

Carbon Nanofibers As Catalyst Support For Efficient Mass Transfer In Liquid Phase Catalytic Reactions

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Introduction

Catalytic multiphase reactors are commonly used in many fine chemical and petrochemical processes. Typical problems encountered in these reactors are mass transfer limitations and pressure drop. One of the ways to overcome these problems is to use structured materials, *i.e.*, to deposit catalyst on a rigid, ordered, porous support body *e.g.*, metal or ceramic foams. Enhancement of surface area is necessary in order to provide sufficient surface area to support active sites. At the same time, the porous structure introduced for that reason should be as porous as possible with low tortuosity to minimize mass transfer limitations. This is especially relevant for liquid phase reactions because of generally sluggish diffusion of reactants and products [1]. Surface area can be increased by preparing a thin layer of Carbon-Nano-Fibers (CNFs) on structured foam support, regarded as 'Hairy foam'. CNF layer can provide a macroporous range of pores with low tortuosity due to its network like structure. The goal of this work is to prepare a stable CNF layer on Ni surface to deposit palladium nano-particles. CNF-foam supported palladium catalyst was studied in liquid phase for the reduction of nitrite as a model reaction.

Materials and Methods

CNFs were grown on Ni foam *via* decomposing ethylene at 440°C. Properties of the CNFs were characterized by electron microscopy, temperature programmed techniques and Raman spectroscopy. Mechanical stability of the CNFs was studied by flowing compressed air (100 L/min) and water (1m/s) through the foam. Palladium was deposited on CNF/Ni foam from palladium acetylacetonate precursor in toluene by rotary evaporator method. Pd distribution over the CNF layer was characterized by CO-Chemisorption and electron microscopy. A fixed bed reactor was used to study the Hairy foam catalyst (Pd-CNF/Ni foam). Hydrogen saturated nitrite solution was used as single phase reactant liquid.

Results and Discussion

Homogenous coverage of CNFs was achieved on Ni foam (figure 1). Microscopic studies at cross-sections of the deposited layer on Ni foam showed the presence of two carbon layers; an apparent dense layer ('C-layer') at the carbon-Ni interface and a CNF layer on top (figure 2). Variation of the growth time showed that both layers develop in parallel. Characterization of carbon deposits on Ni surface by

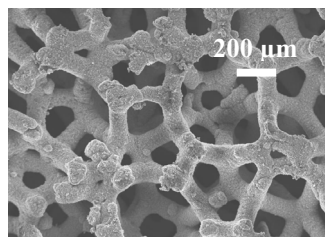


Figure 1 Ni foam covered with CNFs grown at 440°C in 25% C₂H₄/N₂

Temperature programmed gasification in H₂, Raman spectroscopy and Transmission electron microscopy confirmed that both layers are graphitic in nature. Addition of hydrogen to the feed varies the properties of C-layer and CNF layer on the foam. Presence of hydrogen limits the deactivation of the Ni particle which is caused by encapsulation. The C-layer thickness reduces with increasing hydrogen concentration, while a maximum CNF layer thickness is achieved at lower hydrogen concentrations. A decrease in the C-layer thickness caused an increase in the weight loss of carbon from the foam during the stability test.

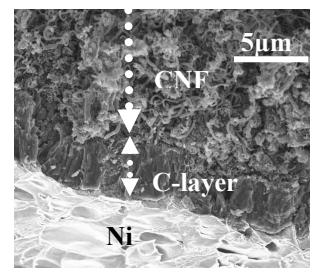


Figure 2 C-layer and CNF layer in CNF/Ni foam sample. The arrows indicate the thickness of the layers.

Scanning electron microscopy at the interface of the metallic nickel surface and the C-layer revealed that both interfaces are very rough and very similar, indicating a strong interaction. Electron microscopy at the interface between the C-layer and CNF layer shows that CNFs are strongly attached via roots that penetrate into the C-layer. Based on a study of the effect of growth time, a model was proposed explaining the growth of these features. The interconnections of Ni surface, C-layer and CNFs induce integrity facilitating stability against shear forces [2].

Hairy foam catalysts were tested in fixed bed reactor for mass transfer limitations and compared with conventional porous catalysts such as alumina, silica, graphite and activated carbon. Nitrite conversion at fixed space time remains constant at liquid linear velocity larger than 0.55 m/min showing external mass transfer limitations. Intrinsic rates were independent of CNF layer thickness (8-30μm) and Pd loading (0.5-2 wt %), demonstrating the absence of any mass transfer limitations. When compared to conventional catalyst, hairy foam catalysts showed five times higher rates of nitrite conversion per mole of surface palladium. The macroporous structure of the CNF layer, which offers low tortuosity, provides accessibility to all the active sites eliminating mass transfer limitations.

A stable CNF layer was prepared on Ni foam. Hairy foam catalysts showed superior performance over conventional catalysts. Effect of support on the selectivities of nitrogen and ammonia during the nitrite reduction is under study.

Significance

This work demonstrates the excellent properties of Hairy foam catalysts for application in fast liquid phase reactions. The improved accessibility of the catalytic site and mass transfer properties enable cleaner, intensified and more selective processes.

References

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2. Chinthaginjala, J.K., Thakur, D.B., Seshan, K., Lefferts, L., *Carbon*, 46, 1638 (2008).