Synthesis and characterization of Ni nanoparticles supported on nitrogen-doped mesoporous carbon

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Abstract. Nitrogen-doped mesoporous carbon (N-MC) was synthesized by the soft-templating method using phloroglucinol/formaldehyde and melamine as carbon and nitrogen precursors, respectively, and Pluronic F127 as a template for the generation of mesopores inside the carbon structure. Scanning electron microscopy analysis revealed that the material had a rough surface, while Raman analysis indicated the existence of sp-hybridized carbon rather than sp, similar to graphite. The increase of the D-band to G-band intensity ratio indicated that N-MC has a more graphite-like structure than pristine mesoporous carbon. X-ray photoelectron spectroscopy analysis confirmed that nitrogen was successfully doped into the carbon framework. The material was then used as a support for Ni nanoparticles (Ni-NPs). The presence of Ni metal in Ni-NP@N-MC was confirmed by X-ray diffraction analysis.

Keywords: mesoporous carbon, Ni nanoparticles, N-doped carbon, soft-templating method

1. Introduction

Industrial activity has steadily increased since the advent of the industrial revolution, leading to ever increasing emission of CO₂ into the atmosphere. Accordingly, the pre-industrial revolution atmospheric CO₂ concentration of 280 ppm has increased to its current level of 380 ppm [1]. This has become a serious environmental problem because of the contribution CO₂ makes to the greenhouse effect, leading to global climate change. Consequently, to reduce this negative effect, it is absolutely vital that we decrease the amount of anthropogenic CO₂ released into the atmosphere.

The current technology used for large-scale CO₂ absorption is based on liquid amine absorption [2, 3]. Amine groups can remove CO₂ from the air owing to their ability to reversibly form carbamate and bicarbonate compounds. However, this method suffers from disadvantages related to high energy consumption, corrosion, and solvent evaporation [4, 5]. A potential strategy for overcoming these problems is the immobilization of the working amine compounds onto the surface of support materials instead of using them in the liquid state [6].

Since its initial development, mesoporous carbon has been used in a wide range of applications, including adsorbents [7], sensors [8], molecule carriers [9], and catalyst supports [10]. However, the use of mesoporous carbon in CO₂ adsorption is still limited as CO₂ is only weakly physisorbed on mesoporous carbon. Recently, our group successfully prepared mesoporous carbon modified with amine compounds [11, 12]. The amine compounds were immobilized in the pores of the mesoporous carbon, enhancing its capacity to adsorb CO₂. However, the effect of nitrogen compounds with both sp and sp² hybridization on the CO₂ sorption properties of mesoporous carbon remains largely unresearched. Accordingly, in this work, a mesoporous carbon framework was doped with nitrogen using melamine as a nitrogen source.
The morphological studies of MC, N-MC, and Ni@N-MC were observed by scanning electron microscopy (SEM), as shown in figure 1. All the materials present rough surfaces. A grass-like structure is observed for the surface of MC, as has been previously reported [14]. This characteristic surface mor-
Figure 2. XRD pattern of MC, N-MC, and Ni@N-MC.

Figure 3. XPS spectra of MC, N-MC, and Ni@N-MC.

Figure 4. Raman spectra of MC, N-MC, and Ni@N-MC.

Figure 5. CO₂ adsorption of MC, N-MC, and Ni@N-MC.

Phosphorylation endows the MC with a high surface area. Both N-MC and Ni@N-MC exist as small particles. There is no observable difference in morphology upon impregnation with Ni nanoparticles.

Figure 2 shows the X-ray diffraction (XRD) patterns for MC, N-MC, and Ni@N-MC. It is clear that all the samples present very similar diffraction patterns. The peaks for 2θ = 25° and 44° are attributed to the (002) and (101) planes, respectively, which are characteristic of graphitic carbon [15]. The similarity of the diffraction patterns indicates that there is no significant change in the structure of the material upon nitrogen doping. For Ni@N-MC, there are additional peaks at 2θ = 45° and 52° owing to the presence of Ni metal [16]. This confirms the success of the Ni nanoparticle impregnation into the mesoporous carbon. The X-ray photoelectron spectroscopy (XPS) spectra (figure 3) further confirm the presence of Ni in addition to C, N, and O in Ni@N-MC.

The Raman spectra (figure 4) reveal Raman shifts at 1339 and 1584 cm⁻¹, which are the characteristic D-band and G-band, respectively, of graphitic materials. The spectral peaks for all the materials occur at the same frequency, indicating that the Raman spectra are not affected by nitrogen doping. However, the D-band to G-band intensity ratio (I_D/I_G) changes from 1.01 for MC to 0.98 for N-MC and Ni@N-MC. This indicates that nitrogen doping increases the abundance of sp² carbon relative to that of sp³ carbon.

The results for the CO₂ adsorption capacities of the materials are shown in figure 5. Although modification with amine compounds has been shown to increase the CO₂ uptake of mesoporous carbon
in previous works [11,12], modification with melamine as the nitrogen source decreases the CO uptake of the N-doped mesoporous carbon. This is most likely due to structural shrinkage of the framework upon nitrogen doping and also the low primary and secondary amine contents, since the nitrogen forms bonding interactions with the carbon framework. Furthermore, the Ni nanoparticles in Ni@N-MC appear to have no significant effect on CO adsorption. Ongoing work is underway in our group to determine the mesoporosity and basicity of these materials, which are important for further application as heterogeneous catalysts for CO fixation reactions.

4. Conclusions
Nitrogen-doped mesoporous carbon was successfully synthesized using a soft-templating method with melamine as nitrogen source. The CO adsorption capacity of N-MC is lower than that of MC. This may be due to structural shrinkage upon nitrogen doping and also the low primary and secondary amine contents. Nevertheless, this material has the potential to be employed as an alternative sorbent for CO capture.

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