Comprehensive Understanding of the Effects of Carbon Nanostructures on Redox Catalytic Properties and Stability in Oxidative Dehydrogenation[1]

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Abstract: The redox catalytic properties and stabilities of 16 different types of carbons were investigated using *n*-butane oxidative dehydrogenation. The results demonstrate that overall activity increased with increasing content of C=O active sites. However, the turnover frequency gradually decreases, while the alkene selectivity increases due to the decreased reducibility of C=O site. Since more C=O sites are present in thermochemically less stable edge sites, the carbons generally exhibit trade-off relationship between activity and stability. However, graphitic carbon with 'coin-stacking' carbon layers showed high activity and stability simultaneously due to its unique structure that provides high graphitic order and abundant edge sites.

Keywords: Carbon nanostructure, Oxidative dehydrogenation, Reducibility

1. Introduction

Oxidative dehydrogenation (ODH) using metal-free carbon materials as catalyst has been investigated extensively in order to understand the intrinsic redox functions of the carbon surface. Earlier studies demonstrated that quinone-type C=O groups are the catalytic active sites responsible for activating C–H bonds of hydrocarbons during ODH reactions through redox cycle involving quinone-hydroquinone interconversion. Although a large variety of carbons with different framework structures are available, a rather limited number of carbon types has been directly compared under the same ODH condition. In the present work, to understand the effects of carbon nanostructures on their intrinsic redox catalytic properties and thermochemical stabilities, various types of carbons were investigated in *n*-butane ODH.

2. Experimental

Catalyst preparation. As-received activated carbon and were treated with concentrated HCl solution to remove metal impurities. OLC was synthesized by heating a nanodiamond in a vacuum furnace. Some portions of CNT and OLC were further treated with HNO_3 to control the number of carbon defect sites and oxygen functional groups. Templated carbons with different framework structures (CMK-3, CMK-3G, and ZTC) were also prepared by following the previously reported procedure.[1]

Catalytic measurements. The *n*-butane ODH reactions were carried out at 450 °C with an O_2-rich reactant composition. The *n*-butane conversion and selectivity measured at a fixed 1 h time-on-stream were extrapolated to zero residence time (1/WHSV) in order to obtain the primary alkene formation rate and selectivity. To check the catalyst half-life ($t_{1/2}$), the reactions were carried out under a fixed WHSV (2.9 h^{-1}).

3. Results and discussion

The redox catalytic properties of the prepared carbon materials were investigated in *n*-butane ODH. To correlate catalytic results with the density of C=O active sites, we carried out quantitative analysis of the oxygen groups in the carbon catalysts with O 1s XPS. We analyzed the carbon catalysts after they had been used in ODH reactions for 1 h, and correlated the results with catalytic data obtained at the same time.

As shown in Figure 1a, *n*-butane conversion rate gradually increases with the amount of C=O groups in the carbons. It is notable, however, that the trend is not completely linear. The nonlinear correlation is attributed to the fact that the catalytic activity per C=O group (*i.e.*, TOF) gradually decreases with increasing C=O group functional group density (Figure 1b). On the other hand, the alkene selectivity monotonically increases with increasing C=O density of the carbon catalysts (Figure 1c).

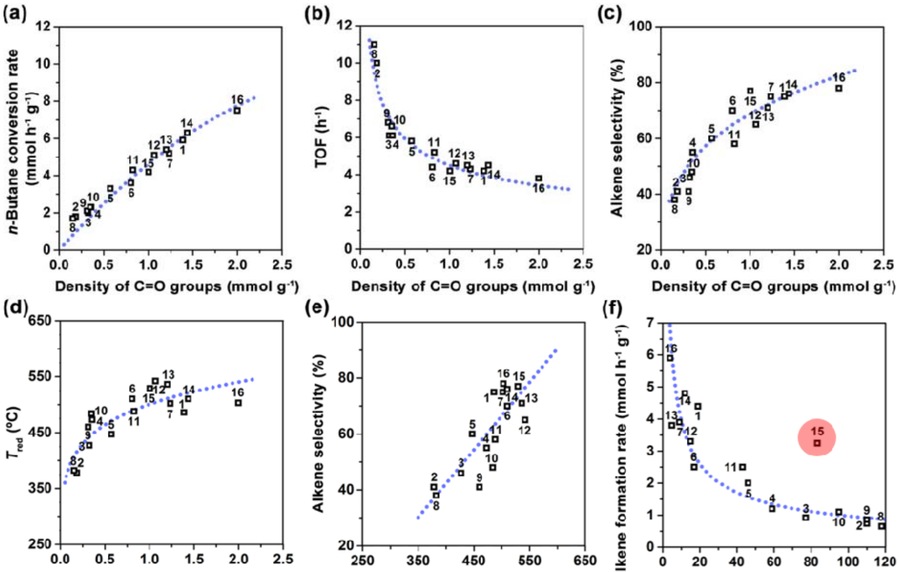
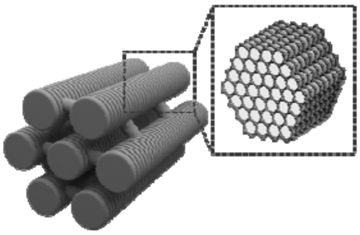


Figure 1. (a) *n*-Butane conversion rate, (b) turnover frequency (TOF) for *n*-butane conversion, (c) alkene selectivity, and (d) T_{red} as a function of the density of the C=O groups in the carbon catalysts. (e) Alkene selectivity as a function of T_{red}. (f) Alkene formation rate as a function of the density of the C=O groups in the carbon catalysts. The numbers inside each plot indicate an entry (1: AC, 2 – 7: CNT and HNO_3-treated CNTs, 8 – 13: OLC and HNO_3-treated OLCs, 14: CMK-3, 15: CMK-G, and 16: ZTC)

To understand the reason for change of catalytic behaviors as a function of the density of C=O groups, we investigated redox property of individual C=O active site by TPR experiments. The reduction temperature (T_{red}, defined as the onset temperature where the H_2 consumption rate reaches 10% of the maximum H_2 consumption rate) generally shifted to higher temperatures as the C=O content increased (Figure 1d). The results verify that individual C=O group reducibility decreases with increasing C=O density. When alkene selectivity is plotted as a function of the T_{red}, selectivity is observed to gradually increase with T_{red} (Figure 1e). Therefore, we conclude that the lower reducibility of each C=O group at higher C=O density results in a lower TOF but a higher alkene selectivity. Because the TOF for *n*-butane conversion and selectivity change in opposite directions with C=O content, the alkene formation rate show a linear correlation with C=O content.

The C=O groups should be located at edge sites of the carbon layers. Therefore, maximizing the number of carbon edge sites increases the number of C=O active sites and, hence, the alkene formation rate. However, such carbons are less resistant to combustion under oxidative conditions. This could be why most of the carbons exhibit a general trade-off relationship between alkene formation rate and catalyst half-life (Figure 1f). However, there is one notable exception that is not located near the trend line; CMK-3G exhibits a high alkene formation rate and stability simultaneously. This may be attributed to the unique framework structure of the CMK-3G which consists of carbon layers stacked perpendicular to the direction of the nanorod-like carbon framework (Scheme 1). Due to the 'coin-stacking' of the carbon layers, CMK-3G can possess a high graphitic order in the framework as well as a large number of edge sites where C=O active sites are located.



Scheme 1. Schematic illustration of ordered mesoporous carbon with a 'coin-stacking' graphitic framework (CMK-3G).

4. Conclusions

In this work, the redox properties and thermochemical stabilities of a variety of nanostructured carbons were investigated in *n*-butane ODH. Regardless of the type of carbon, the TOF decreases while the alkene selectivity increases with increasing C=O active sites. This is attributed to the lower reducibility of each C=O group at higher C=O density. Because more C=O active sites are present in thermochemically less stable amorphous carbon framework, the carbons generally exhibit a trade-off relationship between catalytic activity and stability. However, a graphitic mesoporous carbon with a 'coin-stacking' arrangement of carbon layers exhibited both exceptionally high catalytic activity and stability. The present study demonstrates that carbon materials can have a wide range of redox catalytic properties depending on their nanostructures.

Reference

1. H. C. Kwon, S. Yook, M. Choi, ACS Catal. 7 (2017) 5257.