Furfural aqueous phase hydrogenation by nickel: how activity and stability are affected by the catalyst architecture

Leon F. Feitosa,[1*] Gabrielle F. Fernandes,[1,2] Mattheus Torquato,[1] Marco A. Fraga,[1] Andréa M. Duarte de Farias,[1*]

[1]*Instituto Nacional de Tecnologia (INT), Av. Venezuela, 82, Saúde, Rio de Janeiro (RJ), 20.081-312, Brasil*
[2]*Instituto Federal do Rio de Janeiro (IFRJ), R. Lúcio Tavares, 1045, Centro, Nilópolis (RJ), 26.530-060, Brasil*
[*] leon.feitosa@int.gov.br, andrea.farias@int.gov.br

Resumo/Abstract

RESUMO – Catalisadores Ni-SiO_2 com arquiteturas encapsulada (NPNi@SiO_2) e suportada (Ni/SiO_2) foram sintetizados, caracterizados e avaliados na reação de hidrogenação de furfural. Imagens de MET indicaram que as NPNi têm morfologia geométrica e confirmaram o seu encapsulamento. Os difratogramas revelaram domínios cristalinos de Ni maiores no NPNi@SiO_2. A porosidade da casca foi confirmada por fisissorção de N_2 e os termogramas mostraram um aumento na temperatura de oxidação do Ni após o encapsulamento. Foi atestado por TPR e DRX que o NPNi@SiO_2 apresenta Ni^0 e não demanda redução. Assim, na avaliação catalítica, o Ni/SiO_2 demonstrou atividade dependente da redução em H_2, enquanto o NPNi@SiO_2 apresentou o mesmo desempenho com ou essa etapa. A maior conversão do Ni/SiO_2 (red.) em comparação às NPNi mostrou um impacto da diferença de tamanho dos domínios cristalinos na atividade. Além disso, a maior conversão das NPNi em relação ao NPNi@SiO_2 mostrou que, apesar de porosa, a casca diminui a acessibilidade do Ni.
Palavras-chave: encapsulamento, casca-núcleo, bioeconomia, beneficiamento de biomassa, álcool furfurílico.

ABSTRACT – Ni-SiO_2 catalysts with encapsulated (NPNi@SiO_2) and supported (Ni/SiO_2) architectures were synthesized, characterized and evaluated in furfural hydrogenation rection. MET images indicated that NPNi present geometrical morphology and confirmed encapsulation. The diffractograms revealed that NPNi@SiO_2 Ni crystal domains are bigger. The shell porosity was confirmed by N_2 physissorption and the thermograms showed that Ni oxidation temperature is increased after encapsulation. TPR and XRD attested that NPNi@SiO_2 presents Ni^0 after synthesis, and do not demand reduction. Therefore, in the catalytic tests, Ni/SiO_2 showed activity dependent on previous reduction in H_2, while NPNi@SiO_2 presented the same performance with and without that. Ni/SiO_2 (red.) higher conversion in comparison to NPNi showed an impact of the different crystal domain sizes in activity. Moreover, NPNi higher conversion in relation to NPNi@SiO_2 indicated that, the shell decreases Ni accessibility.
Keywords: encapsulation, core-shell, bioeconomy, biomass upgrading, furfuryl alcohol.

Introduction

Residual biomass is a renewable source of energy that emerges as an alternative to mitigate CO_2 emissions arising from the consumption of fossil fuels. Its upgrading involves several chemical processes (1). Some of them involve the use of heterogeneous catalysts and are performed either in aqueous phase or in a system where water is a byproduct. Therefore, catalysts, which are stable in aqueous media, are important for those applications. Noble metals are well known as active phases with remarkable activity, selectivity, and stability. However, their scarcity and high prices are an economical drawback for large-scale application. Nickel is significantly less expensive and successfully used as active phase in hydrogenation reactions. Despite that, it can suffer severe deactivation in liquid/aqueous media. The use of catalysts with non-conventional architectures is a strategy to improve Ni stability and avoid that issue.

The proposal of the present study is to synthesize Ni-SiO_2 catalysts with encapsulated (core-shell) and supported architectures and compare their properties and catalytic performance. Aqueous phase furfural hydrogenation was selected as catalytic system due to furfural importance as platform molecule in lignocellulosic biomass upgrading (2).

Experimental

Synthesis

The silica encapsulated nickel catalyst (NPNi@SiO_2) was synthesized by a procedure detailed elsewhere (3). It consists of two steps: i) synthesis of nickel nanoparticles (NPNi) by polyol method, and ii) NPNi encapsulation by silica using Stöber method. Each step was scaled up in relation to the literature (5 and 3 times, respectively) and was performed in triplicate to evaluate reproducibility.

The silica supported nickel catalyst (Ni/SiO_2) was prepared by incipient wetness impregnation. A commercial SiO_2 gel was impregnated with nickel(II) nitrate aqueous solution, dried (110 °C / 12 h) and calcined (500 °C / 2 h).

Characterization

Thermogravimetric analysis (TGA) was used to verify the presence of organic matter and to evaluate Ni oxidation. Transmission electron microscopy (TEM) was employed to

evaluate NPNi morphology and particle size distribution, and to confirm Ni encapsulation. The catalysts' reducibility was analyzed by temperature-programmed reduction (TPR). Ni crystal phases were identified by X ray diffraction (XRD), and Ni crystal domain sizes were estimated by Scherrer equation. Ni contents were quantified by X ray fluorescence spectrometry (XRF). Textural properties were evaluated by N_2 physisorption.

Catalytic tests

Aqueous phase furfural hydrogenation was conducted in a custom made 100 mL batch reactor. The samples were tested with and without previous reduction in H_2 (500 °C / 2h). All reactions were conducted at 150 °C and 30 bar H_2, using a furfural:nickel ratio of 10:1 and 25 mL of a 100 mmol/L furfural 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

Based on characterization data, NPNi and NPNi@SiO_2 synthesis proved to be reproductive and scalable. TEM images indicated the formation of nanoparticles with geometric morphology. TGA attested PVP removal and a mass gain event (Ni→NiO) at *ca.* 460 °C indicating the presence of Ni^0. No reduction peak was observed by TPR, and XRD presented peaks attributed to Ni^0 cubic phase, with crystal domains of 25 nm. TEM images showed that NPNi was encapsulated by SiO_2, and textural properties confirmed that the shell is porous. TPR and XRD data indicated that Ni crystalline phase and domain size were preserved after encapsulation. Ni oxidation on NPNi@SiO_2 occurred at *ca.* 580 °C (TGA), showing that Ni stability against oxidation was improved after encapsulation. The presence of NiO in Ni/SiO_2 was confirmed by a TPR peak at 378 °C and XRD peaks attributed to cubic NiO. Table 1 presents further details on NPNi@SiO_2 and Ni/SiO_2 properties. Sg and Vp, which come from each SiO_2 matrix, are remarkably distinct. For a supported catalyst, high Sg is important to provide enough space for active phase particles to be deposited. On encapsulated catalysts, it must be enough to recover the nanoparticles and provide porosity for the shell. Ni loadings are also quite different. Low metal loadings on supported catalysts favor dispersion, while encapsulated catalysts can have an amount of shell just enough to cover the particles.

Table 1. NPNi@SiO_2 and Ni/SiO_2 composition and texture.

Catalyst	%Ni (w/w)	D_{XRD} (Ni) (nm)	Sg (BET) (m^2/g)	Vp (BJH) (cm^3/g)
NPNi@SiO_2	82.1	25	25	0.074
Ni/SiO_2	12.5	18[(a)]	209	0.667

[(a)] After reduction in H_2 (500 °C / 2 h).

The data in Figure 1 attests that Ni/SiO_2 demands a reduction step to be active in furfural hydrogenation. On the other hand, NPNi@SiO_2 presents the same performance with and without reduction. Therefore, NPNi@SiO_2 has the advantage of eliminating a process step which involves H_2 consumption and heating. However, reduced Ni/SiO_2 presented higher conversion than NPNi and NPNi@SiO_2. In relation to NPNi, this result can be due to Ni/SiO_2 smaller crystal domains, which possibly led to a greater availability of Ni active sites. Once Ni crystal domains sizes are the same on NPNi and NPNi@SiO_2, that explanation is valid for both materials. Considering that NPNi@SiO_2 presented the lowest conversion, an additional phenomenon occurs on that catalyst. The plausible explanation here is that NPNi encapsulation decreases Ni accessibility, decreasing NPNi@SiO_2 activity. However, the benefit of SiO_2 encapsulation on stability can be seen by comparing NPNi and NPNi@SiO_2 conversions with and without reduction. While no relevant impact was observed on NPNi@SiO_2, a huge drop was observed on NPNi after reduction, which is possibly due to Ni particles' sintering during reduction.

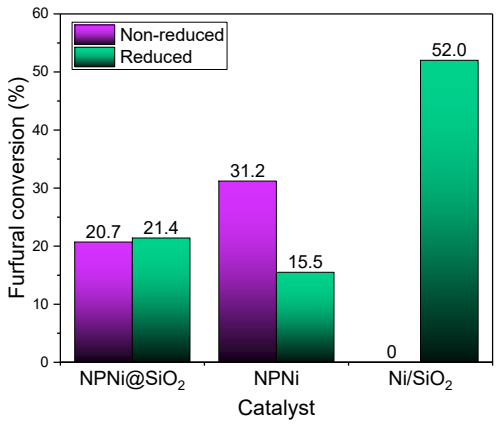

Figure 1. Furfural conversions of reduced and non-reduced Ni catalysts (150 °C, 30 bar H_2, 10furfural:1Ni, 0.1 mol/L, 2 h).

Conclusions

NPNi@SiO_2 synthesis led to catalysts which do not need a reduction step. Encapsulation proved to be effective in improving Ni stability. However, the decrease in Ni accessibility by encapsulation impacted on its performance in furfural hydrogenation. Investigations into those catalysts selectivity and stability after recycling are in course.

Acknowledgments

The authors thank CNPq for financial support, and UFF and LABNANO/CBPF for TEM analyses.

References

1. M. K. Awasthi *et al.*, *Sustainable Chemistry and Pharmacy* **2024**, *38*, 101450.
2. H. Tian *et al.*, *Molecular Catal.* **2021**, *510*, 111697.
3. W. Yang *et al.*, *Catal. Today* **2016**, *259*, 438-445.