Correlation Between Oxygen Reduction Reaction and Oxidative Dehydrogenation Activities Over Nanostructured Carbon Catalysts

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Introduction

Nanostructured carbons are promising materials for a number of catalytic applications. Variations in preparation parameters can cause significant changes in fiber nanostructure which, in turn, can cause changes in performance. The oxygen reduction reaction (ORR) and the oxidative dehydrogenation reaction (ODH) are two potential applications where nanofiber structure may influence reaction performance.

It is desirable to reduce the use of platinum in PEM fuel cell cathodes. Researchers have reported that active ORR catalysts can be prepared by pyrolysis of a variety of nitrogen, iron and carbon containing precursors [1-3]. The preparation of these active ORR catalysts is strikingly similar to the preparation of carbon fibers.

Unsaturated hydrocarbons are feedstocks for many industrially significant processes. The oxidative dehydrogenation (ODH) of lower alkanes has received much attention in recent years [4, 5] and offers many benefits compared to traditional production of unsaturated hydrocarbons by steam cracking and direct dehydrogenation. Research has shown that during certain ODH reactions, coke deposition actually improves performance [6, 7]. This observation has led researchers to investigate the activity of other carbonaceous materials such as carbon nanofibers [8, 9].

This research investigates the link between carbon nanostructure and performance in ORR and ODH reactions.

Materials and Methods

Nitrogen-containing carbon fibers were prepared by the pyrolysis of acetonitrile precursors over various supported metal oxide catalysts. Al_2O_3, MgO and SiO_2 were impregnated with Fe or Ni acetate. The metal and support were subsequently removed by acid and/or alkaline washing. ODH reaction performance was measured using a packed bed reactor system with Agilent 3000A microGC. ORR activity was measured using a Rotating Ring Disk Electrode (RRDE) half-cell setup. The fibers were characterized using Transmission Electron Microscopy (TEM), BET surface area analysis and X-Ray Photoelectron Spectroscopy (XPS).

Results and Discussion

A strong correlation between ORR and ODH activity is observed. The nitrogen-containing carbon fiber catalysts have significant ORR activity [10, 11] and possess substantial activity for certain ODH reactions. Fibers grown over iron impregnated supports performed best. Nickel impregnated samples led to the formation of multiwalled nanotubes with little edge plane exposure. Iron impregnated supports, on the other hand, tended to form herringbone structured fibers with substantial edge plane exposure. These edge planes are presumed to contain the active sites for both ORR and ODH reactions. Additionally, the most active samples contain the highest proportion of pyridinic nitrogen, as determined by XPS. This may also be an indicator of higher edge plane exposure as pyridinic nitrogen is contained in the edge plane of a graphitic sheet.

Significance

Carbon nanofibers are potential catalysts for ORR and ODH reactions. This research elucidates the relationship between nanostructure and performance providing insight that will allow better catalysts to be synthesized in the future.

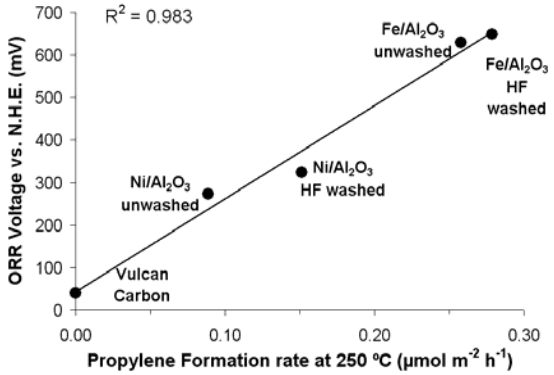

Figure 1. Correlation between ODH reaction performance and ORR activity for a number of carbon nanofibers grown on different supports.

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