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Synthesis of nitrogen-doped ordered mesoporous carbons for catalytic dehydrochlorination of 1,2-dichloroethane

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ABSTRACT

Nitrogen-doped ordered mesoporous carbons (N-OMCs) were prepared via a two-step approach, using resorcinol (R) and formaldehyde (F) as the carbon precursor and dicyandiamide (DCD) as the nitrogen precursor. In this approach, dicyandiamide, formaldehyde and resorcinol were pre-polymerized in the first step using a basic catalyst to produce DCD-RF resol. The DCD-RF resol was mixed with a solution of triblock copolymer Pluronic F127 followed by the addition of an acid catalyst to facilitate the self-assembly and condensation in the second step. After calcination, N-OMCs were obtained and further characterized by nitrogen sorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The well-prepared N-OMCs were evaluated for the catalytic dehydrochlorination of 1,2-dichloroethane and exhibited superior catalytic performances and excellent stability over 72 h.

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1. Introduction

Ordered mesoporous carbons (OMCs) have attracted great interest due to their high surface area, large pore volume, uniform pores, and tunable pore sizes [1,2]. Their performances are influenced not only by their structural parameters but also by their chemical compositions and surface functionalities [3,4]. Particularly, the incorporation of nitrogen species into the framework of OMCs could change the properties of carbon, and improve their performance in certain catalytic, capacitive, and adsorptive applications [5].

Nitrogen-doped ordered mesoporous carbons (N-OMCs) have been prepared by different approaches with many efforts. The conventional methods to synthesize N-OMCs involve a nanocasting strategy, which employed nitrogen-containing molecules, such as acetonitrile [6], ethylenediamine [7], polyacrylonitrile [8], aniline [9], polypyrrole [10] and diaminobenzene [11] as the carbon and nitrogen precursors, and ordered mesoporous oxides as the hard templates. Hard material templating is typically time-consuming and expensive to carry out at large scale. Therefore, a soft-template method based on supramolecular assemblies of surfactants and carbon precursors is highly desired as an alternative option. However, the synthesis of N-OMCs by the self-assembly approach is difficult to achieve for two main reasons. Firstly, the nitrogen precursor must be capable to co-polymerize with the chosen polymeric carbon precursor for the formation of ordered mesostructures. Secondly, the involved nitrogen species must be highly thermal stable to retain in carbon framework during pyrolysis. Recently, several

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groups reported the synthesis of N-OMCs via soft-template process by using phenolic resins as carbon sources and m-aminophenol [12], 1,6-diaminohexane [13], urea [14], melamine [15,16], or dicyandiamide [17] as nitrogen sources. Besides, nitrogen can be also introduced into OMCs by treated with nitrogen-containing molecules, which decompose into reactive radicals at high temperature [18,19].

Previously, we demonstrated a reproducible synthesis of ordered mesoporous resorcinol–formaldehyde (RF) polymers and carbons by a two-step method [20]. In this method, resorcinol and formaldehyde is pre-polymerized in the first step using a basic catalyst to produce RF resol. Then, the RF resol is mixed with a triblock copolymer Pluronic F127 solution followed by the addition of an acid catalyst to allow the rapid self-assembly and condensation in the second step. In the present work, we added dicyandiamide (DCD) to the synthetic solution in the first step and fabricated a series of N-OMCs. The structure and nitrogen content of N-OMCs can be controlled by adjusting the dicyandiamide content. Furthermore, the obtained N-OMCs showed excellent activities in the catalytic dehydrochlorination of 1,2-dichloroethane reaction. The conversion of 1,2-dichloroethane increased along with the nitrogen content and the selectivity of vinyl chloride were all above 99.5%.

2. Experimental

2.1. Chemicals

All chemicals were used as received without further purification. Pluronic F127 (M_{av} = 12,600, $EO_{106}PO_{70}EO_{106}$) was purchased from Sigma–Aldrich. Formaldehyde (37 wt.%), Ethanol and Na_2CO_3 were purchased from Tianjin Kermel Chemical Reagent Corp. Ltd. HCl (37 wt.%) was purchased from Tianjin Windship Chemistry Technological Corp. Resorcinol and dicyandiamide were obtained from Sinopharm Chemical Reagent Corp.

2.2. Synthesis of mesoporous nitrogen-doped polymers and carbons

In a typical synthesis, 0.0056 g of Na_2CO_3 and 0.168 g of dicyandiamide was dissolved in 1.13 g of formaldehyde solution (37 wt.%) in a water bath at about 18 °C, then 1.10 g of resorcinol was added to the solution to produce a DCD-RF resol. After stirring for 4 h, the DCD-RF resol solution was mixed with a solution composed of 0.80 g of F127, 4.00 g of H_2O and 5.00 g of ethanol, and then 1.00 mL of 2 M HCl was quickly added to this solution. After vigorously stirring for about 0.5 min, the transparent solution turned turbid, indicating a phase separation and the formation of DCD-RF-F127 nano-composite. The mixture was stirred for 1 h and then left standing for 10 h to obtain the polymer rich gel phase. Finally, the polymer rich gel was calcined under N_2 atmosphere at 350 and 800 °C for 3 h, respectively, to get the ordered mesoporous polymer 0.2DCD-RF-350 and the ordered mesoporous carbon 0.2DCD-RF-800. The other samples were prepared by varying the molar ratios of the reactants (dicyandiamide and formaldehyde, see Table 1), while maintaining the molar ratio of resorcinol to F127, and the mass ratio of water to ethanol.

2.3. Characterization

The X-ray diffraction (XRD) measurement was taken on a PANalytical X'Pert PRO powder X-ray diffractometer using Cu Kα radiation. Transmission electron microscopy (TEM) was conducted on a Tecnai G2 Spirit electronic microscope. The acceleration voltage was 100 kV. The samples for TEM observations were ultrasonically dispersed in ethanol and dropped onto a holey carbon film on a Cu grid. Nitrogen sorption analysis was performed on a Micromeritics ASAP 2010 apparatus at −196 °C. Prior to the measurements, the samples were degassed at 200 °C for about 6 h. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface areas, S_{BET}. The pore size distributions (PSD) were calculated from the adsorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) method. The pore size, D_p, was determined by the maxima in the pore size distribution curves. The total pore volume, V_p, was determined from the adsorbed amount at a relative pressure (P/P_0) of 0.998. The micropore volume, V_{micro}, was estimated according to the t-plot method. X-ray photoelectron spectroscopy (XPS) was performed on ESCALAB250 (Thermo VG Corporation) equipped with an Al Kα radiation source (1486.6 eV, 15 kV, 10 mA, 150 W). All binding energies (B.E.) were calibrated with graphitic carbon C1s peak at 284.5 eV as a reference.

2.4. Catalyst evaluation

Dehydrochlorination of 1,2-dichloroethane was performed in a tubular quartz micro reactor (4.8 mm) under atmospheric pressure. Under each catalysis condition, 0.10 g of catalyst was supported on a fritted disk. The 1,2-dichloroethane was metered into the reaction system by flowing a sweep gas of He (20 mL/min) through a saturator filled with the liquid 1,2-dichloroethane. A constant 1,2-dichloroethane concentration was ensured by maintaining the saturator at a fixed temperature of 0 °C using an ice-water bath. The reaction was run at 300 °C for 72 h and sampled every 2 h. The catalytic activities were measured with time on stream at a fixed temperature. The outlet gases were analyzed on line with an Agilent Technologies 6890N gas chromatograph equipped with a FID detector using a 30 m Poraplot Q capillary column.

3. Results and discussion

3.1. Synthesis and characterization of nitrogen-doped mesoporous polymers

In the present work, dicyandiamide was introduced to the synthetic solution in the first step of the two-step method [20]. Just like resorcinol, in the presence of a base catalyst, dicyandiamide also reacted with formaldehyde rapidly at low temperatures to produce the hydroxymethyl compounds. Resorcinol and hydroxymethylated resorcinol could be connected with hydroxymethylated dicyandiamide either by methylene or ether bridges to give a dicyandiamide modified

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