Phosphate-Modified Carbon Nanotubes in the Oxidative Dehydrogenation of Isopentanes


Ketonic/quinonic $\equiv$O groups on the surface of a carbon matrix are capable of abstracting hydrogen in C–H bonds from hydrocarbons and enable them to selectively convert into corresponding unsaturated hydrocarbons; this process is the oxidative dehydrogenation (ODH) reaction. However, a variety of inevitable defects or graphene edges and other oxygen-containing groups on the carbon matrix are detrimental to the selective production of alkenes due to their high activity towards overoxidation. Herein, we show that phosphate can not only impede the total oxidation but also cover the selective ketonic/quinonic $\equiv$O groups, hence allowing its use as a modulator to defects and oxygen-containing functional groups on the multiwalled carbon nanotubes, regulating the distribution of active sites and related catalytic targets.

Introduction

Surface modification of catalysts, by means of passivating or prepoisoning, plays an indispensable role in chemical science for the synthesis of desirable targets.[1] Heterogeneous metal-free catalysts, as novel alternatives to the conventional transition-metal-based catalysts, offer great environmental and economical advantages.[2] Among them, surface-modified carbon materials have been well studied as alternatives to metal oxide catalysts for oxidative dehydrogenation (ODH) of light (i.e., C2–C4) alkanes, such as ethane,[3] propane,[4] n-butane,[5] and isobutane.[6] However, processes using these catalysts have not been industrially applied. One (critically important) reason is deep oxidation of the alkane and of the produced alkene in consecutive reactions. Higher alkanes (i.e., C4, C5) have an abundance of secondary and tertiary C–H bonds (with bond energies of 401 kJ mol$^{-1}$ and 390 kJ mol$^{-1}$, respectively) and are much more reactive towards gaseous oxygen than lower alkanes (i.e., C2, C3) (see Supporting Information, Table S1). The corresponding dehydrogenation products contain the very active allylic C–H bond (361 kJ mol$^{-1}$), which is easily oxidized to CO$\_2$.[7] Numerous studies reveal that the molar ratio of combustion/dehydrogenation (hydrocarbon; HC) products (CO$\_2$/HC) in ODH reactions increases with the chain length of reactants. This tendency is summarized in Figure 1,[7–12] it is more difficult to suppress the formation of CO$\_2$ during ODH of isopentane than during ODH of lower alkanes (C2–C4). On the other hand, there is increased demand for C5 olefins and diolefins from dehydrogenation of C5 paraffins for use in resins, elastomers, and fine chemicals.[12] Unfortunately, there are only few studies on the dehydrogenation of C5 alkanes, and most of these use metal oxide catalysts: under oxidative conditions, the selectivity towards the dehydrogenation products is lower than 65 %.[12]

In carbon technology, phosphorous modification is a well-established means of enhancing the oxidation resistance of carbon materials, especially in case of activated carbon. Phosphorus is present in carbon matrices as red phosphorus, in phosphates, and/or in chemically bonded form, for example in $\equiv$C–P– bonds or $\equiv$C–O–P– bonds.[13] Recently, phosphorous modification was used in carbon catalysis to increase the selectivity of oxidative dehydrogenation, suppressing the deep oxidi-

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By studying oxidative dehydrogenation of isobutane on phosphorous-modified graphitic mesoporous carbon, Schwartz et al. revealed that phosphorous groups do not change the nature of the active sites but affect the availability of the sites, depending on the phosphorous content loaded onto the carbon catalyst. The decline of olefin selectivity at high phosphorous loadings cannot be clearly assigned to the coverage of selective ketone sites or to the generation of additional active sites favorable to total oxidation.

Herein, we show for the first time that isopentane can be dehydrogenated with only carbon as catalyst. By using carbon nanotubes (CNTs) as catalyst, we systematically studied the effect of phosphate modification on the oxidative dehydrogenation of isopentane involving the formation of active allylic C–H bonds that can be easily oxidized to CO$_2$. We found that the surface chemistry and the distributions of active sites of CNTs are strongly dependent on the loading of phosphate. An addition of phosphate of up to 1 wt% is capable of inhibiting the sites for deep oxidation, and thus increasing the selectivity of isopentane dehydrogenation—the selectivity was doubled. Phosphorus or phosphorous oxides act as electron-attracting dopant, inhibiting the generation of electrophilic oxygen species and thus suppressing the combustion of hydrocarbons. However, a higher loading is not beneficial for the reaction. The nucleophilic ketonic/quinonic groups are blocked by electrophilic phosphate, thus diminishing the number of active sites for ODH. We reveal that phosphorous oxides not only act as an inhibitor of non-selective electrophilic oxygen species but also cover the selective sites (C=O groups) with increasing loading.

**Results and Discussion**

**What level of phosphate loading is favorable for dehydrogenation?**

Pristine CNTs, oxidized CNTs (oCNTs), and phosphate-modified oCNTs with different loadings (denoted as xP-oCNTs, with x = 0.1–5 wt% P$_2$O$_5$) were employed in the ODH of isopentane. For comparison with metal oxides, V-Mg-O systems (Mg$_3$V$_2$O$_8$ and Mg$_2$V$_2$O$_7$) were used. Figure 2 shows that all of the catalysts are active towards the reaction, but the selectivity towards dehydrogenated products (Figure 2a) on xP-oCNTs (x < 3 wt%) is higher than those of oCNTs at the same conversion of isopentane. This demonstrates that phosphate modification of CNTs is beneficial to inhibit the formation of CO, in the ODH of isopentane. As depicted in Figure 2, the selectivity of all catalysts could not reach 100% when the conversion was extrapolated to 0, indicating a reaction network with parallel and consecutive hydrocarbon combustions (Scheme 1).

This correlation did not change with time-on-stream during a lifetime test of the catalyst (Supporting Information, Figure S2). Among all of the tested samples, the 1P-oCNTs catalyst exhibits an outstanding performance and stability: the conversion of isopentane remained almost unchanged (9.5%) and the alkene selectivity stayed above 62%.

The products distributions over different catalysts, obtained by sampling at 2.5% isopentane conversion and shown in Figure 3, reveal that an increase of phosphate loading from 0 to 3 wt% leads to an increase of the selectivity towards monoolefins (2M1B, 2M2B, and 3M1B) and di olefins (isoprene). However, when the phosphate loading is higher than 3%, the selectivity of dehydrogenation declines accompanied with an increase of CO$_2$. Ultimately, the isopentane cannot be converted into any products when the phosphate loading reaches 15 wt%. Interestingly, after sufficient washing with distilled water by centrifugation, the activity of 15P-oCNTs can match that of 0.1P-oCNTs. This demonstrates that excessive phosphorus or phosphorous oxides act as electron-attracting dopant, inhibiting the generation of electrophilic oxygen species and thus suppressing the combustion of hydrocarbons. However, a higher loading is not beneficial for the reaction. The nucleophilic ketonic/quinonic groups are blocked by electrophilic phosphate, thus diminishing the number of active sites for ODH. We reveal that phosphorous oxides not only act as an inhibitor of non-selective electrophilic oxygen species but also cover the selective sites (C=O groups) with increasing loading.

**Figure 2.** Product selectivity versus isopentane conversion obtained by variation of reaction temperature, with V-Mg-O as a reference (Supporting Information, Figure S1).

**Scheme 1.** Schematic illustration of the reaction network of isopentane oxidative dehydrogenation over CNTs.
Does the nature of the active sites change with phosphate loading?

To understand the nature of active sites, the steady-state apparent activation energy ($E_a$) of different C5 hydrocarbons was obtained by using C$_5$H$_{12}$, C$_5$H$_{10}$, and C$_5$H$_8$ as substrates. Figure 4 reveals that the activation energy of C$_5$H$_8$ increases from 121 kJ mol$^{-1}$ over oCNTs catalyst to 145 kJ mol$^{-1}$ over the 3P-oCNTs catalyst, as expected considering that the modification with phosphate suppresses C$_5$H$_8$ combustion. The activation energy of C$_5$H$_{12}$ is nearly constant, at about 85 ± 5 kJ mol$^{-1}$. Notably, the activation of C$_5$H$_{10}$ is suppressed on the oCNTs with 1 wt% phosphate loading (an increase of activation energy by 31 kJ mol$^{-1}$), but a decrease of the activation energy by 19 kJ mol$^{-1}$ is observed at higher phosphate loading. Considering the information in both Figure 3 and 4 leads to the conclusion that the increased selectivity towards mono- and diolefins at low phosphate loading (0.1–1 wt%) is mainly due to inhibited C$_5$H$_{12}$ and C$_5$H$_8$ combustion. At high phosphate loadings (>1 wt%), the increased formation of diolefins comes at the expense of mono-olefins, seldom affecting consumption of the relatively stable paraffin C$_5$H$_{12}$. Probably, phosphorus-bound oxygen functional groups or phosphorus oxides activate C$_5$H$_{10}$, but this needs further investigation.

Structure–performance correlation

The structural properties, surface properties, and thermal stability of the catalysts before and after reaction were characterized by N$_2$ physisorption, X-ray photoelectron spectroscopy (XPS), scanning and transmission electron microscopy (SEM and TEM), Raman spectroscopy, and temperature-programmed techniques (oxidation: TPO and desorption: TPD). N$_2$ physisorption and surface analysis by XPS (see Table S2, Supporting Information) show that the addition of phosphorus leads to a decline of the specific surface area, from 283 m$^2$ g$^{-1}$ on the oCNTs to 210 m$^2$ g$^{-1}$ on the 5P-oCNTs, accompanied by an increase of the surface oxygen content and P/O atomic ratio from 4.68% to 5.76% and 0 to 0.20, respectively, while the pore diameter is nearly constant. This indicates that the added phosphorus mainly covers the surface of the CNTs, resulting in rearrangement of the surface oxygen-containing groups (see Supporting Information, Table S2). It can also be concluded from SEM and TEM images as well as the Raman results that the addition of phosphate has an extremely minor impact on the texture and framework of CNTs, but results in a slightly increased degree of disorder due to carbon debris or phosphorus oxides (see the Supporting Information, Figures S3 and S4).

The interactions between phosphates and defect sites

CNTs undergo oxidation (combustion) in the presence of oxygen at high temperature. The combustion starts at sites on CNTs that can dissociate the adsorbed oxygen molecules. The interaction between CNTs and O$_2$ gas was investigated by TG analysis in air, and the maximum temperatures $T_{\text{max}}$ of the exothermic differential scanning calorimetry (DSC) curves are summarized in Table S2 (Supporting Information). Phosphate loading increases the $T_{\text{max}}$ as expected and well reported in literature.[15] Phosphorus compounds are known to selectively block the defect sites,[14] thus improving the carbon materials’ resistance to oxidation.[15] These defect sites convert O$_2$ molecules to highly reactive electrophilic oxygen species (superoxide, O$_2^-$; peroxide, O$_2$$_2^-$),[16] They are the starting sites for CNT oxidation or they can attack the electron-rich C=C bonds in the ODH reaction, leading to the rupture of the carbon skeleton and subsequent deep oxidation.[15]

The correlation of $T_{\text{max}}$ with the consumption rate of substrates during ODH reaction in Figure 5 shows that the declin-
ing trends of substrate consumption accurately coincides with the rising tendencies of combustion resistance of phosphate-modified CNTs: lower loadings of phosphate (0–1 wt %) have a marked inhibition effect, while the effect is only moderate at higher loadings (1–5 wt %). This means that active sites on the surface of CNTs blocked by phosphate have an equivalent effect on the combustion of CNTs and on the oxidative dehydrogenation of isopentane. A loading of up to 1 wt % gives a pronounced enhancement of the combustion resistance of phosphate-modified CNTs: lower loadings of phosphate (0–1 wt %) have only a moderate inhibition effect on the consumption of substrates (Figure 5), while a reduction of CO on oCNTs down to 18 % CO at high temperature and at high phosphate loading is assigned in Figure 3. Also, an abrupt decline of substrates consumption is observed in Figure 5. Consistent with the elevated activation energies of C5H10 and C5H8 in Figure 4, it is deduced that lower amounts (0–1 wt %) of phosphates preferentially occupy or cover the defect sites on CNTs where usually the electrophilic oxygen species were generated.

In contrast, high phosphate loadings (> 1 wt %) have only a moderate inhibition effect on the consumption of substrates and the combustion of CNTs (Figure 5), a slower decline of the red dashed and blue dashed lines, and a relatively gradual rise of the black lines at wp2O5 > 1 wt %). The inset in Figure 5 shows that the consumption rate of C5H12 decreased faster than the consumption rate of oxygen (wp2O5 = 1–5 wt %), which indicates that the inhibition effect on the consumption of C5H12 is stronger than the consumption of O2. This means that excessive phosphate (> 1 wt %) selectively suppresses the sites active for dehydrogenation (nucleophilic oxygen species: ketonic/quinonic C=O).

The interaction between phosphates with oxygen-containing groups

Attenuated total reflection (ATR)–IR spectroscopy was used to study the interaction between phosphorus species and oxygen-containing groups. Figure 6 reveals that the C=O stretching peak of ketones, aldehydes, lactones, or carboxyl groups shifts from 1704 cm−1 on oCNTs (black line) to 1724 cm−1 on phosphate-modified CNTs (colored lines, 1P, 3P, 5P-oCNTs).[17] The intensity of the C=O stretching peak, relative to the intensity of C=C (1563 cm−1) in the aromatic rings of CNTs, declines with increased loading of phosphate, while the peak due to C=O−P stretching vibrations (1087 cm−1, overlapping with C=O stretching vibrations), as well as asymmetric stretching vibrations of C=O−P and P=O−P (1000–750 cm−1) increases.[20] This means that the excess phosphate reacts with the oxygen-containing groups on the CNTs, forming C=O−P bonds.[21] This is most likely due to esterification or dehydration of −COOH/−C=O bonds on the surface of the CNTs with the −OH groups of phosphate.[20] In addition, the linkage of excessive phosphates to the ketonic/quinonic C=O groups cannot be ruled out, because the dehydrogenation selectivity decreases. Nevertheless, the binding of C=O groups to phosphate likely involves very weak physical forces, but not chemical bonding because the activity can be easily recovered after washing with distilled water, as shown in Figure 3.

TPD experiments revealed two significant changes in the evolution of CO2 desorption (Figure 7a) and CO desorption (Figure 7b). The first was a gradual shift of the evolution to higher temperatures when the loading of phosphate increased. The second change was in the shape of the CO2/CO evolution signals: the peak intensity in the lower-temperature regime decreased while the evolution in the higher-temperature regime became stronger. Clearly, phosphate modification retards the decomposition of the corresponding functional groups. It is noteworthy that the interaction between phosphate and the functional groups becomes more and more significant when the loading of phosphate was more than 1 wt %. In particular, a sharp peak appears in the CO profiles at about 1180 K at a loading of more than 3 wt %. The signals due to anhydride and lactone in CO2 profiles shifted to higher temperatures with increased phosphate loading. This change of CO2/CO evolution at high temperature and at high phosphate loading is assigned to the presence of highly stable C=O−PO3 groups,[19a,22] formed
due to the interaction between phosphorus oxides and oxygen groups and dissociated at high temperature.\[^{29}\]

The effects caused by phosphate modification were analyzed in detail by deconvolution of TPD profiles\[^{26}\] as shown in Figure 7. The evolution of CO\(_2\) is assigned to strongly acidic carboxylic groups at ~560 K, weakly acidic carboxylic groups at ~620 K, carboxylic anhydrides at ~750 K, and lactones above 800 K.\[^{25}\] For CO, the dominant contributions are attributed to adsorbed CO at ~550 K\[^{23}\], carboxylic anhydrides at ~850 K, phenols at ~1000 K, carbonyls/quinones at ~1150 K, as well as stable C–O–PO\(_3\) groups at ~1180 K.\[^{19, 20}\] Although the results of TPD analysis were not quantified, the decline of carboxyl acidic groups and carbonyl groups with increased phosphate loading is apparent. The reduction of carboxyl acidic groups likely results from neutralization by phosphate ammonia. The reduction of signals attributable to carbonyls agrees well with the conclusions derived from IR measurements.

**Schematic evolution of different active sites on the surface of CNTs**

Based on the observations mentioned above, a conceivable mechanism of the role of phosphate-modified CNTs in the ODH of isopentane is proposed in Scheme 2. With different phosphate loadings, three distinct stages are observed:

1) At low phosphate loadings (0.1–1 wt %), defect sites where the highly active oxygen species (superoxide O\(_{2}^-\), peroxide O\(_{2}^2^-\)) could be formed are blocked. This inhibits the deep oxidation of isopentane to carbon oxides, either directly or consecutively, and gives a maximum dehydrogenation selectivity (82%). The blocking of such defect sites also renders the modified CNTs a high oxidation resistance.

2) At loading of phosphate above 1 wt %, selective C–O sites are covered: the number of ketone C–O groups is lowered which results in a decline of the dehydrogenation selectivity.

3) Higher loadings (more than 1 wt %) may lead to the accumulation of phosphorus oxides, PO\(_3\). The role of the accumulated PO\(_3\) particles in the reaction needs to be explored further.

**Conclusions**

Phosphate-modified carbon nanotubes (CNTs) as novel catalysts for isopentane oxidative dehydrogenation (ODH) show a predominant selectivity towards dehydrogenation as compared to the conventional V-Mg-O catalysts. Moreover, the impact of phosphate on the structure–activity relationship is investigated in detail. We reveal that different phosphate loadings strongly impact on the catalytic properties, either positively or negatively. Low phosphate loadings (0–0.1 wt %) result in improved dehydrogenation selectivity by blocking the combustion sites. The catalytic behavior mainly originates from oxygen-containing groups on the surface of the CNTs. High loadings (1–5 wt %) lead to a decline of the dehydrogenation selectivity, due to the partial coverage of selective sites (C=O groups). Meanwhile, the catalytic behavior is dominated by a synergistic effect of oxygen groups and phosphorous oxides. Excessive phosphate loading (15 wt %) results in a full coverage of active sites from CNTs and no paraffin conversion. Based on these results, in order to get a desired product we can control the product distribution of ODH by adjusting the loading of phosphate on CNT surfaces. Furthermore, our work implies a universal principle on metal-free nanocarbon catalysis: by tuning oxygen active sites, we can design a vast variety of catalysts with controllable selectivity involved in the oxidative dehydrogenation of light alkanes and alkenes.

**Experimental Section**

**Material synthesis**

Pristine CNTs were provided by Tsinghua University (PR China) with a length in the range of 5–15 μm, average diameter 12 ± 1 nm, and wall thickness 4 ± 1 nm. The CNTs were dried in a 5 M hydrochloric acid aqueous solutions (500 mL g\(^{-1}\)) at room temperature for 12 h and then were rinsed with distilled water until neutral pH and dried overnight at 393 K. These samples were denoted as CNTs. Oxidized CNTs (oCNTs) were obtained by hydrothermal oxidation with 0.3 M nitric acid aqueous solution (60 mL g\(^{-1}\)) in a 100 mL Teflon-lined autoclave at 473 K for 2 h. Phosphate-modified samples were first prepared by impregnation of oCNTs (10 mLg\(^{-1}\)) using aqueous solutions of (NH\(_4\))\(_2\)PO\(_4\) (Sigma Aldrich, > 99 %) and...
were sonicated until all the water had evaporated, and then dried at 393 K for 24 h. Different samples with $P_{2}O_{5}$ contents of 0.1, 0.5, 1, 3, and 5 wt% were labeled as 0.1–5 P-oCNT. Mg$_{3}$V$_{2}$O$_{13}$ (pyrovan- date) and Mg$_{2}$V$_{2}$O$_{13}$ (orthovanadate) samples were synthesized according to reference [7]. An appropriate amount of solid MgO was added into a hot aqueous solution of NH$_{4}$VO$_{3}$. The supernuous water was evaporated and then dried at 353 K. The received solid was crushed and calcined at 823 K for 6 h. The XRD patterns of samples shown in Figure S1 (Supporting Information) are consistent with previous studies.\[16\]

**ODH reactions of isopentane**

On average, 50 mg of catalyst sample (100–400 mesh) mixed with 1 g of quartz sand was placed in a quartz tubular reactor and kept at 673 K in a 16.7 mL min$^{-1}$ flow with i-C$_{5}$H$_{12}$/O$_{2}$/He = 1:2:38 until constant conversion was achieved. The apparent activation energy was determined by stepwise heating (10 K steps) from 623–673 K at 25 mL min$^{-1}$ (20 mg oCNTs, 50 mg 1P-oCNTs, 100 mg 3P-oCNTs). The reactants and products were analyzed by using an on-line gas chromatography system (Agilent 7890A) with two Hayesep Q columns, a HP-PLOT/Al$_{2}$O$_{3}$ column (50 m × 0.32 mm × 8 μm), and a molecular sieve column. CO and CO$_{2}$ were detected with a thermal conductivity detector and hydrocarbons were detected with a flame ionization detector.

**Catalyst characterization**

Fourier-transform infrared spectroscopy was performed using a Nicolet FTIR infrared microscope with an ATR attachment (ATR-KBr). Specific surface areas (BET) and pore size distributions (Barrett–Joyner–Halenda (BJH)) of the CNT samples were determined by N$_{2}$ physisorption at 77 K utilizing a Micromeritics ASAP 3020 BET apparatus. The oxidation stability was carried out by a thermogravimetric analyzer (Netzsch 449 F3). 5–10 mg of sample was heated linearly in a corundum crucible from 323 to 1100 K in 50 mL min$^{-1}$ of 10 vol% O$_{2}$ in Ar. Temperature-programmed desorption (TPD) experiments were performed in He atmosphere. The temperature program involved heating at 10 K min$^{-1}$ from ambient temperature to 423 K, that temperature was kept for 30 min, the temperature was then raised to 1200 K, which was again kept for 30 min, and ultimately the sample was cooled to room temperature in a helium atmosphere. The product gases were analyzed by on-line MS (Pfeiffer-Balzer Omnistar); the masses 28 and 44 were monitored with a time-resolution of 0.1 s. The product gases were analyzed by on-line MS (Pfeiffer-Balzer Omnistar); the masses 28 and 44 were monitored with a time-resolution of 0.1 s. The product gases were analyzed by on-line MS (Pfeiffer-Balzer Omnistar); the masses 28 and 44 were monitored with a time-resolution of 0.1 s. The product gases were analyzed by on-line MS (Pfeiffer-Balzer Omnistar); the masses 28 and 44 were monitored with a time-resolution of 0.1 s. The product gases were analyzed by on-line MS (Pfeiffer-Balzer Omnistar); the masses 28 and 44 were monitored with a time-resolution of 0.1 s. The product gases were analyzed by on-line MS (Pfeiffer-Balzer Omnistar); the masses 28 and 44 were monitored with a time-resolution of 0.1 s. 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