Ni encapsulation by SiO2: improvement of metal stability and activity in aqueous phase furfural hydrogenation

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Resumo/Abstract

RESUMO – Neste trabalho, foram avaliadas a estabilidade e atividade catalítica de um catalisador Ni-SiO2 com arquitetura encapsulada (*core-shell*). Dois métodos de síntese de nanopartículas foram estudados e aquele que levou à obtenção de partículas menores foi usado para preparar o catalisador encapsulado. Resultados de TGA indicaram que houve um aumento da resistência das nanopartículas a oxidação em ar após o encapsulamento. Nos testes de hidrogenação de furfural em fase aquosa, foi observada uma diminuição na conversão em comparação ao observado com um catalisador Ni/SiO2 suportado. Ainda assim foi possível alcançar 62,5 % de conversão, indicando o potencial para aplicação do catalisador encapsulado para essa reação.

*Palavras-chave: níquel, casca-núcleo, estabilidade, biomassa, hidrogenação*

ABSTRACT – In this study, the stability and catalytic activity of a Ni-SiO2 catalyst with encapsulated architecture (core-shell) were evaluated. Two nanoparticles synthesis methods were studied and the one which obtained smaller particles was used to synthesize the encapsulated catalyst. TGA data indicated that the nanoparticles resistance to oxidation in air was improved after encapsulation. In aqueous phase furfural hydrogenation tests, a decrease in conversion was observed in comparison to a Ni/SiO2 supported catalyst. Despite that, 62.5 % of furfural conversion was achieved, showing that the encapsulated catalyst has potential to be used in the studied reaction.

*Keywords: nickel, core-shell, stability, biomass, hydrogenation*

## Introduction

Noble metals are well known as active phases with remarkable activity, selectivity, and stability for a wide variety of catalytic systems. However, their scarcity and elevated prices (1) are an economical drawback for the large-scale production of noble metal-based catalysts. Nickel is an earth-abundant metal and significantly less expensive (1). Besides, it is well known as an excellent active phase for a wide variety of catalytic systems. Despite that, nickel-based catalysts can suffer severe deactivation depending on the reaction system and operation conditions. A strategy to avoid that is the use of catalysts with non-conventional architectures which promote a higher protection of Ni particles.

The proposal of the present study was to synthesize and characterize a silica encapsulated nickel catalyst (core-shell Ni@SiO­2). Its catalytic activity was evaluated in aqueous phase furfural hydrogenation. Furfural was chosen because it is a platform molecule inserted in the context of lignocellulosic biomass upgrading which can be hydrogenated to different valuable products (2).

## Experimental

*Synthesis*

Ni@SiO2 was synthesized via encapsulation of nickel nanoparticles (NiNP). Two different versions of poliol method were used to obtain NiNP.

The first of them was performed in inert atmosphere (N2). 1,5-pentanediol (1,5-PDO) and Ni(acac)2 were added to a round flask connected to a reflux system and heated up to 200 °C and kept under stirring. After 10 min of N2 bubbling, a solution of polyvinylpyrrolidone (PVP, Mw = 10,000) in 1,5-PDO was added. After 1 h, the temperature was raised to 220 °C (4 h). After cooling down, acetone was added and the solid was centrifuged and washed with ethanol 4 times and dried (80 °C / 4 h).

The second method used an additional reducing agent (NaBH4). A reflux system was heated up to ethylene glycol (EG) boiling point. EG and NaBH4 were added and, after 5 min, NiCl2 and PVP (Mw = 40,000) solutions in EG were simultaneously dropped in the system. After 1 h, the obtained mixture was centrifuged, the solid was separated, washed with ethanol 4 times and dried (80 °C / 4h).

For the synthesis of Ni@SiO2, NiNP were dispersed in ethanol and NH4OH was added to the suspension. Then, octadecyltrimethoxysilane (C18TMS) was added and dispersed. Finally, tetramethyl orthosilicate (TMOS) was dropped in the suspension and kept under stirring at room temperature (1 h). The solid was centrifuged and washed 4 times and dried (80 °C / 4 h).

A supported catalyst (Ni/SiO2) was prepared by incipient wetness impregnation. An aqueous solution of Ni(NO3)2 was impregnated in a commercial SiO2 gel (Aldrich, 500 m2 g-1). The sample was dried (110 °C / 12 h) and then calcined in air (500 °C / 2 h).

*Characterization*

Thermogravimetric analysis (TGA) in oxidant atmosphere was used to verify the presence of PVP in synthesized NiNP and to evaluate Ni oxidation to NiO. Scanning transmission electron microscopy (STEM) was used to investigate NiNP morphology, determine their particle size distribution, and confirm Ni encapsulation.

*Catalytic tests*

Aqueous phase furfural hydrogenation was conducted in a homemade batch system able to simultaneously perform 10 catalytic tests. The catalysts were previously reduced in H2 (500 °C / 2h). All reactions were conducted at 150 °C and 30 bar H2, using 5 mL of a 100 mmol/L furfural aqueous solution as reaction medium. After 2 h of reaction, the system was cooled down and the liquid reaction samples were analyzed by gas chromatography (CG).

## Results and Discussion

NiNP thermograms presented no mass loss, indicating no presence of PVP. Therefore, ethanol washing used in both procedures was effective to remove it. Moreover, the relative mass of all samples raised *ca.* 24.5 %, with mass derivative minima located between 380-415 °C. Considering the theoretical relative mass gain from Ni0 oxidation to NiO (27.3 %), this result indicates that NiNP are basically composed of Ni0 particles. This is in accordance with the magnetic nature of the samples.

STEM images indicated that both methods are reproductive in terms of particle size distribution and morphology. However, some differences were observed from one methodology to the other. NiNP synthesized in N2 atmosphere presented some spherical particles, but also others with geometric morphologies (tetragonal and octahedral). NiNP obtained using NaBH4 were only spherical. Moreover, NiNP particle size from N2 atmosphere synthesis (61 nm) was smaller than the one from NaBH4 (127 nm). Therefore, the former were selected to be encapsulated.

Ni@SiO2 STEM images confirmed that NiNP were encapsulated by SiO2. Moreover, a mononuclear configuration was achieved (one Ni particle per SiO2 shell). EDS data indicated a high Ni content (84±4 % wt.). Ni@SiO2 thermogram presented a relative mass gain of 19.2 %, indicating that there was Ni0 after encapsulation. Considering Ni content determined by EDS and assuming all Ni is Ni0, a mass increase of 22.9 % would be expected. Therefore, even after encapsulation, NiNP are basically Ni0. Moreover, the mass derivative minimum of this transformation occurred at 518 °C. The increase of more than 100 °C in Ni oxidation temperature is an indicative that SiO2 shell increased NiNP resistance to oxidation.

Aqueous phase furfural hydrogenation data are presented in Table 1. Once Ni loadings were different on Ni@SiO2 and Ni/SiO2 (84 and 10 % wt., respectively), two tests were performed with Ni@SiO2: one with the same catalyst mass of Ni/SiO2 test and other with the same Ni mass of Ni/SiO2 test. As can be seen in Table 1, Ni-SiO2 catalysts were active for furfural conversion in both supported and encapsulated architectures. However, Ni@SiO2 achieved lower furfural conversions than Ni/SiO2 in both tests. One possible explanation to this fact is that furfural needs to diffuse through the SiO2 shell to be hydrogenated by Ni. On the other hand, Ni particles are directly exposed to the reaction medium, and consequently to furfural, in the supported catalyst. Despite that, the tests with the same catalysts mass showed that Ni@SiO2 can reach levels of furfural conversion similar to those of Ni/SiO2. In all performed tests, furfuryl alcohol and cyclopentanone appeared as main reaction products, indicating that the use of different catalysts architectures led to no relevant changes in selectivity.

**Table 1.** Aqueous phase furfural hydrogenation over Ni-SiO2 catalysts. Reaction conditions: 150 °C; 30 bar H2 (25 °C); 5 mL of a 100 mmol/L furfural aqueous solution.

|  |  |  |  |
| --- | --- | --- | --- |
| **Catalyst** | **Catalyst mass (mg)** | **Ni mass (mg)** | **Furfural conversion (%)** |
| No catalyst | - | - | 3.4 |
| Ni/SiO2 | 48.0 | 4.8 (a) | 71.5 |
| Ni@SiO2 | 48.0 | 40.3 (b) | 62.5 |
| 5.7 | 4.8 (b) | 28.0 |
| (a): Calculated from the catalyst Ni nominal loading (10 % wt.).(b): Calculated from Ni@SiO2 loading determined by EDS. |

## Conclusions

In the present study, it was shown that it is possible to improve Ni particles stability by using an encapsulated architecture (core-shell). It was also shown that Ni@SiO2 can be used as a hydrogenation catalyst to furfural conversion in aqueous phase.

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