface concentration of major oxygen functional groups (hydroxyl, carboxylic acid, and ketonic carbonyl groups) on nanocarbon catalysts.[26] The chosen titrants would selectively and quantitatively react with certain oxygen functionalities on carbon catalysts, and the surface concentration of oxygen groups could be calculated by in situ monitoring the consumption of the titrants. Furthermore, the different ODH catalytic activities of various titration derivatives suggest that ketonic carbonyl groups are the only active sites, and hydroxyl or carboxylic acid groups do not have any direct effects in EB ODH reactions.[26] The chemical titration method has shown its unique advantages in quantification of the oxygen functionalities on carbon catalysts. It could provide the absolute value of surface concentration of oxygen functionalities, which avoids the subjectivity caused by deconvolution and peak identification process in traditional spectroscopy-based quantification techniques (e.g., XPS or TPD), the result of which obviously depends on the operator's experience. However, it should be noted that the quantification results depend on the nature of the titrants selected in this method. An ideal titrant needs to have similar size and polarity as reactant. For example, phenyl hydrazine, which has a similar molecular structure as EB, is selected as the titrant in the reported literature.[26] The titrated concentration may not reflect the total number of ketonic carbonyl groups on nanocarbon catalysts, but it indicates the number of sites that are accessible and active in the catalytic ODH reactions.

Another direct evidence for the identity of the active sites comes from the relatively high activity of the model catalysts.[29] Metal-free phenanthrenequinone cyclotrimer, which contains only ketonic carbonyl groups on its periphery, exhibits a relatively high EB ODH activity comparing with oxidized nanocarbon catalysts. More importantly, the kinetic parameters (reaction order for EB and O_2, the activation energy, etc.) derived from phenanthrenequinone cyclotrimer are identical to that from o-CNT catalyzed reaction systems, confirming the similarity of the catalytic mechanism and also suggesting that the active sites for ODH reactions on carbonaceous catalysts are ketonic carbonyl groups.[29]

DFT calculations also suggest that neocleophilic quinone or ketone groups are thermodynamically favorable in hydrocarbon activation.[30] It has been reported that dissociations of ethane molecules at the lactone, anhydride, carboxyl, and ether sites are highly endothermic process. On the other hand, the dissociations of ethane on ketone and quinone sites are exothermic. For example, the dissociation energy for ethane molecules at quinone sites is over 5 eV lower than that at ether groups,[30] suggesting quinone or ketone groups are promising active sites for hydrocarbon ODH.

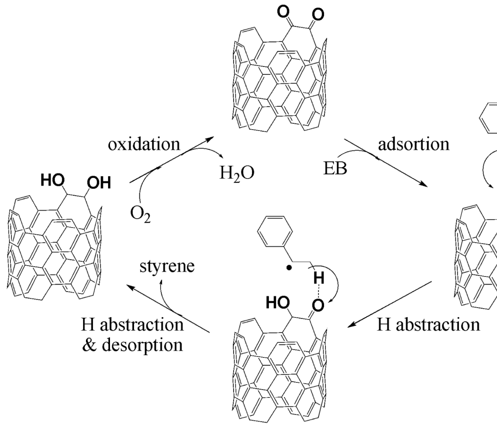
Taken together, both in situ characterization measurements and activity comparisons from titration or model catalysts indicate that the nucleophilic ketonic carbonyl groups on carbon catalysts are active sites for ODH reactions. However, it has to be pointed out that most of the research works related to the identification of active sites on carbon catalysts focus on CNTs or OLCs, which has a closed graphene-like surface. It has also been reported that the situation is different for few-layer graphene sheet catalysts, which have a larger fraction of edge defects and also more oxygen functionalities on basal planes. Schwartz and co-workers first found that there was no obvious relationships between ODH activity and the total oxygen content in fresh catalysts, and the catalytic activity positively depends on the fraction of sp^3 hybridization as well as the number of edge sites of layered graphene catalysts.[31] In fact, the transformation of edge defects to different types of oxygen functionalities should be a very complicated process under reaction conditions and which should also be considered in structural or kinetic analysis for carbon catalysts. Based on this hypothesis, one of the most recently published results from the same group also found that ketonic carbonyl groups are real active sites for ODH reactions,[32] and the results from nanocarbon catalysts composing planar or curved graphene structure finally reach consistence.

4. MECHANISTIC STUDY

The mechanistic study is the basis for comprehensive understandings of the nature of catalytic process at molecular level and which is the key point in the field of carbon catalysis. As shown above, the nucleophilic oxygen functionalities on carbon catalysts, especially ketonic or quinoidic carbonyl groups, play a vital role in ODH catalytic process. It is generally accepted that ODH on carbon catalysts is a consecutive reaction sequence of activation and dehydrogenation of hydrocarbons at ketonic sites and water formation and reoxidation steps with active oxygen species. However, the detailed catalytic mechanism at the molecular level and the elementary steps are still not clear. The first half of the catalytic process, which is the abstraction process of the hydrogen atoms from the adsorbed alkanes by nucleophilic ketonic groups, is somewhat easy to understand. The water formation and the reoxidation steps during ODH on carbon catalysts remain the subjects of debate.

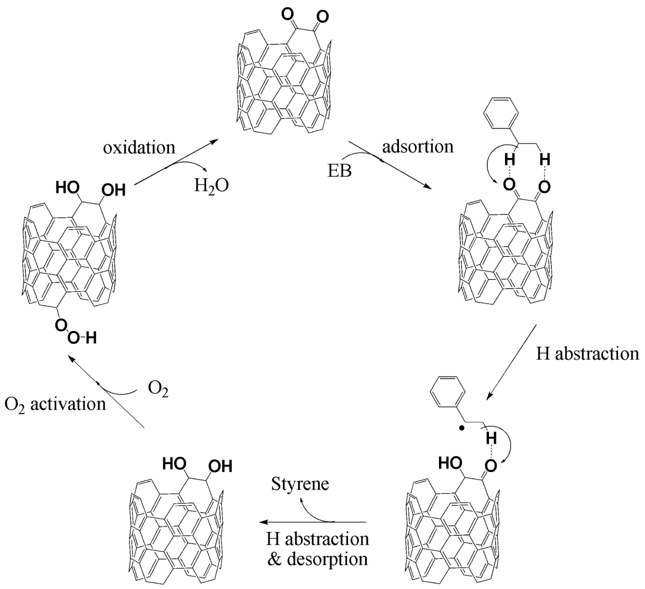
As implied by the widely accepted ODH reaction mechanism over metal oxide catalysts, carbon-catalyzed ODH reactions are initially believed to follow the Mars−van Krevelen (M−K) mechanism,[33] and the elementary steps of which at molecular level could be summarized as shown in Scheme 1. Chemical adsorption of EB molecules first happens on ketonic carbonyl groups on nanocarbon catalysts, and after the sequential hydrogen abstraction and product (styrene) desorption process, reduced nanocarbon catalysts are formed. Molecular oxygen reoxidizes the catalysts, and the catalytic cycle is finished after desorption of H_2O.

Scheme 1. Schematic Drawings of Carbon Catalyzed EB ODH Reactions through the M−K Mechanism



On the other hand, it has also been reported that M−K mechanism cannot fully describe the ODH process on carbon, especially nanocarbon catalysts.[34] The kinetic analysis on EB ODH reactions over CNT catalysts suggests that the catalytic process follows Langmuir−Hinshelwood (L−H) mechanism, as summarized in Scheme 2.[35] The major differences between M−K and L−H mechanism are in oxygen activation and reoxidation steps. Oxygen molecules are first activated at defect sites on carbon catalysts. The forming reactive atomic oxygen diffuses on the basal plane of sp^2 carbon, and it eventually reaches and oxidizes the active sites under reduced state (hydroxyl groups in Scheme 2). The isotopic effect demonstrates that hydrogen abstraction is the kinetic relevant step in EB ODH reactions under the catalysis of CNTs,[35] which is consistent with the L−H mechanism. It should be pointed out that Scheme 2 is just to show the catalytic reaction cycle through the L−H mechanism, and the hydrogen abstraction and oxygen activation are actually not sequential steps. The kinetic results suggest that ODH reactions catalyzed by CNTs follow dual site L−H mechanism, and the hydrogen abstraction and oxygen activation steps are not competitive processes or kinetically relevant with each other.[35] Theoretical calculations suggest the possibility of the L−H mechanism.[32] Abstraction of the first hydrogen atom from alkanes has the highest energy barrier (0.92 eV for butane molecules[25]), and it is considered as the rate-determining step in the L−H process. DFT calculations also suggest that H_2O_2 may serve as the oxidation product during the regeneration of quinone sites (step of oxidation in Scheme 2), which is more thermodynamically favorable than forming H_2O.[30,32] However, this is not verified experimentally, because H_2O_2 will decompose quickly under ODH reaction conditions.

Scheme 2. Schematic Drawings of Carbon-Catalyzed EB ODH Reactions through the L−H Mechanism



One commonly accepted difference between the M−K and L−H mechanism is whether lattice oxygen species participate in the catalytic process. Nanocarbon materials do not contain lattice oxygen species. It should also be pointed out that L−H mechanism typically involves two types of active surface species. Most of the research results suggest that carbon catalysts could activate both alkanes and oxygen reactants, thus supporting the dual-site L−H mechanism. Activation of oxygen is generally believed to occur at defect sites on nanocarbon materials. However, the detailed activation mechanism is still unclear because of the complexity of the defects.

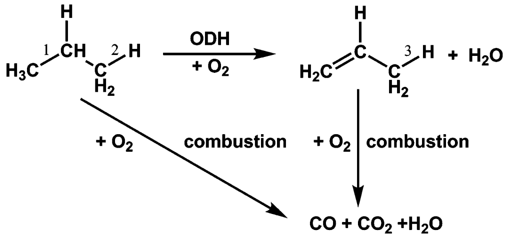
In summary, there are still arguments on the in-depth understanding of the detailed catalytic mechanism of the carbon-catalyzed ODH process at the molecular or atomic level. One possible explanation on the inconsistent comprehension on ODH mechanism is the difference in the chemical nature of selected carbon catalysts. It is generally accepted that active carbon or graphene oxides have more edge defect sites or oxygen species at graphene basal planes compared with CNTs. Thus, it leads to more complicated transformations of oxygen functionalities on carbon catalysts under reaction conditions and which should be definitely considered in the proposal of kinetic models. For example, it has been reported that the kinetics of isobutane ODH on few-layered graphene catalysts also follows L−H mechanisms based on the accurate evaluations of the structural changes during reactions.[32]

Another important reason that could lead to inconsistent understanding on catalytic ODH mechanism on carbon catalysts may be the incomplete kinetic measurements. As shown above, the only difference between the L−H and M−K mechanism is the oxygen activation process, and the rate equations derived from the two mechanisms should be similar under the high oxygen partial pressure region, where the contribution of reoxidation is negligible and the elementary steps of reduction are kinetically relevant. Considering the above premises, we believe that full kinetic measurements that could distinguish the L−H and M−K mechanism and reliable in situ characterizations of the catalysts that could reflect the changes of the chemical state of the catalysts are still needed for mechanistic studies of carbon catalyzed ODH reactions.

5. EFFECT OF HETERO-ATOM DOPINGS AND SURFACE MODIFICATIONS

The selectivity of styrene is normally high (~95%) in EB ODH reactions catalyzed by carbon catalysts because of the kinetic stability of styrene products with conjugated structure. However, the selectivity for target alkene products in the ODH process of light alkanes (C_2−C_5) decreases dramatically due to the high reactivity of olefin products.[16] It is well-known that the chemical bonding of C−C and C−H is weaker in alkene molecules than in the corresponding alkane chains. As shown in Scheme 3, the dissociation energy for the C−C bond in propane (bond 1) and the C−H bond in propylene (bond 3) is 360 kJ mol^{-1} and 370 kJ mol^{-1} respectively, which is much lower than that for C−H bond in propane (bond 2, 420 kJ mol^{-1}), indicating the priority of combustion and decomposition of light alkanes and alkenes comparing with oxidative dehydrogenation reactions.[36] For example, the optimum yields for light alkenes are normally under 15% (as shown in Table 1) under the catalysis of nanocarbon materials due to the low selectivity, and which makes the practical applications nearly impossible. Thus, the selectivity for olefin products is a key parameter to evaluate ODH performance for carbon catalysts, and significant efforts have been devoted in related fields.

Scheme 3. Schematic Drawings of ODH, Decomposition and Combustion Reactions of Propane



Surface modifications with phosphorus or boron oxide is one of the most successful solutions to improve the selectivity of carbon catalysts. As discussed above, CO, CO_2, and H_2O originated from combustion and decomposition reactions are the main byproducts in light alkane ODH reactions over carbon catalysts. It has been reported that the total olefin selectivity (including 1-butene, 2-butene, and butadiene) in ODH of butane is less than 20% under the catalysis of o-CNTs, and most of the reactants convert to carbon oxide through combustions.[25] The electrophilic oxygen species, such as O_2^{2-}, O_2^-, and O^-, are responsible for activation of O_2 molecules that ultimately cause total oxidation of alkanes.[37] The electron-attracting dopants, such as phosphorus or boron oxide, prefer to deposit on the electrophilic oxygen functionalities (acidic groups) and thus inhibit the facile auto-oxidation process.[25] This selective deposition and deactivation of electrophilic oxygen functionalities by electron-attracting dopants is a commonly accepted principle in carbon material science,[38] and which is also proved to be effective in nanocarbon catalytic fields.[16,25] It has been reported that the selectivity for alkene increases by a factor of 2 in ODH of butane or propane after surface modification of o-CNTs with phosphorus or boron oxide.[16,25] The catalytic performance of the modified o-CNTs is as competitive as that of supported vanadia catalysts, which are normally used in chemical industrial ODH process.[25] Temperature-programmed oxidation (TPO) measurements reveal an improvement of resistance to oxidation after boron oxide modifications on o-CNT catalysts.[16] Further kinetic studies indicate that phosphorus or boron oxide modifications exhibit a minor impact on the activation of hydrocarbons, and it improves the ODH catalytic performance of o-CNT catalysts through suppressing the activation of nonselective oxygen species.[16]

Another typical strategy that is commonly used to improve the selectivity of carbon catalysts is doping of nitrogen or boron heteroatoms into graphene frameworks. The nitrogen-doped CNTs could be synthesized through CVD process with organic precursors containing nitrogen species (for example, imidazole, etc.), and it shows significant selectivity improvement for olefin products in ODH of alkanes, especially at high conversions.[39] Detailed structure analysis on fresh and used catalysts reveals that graphitic nitrogen species plays a vital role in enhancing the catalytic performance of CNT catalysts. Apparent activation energy and reaction order of oxygen significantly decreases with the increasing of the graphitic nitrogen content in CNT catalysts for propane ODH reactions, indicating the promotion of oxygen activation with nitrogen doping.[39] DFT calculations have shown that the incorporation of nitrogen atoms into graphene frameworks will lead to a local electron deficiency of CNTs. The obvious positive charge of carbon atoms around nitrogen could benefit the oxygen adsorption process.[40] An electronic transition of O_2 accompanies with the adsorption process on nitrogen functionalized CNTs (NCNTs) forming activated oxygen species with high reactivity.[40] Further calculation studies on boron-doped CNTs prove that oxygen molecules dissociate on positively charged carbon atoms around boron, and the activated oxygen is able to break the C−H bond in hydrocarbon that adsorbed on oxygen functionalities on CNTs.[41] The energy barrier for hydrocarbon activation is 0.95 eV in the presence of boron and defects on CNTs, which is significantly lower than other typical catalysts adopted in ODH process (e.g., Pd-doped ceria at 1.08 eV).[41] Such a promotion effect for adsorption and activation of oxygen or hydrocarbon molecules from theoretical calculations is consistent with experimental observations, and which is considered as the origin of the excellent catalytic performance of nitrogen or boron-doped CNTs.

This part summarizes two important modification methods for carbon catalysts that could effectively improve olefin selectivity especially in low alkane ODH reactions, namely, surface modifications with oxides and doping with heteroatoms, respectively. The nature on these two promotion effects is different. Surface modifications with phosphorus or boron oxide could block combustion sites, thus increasing alkene selectivity. Nitrogen or boron doping into graphene frameworks actually will affect the electronic structure of CNT catalysts and facilitate the activation of oxygen or hydrocarbon molecules.

6. SUMMARY AND OUTLOOK

Nanocarbon materials have shown outstanding and stable performance in many redox catalytic reactions, especially in ODH reactions, and which are attractive options for alternatives for metal or metal oxide catalysts. Based on the current understanding of the nature of carbon-catalyzed ODH reactions, nucleophilic ketonic carbonyl groups and defect sites on graphene layers are considered as active sites and play a vital role in the ODH process. The kinetic studies prefer to reach the conclusions that ODH reactions catalyzed by carbon catalysts follow dual site L−H mechanism. Surface modifications or chemical structure adjustments to nanocarbon catalysts are effective strategies to promote olefin selectivity, especially in light alkane ODH reactions.

Although the above basic concepts and commonly accepted regularities for carbon catalysis have been well-established, the in-depth understanding on the nature of carbon-catalyzed ODH reactions is still missing. For example, the detailed kinetic studies and in situ quantitative structure analysis are urgently needed to reveal the mechanism of carbon-catalyzed reactions at the molecular level. The establishment of integral structure—function relations for carbon catalysts is also an important subject in related fields, which could provide a guidance for the synthesis of carbon catalysts with high activity. Besides the fundamental mechanistic or kinetic studies, the synthesis and fabrication approaches for carbon-related materials also need further developments to meet the demanding for potential industrial applications. For example, the fabrication of carbon catalysts with certain single functionality through a "bottom-up" organic synthetic strategy or surface chemical method is still a persistent and hot topic in related fields, which could help avoiding the structure ambiguity and side effect on catalytic performance brought by other undesired functionalities. Another important subject is the shaping of the carbon catalysts to improve their processability, which are originally in powder form and severely hinder the heat and mass transfer process in ODH reactions. The last concern is the development of preparation technology for nanocarbon materials at large scale and low cost, which is also a key factor for their practical applications.

The authors hope to have shown that carbon (especially nanocarbon) is one of the promising catalysts in ODH process for alternation or complement of traditional metal or metal oxide catalysts. Significant progress has been made in "a not very long history" of carbon catalysis, and which is still a hot topic in material science, catalysis, and sustainable chemistry. However, as shown above, there is still a lot of work to do to push related fields to real practical chemical industries.

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Notes

The authors declare no competing financial interest.

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