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Grignard reagent reduced nanocarbon material in oxidative dehydrogenation of *n*-butane

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ABSTRACT

A modification route of nanocarbon catalyst based on Grignard reagent reduction of oxidized carbon nanotubes (o-CNTs) has been developed for oxidative dehydrogenation (ODH) of *n*-butane. The o-CNTs contain considerable amount of electrophilic oxygen species which are responsible for deep oxidation side-reactions and the alkene selectivity in ODH is low. After Grignard reduction, the corresponding electrophilic oxygen groups on the surface of the catalyst were eliminated and the basicity increased. As a result, the side-reactions in ODH were prohibited and the alkene selectivity was significantly improved compared with o-CNTs. The chlorine containing Mg/Cl species were found to have positive effect on the improvement of C_4H_8 alkene yield. This study provides a method of the preparation of nanocarbon catalyst to achieve higher alkene selectivity for the dehydrogenation reaction.

1. Introduction

Oxidative dehydrogenation (ODH) of *n*-butane is a promising process to produce high value butenes and butadiene from low-cost butane. Traditional metal oxides such as supported vanadium and molybdenum oxide catalysts have been widely employed to catalyze this reaction [1,2]. Among the reported metal oxide catalysts, the V—Mg—O catalyst presents the highest selectivity to C_4 alkenes [1–6]. However, the traditional metal oxide catalysts are unfavourable in side-reaction controlling and suffer serious deactivation by the coke formation during ODH reaction, which restrains their further application.

Nanocarbon materials are attracting considerable interest in catalyzing C—H bond activation such as ODH of light alkanes, owing to their competitive catalytic activity and remarkable coke-resistance [7,8]. It has been proven that the electron-rich quinone groups on the surface of nanocarbon are active sites to catalyze ODH reactions through a redox mechanism [8–10], and the electrophilic oxygen groups (peroxide O_2^{2-} and superoxide O_2^-) attack C=C bonds and are responsible for deep oxidation of the desired alkene products [8]. A variety of heteroatom-doping treatments have been explored on nanocarbons to enhance the catalytic performance focusing on O, N, B and P doping [8,11–13], however, the employed modification approaches for ODH reaction are still limited and the catalytic influence of other elements has not been investigated. Moreover, further industrial application of nanocarbon catalysts in ODH of *n*-butane requires higher alkene selectivity which is a priority in developing new modification strategies.

Grignard reagent is a reductant presented as RMgX (R is alkyl or aryl and X is halogen). Reduction of graphene oxide with Grignard reagent has been reported to form functional nanocomposites [14,15], but the impact of Grignard reagent reduction on the catalytic performance of nanocarbon materials hasn't been discussed. Herein, a modification route of nanocarbon materials was developed based on Grignard reagent reduction of oxidized carbon nanotubes (o-CNTs) to control the distribution of the surface oxygen groups and to introduce heteroatoms on carbon nanotubes (CNTs) that have potential effects on the catalyst. We employed $C_6H_5CH_2$-MgCl as the reductant and Cl/Mg precursor to reduce the electrophilic oxygen species on the surface of o-CNT which cause deep oxidation side-reactions, and examined the effect of Cl/Mg dopant on the catalytic behavior in ODH of *n*-butane. The C_4 alkene selectivity of Grignard reduced o-CNT catalyst (Gr-oCNT) was significantly improved, providing new insights into heteroatom-doped carbon-mediated catalyst. The catalytic roles of electrophilic oxygen, Mg and Cl species in ODH reactions were systematically discussed in this work.

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2. Methodology

2.1. Catalysts preparation

Commercial available CNTs were purchased from Shandong Dazhan Nano Materials Co., Ltd., and used directly without any purification. The length, inner diameter and purity of CNTs were: 3–12 μm, 12–15 nm and 96%, respectively. 10 g CNTs was oxidized in 125 mL of concentrated HNO_3 (65–68%) and 375 mL of concentrated H_2SO_4 (95–98%) under sonication at 50 °C for 6 h, and the precipitate was filtered out and washed several times with deionized water until the pH of the filtrate reached 7. The precipitate was dried in the atmosphere at 120 °C for 12 h to obtain oxidized carbon nanotubes (o-CNTs).

The Grignard reduction of o-CNT was performed as follows. 2 g o-CNTs was added in 20 mL of $C_6H_5CH_2MgCl$ (1.0 M, solution in diethyl ether, Aldrich Chemical Company). After the solution had been stirred under N_2 protection for 2 h at 25 °C, the temperature was increased to 65 °C and held for 12 h. Excess $C_6H_5CH_2MgCl$ was washed off by tetrahydrofuran (THF) for several times and the precipitate was filtered out and dried in the atmosphere at 80 °C for 12 h to obtain Gr-oCNT.

The samples involved in control experiments include Mg-oCNT, Cl-oCNT, Gr-CNT and Me-oCNT. The preparation procedure was as follows:

Mg-oCNT: 2 g o-CNT was added into 20 mL of Dibutylmagnesium (1.0 M, solution in heptane, Aldrich Chemical Company). After the solution had been stirred under N_2 protection for 2 h at 25 °C, the temperature was increased to 65 °C and held for 12 h. Excess Dibutylmagnesium was washed off by tetrahydrofuran (THF) for several times and the precipitate was filtered out and dried in the atmosphere at 80 °C for 12 h to obtain Mg-oCNT.

Cl-oCNT: 1 g o-CNTs was added into 20 mL of CCl_4. After the solution had been stirred under N_2 protection for 2 h at 25 °C, the temperature was increased to 80 °C and held for 12 h. The precipitate was filtered out and dried in N_2 at 80 °C for 12 h to obtain Cl-oCNT.

Gr-CNT was obtained following the same procedure as Gr-oCNT except that o-CNTs was replaced by pristine CNTs.

Me-oCNT was obtained following the same procedure as Gr-oCNT except that $C_6H_5CH_2MgCl$ was replaced by CH_3MgCl (1.0 M, solution in diethyl ether, J&K Scientific Ltd).

2.2. Iodometric titration method

In this work, we used iodometric titration to determine the surface amount of electrophilic oxygen species on CNTs samples [16]. Electrophilic peroxide and superoxide species can oxidize aqueous I^- into I_2 for subsequent titration with $Na_2S_2O_3$. Herein, we suppose the electrophilic oxygen species are mostly composed of peroxides and designate peroxide as electrophilic oxygen for convenient calculation. The titration of electrophilic oxygen groups on CNTs samples was performed as following procedure. A 0.3 g CNT sample was added in a KI solution that consisted of 10 mL of KI (100 g/L), 5 mL of H_2SO_4 (0.1 mol/L), 30 mL of deionized water, and 3 drops of $(NH_4)_6Mo_7O_{24}$ (30 g/L). The reaction between peroxides on the surface of CNTs and KI is shown in (1). After 30 min under sonication at 25 °C in the dark, I^- was oxidized into I_2. Then the precipitate was filtered out and washed six times. I_2 in the filtrate was titrated with $Na_2S_2O_3$ (0.002 mol/L) as presented in (2) and the concentration of electrophilic oxygen (mol/g) on CNTs was calculated with (3) where c (mol/g), V (mL) and m (g) represent the electrophilic oxygen concentration, the volume consumption of $Na_2S_2O_3$ solution and the mass of CNT samples for titration, respectively. The obtained iodometric titration data were validated with similar results from repeated experiments.

$$O_2^{2-} + 2KI + 2H_2SO_4 \rightarrow O^{2-} + 2KHSO_4 + I_2 + H_2O \quad (1)$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6 \quad (2)$$

$$c(\text{electrophilic oxygen}) = 2 \times 10^{-6}\ \text{V/m} \quad (3)$$

The titration results were validated by the control experiments where no electrophilic oxygen species were detected on pristine CNTs and blank sample (without CNTs).

2.3. Catalyst performance test

The catalytic activity of CNT samples in the reaction of oxidative dehydrogenation of butane was measured at 723 K using a 10 mm diameter fixed-bed quartz tube reactor at atmospheric pressure over 300 min. Reactant and product concentrations (weight percent) were measured by online gas chromatography (Agilent model 7890B) equipped with a HayeSep Q column, a HayeSep N column and a molecular-sieve column connected to a thermal conductivity detector, and a HP-PLOT $A1_2O_3$ column (50 m × 0.53 mm × 15 μm) connected to a flame ionization detector. Reactant mixtures (Beijing AP BAIF Gases) contained 0.7 wt% butane, 1.4 wt% O_2 and 97.9 wt% N_2 with a typical gas flow rate of 4500 mL of gas h^{-1} (g of catalyst)$^{-1}$.

The selectivity of alkene products is calculated as follows:

$$sel_{\text{butene}} = \frac{c_{\text{butene}} \times 1.034}{[c_{\text{butane}}]_{\text{in}} - [c_{\text{butane}}]_{\text{out}}} \times 100\%$$

$$sel_{\text{butadiene}} = \frac{c_{\text{butadiene}} \times 1.074}{[c_{\text{butane}}]_{\text{in}} - [c_{\text{butane}}]_{\text{out}}} \times 100\%$$

where sel_i (percent) and c_i (weight percent) are selectivity and concentration, respectively, of each C_4 alkene product in the outlet gas and $[c_{\text{butane}}]_{\text{in}}$ and $[c_{\text{butane}}]_{\text{out}}$ are the n-butane concentrations in the inlet and outlet gas mixture, respectively.

The side-reaction refers to total oxidation of hydrocarbon to form CO_x. The calculations of side-reaction rates (moles per gram per second) are based on the reaction conditions (gas flow rate and butane concentration) and the catalytic performance. The calculating formula for the side-reaction rate is presented as

$$v_s = 0.189 \times 10^{-6}\text{conv}(1 - \text{sel})$$

where v_s (moles per gram per second), conv (percent) and sel (percent) represent the side-reaction rate, the conversion of butane and the C_4 alkene selectivity, respectively.

A control experiment was conducted under the same reaction condition except there was no catalyst sample added into the reactor. The conversion rate of n-butane was 0%, and neither alkene nor the side reaction product was detected by gas chromatography.

2.4. Characterizations

Transmission electron microscopy (TEM) measurements were taken on a FEI Tecnai F20 microscope with an accelerating voltage of 200 kV. Raman spectra were recorded under ambient conditions on a JY LabRAM HR Raman spectrometer with a 325 nm laser beam. The weight concentrations for element C, H, and O were determined on an Elementar Micro Cube elemental analyzer. The weight concentrations for element Mg and Cl were obtained by Rigaku 3013 X-ray Fluorescence Spectrometer (XRF). X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. The base pressure was ~3×10^{-9} mbar.