

Preparation and Characterization of Ni/Al₂O₃ Catalyst for Carbon Nanofibers by Conversion of Carbon Dioxide

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Abstract

In this study, Ni/Al₂O₃ was prepared with an impregnation method for CO₂ hydrogenation into carbon nanofibers (CNFs). High purity CNFs were acquired from CO₂ hydrogenation at 500 °C and 1 atm over Ni/Al₂O₃ catalyst after a liquid phase extraction process, removing the used catalysts and by-products. The particle properties of as-prepared Ni/Al₂O₃ have been well characterized for comparison with the commercial ones. The results of XPS spectra and XRPD patterns indicated that the commercial, as-prepared, and used Ni/Al₂O₃ were multicomponent with various crystal phases. The as-prepared Ni/Al₂O₃ can be sufficiently exposed in CO₂ atmosphere for higher catalytic performances owing to its unique microstructure with higher specific surface area (429.2m²/g). Both EXAFS and XANES spectra have shown that the first shell of Ni atom in commercial, as-prepared, and used Ni/Al₂O₃ were Ni-O with bond distances of 1.61, 1.63, and 1.62 Å, respectively. The configuration of fabricated CNFs was characterized by its unique ID/IG (Intensities of D-band/G-band) ratio of 0.23 in the Raman spectrum. Solid tubular shape with 30 nm diameter of CNFs was observed using FE-SEM and HR-TEM. Thermodynamic analyses indicate that CO₂ hydrogenation into CNFs is a spontaneous and exothermic reaction with an optimal temperature of 500 °C.

Keywords - CO₂ hydrogenation, Carbon nanofiber, Ni/Al₂O₃ catalyst, EXAFS/XANES.

Introduction

The environmental and ecological problems caused by a large amount of greenhouse gas CO₂ emissions are becoming increasingly prominent. CO₂ conversion is regarded as an ideal strategy to use CO₂ and to produce chemicals and fuels, such as methane (CH₄), methanol (CH₃OH), formic acid (HCOOH), dimethyl carbonate (CH₃O)₂CO, dimethyl ether (CH₃OCH₃), and syngas (CO+H₂) with the aid of catalytic reactions [1]. In recently work prepared nickel (Ni)-based catalysts with additive potassium (K) and sodium (Na) as promoters to induce the carbon nanofiber (CNF) deposition on the catalyst surfaces [2]. Moreover, graphene, carbon nanotube, and CNF can also be fabricated from CO₂ reductions. A deposition-rate-controlled electrolytic synthesis route was carried out in the molten electrolyte liquid to produce carbon nanoparticle, ultrathin carbon sheets, and hollow carbon spheres for lithium storage usage. The wide application of Ni/Al₂O₃ catalytic materials demonstrates their efficiency, reliability, and high stability. Similarly, owing to its cost effectiveness, easy availability, and high activity, Ni-based catalysts have emerged as promising catalysts. Ni/Al₂O₃ catalysts are found to be efficient promoters for CO₂ hydrogenation and methanation, and aluminum oxide (Al₂O₃) is active for CO₂ adsorption [3].

In present work, Ni/Al₂O₃ catalysts were synthesized using an impregnation method for CNF fabrication from CO₂ hydrogenation. The physiochemical property differences between commercial, as-prepared, and used Ni/Al₂O₃ catalysts were characterized and identified with various instruments thoroughly. The CNFs were

fabricated using a self-assembled fixed-bed reactor with a 70 mL min⁻¹ of CO₂/H₂ (1/1, vol/vol) inlet flow at 500 °C and 1 atm for 6 h. Microstructures of as-prepared/used Ni/Al₂O₃ and fabricated CNFs were investigated based on the analyzed results. Thermodynamic analyses were adopted to estimate the tendency of CO₂ hydrogenation into CNFs for further yield enhancement.

Experimental

Ni/Al₂O₃ catalyst was prepared by impregnation method in present work. The catalyst support, γ-Al₂O₃ particles (0.97 g) were poured into a 100 mL aqueous nickel nitrate hexahydrate solution (Ni(NO₃)₂·6H₂O) with 12 wt% Ni for a 2-h mixing. These particles were filtered by a centrifuge at 600 rpm for 30 min, and then dried at 110 °C overnight. Ultimately, Ni/Al₂O₃ catalysts were obtained after calcined in a flowing air and reduced in a flowing hydrogen (H₂) stream at 25 mL min⁻¹ and 500 °C for 5 h. To further investigate the structure of the active nickel species in NiO/Al₂O₃ catalysts, X-ray absorption (XAS) spectra of the catalyst were also measured. The Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectra of commercial, as-prepared, and used Ni/Al₂O₃ catalysts were collected at Wiggler beamline 17C1 of Taiwan National Synchrotron Radiation Research Center (NSRRC).

Results

The XANES spectra of the NiO/Al₂O₃ catalysts for CO₂ reduction is shown in (Fig. 1(a)). Even through the

microstructures of commercial, as-prepared, and used Ni/Al₂O₃ catalysts have been characterized, the valence and fine structure of the core nickel in particles still required to be analyzed. The absorption peak positions of commercial, as-prepared, and used Ni/Al₂O₃ catalysts approach to that of Ni(II) at 8350 eV. The XANES spectrum of NiO/Al₂O₃ catalysts displays weak absorbance feature for the 1s to 3d transition which is restricted by the selection rule in the case of perfect octahedral symmetry. Moreover, the features of their spectra are similar with that of Ni(II). It represents that commercial, as-prepared, and used Ni/Al₂O₃ particles have a solid Ni(II)/Al₂O₄ cores. The XANES spectra work particularly well in distinguishing of Ni(I) and Ni(II) coexisted in the NiO/Al₂O₃ catalysts. Generally, the EXAFS spectroscopy can provide the information on the atomic arrangement of catalysts in terms of bond distance, number, and kind of near neighbors, thermal and static disorder. Over 99 % reliability of the EXAFS data fitting for Ni species in Ni/Al₂O₃ catalysts was obtained (Fig. 1(b)). The fine structures of commercial, as-prepared, and used Ni/Al₂O₃ were analyzed with EXAFS Fourier transformed (FT) spectra and then model-fitted with the crystal parameters of a Ni(II) species, as displayed. Both of their EXAFS FT spectra were well-fitted with that of Ni(II) model. Generally, the neighbor atom (oxygen) with lighter atomic weigh is prior to bind with the central metallic atom (nickel) compared with other metallic atoms. Thus, two peaks with shorter and longer bond distances were marked as Ni-O and Ni-Ni bonds, respectively. The model-fitted results were illustrated in Table. It shows that the first shells of commercial, as prepared, and used Ni/Al₂O₃ catalysts are coordinated by Ni-O with the coordination numbers of 5.89, 5.18, and 5.21 at bond distances of 1.61, 1.63, and 1.62 Å, respectively. On the basis of previous characterized results, it exhibits that the as-prepared Ni/Al₂O₃ has the porous Ni/Al₂O₄ shells, the surficial metallic nickel sub-particles, and a Ni/Al₂O₃ core.

Discussion

The commercial Ni/Al₂O₄ is a solid Ni/Al₂O₄ spinel particles attached on γ -Al₂O₃. The coordination number and bond distance of as-prepared Ni/Al₂O₃ are respectively less and more than that of commercial and used ones. This is because the as-prepared Ni/Al₂O₃ has more steric defects and vacant intermolecular spaces. For the coordination number of the used catalyst to be slightly more than that of as-prepared might be due to oxidation that occurred during the reaction process. Moreover, in all EXAFS data analyses, the Debye-Waller factors ($\Delta\sigma^2$) are less than 0.07 ($\Delta\sigma < 0.1$ Å in general).

Fine structural parameters of Ni species in commercial, as-prepared, and used Ni/Al₂O₃ catalysts using EXAFS spectra.

Sample	First shell	CN ^a (± 0.05)	R ^b (± 0.01 Å)	$\Delta\sigma^2(\text{Å}^2)^c$
Commercial	Ni-O	5.89	1.61	0.00310
As-prepared	Ni-O	5.18	1.63	0.00778
Used catalyst	Ni-O	5.21	1.62	0.00231

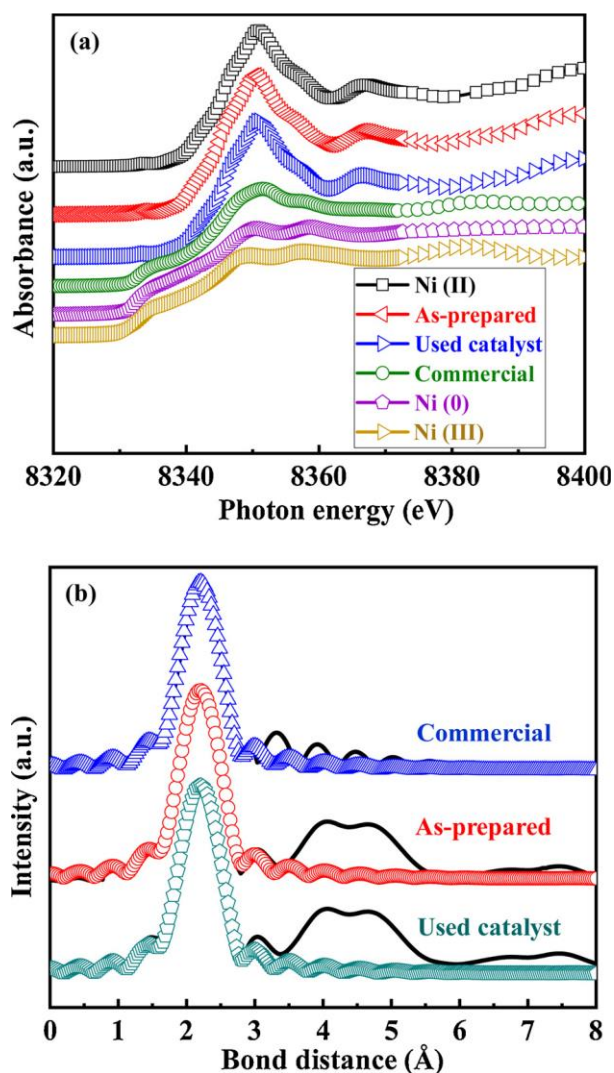


Fig. 1. Ni K-edge (a) XANES and (b) EXAFS Fourier transformed (FT) spectra of commercial, as-prepared, used Ni/Al₂O₃ catalysts and nickel standards.

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