



Transesterification of dimethyl oxalate with phenol over nitrogen-doped nanoporous carbon materials

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ABSTRACT

A series of nitrogen-doped nanoporous carbon (NNC) materials were prepared by directly carbonizing sol–gel composites containing aluminum phosphate, citric acid and hexamethylene tetramine (HMT). The structure and surface properties of these NNC materials were characterized by means of elemental analysis, N₂ adsorption, X-ray powder diffraction (XRD), scanning electron microscope (SEM), high-resolution transmission electron microscopy (TEM), Fourier transform infrared spectra (FT-IR), and X-ray photoelectron spectra (XPS). Besides possessing various oxygen-containing groups, these NNC materials also contain different types of nitrogen-containing groups, including pyridinic-N, pyrrolic-N and quaternary-N groups. The resulting NNC materials are highly active and selective heterogeneous catalysts for the transesterification of dimethyl oxalate (DMO) with phenol to produce methyl phenyl oxalate (MPO) and diphenyl oxalate (DPO), and can be easily recycled by simple filtration. The presence of suitable surface basic sites should be mainly responsible for the excellent catalytic performance of NNC materials in the transesterification reaction.

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1. Introduction

Diphenyl carbonate (DPC) is an important chemical intermediate for the synthesis of many organic compounds and polymer materials [1]. Transesterification of dimethyl oxalate (DMO) with phenol to produce MPO and DPO, following a decarbonylation reaction, is an attractive route for the green synthesis of DPC [2]. So far, a variety of metal oxides bearing weak acidity have been investigated as heterogeneous catalysts for the transesterification of DMO with phenol, including TiO₂/SiO₂, MoO₃/SiO₂, SnO₂–MoO₃/SiO₂, CuNi-containing hydrotalcites and Sn-modified zeolites [3–9]. Our recent work suggested that some organic bases grafted solid materials, such as pentamethylcyclopentadienyl (Cp) functionalized MCM-41 material (Cp-MCM-41) and amino-modified MCM-41 materials (amino-MCM-41), can also act as active catalysts for the transesterification of phenol with DMO [10,11]. However, the catalytic performance of these metal-free hybrid catalysts is still not very satisfied concerning the thermal stability and/or recyclability. For example, a post-treatment with diluted basic agents is required in order to fully recover the catalytic activity of the used amino-MCM-41 catalysts. Besides, relatively high side-product selectivity (i.e.,

to anisole) was usually observed when a high DMO conversion was achieved over these catalysts, which make it less attractive for practical application. Therefore, interest is still remaining to develop more active and selective heterogeneous catalysts with excellent stability and recyclability for the transesterification of DMO with phenol to produce MPO and DPO.

Recently, carbon materials with different morphologies that contain heteroatoms such as B, Si and N have received considerable attention for their improved properties such as extreme hardness, oxidation resistance, and potential applications in fuel cells, energy storage and catalysis [12–19]. In particular, the incorporation of nitrogen into the carbon matrix can offer basic sites in the form of various N-containing groups such as amine, imine and pyridinic-N, thus might be utilized as efficient solid base catalysts for various catalytic reactions, such as including transesterification of β -keto esters (e.g., aryl, aliphatic, and cyclic primary alcohols), Friedel–Crafts reactions, Knoevenagel condensation and the reaction of benzene and CO₂ [20–23].

Previously, our group reported a simple and efficient sol–gel route to prepare a kind of nanoporous carbon (NC) materials using in situ-formed aluminum phosphate as template, and citric acid and sucrose as carbon sources. The resultant NC materials possess abundant surface oxygen-containing functional groups, and can be directly used as active catalyst for the aerobic oxidation of benzyl alcohol, or used as catalyst support for the preparation of

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