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FACILE SYNTHESIS OF Ni- AND NiCo-MODIFIED MESOPOROUS CARBON AND ITS CATALYTIC ACTIVITY FOR PHENYLACETYLENE REDUCTION TO STYRENE UNDER AN ATMOSPHERIC HYDROGEN

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ABSTRACT

Mesoporous carbon (MC) has been successfully synthesized via the soft template method and further impregnated with monometallic Ni and bimetallic Ni-Co to give Ni-modified MC (Ni/MC) and NiCo/MC, respectively. The modified MC materials were characterized using XRD, SEM-EDX, SAA, and TEM. The results of the TEM analysis showed that the metal was homogeneously distributed on MC with the average particle sizes of Ni and bimetallic NiCo being 23.1 and 10.4 nm, respectively. The results of BET analysis show that the materials have a high surface area of 304, 289, and 313 m^2/g for MC, Ni/MC, and NiCo/MC, respectively. Both Ni/MC and bimetallic NiCo/MC were then used as catalysts in phenylacetylene hydrogenation under atmospheric hydrogen pressure.

Keywords: Mesoporous Carbon, Hydrogenation Reaction, Nickel, Bimetallic NiCo, Phenylacetylene.

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INTRODUCTION

Polystyrene, a polymer composed of styrene monomer, is widely used as the main raw material in food container production. However, phenylacetylene always exists in the styrene-containing feedstock, and even a small amount of phenylacetylene will poison the catalyst used in the polymerization process.[1] considering the similar chemical structures of phenylacetylene and styrene, it is very difficult to separate them from one another. The most effective way to eliminate phenylacetylene from styrene is through the hydrogenation reaction.[2] Therefore, developing highly selective and inexpensive catalysts for phenylacetylene hydrogenation to styrene remains a challenge. Among the transition metal alternatives, the most attractive are those that are abundant, non-toxic, and inexpensive such as Mn,[3] Fe[4], and Ni.[5] Nickel is a transition metal that was reported for its capability to enhance hydrogen adsorption in porous media.[6] Supported nickel catalysts were mostly studied for alkynes hydrogenation. Nickel is also known for its high alloying efficiency with all noble metals as well as many transition metals, which makes it easier to develop a wide range of composition-dependent bimetallic Ni systems for diversified catalytic applications. Bimetallic catalysts, which often have electronic and chemical properties that are distinct from those of their parent metals, may show enhanced performances. Bimetallic catalysts have attracted considerable interest in heterogeneous catalysis from both a fundamental and an applied point of view because their catalytic properties are superior to those of monometallic catalysts for many reactions. There have been many reports on the facile synthesis of bimetallic Ni systems, which have shown the potential to replace expensive noble metal catalysts in terms of catalytic activity and stability.[7] Recently, cobalt and nickel metals in graphite-like carbon layers have been developed as heterogeneous catalysts for the efficient hydrogenation of various unsaturated compounds at high hydrogen pressure.[8] From previous studies it was reported that cobalt as second metal can effectively improve the selectivity and conversion for hydrogenation reactions. In addition, Li *et al.* reported having successfully synthesized a NiCo/silica-titania catalyst for phenol hydrogenation reactions with an optimal conversion of 98.2% and selectivity >99% and

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showed good performance in reducing unstable oxygenated compounds in bio-oil.[9] Most recently, Ridwan *et al* reported the catalytic activity of bimetallic NiCo (1:3) supported various support for dehydrogenation of hydrazine hydrate. They observed that $NiCo_3/TiO_2$ gave the best catalytic activity with hydrazine hydrate conversion of 29.7% achieved for a 5-minute reaction.[10] In another hand, mesoporous carbon has been regarded as promising catalyst support due to its unique benefits such as high specific surface area and large pore volume in combination with good chemical and mechanical stability.[11] Previously, Artanti *et al*. reported the use of mesoporous carbon prepared via a hard-template method as NiMo catalyst support for hydrocracking of lubricant waste.[12] Hwang *et al* reported the effective use of mesoporous carbon as Fe catalyst support in CO_2 hydrogenation to liquid hydrogenation.[13] We also previously utilized mesoporous carbon as some metal catalyst support such as Ni and Cu for CO_2 capture and utilization in the carboxylation of unsaturated hydrocarbon.[14-16] Considering the above-mentioned previous works on the importance of mesoporous carbon as well as a nickel-based catalyst, herein we report our work on the facile synthesis of monometallic Ni/MC and bimetallic NiCo/MC via the wet impregnation method. The catalysts were evaluated their properties using some characterizations such as XRD, SEM-EDX, TEM imaging and BET surface area analysis, and were then applied as a catalyst in the hydrogenation of phenylacetylene under an atmospheric pressure of hydrogen gas.

EXPERIMENTAL

Materials

Phloroglucinol (≥ 98.0%), formaldehyde (37%), pluronic F-127, phenylacetylene (≥98%), styrene (≥99%), and methanol were obtained from Sigma Aldrich. Ethanol, methanol, nickel nitrate hexahydrate, and cobalt nitrate tetrahydrate were provided by Merck. HCl (37%) was purchased from Smart-Lab. All ultra-high purity gases, i.e., H_2 and N_2, were obtained from CV Retno Gas.

General Procedure for the Synthesis of MC, Ni/MC, and NiCo/MC

The synthesis of mesoporous carbon was carried out using a previously reported procedure.[17] Phloroglucinol and formaldehyde were used as a carbon source while pluronic F127 was employed as the template. The resulting monolith was placed in an autoclave and cured in an oven at 100 °C for 24 h, then was further carbonized in a tubular furnace under nitrogen gas flow at 850 °C for 2 h. Synthesis of Ni-modified mesoporous carbon was performed using the wet impregnation method. In a typical procedure, a total of 0.1238 g $Ni(NO_3)_2.6H_2O$ were dissolved into 2.5 ml ethanol and 2.5 ml deionized water. Then, 0.5 g mesoporous carbon was added into the aqueous solution of nickel(II) nitrate. The mixture was ultrasonicated for 10 min to uniformly distribute the catalyst in the solvent, then the mixture was stirred at room temperature for 48 h. Finally, the catalyst was reduced at 400 °C for 6 h under a hydrogen gas stream (flow rate of 20 cc/min). NiCo-modified mesoporous carbon was synthesized using a similar procedure to that of the Ni/MC by using an equimolar aqueous solution of nickel nitrate and cobalt nitrate.

Materials Characterization

The as-synthesized mesoporous carbon as well as Ni- and NiCo-modified MC were characterized by XRD (PANalytical X'Pert PRO), SEM-EDX (JEOL JED-2300 Analysis Station), TEM (Tecnai G2 SuperTwin TEM) and SAA (Quantachrome Quadrasorb-Evo Surface Area and Pore Size Analyzer).

Catalytic Phenylacetylene Hydrogenation

The catalytic activity of Ni/MC and NiCo/MC catalysts in the hydrogenation of phenylacetylene (PA) was examined under atmospheric hydrogen pressure. First, 0.1097 ml of phenylacetylene, 5 ml of methanol as solvent, and 0.0586 g of catalyst were introduced into the glass reactor. Next, hydrogen gas flowed into the reactor to remove the air, and then a balloon filled with hydrogen gas was connected to the reactor through a glass pipe connection. Finally, the reactions were carried out under magnetic stirring at 30 °C and 50 °C in an oil bath for 5 hours. The remaining reactant (PA) and the reaction products (styrene) were analyzed by Shimadzu gas chromatography using a flame ionization detector (FID). A known amount of styrene solution was used as an internal standard in this analysis.

RESULTS AND DISCUSSION

The XRD patterns of mesoporous carbon, Ni/MC, and NiCo/MC catalysts are shown in Fig.-1. The diffraction peaks of MC appear at 22.97°, and 43.3° which is similar to that of MC standard according to

JCPDS index, no. 75-1621. A broad peak indicates that mesoporous carbon contains amorphous carbon.[18] XRD pattern of Ni/MC catalysts shows three typical nickel peaks at 2θ of 44.39°, 51.74°, and 76.61° which are assigned to the diffraction peaks of metallic Ni (111), (200), and (220) respectively.[19] This result shows that mesoporous carbon has been impregnated successfully with nickel metal.[20] Similar XRD pattern was also observed for NiCo/MC, indicating the existence of alloy structure between Ni and Co on mesoporous carbon. Alloying of cobalt and nickel was also previously reported by Motlak *et al*.[21] However, compared to Ni/MC catalysts, the bimetallic catalysts possessed lower intensity, which related to the variation in crystallinity. The NiCo/MC catalyst show diffraction peaks located at 2θ = 44.39°, 51.58°, dan 76.85° corresponding to (111), (200), and (220) lattice planes of cubic Ni (JCPDS No. 04-0850) and Co (JPDS No. 15–0806), indicating that NiCo has the similar crystal structure to Co and Ni metals.[22] Based on a calculation using Scherrer's equation for the strongest diffraction peak (111), the crystallite size of Ni/MC and NiCo/MC catalyst was 5.59 nm, and 5.50 nm, respectively.

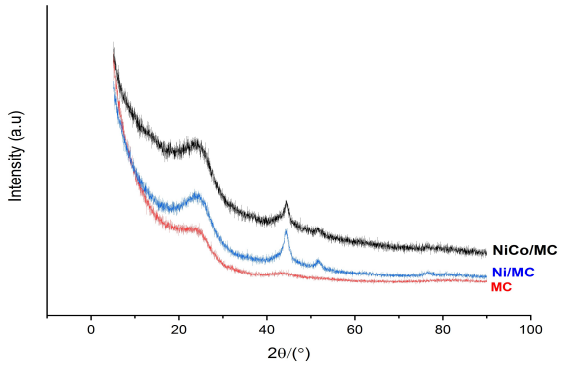
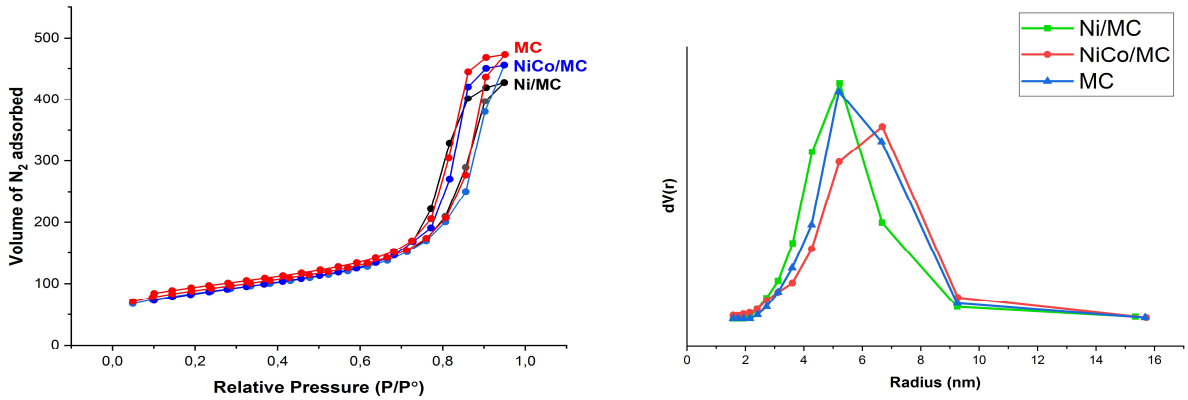


Fig.-1: XRD Patterns of MC, Ni/MC, and NiCo/MC

The nitrogen adsorption-desorption isotherms of MC, Ni/MC, and NiCo/MC are shown in Fig.-2(a). All samples show a type IV isotherm as per IUPAC classification with H1 (the two branches are almost vertical and almost parallel over a wide range of gas uptake). The type IV of adsorption isotherm indicates the presence of mesopores structure in the materials, as expected in this work.[23] Fig.-2(b) shows the pore size distribution of MC, Ni/MC, and NiCo/MC. Based on the Figure, after being impregnated with Ni, there was a slight decrease in pore size distribution (green curve), which indicates that some of the Ni entered the MC pores.



(a) (b)

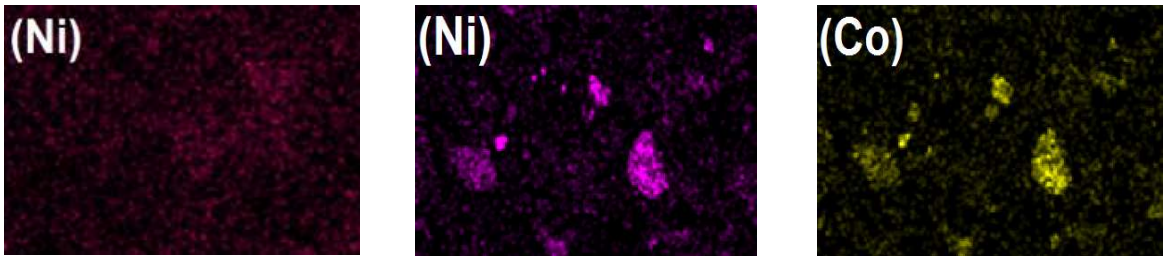
Fig.-2: (a) Nitrogen Adsorption and Desorption Isotherm of MC, Ni/MC, and NiCo/MC, (b) Pore Size Distribution of MC, Ni/MC, and NiCo/MC Calculated by the BJH Method

In addition, the surface area decreased from 304 m^2/g to 289 m^2/g (Table-1). This is because the metal particles were dispersed inside the pores and matrices of the carbons, which resulted in a decrease in available surface area as well as nitrogen uptake.[24] In contrast, MC impregnation with NiCo slightly increased the size of the pore, as well as its surface area. These results indicate that the bimetallic NiCo particles formed in the MC pores are smaller than Ni in Ni/MC, which means that the presence of these

particles can increase the surface area measured in nitrogen adsorption-desorption measurements. These results are also in line with the data obtained from TEM characterizations. The complete textural properties of the three materials are presented in Table-1.

Table-1: Textural properties of the materials

Catalyst	S_{BET} (m^2/g)	S_{ekt} (m^2/g)	V_{tot} (cc/g)	V_{meso} (cc/g)	V_{micro} (cc/g)	Pore size (nm)
MC	304	288.7	0.7	0.61	0.10	10.4
Ni/MC	289	216.7	0.6	0.61	0.03	10.4
NiCo/MC	313	223.6	0.7	0.65	0.04	13.4



(a) (b) (c)

Fig.-3: EDX-Mapping of (a) Nickel at Ni/MC, (b) Nickel at NiCo/MC, and (c) Cobalt at NiCo/MC Catalyst

Fig.-3(a) shows the EDX-elemental mapping pattern of Ni/MC, with Ni atoms marked in red. The impregnation of mesoporous carbon with nickel could be demonstrated by an evenly distributed red distribution pattern. Fig.-3(b) and Fig.-3(c) show that particle agglomeration is observed in NiCo/MC catalyst. However, the mapping image also shows the similarity in the present position and density distribution of Ni and Co. This result demonstrates the occurrence of an alloy between Ni and Co as described in the XRD analysis.

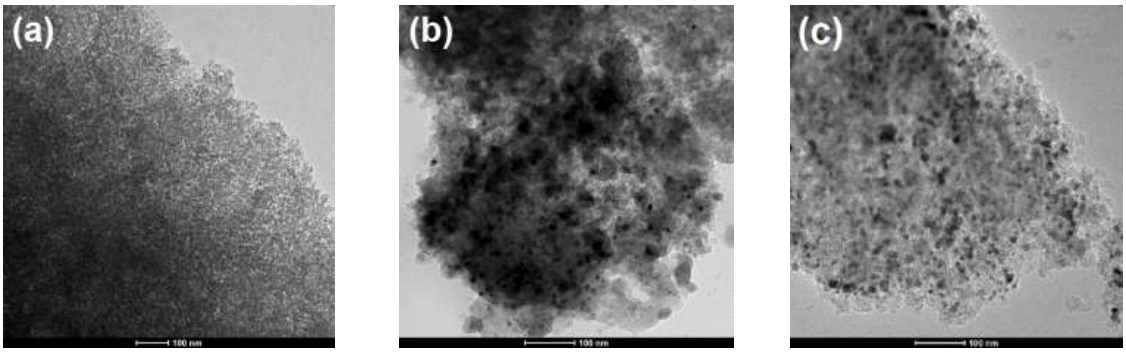


Fig.-4: TEM Images of (a) MC, (b) Ni/MC, and (c) NiCo/MC

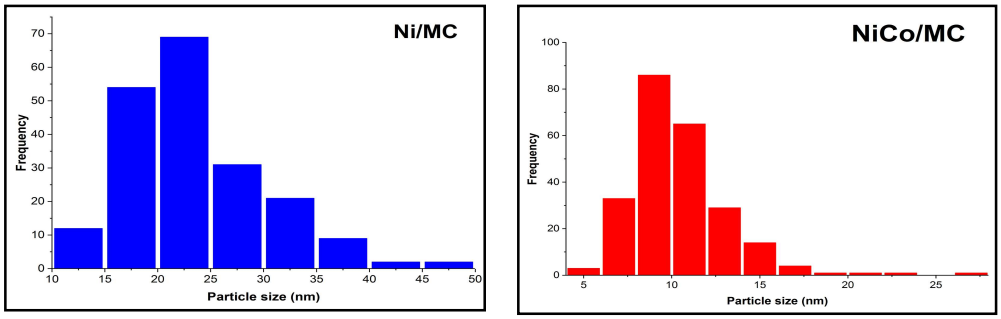


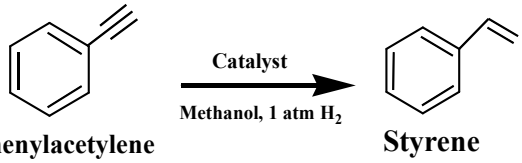
Fig.-5: Particle Size Distribution of Ni and NiCo on MC

TEM images of MC, Ni/MC, and NiCo/MC catalysts are presented in Fig.-4. The MC shows an irregular morphology and a worm-shaped channel (wormhole-like channel).[25] This could be due to the partial collapse of the carbon structure during the carbonization process.[26] Fig.-4(b) shows the presence of black

spots on a large, faded surface, which indicates that Ni metal exists in mesoporous carbon. Fig.-4(c) reveals the black spot demonstrates the formation of NiCo alloys in mesoporous carbon. TEM images also show that the NiCo alloys are distributed more evenly on the surface of MC with a smaller particle size than that of monometallic Ni. However, some agglomeration was observed in both catalysts. Particle size distribution of Ni/MC and NiCo/MC samples were calculated using Image J software based on TEM imaging analysis as shown in Fig.-5. Ni/MC exhibited particle size in the range of 10-50 nm with an average size of 23.1 nm. While in the case of NiCo/MC catalyst, the average particle size is 10.4 nm.

Attempts of Phenylacetylene Hydrogenation under an Atmospheric Hydrogen Pressure

The catalytic activity of the catalysts was evaluated in the hydrogenation of phenylacetylene reaction leading to the formation of styrene as shown in Scheme-1.



Scheme-1: Hydrogenation of Phenylacetylene to Styrene

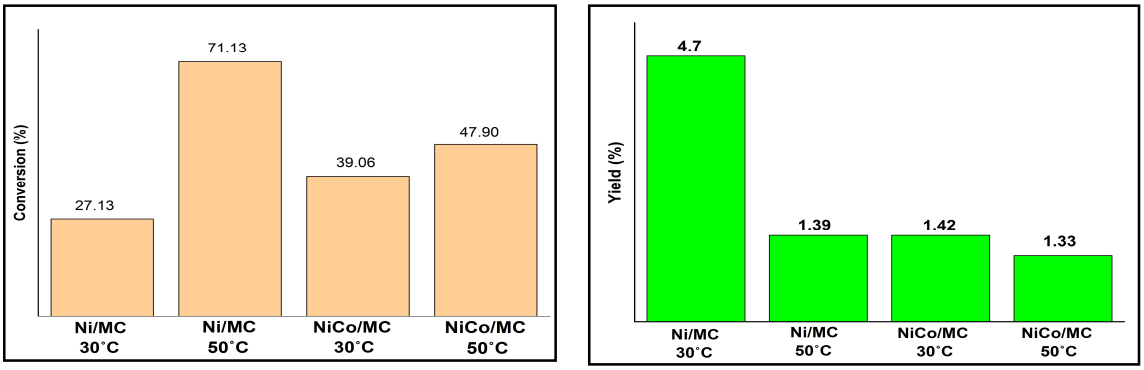


Fig.-6: Results of Phenylacetylene Hydrogenation over Ni/MC and NiCo/MC Catalyst under an Atmospheric H_2 Pressure)

The conversion of phenylacetylene and the yield of styrene obtained under various reaction conditions are presented in Fig.-6. It is shown that at 30 °C, a lower phenyl acetylene conversion was obtained, this was due to the relatively low kinetic energy thus there are fewer collisions between reactants and catalysts. However, the yield of styrene decreases with increasing reaction temperature. The low yield of styrene obtained for both catalysts could be attributed to the low hydrogen pressure used and the relatively short reaction time. These preliminary results show that although the yield of styrene is still quite low, the Ni/MC, and NiCo/MC have potential as catalysts for the selective hydrogenation of phenylacetylene, even at low hydrogen pressure.

CONCLUSION

Monometallic Ni and bimetallic NiCo modified mesoporous carbon was successfully prepared by the wet impregnation method followed by reduction under hydrogen gas. The presence of the nanoparticles on mesoporous carbon was provable by XRD, TEM, SEM, and SAA analyses. Characterization with XRD showed the formation of NiCo alloy on mesoporous carbon. Preliminary studies on the catalytic activity of the two materials show that Ni/MC provides a better yield of the product than NiCo/MC.

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