

## Oxidative dehydrogenation of *n*-butane on nano-carbon catalysts having graphitic structures

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Received: 31 May 2011 / Accepted: 21 July 2011 / Published online: 24 September 2011  
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**Abstract** The catalytic activity of well-nanostructured carbon, for example glassy carbon spheres, SWCNT, graphene, and graphite, has been demonstrated in the oxidative dehydrogenation (ODH) of butane to obtain olefins. The catalytic performance of the carbon samples was stable, with prolonged reaction time. The proportion of butenes in the product decreased as the reaction temperature increased, whereas selectivity for ethene and propene increased with increasing temperature. Pd-containing carbon nanofibers (CNF) had superior selectivity for butadiene formation than Pd free CNF catalyst. Carbon with graphitic structures was highly selective for propylene and butenes without severe combustion in ODH of butane.

**Keywords** SWCNT · Oxidative dehydrogenation · Butane · Alkene selectivity

### Introduction

Butenes, butadiene, and propylene, which are useful intermediates for the synthesis of synthetic rubbers, plastics, and a number of industrially important chemicals, are synthesized traditionally by oxidative dehydrogenation (ODH) of *n*-butane or propane over various mixed metal oxides [1–10]. Despite a great deal of research, alkene selectivity is severely limited in this ODH reaction [11]. One important reason is that the unsaturated products are much more readily oxidized to CO<sub>2</sub> than is the starting alkane. A high oxygen-to-butane ratio is required to maintain the activity of such catalysts, which leads to unwanted oxidation of products. Carbon materials have been reported to catalyze the ODH of saturated hydrocarbon molecules, for example propane, butane, and ethylbenzene [12–15]. However,

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conventional types of carbon, for example particular active carbons, underwent unavoidable deactivation because of coking or combustion [16–19]. Recently, it was shown that only well-nanostructured carbons are stable and coke-free catalysts for these reactions [19]. Su group has shown that carbon nanotubes with modified surface functionality efficiently catalyze the ODH of less active *n*-butane to butenes [12, 14, 15]. Compared with metal oxide-based catalysts, CNTs had enhanced selectivity for C<sub>4</sub> alkenes, especially butadiene. For low O<sub>2</sub>-to-butane ratios, high selectivity to alkenes was achieved for periods as long as 100 h. They concluded that such high selectivity may occur as a result of ketonic C=O groups formed via a combination of parallel and sequential oxidation steps under the mild conditions. In their study, addition of a small amount of phosphorus greatly improved the selectivity by suppressing combustion of hydrocarbons. This progress in ODH leads to new applications of nano-structured carbon with enormous possibilities.

In this work, we demonstrated the catalytic activity of well-nanostructured carbon, for example CNTs, graphene, and graphite, in the ODH reaction to obtain the olefins. The effects of carbon structure, surface properties, and reaction conditions on the selectivity for the olefins was investigated. Carbon with graphitic structures had high selectivity for propylene and butenes without severe combustion of butane during ODH. Furthermore, in this work we synthesized carbon nanofibers (CNF) in the presence of palladium, and these were used as catalyst in the ODH reaction to obtain the olefins. Pd-containing CNF had superior selectivity for butadiene formation than Pd-free CNF catalyst.

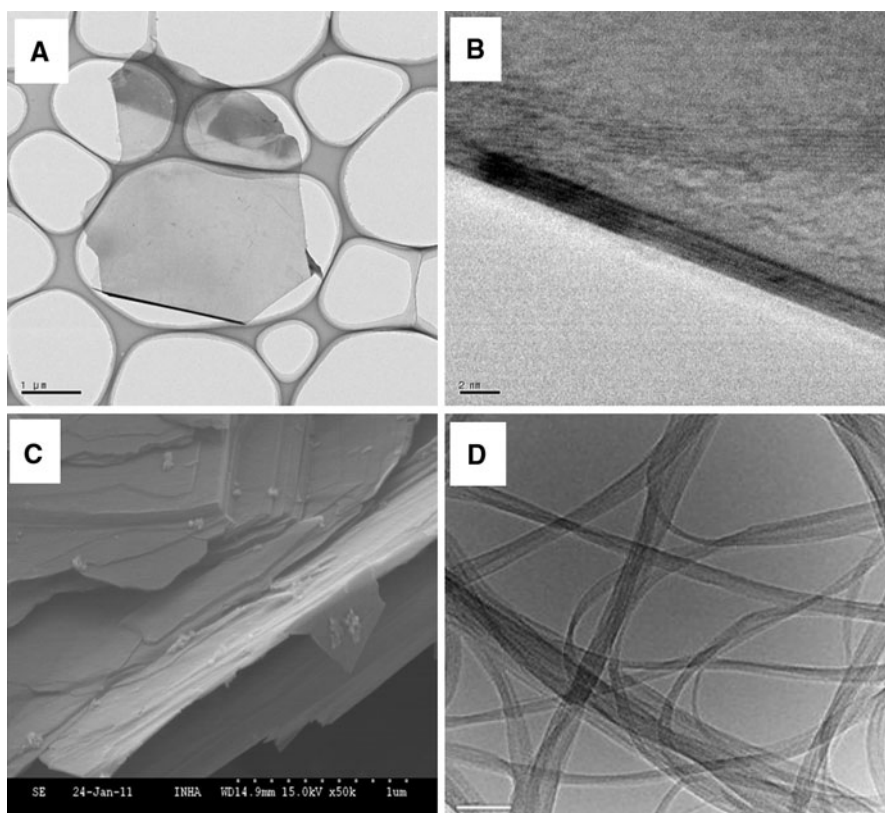
## Experimental

Single-wall CNT (Nano Solution; 1–1.5 nm single wall), glassy spherical carbon powder (Sigma–Aldrich; 99%), graphene (Cheap tubes, USA; 99%, 2 μm, surface area; 100 m<sup>2</sup>/g), graphite (Timlex KS44; 44 μm) and active carbon (Oriental Chemical) were used as catalysts without further purification. For oxidation of CNT, 2 g pristine CNT was heated under reflux in 200 ml concentrated HNO<sub>3</sub> solution for 2 h. The mixture was filtered, washed with deionized water, and dried at 80 °C in air, overnight. The resulting solid was then calcined in nitrogen at 450 °C for 30 min. P-modified graphite was prepared by incipient wetness impregnation of fresh graphite (2 g) with aqueous solutions of (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub> (Aldrich, >99%), to achieve loadings of 2 wt% P<sub>2</sub>O<sub>5</sub>. Impregnated samples were dried in air at 120 °C overnight for use as a catalyst. The dried solids were further calcined in nitrogen for 30 min. The catalytic tests were performed at atmospheric pressure and 400–600 °C in a continuous-flow, fixed-bed quartz tube with a total flow rate of 150 ml min<sup>-1</sup>. For each run, 500 mg catalyst was used and the reactant mixture usually comprised *n*-butane–air–N<sub>2</sub> (*n*-butane–O<sub>2</sub> = 1:1–2:4, with N<sub>2</sub> as balance). Gas mixtures were analyzed on a gas chromatograph (GC; Hewlett–Packard, HP-6890) with FID and TCD detectors. The morphology of carbon samples was characterized by field emission transmission electron microscopy operating at 200 kV (FE-TEM, S-4200) and scanning electron microscopy (SEM) with an Hitachi S-4200 microscope. Elemental analysis of carbon samples was conducted by use of an XPS

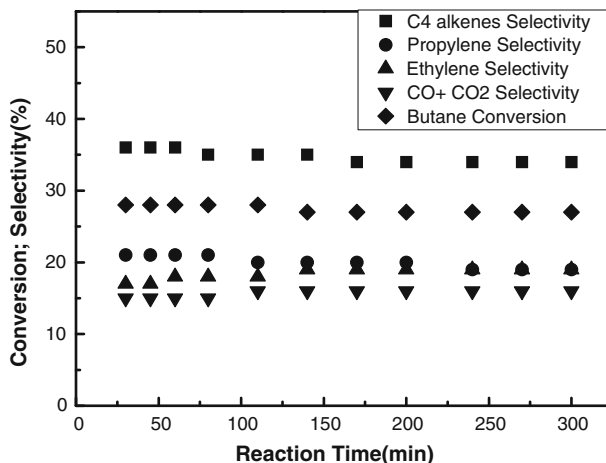
(Sigma-Probe (Thermo VG, UK) spectrometer, with  $\text{MgK}_{\alpha}$  radiation as excitation source ( $h\nu = 1253.6 \text{ eV}$ )).

## Results and discussion

For a comparative study of catalytic performance in ODH of butane, we evaluated pristine SWCNT, oxidized CNT, graphene, glassy carbon, active carbon, graphite, and 2 wt%  $\text{P}_2\text{O}_5$ -loaded graphite. The carbon samples were analyzed by SEM and TEM; the photographs are shown in Fig. 1. The graphene was very transparent because of its thin layers, as can be seen in Fig. 1a. It was composed of approximately 10 carbon layers (Fig. 1b). The graphite has a flake shape with an average size of  $45 \mu\text{m}$  (Fig. 1c). In addition, single-wall CNT was chosen as a typical carbon catalyst. The characteristic of single-wall CNT can be seen in the TEM image (Fig. 1d). XPS analysis showed that all the carbon samples contained metal compounds in trace amounts (less than 0.5%). As a result, co-operative



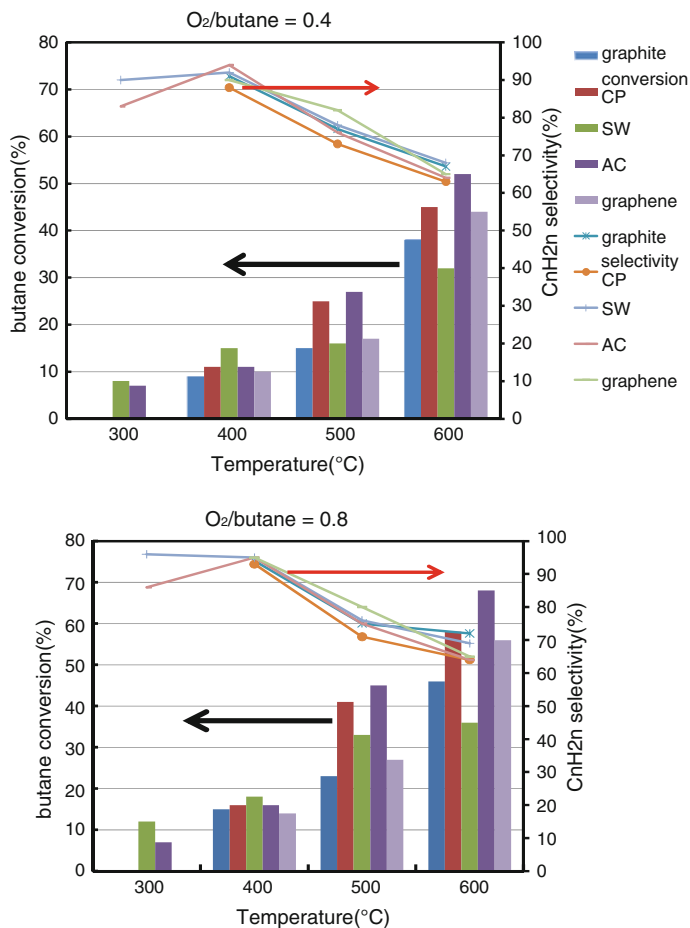
**Fig. 1** SEM and TEM images of carbon catalysts; **a** and **b** graphene, **c** graphite, **d** single-wall CNT



**Fig. 2** Stability with reaction time of graphite catalyst in ODH of butane (0.5 g catalyst,  $O_2$ -to-butane ratio = 0.8, 500 °C)

catalysis of the reactions by metal species could be ruled out. Reactions in the gas phase could also be excluded by blank experiments. All the samples had a stable catalytic performance after a few hours on-stream, and their activity and selectivity were investigated in detail by variation of reaction temperature and oxygen-to-butane ratio. We conducted the reaction at 400–600 °C with  $O_2$ -to-butane ratios of 0.4–0.8. The product mixture contained methane, ethene, propene, butenes, butadiene, CO, CO<sub>2</sub>, and residual reactants; the resulting carbon balance was almost 100%. At the  $O_2$ -to-butane ratio of 0.8, SWCNT, graphite, and graphene catalysts had outstanding stability in the ODH of butane. During reaction for 24 h on the graphite catalyst, butane and oxygen conversion remained almost unchanged, and selectivity for butenes stayed above 35%, as shown in Fig. 2. Dissociative conversion of butane into ethene and propene was observed under these conditions. Considering the high stability of graphite in  $O_2$ , we conclude that the CO<sub>2</sub> during the reaction mainly originated from oxidation of the hydrocarbon feedstock and not from burning of the carbon catalysts.

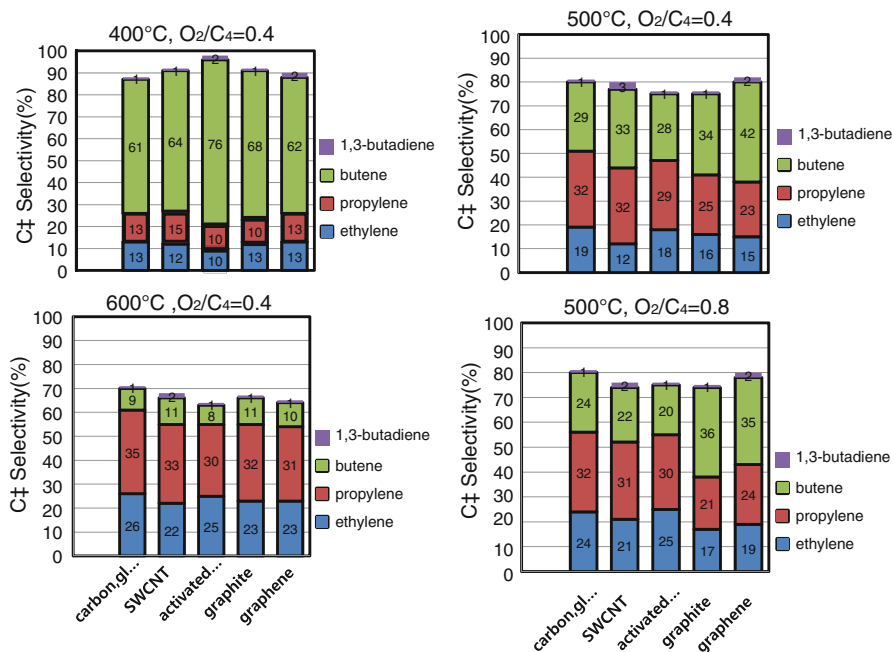
In Fig. 3, we show the ODH activity of different carbon catalysts as a function of reaction temperature and  $O_2$ -to-butane ratio. Conversion increased as the reaction temperature increased whereas selectivity for total olefins decreased. Conversion values improved on increasing the  $O_2$ -to-butane ratio from 0.4 to 0.8 at the same reaction temperature. All the catalysts had almost the same selectivity for alkenes as the concentration of oxygen was doubled. As shown in the figure, amounts of the olefins obtained on the graphite and graphene catalysts were higher than on the other types of carbon. For glassy carbon, although conversion of the reactant butane was high, total olefin selectivity was lowest among the carbon catalysts. Conversion values were highest for active carbon, with promising selectivity, but this catalyst was consumed by combustion during the reaction, because of the presence of oxygen.



**Fig. 3** Effect of reaction temperature and O<sub>2</sub>-to-butane ratio on olefin selectivity and butane conversion (0.5 g catalyst, O<sub>2</sub>-to-butane = 0.4 and 0.8, 300–600 °C)

We then functionalized surfaces of pristine CNT by heating under reflux and oxidation in concentrated HNO<sub>3</sub>. With the resulting oxidized CNT as a catalyst, we observed no improvement in the yield of alkenes. The oxidized CNT was unstable during the reaction, and was combusted in the ODH of butane. Only 10% of the CNT catalyst remained after ODH reaction at 600 °C. Over the oxidized CNT, more than 80% of the converted butane was combusted, yielding less than 2% alkenes. After heating CNT under reflux in HNO<sub>3</sub>, defect sites were functionalized by use of O<sup>2-</sup> anions into various functional groups. Then, at the reaction temperature, desorption of less stable groups may result in many defects that subsequently generate new electrophilic oxygen sites, thus partially limiting the selectivity for alkenes of the oxidized CNT.

To compare catalytic activity, we evaluated different types of carbon in ODH of *n*-butane at different reaction temperatures. The effects of reaction temperature and

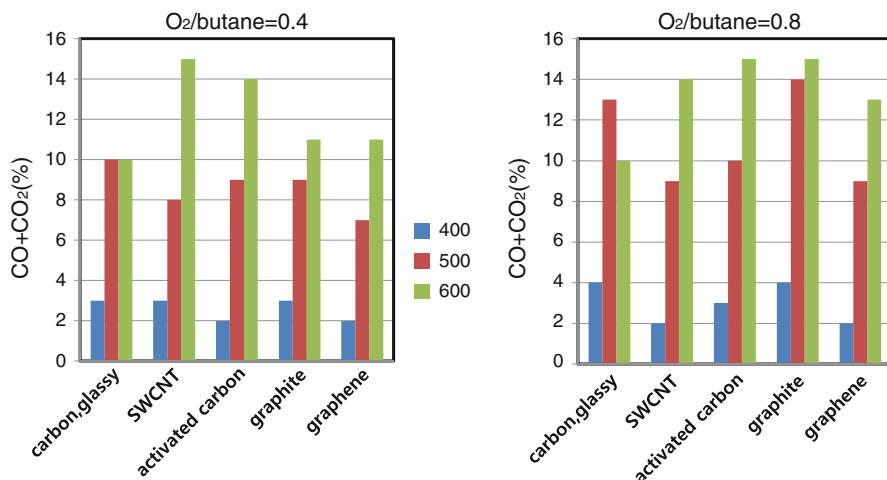


**Fig. 4** The product distribution obtained in the ODH of butane over different carbon catalysts at reaction temperatures of 400–600 °C (0.5 g catalyst, O<sub>2</sub>-to-butane ratio = 0.4 and 0.8)

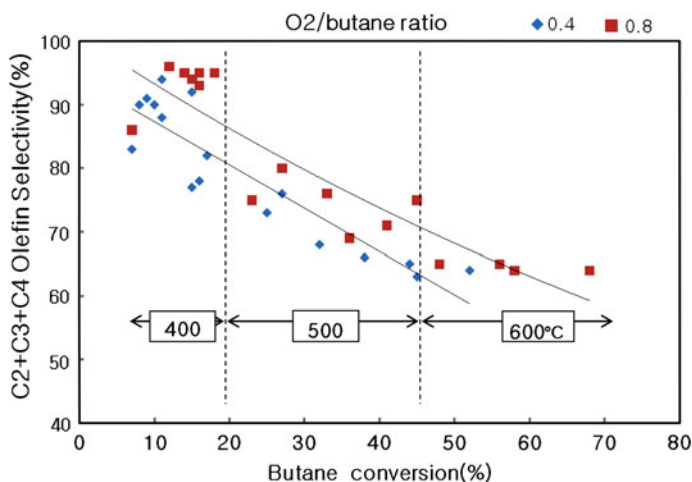
O<sub>2</sub>-to-butane ratio on olefin selectivity were investigated in detail; the product distribution obtained over the different carbon catalysts is summarized in Fig. 4. As mentioned above, higher selectivity for total alkenes was obtained with at decreased temperature and lower O<sub>2</sub>-to-butane ratio. In the product olefins, the higher proportion was butenes at a reaction temperature of 400 °C. The amount of butenes decreased as the reaction temperature increased. Instead, selectivity for ethene and propene increased with increasing temperature. This means that dissociation of CH bonds was predominant at the higher reaction temperature in the presence of carbon catalysts. The trend in the change of product distribution was very similar for every carbon catalyst.

Selectivity for CO and CO<sub>2</sub> was determined over the carbon catalysts, and the result is shown in Fig. 5. In general, CO and CO<sub>2</sub> selectivity increased as the O<sub>2</sub>-to-butane ratio and the reaction temperature were increased. At relatively low O<sub>2</sub>-to-butane ratios, for example 0.4, graphite and graphene had low CO, CO<sub>2</sub> selectivity compared with the other catalysts. The low yield of CO<sub>2</sub> means improvement in the selectivity for alkenes in the ODH reaction of butane.

Figure 6 shows the relationship between conversion and selectivity for total olefins in ODH of butane over different catalysts. At the higher level of conversion, alkene selectivity decreased. However the carbon catalysts had enhanced selectivity for olefins at the high oxygen concentration, as indicated in the results shown in Fig. 6. This phenomenon was investigated in detail by comparing conversion vs. selectivity for each olefin, for example dissociated product ethene and propene, and



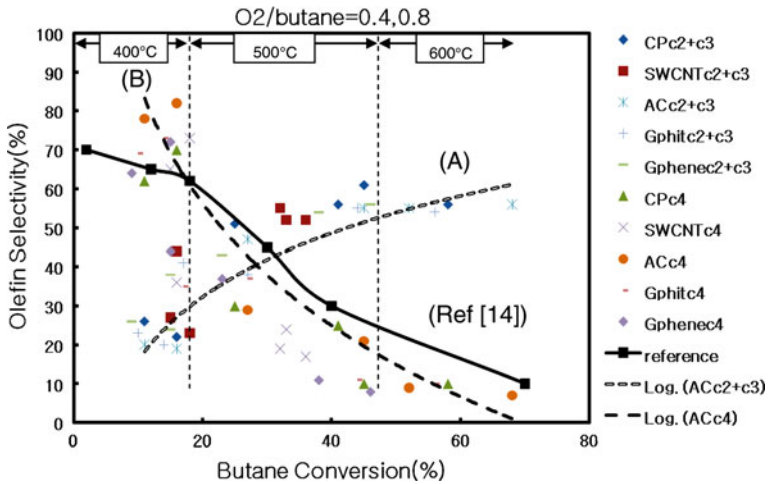
**Fig. 5** Selectivity for CO and CO<sub>2</sub> in the ODH of butane over different carbon catalysts at reaction temperatures of 400–600 °C (0.5 g catalyst, O<sub>2</sub>-to-butane ratio = 0.4 and 0.8)



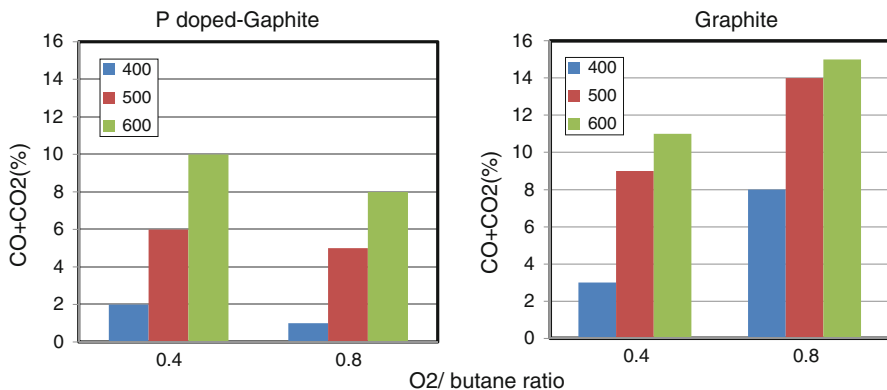
**Fig. 6** Plot of conversion vs. total olefin selectivity in the ODH of butane over carbon catalysts (0.5 g catalyst, O<sub>2</sub>-to-butane ratio = 0.4 and 0.8, 400–600 °C)

butene. Selectivity for butenes decreased with progressively increasing conversion values. The same trend and the similar values in the plot of conversion vs. C<sub>4</sub> olefin selectivity have been reported in the paper by the Su group, as shown additionally in Fig. 7 [14]. However concentrations of ethene and propene increased at the high level of butane conversion.

The effect of addition of phosphorus as a promoter was investigated in the ODH reaction. Selectivity for CO, CO<sub>2</sub>, and alkenes in the ODH of butane were determined over graphite and 2 wt% P-doped graphite catalyst at reaction



**Fig. 7** Plot of conversion vs. butenes (b) and ethane + propene selectivity (a) in the ODH of butane over different carbon catalysts (0.5 g catalyst,  $O_2$ -to-butane ratio = 0.4 and 0.8, 400–600 °C, Ref [14])

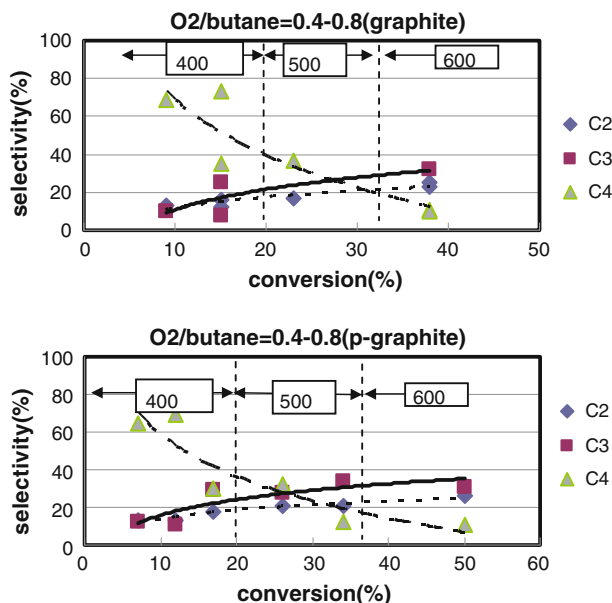


**Fig. 8** Selectivity for CO and  $CO_2$  in the ODH of butane over graphite and 2 wt% P-doped graphite catalysts at reaction temperatures of 400–600 °C (0.5 g catalyst,  $O_2$ -to-butane ratio = 0.4 and 0.8)

temperatures of 400–600 °C. Selectivity for CO and  $CO_2$  is shown in Fig. 8. The P-loading on CNT reduced selectivity for CO and  $CO_2$  by suppressing the combustion rate, rather than enhancing the rate of formation of alkenes. Modification with phosphate is indeed reported to block the combustion sites serving as a point of attack for gaseous oxygen, and thus to suppress the combustion of the carbon framework at elevated temperatures [19].

Figure 9 shows the relationship between conversion and selectivity for each olefin, e.g. ethene, propene, and butene. At the higher level of conversion, alkene selectivity decreased for both carbon catalysts. At the same conversion of butane, fresh graphite had the same selectivity for olefins as the 2 wt% P-doped graphite catalyst.



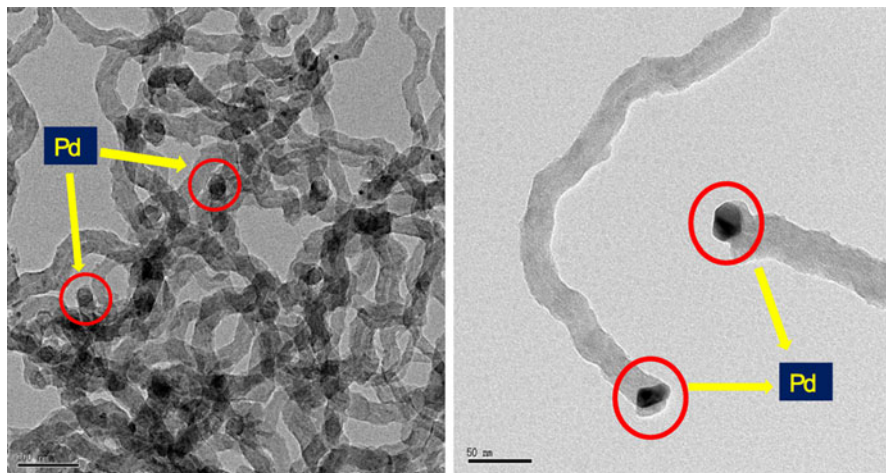


**Fig. 9** Plot of conversion vs. butane, ethane, and propene selectivity in the ODH of butane over graphite and 2 wt% P-doped graphite catalysts at reaction temperatures of 400–600 °C (0.5 g catalyst, O<sub>2</sub>-to-butane ratio = 0.4 and 0.8)

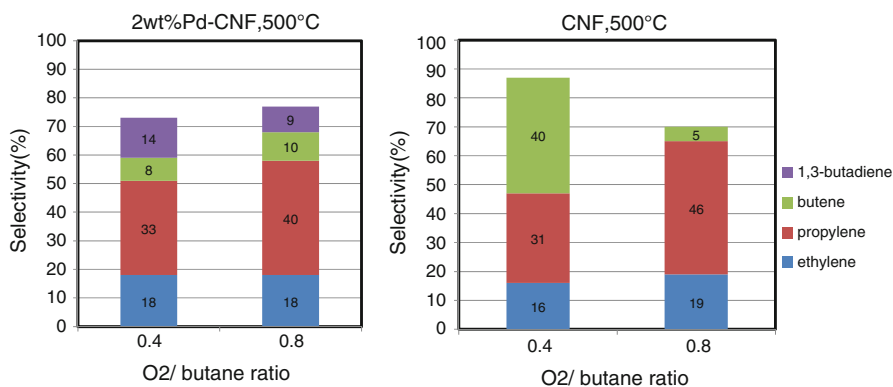
We have synthesized CNF on Pd particles supported on silica. The nano-sized Pd particles were embedded at the end of CNF, as shown in Fig. 10. After dissolution of Pd by nitric acid, we conducted the ODH reaction of butane using the as-synthesized Pd-containing CNF and HNO<sub>3</sub> treated CNF as catalysts. Different product distributions were observed. The results obtained are compared in Fig. 11, from which it can be seen that Pd-containing CNF have superior selectivity toward butadiene formation than Pd-free CNF catalyst. Such a pronounced enhancement can be related to the high dehydrogenation activity of Pd species. However, selectivity for butenes was dramatically reduced in the presence of Pd-containing CNF. At the high O<sub>2</sub>-to-butane ratio, selectivity for ethene and propene was enhanced for both catalysts.

However, interaction of butane with oxygen-treated surfaces of the carbon catalysts is important to yield alkenes such as propene and butenes. Butane molecules are activated by the surface oxygen groups to yield alkenes with remarkable selectivity. The surface of carbon materials is terminated by a variety of functionalized oxygen groups [11]. In these surface species, ketonic groups have great potential to coordinate a redox process, because they are rich in electrons. It is well known that Lewis basic sites can abstract hydrogen atoms from CH bonds of alkanes to produce the corresponding alkenes. The reaction between the gas-phase oxygen and the abstracted hydrogen will regenerate the active sites with the formation of water [14, 15].

In XPS spectra for C1s, the ketonic C=O bond has a peak at 287.8 eV. Fresh graphite and that used in the ODH reaction were analyzed by XPS. The small



**Fig. 10** TEM images of carbon nanofiber (CNF) as-synthesized on the nano-size Pd particles: this Pd-containing sample and acid-treated Pd-free CNF were used as catalysts in the ODH of butane

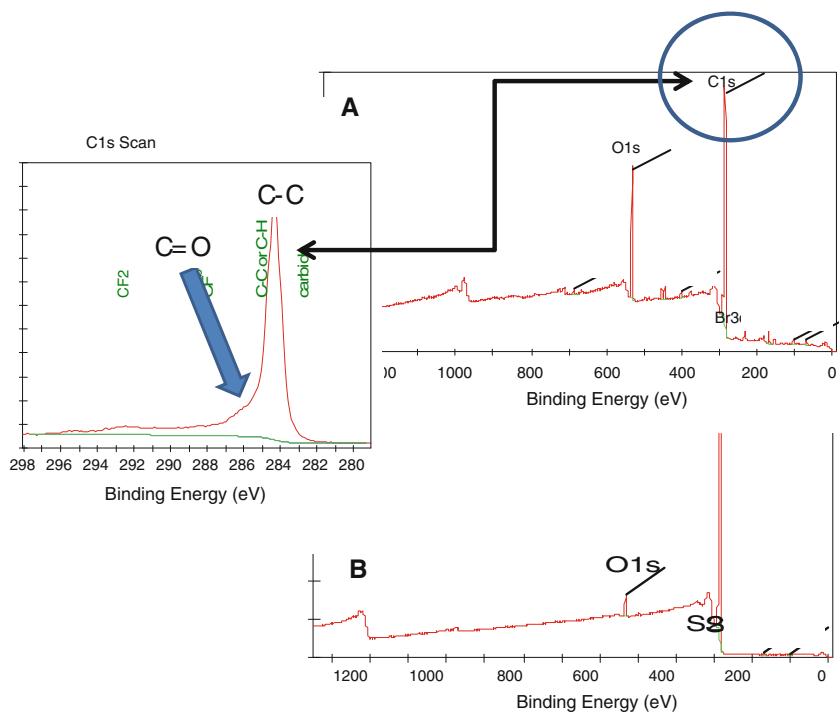


**Fig. 11** Selectivity for olefins in the ODH of butane over the Pd-containing carbon nanofiber (Pd-CNF) and HNO<sub>3</sub>-treated Pd-CNF carbon catalysts at a reaction temperature of 500 °C (0.5 g catalyst, O<sub>2</sub>-to-butane ratio = 0.4–0.8)

shoulder near 288 eV for ketonic C=O bonds was observed in the C1s peak as shown in Fig. 12. It is believed that these groups present on the carbon surfaces may be critical components of the active sites, as reported by Su et al. [14]. The presence of oxygen was confirmed in the same XPS analysis, and an increase of oxygen species on the surface was found after use in the ODH reaction.

## Conclusion

In this work, the catalytic activity of well-nanostructured carbon, for example glassy carbon spheres, SWCNT, graphene, and graphite were demonstrated in the ODH



**Fig. 12** XPS spectra of fresh graphite (b) and of graphite used (a) in the ODH of butane

reaction of butane to obtain olefins. These carbon samples had stable catalytic performance with prolonged reaction time. Higher selectivity for total alkenes was obtained at lower temperatures and lower  $O_2$ -to-butane ratios. The proportion of butenes in the product decreased as the reaction temperature was increased, whereas selectivity for ethene and propene increased with increasing temperature. Furthermore butene selectivity decreased with progressively increasing conversion. P-loading of the CNT reduced the selectivity for CO and  $CO_2$  by suppressing combustion. Pd-containing CNF has superior selectivity for butadiene formation than Pd-free CNF catalyst. Carbon with graphitic structures had high selectivity to propylene and butenes without severe combustion of butane in ODH.

**Acknowledgment** This research is supported by Korea Ministry of Environment as “Converging technology project”.

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