Phosphate modified carbon nanotubes for oxidative dehydrogenation of n-butane[☆]

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ABSTRACT

Catalytic performance of phosphate-modified carbon nanotube (PoCNT) catalysts for oxidative dehydrogenation (ODH) of n-butane has been systematically investigated. The PoCNT catalysts are characterized by SEM, TEM, XPS and TG techniques. We set the products selectivity as a function of butane conversion over various phosphate loading, and it is found that the PoCNT catalyst with the 0.8% phosphate weight loading (0.8PoCNT) exhibits the best catalytic performance. When the phosphate loading is higher than 0.8 wt%, the difference of catalytic activity among the PoCNT catalysts is neglectable. Consequently, the ODH of n-butane over the 0.8PoCNT catalyst is particularly discussed via changing the reaction conditions including reaction temperatures, residence time and n-butane/O_2 ratios. The interacting mechanism of phosphate with the oxygen functional groups on the CNT surface is also proposed.

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1. Introduction

Butadiene as one of the most important basic petrochemical products is widely used in the manufacture of rubbers and fine chemical synthesis, which is generally synthesized via a catalytic oxidative dehydrogenation (ODH) process using transition metal oxides catalysts [1–3]. But the metal oxide catalysts usually require high O_2/butane ratios or large amounts of steam to avoid the coking during the ODH reaction, resulting in the massive energy consumption [4]. Recently, carbon nanotubes (CNTs), as a new type of carbon materials, have drawn much attention owing to their unique physical and chemical properties [5–9]. Many studies demonstrate that CNTs show excellent catalytic performance in several reactions [10–15]. In our previous studies, it was found that the phosphate modified CNTs (PoCNT) catalysts exhibit the best catalytic activity and selectivity for the ODH of n-butane without the protection of steam, compared with that of the traditional

activated carbon and transition metal oxides catalysts [16,17]. The modification of phosphate on the CNT surface could decrease the activity and increase the selectivity by suppressing the combustion of n-butane. The ketonic and quinonic C=O groups on the CNTs surface have been identified as the active sites to catalyze the oxidative dehydrogenation (ODH) of n-butane [17]. In this paper, we systematically investigate the PoCNT catalysts with different phosphate loading for the ODH of n-butane. The results reveal that the PoCNT with 0.8 wt% phosphate loading (0.8PoCNT) presents the highest selectivity to alkenes. The interacting mechanism of phosphate with the oxygen functional groups on the CNT surface is proposed. After the comprehensive analysis of the PoCNT catalysts by XPS, TEM and TPO tests, we choose 0.8PoCNT as the target catalyst and study the effect of reaction conditions including reaction temperature, residence time and n-butane/O_2 ratios.

2. Experimental

2.1. The preparation of CNTs

Pristine MWCNTs synthesized by Chemical Vapor Deposition (CVD) were purchased from Shandong Dazhan Nano Materials Co, ltd. 5 g pristine CNTs were oxidized by refluxing them in 500 mL concentrated HNO_3 solution for 2 h. The mixture was filtered, fully washed by deionized water, and dried at 393 K under air
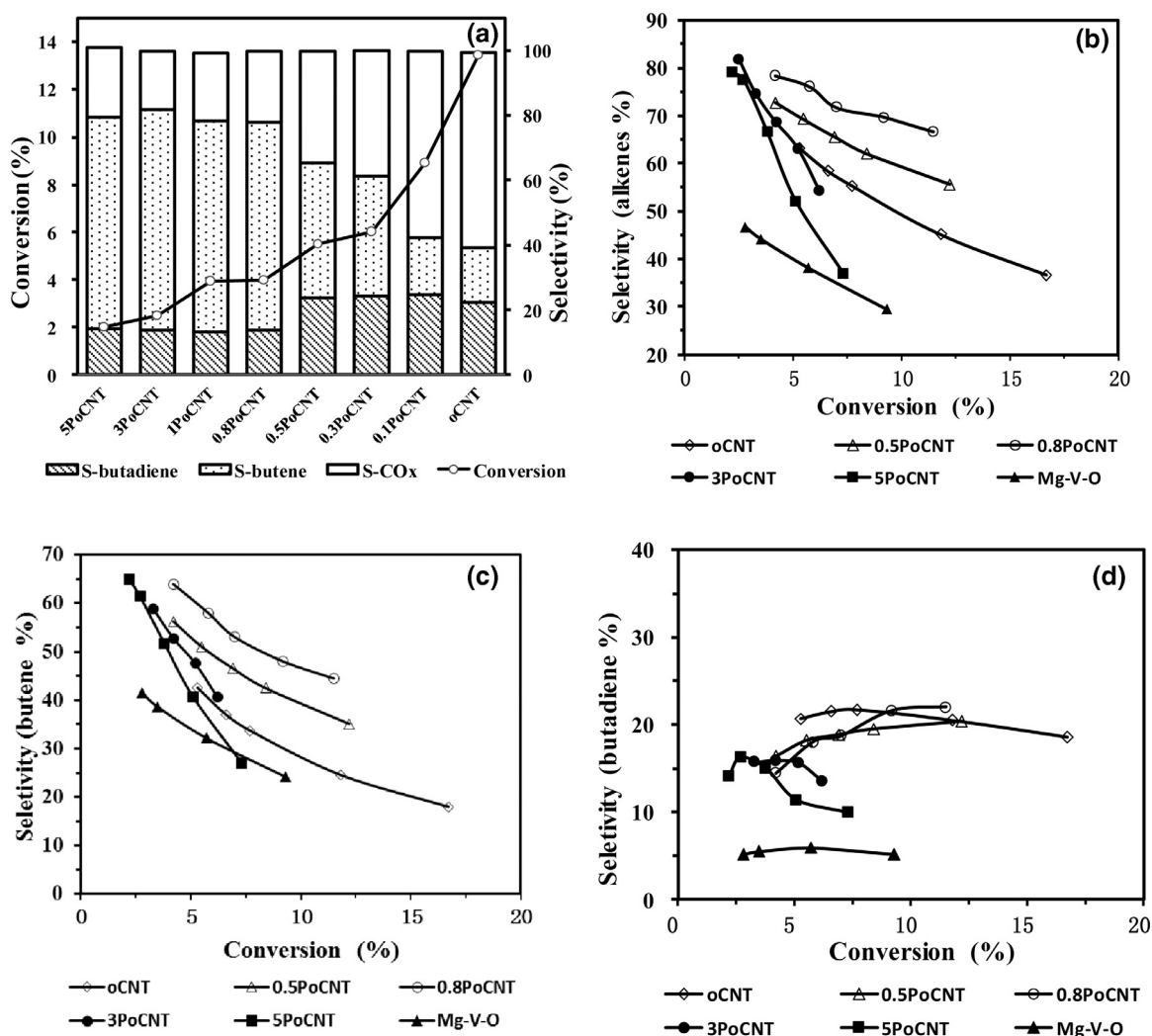
Fig. 1. (a) Performance of various CNTs for ODH of butane under oxygen-rich conditions: 0.1 g catalyst, 400 °C, 1.98% butane, O_2/butane = 2, 15 mL/min. (b–d) The product selectivity versus n-butane conversion obtained by variation of residence time, with Mg–V–O as a reference. Reaction conditions: 5PoCNTs 300 mg; 3PoCNTs 200 mg; 0.8PoCNTs, 0.5PoCNTs 100 mg; oCNTs 50 mg; 1.98% n-butane, O_2/butane = 2, 5–35 mL/min, 400 °C.

overnight. The as received samples were named as oCNTs. The oC-NTs were then modified by $(NH_4)_2HPO_4$ as phosphorus precursor via a traditional impregnation method. The series catalysts labeled as xPoCNTs that theoretical content of P_2O_5 (x) ranges from 0 wt% to 3 wt%. Mg–V–O ($Mg_3V_2O_8$) samples were synthesized according to the reference [1].

2.2. Catalytic test

The performances of xPoCNTs for the ODH of n-butane were investigated at 673 K. The catalytic reaction was carried out in a quartz tube reactor, holding 0.1 g catalyst powder between two quartz wool plugs in the isothermal zone. The n-butane mixed with oxygen was diluted in He, corresponding to an n-butane concentration 2 vol%. The total flow rate was 15 mL/min at ambient pressure. The 0.8PoCNT was employed for the optimization experiment. The range of operating conditions was as follows: temperature, 673 K to 773 K; residence time, 100 to 300 $g_{cat} \cdot h/mol_{C4}$; oxygen, 2 to 8 vol%, n-butane, 1.98 vol%; with He as balance. Analyses of reactants and products were carried out by the on-line gas chromatographs Agilent 7890 with FID and TCD detectors.

2.3. The characterization techniques

The xPoCNTs were characterized by scanning electron microscopy (SEM, FEI Nova NanoSEM 450) and transmission electron microscopy (TEM, FEI Tecnai G^2 spirit 120 kV). The X-ray photoelectron spectroscopy (XPS) was carried out on ESCALAB 250 with Al $K\alpha$ radiation (1486.7 eV) and a power of 150 W. Thermoprogrammed oxidation (TPO) experiment of fresh 0.8PoCNT was carried out using the gas mixture containing 10 vol% O_2 diluted in 90 vol% He with a flow rate of 50 mL/min. The mass loss was tested by thermogravity instrument (NETZSCH STA 449 F3).

3. Results and discussion

3.1. Oxidative dehydrogenation of n-butane

The catalytic performance of ODH reaction are evaluated over the serial PoCNT catalysts with different phosphate loading. The surface compositions of the xPoCNTs analyzed by the XPS are displayed in Table S1.

Fig. 1 shows the catalytic performance of PoCNTs with different phosphate loading. In Fig. 1(a), it can be observed that the selectivity to CO_x decreases accompanying with the increase of