

# Nickel Nanoparticles Dispersion on Carbon Molecular Sieve by Electroless Deposition

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**Abstract** This work presents a novel one step process to synthesize nickel nanoparticles dispersed on activated carbon. This technique is widely used for the plating of metal surfaces and consists of the immersion of substrate on a stabilized bath that contains the metal precursor, a complexing agent, an additive for pH control, and chemical stabilizer to avoid the spontaneous reduction of metal in bath solution. By this process, nickel was dispersed on chemical activated carbon (carbon molecular sieve, CMS) obtaining a catalyst which showed better catalytic activity on benzene dehydrogenation than the observed for unsupported nickel nanoparticles and a commercial catalyst composed by nickel nanoparticles supported in  $\text{Al}_2\text{O}_3$ – $\text{SiO}_2$ .

**Keywords** Electroless nickel plating · Benzene hydrogenation · Nanoparticles

## 1 Introduction

Even benzene increases the octane number in gasoline blends, due to environmental regulations its content on gasoline has been limited to less than 1% (v/v), and for total aromatics the content must be lower than 35% (v/v) [1], thus hydrogenation of aromatics is an important chemical process in hydrocarbon refining [2, 3]. In the study of aromatic feedstock hydrogenation, benzene has been commonly used as model molecule [4]. Although palladium is considered one of the most active metal catalysts for hydrogenation, nickel is the choice for industrial purposes due to the lower cost. Metal particle size, dispersions, support nature and surface area of support are the main variables considered on the design of catalyst for hydrogenation [5]. The use of activated carbon as support for hydrogenation is well known, however main studies have been made on commercial activated carbon with moderated surface area [6–8]. The conventional process to prepare a metal, dispersed on activated carbon consists of the impregnation or ion exchange of precursor and drying. The metallic state of precursor is obtained by a reduction treatment, which can be made in situ previously to catalytic evaluation [8, 9], or after catalyst preparation in an ex situ treatment under reductive conditions [10].

Recently we report the synthesis of carbon based molecular sieves (CMS) with high content of microporosity and surface area above  $2500 \text{ m}^2/\text{g}$  [11]. In this work we present the results obtained in the formation of nickel nanoparticles on the surface of the CMS in a single step using the electroless deposition process.

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## 2 Experimental

Chemical activation of *Quercus agrifolia* char was described elsewhere [11]. For this work the activation was made with KOH as activating agent. Weight ratio of KOH/char was 4/1. KOH was ground to powder and then physically mixed with the char. The mixture was placed in a stainless steel rotary reactor and heated in a horizontal tube furnace until 760 °C under a constant N<sub>2</sub> flow of 250 mL/min. The activation was performed for 1 h and then cooled down under the same gas flow. The product was first washed with distilled water, followed by a hydrochloric acid (5 M) treatment and distilled water rinse again. Finally it was dried at 110 °C for 8 h. For comparative purposes, nanoparticles of nickel (32 m<sup>2</sup>/g) were also tested on benzene hydrogenation as well as a commercial catalyst Ni (65% w/w) on Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> from Aldrich (190 m<sup>2</sup>/g). According to surface area and TEM analysis, the mean size diameter of unsupported Ni nanoparticles is 18–25 nm, and for Ni on silica/alumina TEM images shown Ni nanoparticles size from 7 to 13 nm.

The conditions of the electroless treatment was taken from the work of Haag and Burgard [12], the original treatment was designed for the plating of metallic surfaces, so the process was slightly modified to favor the deposit on the activated carbon substrate. Electroless plating bath formulation and operating parameters are given in Table 1.

Sodium hydroxide was used to control pH around 9.6. Electroless baths were prepared from analytical grade chemicals and distilled water in a beaker. Electroless plating was conducted on a hot plate with a magnetic stirrer. Before plating treatment, the activated carbon was degassed at 300 °C during 2 h to eliminate gases and moisture adsorbed on the surface. After electroless treatment, the activated carbon was separated from the solution by filtration and the sample was rinsed several times with distilled water and dried at 110 °C. By means of this treatment, the nickel is deposited on AC surface in its reduced form. Sample CMS with 10% w/w of nickel (10Ni/CMS) was obtained for immersion time of 5 min and 16% w/w was obtained for immersion time of CMS of 30 min (16Ni/CMS).

The nickel content on CMS was determined by inductively coupled plasma (ICP) analysis. X-ray diffraction (XRD) analysis were made in a Phillips diffractometer X'pert model, with Cu–K $\alpha$  radiation ( $\lambda = 1.5405$  Å).  $2\theta/\theta$  diffractograms were obtained in the 20–100° range, with a step of 0.05° and measuring time of 5 s per step. Only samples analyzed by XRD were thermally treated at 400 °C during 1 h under argon atmosphere in order to promote the formation of crystalline phase of nickel nanoparticles. Morphology of samples was studied using a Jeol JSM-5800LV scanning electron microscope (SEM) adapted with energy dispersive spectrometry system (EDS) for chemical analysis. Some images were obtained by transmission electron microscopy (TEM) Philips model CM-200, equipped with EDS Prime. X-Ray spectroscopy was useful to characterize the nickel nanoparticles.

Catalytic activity of samples for benzene hydrogenation was made in tubular fix bed reactor using 50 mL/min of gas flow mixture composed by benzene (2% mole), hydrogen (40%) and helium (58%), for all test 0.05 g of catalyst was used. Temperature of reaction was studied from 50 to 210 °C.

## 3 Results and Discussion

Hydrazine is frequently used as reducing agent for the synthesis of supported metal catalyst, the most common method consist of the preparation of a solution containing nickel precursor and hydrazine where catalytic support is immersed, being temperature and precursors nature main variables of study in this process [5, 13], also a two steps method has been reported where nickel is impregnated in support, then the solvent evaporated, and in a second step the impregnated support is suspended in water and hydrazine is added [14]. This process is similar to the preparation where metal ion is exchanged with cations of support and afterwards the exchanged support is treated with hydrazine to reduce the metal and obtain high metal dispersion [15]. Main differences of conventional methods and the method here reported is that there is one step where the deposition

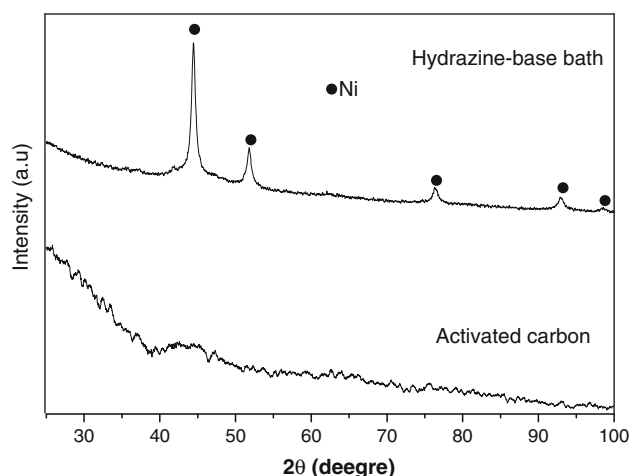
**Table 1** Electroless plating bath formulation and operating parameters

	Bath composition		Operating parameters	
Nickel precursor	Nickel acetate Ni(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	29.86 g/L	Temperature	60 °C
Stabilizer agent	Lactic acid	13.51 g/L	Plating time	5–30 min
Complexing agent	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	5.96 g/L	pH	9.6
	Na <sub>2</sub> EDTA			
Reducing agent	C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> Na <sub>2</sub> O <sub>8</sub> ·2H <sub>2</sub> O	12.82 g/L		
	Hydrazine			
	N <sub>2</sub> H <sub>4</sub>			

on support surface and the reduction is made simultaneously. In this process the amount of nickel deposited on surface as well as the size of particles is a function of the immersion time on the deposition bath. The design of bath chemical composition is based on the process used to plating metallic surfaces, thus the bath has an excess of nickel precursor and the EDTA has the roll of complexing agent to keep the nickel available in solution and the rate of nickel deposition depends of nickel complex concentration, hydrazine availability and the substrate surface interaction with nickel.

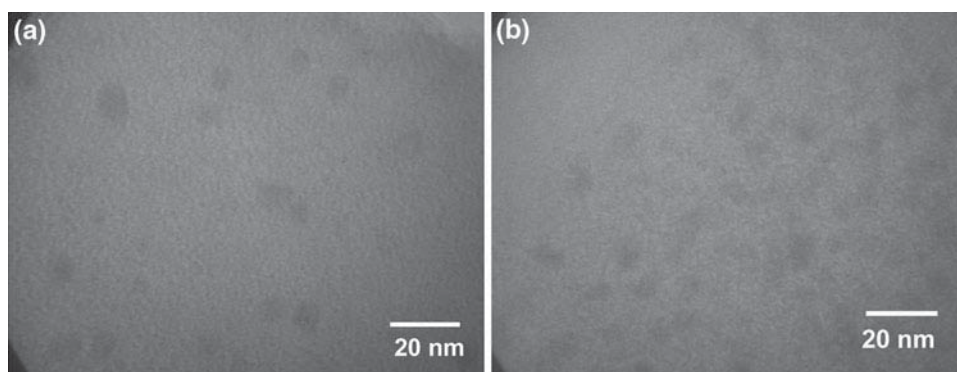
CMS with 10% w/w of nickel (10Ni/CMS) was obtained for immersion time of 5 min and 16% w/w was obtained for immersion time of CMS of 30 min (16Ni/CMS). According to XRD patterns for both samples only a metallic phase of nickel is formed (JCPDS No. 00-004-0850) and no nickel oxides were detected as can be seen in Fig. 1.

Surface area determined by  $N_2$  adsorption was 3081  $m^2/g$  for CMS, 1797  $m^2/g$  for 10Ni/CMS and 1396  $m^2/g$  for 16Ni/CMS. Main contribution of surface area for CMS is



**Fig. 1** Results of XRD analysis of carbon molecular sieve (activated carbon) before nickel deposition and sample 16Ni/CMS. All signals obtained in the sample 16Ni/CMS correspond to metallic nickel

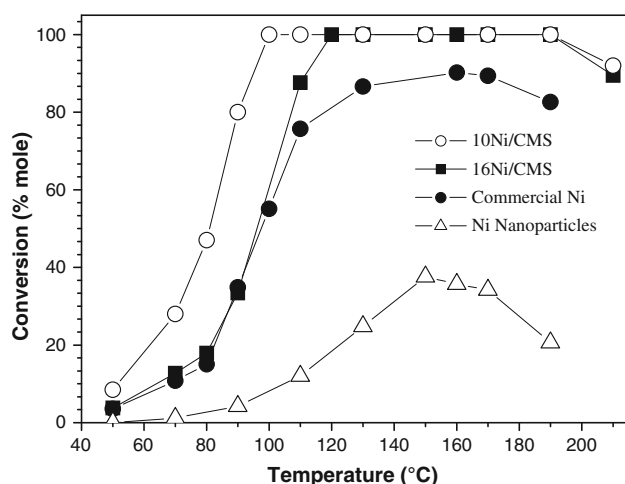
**Fig. 2** TEM images of nickel nanoparticles supported on CMS. **a** 10Ni/CMS, and **b** 16Ni/CMS. Particle size seems to be independent of the amount of nickel deposited on CMS, and main difference is the amount of particles on CMS surface



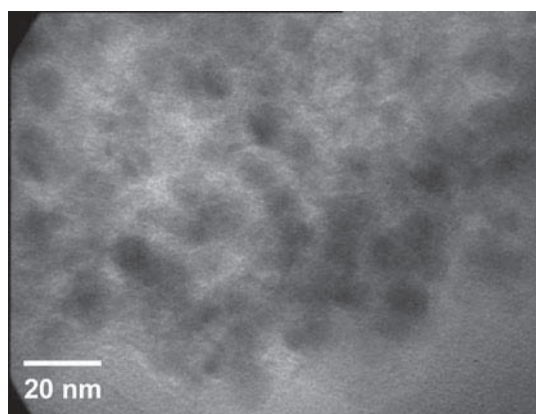
microporosity, being most micropores of 5–6 Å of diameter [11]. The loss of surface area is related to the obstruction of the access to micropores. Figure 2 shows the nickel nanoparticles on 10Ni/CMS, and 16Ni/CMS catalysts and as can be seen, typical particle size is between 5 and 12 nm, independently of the amount of nickel deposited on CMS. Inasmuch the particle size of nickel deposited on CMS surface is larger than the diameter of micropores (around 0.5 vs. 5–12 nm), then nickel particles are located in the access to microporosity and the internal channels of microporosity are free of nickel. Considering that the contribution of meso and macroporosity to surface area in CMS support is around 3%, then, nanoparticles of Ni are dispersed on approximately 90  $m^2/g$ . Since the mean particle size is 8.5 nm for 10Ni/CMS, the surface area of all deposited Ni nanoparticles is lower than 10  $m^2/g$ , thus the availability of surface area concerning meso and macroporosity in CMS is enough to disperse all the deposited nickel nanoparticles.

Figure 3 shows the results of catalytic activity of the studied catalysts, and as can be seen, the typical volcano shape curve of conversion-temperature [16] was obtained for all samples. The best results for benzene hydrogenation were obtained for catalysts based on CMS, in spite of the low content of nickel. Considering the size of nickel particles on catalysts, the available surface area of nickel was around 3.0 times higher for catalytic hydrogenation made with unsupported nanoparticles than the catalytic reaction made with Ni/CMS catalysts, and in spite of that, the performance of Ni/CMS catalysts was better. These results can be related to the role of the support which enhanced the capability of nickel nanoparticles to split hydrogen and to favor the benzene activation for its hydrogenation.

The comparison with Aldrich catalyst also shows a better performance for Ni/CMS catalysts. According to the nickel particle size of materials, the available nickel surface was around five times higher for commercial supported Ni than Ni/CMS catalysts. In spite of the large surface area of support, commercial catalyst has surface crowded of nickel nanoparticles as can be seen in Fig. 4,



**Fig. 3** Conversion of benzene to cyclohexane versus temperature for Ni catalysts



**Fig. 4** TEM image of nickel nanoparticles dispersed on  $\text{Al}_2\text{O}_3\text{-SiO}_2$  (commercial catalyst)

which could be detrimental for catalytic reaction. The nature of support also can be a disadvantage for this catalyst against Ni/CMS.

Finally, the lower activity of 16Ni/CMS when compared with 10Ni/CMS can be explained by a lower interaction among Ni particles in 10Ni/CMS catalyst, since the size of particles is almost the same for both catalysts, and thus the number of nanoparticles in the same support is 30% lower for 10Ni/CMS. This lower population on support surface of nickel nanoparticles for 10Ni/CMS catalyst also could promote a better metal-support interaction.

## 4 Conclusions

According to our results, electroless nickel deposition process allows the synthesis of high disperse nickel nanoparticles on carbon based substrates with a narrow particle size distribution in a single step. This process also allows the regulation of the amount of particles deposited in catalyst support by the control of immersion time of substrate on electroless bath. The obtained nickel supported catalysts showed better catalytic activity for benzene hydrogenation than the observed for unsupported nickel nanoparticles and nickel supported on  $\text{Al}_2\text{O}_3\text{-SiO}_2$ , even the amount of active phase was higher for these catalysts.

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