

Surface Modified Carbon Nanotubes as Highly Selective Dehydrogenation Catalyst

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Introduction

Transition-metal oxides have been widely used as catalysts for the conversion of butane to C₄ alkenes, important industrial precursors for producing synthetic rubbers, plastics, and a number of industrially significant chemicals. Despite a great deal of research, alkene selectivity in the current butane-to-butadiene process is still limited. One important reason is that the unsaturated products are much more readily oxidized to CO₂ than the starting alkane. The chemical complexity of real polyvalent metal oxides was found to be necessary for activity but likewise rendered it hard to achieve satisfactory selectivity through isolation of active sites. Here we show that carbon nanotubes (CNTs) can, when modified with oxygen and phosphorus, in the presence of excess oxygen, improve the selectivity to alkenes. When compared with metal-based catalysts, CNTs displayed a significantly enhanced selectivity to C₄ alkenes, especially to butadiene [1].

Materials and Methods

Multi-walled CNTs from Nanocyl Corp., Belgium, were used. Typically, 2g pristine CNTs were oxidized by refluxing in 200 ml concentrated HNO₃ solution for 2 hours. The mixture was filtered, fully washed by deionized water, and dried at 80°C under air overnight. The resulting solid was then calcined in helium at 450°C for 30 min (oCNTs). The phosphorus modified CNTs (P-oCNTs, 0.5±0.1wt% of P) were prepared via conventional impregnation method by using oCNTs as support and (NH₄)₃PO₄ as phosphorus precursor. The dried solids were further calcined in helium for 30 min. Catalytic tests were carried out at atmospheric pressure and 400–450°C in a continuous-flow fixed-bed quartz tube with a total flow rate of 10–15ml min⁻¹. For each run, 10–180 mg of catalyst was used and the reactant mixture usually comprises *n*-butane, O₂ and He (O₂/*n*-butane=0.5–2, He as balance). Gas mixture was analyzed on a GC chromatograph (Varian Micro-GC 4900) with four TCD detectors.

Results and Discussion

Over pristine CNTs, 88.9% of the converted butane was burnt producing mainly CO₂. The yield to alkenes is only 1.6 %. With oCNTs as catalyst, we observed an improved yield of 6.7% to alkenes. The alkene yield was further enhanced to 13.8% after the oCNTs catalyst was additionally modified by passivating defects with P-oCNTs catalyst [1]. To compare the present reaction conditions to those previously used, two V/MgO samples were synthesized and then evaluated. As it is shown in Figure 1, at the same conversion of butane, the Mg₃V₂O₈ and Mg₃V₂O₇ samples were less selective than P-oCNTs; in particular, P-oCNTs gave twice the selectivity to butadiene than Mg₃V₂O₇, *i.e.* 16.2%. In addition to the excellent improvement in the selectivity, CNTs are highly stable over long-term test. Neither combustion of the CNTs nor coke formation was observed after a 100 h test.

The observed improvement in selectivity to alkene is explained by the following [1]: Surface oxygen species on carbon were classified into electrophilic (superoxide O₂⁻, peroxide O₂²⁻) and nucleophilic (O²⁻) types. Electrophilic oxygen species are electron-deficient and attack the electron-rich C=C bonds in alkenes, leading to the rupture of the carbon skeleton and subsequent combustion. It is well known that CNTs exhibit defect sites or edges of graphene that convert O₂ molecules to electrophilic oxygen species. These species can thus cause low selectivity to alkenes. After refluxing in HNO₃, defect sites were functionalized by O²⁻ anions into various functional groups. For example, the nucleophilic ketonic C=O with its high electron density preferentially reacts with electron-poor saturated bonds. However, at the reaction temperature, desorption of less stable groups results in new graphitic defects that subsequently generate new electrophilic oxygen sites, thus partially limiting the selectivity to alkenes on oCNTs. The addition of phosphate reacting with these defects suppresses the formation of electrophilic oxygen species. Thus, P-oCNTs displayed a lower overall activity but a much better selectivity.

Significance

Our work shows that it is possible to imitate heterogeneously the concepts of homogeneous metal-free catalysis. The function of oxygen heteroatoms in molecular catalysts is reproduced by defects of bent graphitic sheets. The operation mode of ODH reactions can be studied on metal-free catalysts with greater precision than metal oxide systems. There is neither lattice nor structural oxygen, but only oxygen at active sites. The present catalysts are free of polyvalent metal sites with complex electronic and spin structures, allowing for a facile theoretical treatment. Finally, the application of heterogeneous CNTs catalyst is attractive because of favorable management of energy over a good thermal and electronic conductor.

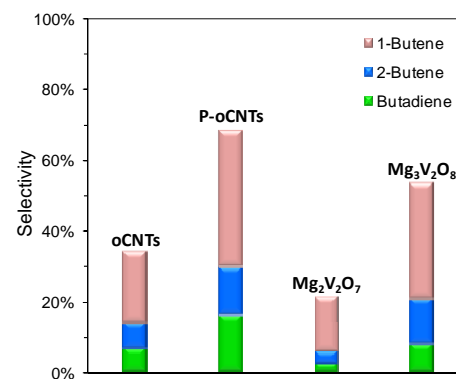


Figure 1. Comparison of selectivity to C₄ alkenes at 5% conversion of butane over various catalysts: 0.02–0.05 g, 2.7% Butane, O₂/butane = 0.5, He as balance, 10 ml min⁻¹, 450°C.

Reference

1. Zhang, J., Liu, X., Blume, R., Zhang, A. Schlögl, R. and Su, D.S. *Science* 322, 73 (2008).