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Supported nickel nitride catalysts for the gas-phase hydrogenation of furfural

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An increasing interest in the development of alternatives to fossil fuels is being paid in the last years due to the growth of the global energy consumption, together with the depletion of the crude reserves and more stringent environmental concerns. In this context, non-fossil carbon resources have emerged as renewable sources for the production of fuels and chemicals from more available feedstock, with lower greenhouse emissions [1]. Lignocellulosic biomass is the most abundant and economical non-fossil carbon resource, and it does not compete with the food chain, being considered the most carbon-sustainable source [2,3]. The hydrolysis and subsequent dehydration of pentosans, mainly xylose, present in hemicellulose, leads to furfural [2], which is an important platform molecule derived from biomass [3]. Furfural hydrogenation, using metal-based catalysts, allows the production of a wide range of value-added chemicals: furfuryl alcohol (FOL), 2-methylfuran (MF), furan, among others. For instance, FOL is an important chemical for the manufacture of foundry resins with excellent chemical, thermal and mechanical properties, whereas furan is used for the synthesis of heterocycles. On the other hand, the search of alternatives to the use of noble metal catalysts for different catalytic processes has prompted the interest of many research groups. This is the case of transition metal carbides and nitrides, which present an electronic structure similar to those of some noble metal and therefore are expected to possess similar catalytic activities to those of platinum-group metals [4]. Well-defined and homogeneous nickel nitride/Ni nanoparticles supported on high surface area matrix can be prepared by a modified sol-gel based process called *urea glass route* (UGR), [5]. Nickel nitride supported on carbon shows, in the hydrogenation of several organic molecules, a conversion similar to that of supported nickel, but a different selectivity pattern. This fact has moved to support nickel nitride on silica and to study its catalytic performance in the gas-phase hydrogenation of furfural, where nickel-based catalysts exhibit a high hydrogenating activity, but with a low selectivity, giving rise to a broad spectrum of hydrogenated products.

A series of catalysts with different nickel loading (2.5-30 wt%) has been prepared by UGR. The preparation of Ni₃N phase was ascertained via Powder X-rays diffraction together with cubic nickel. The elemental chemical analysis and XPS data confirm the presence of the nitride phase. Their catalytic performance points out that catalysts with loading of 5-10 wt% Ni exhibit a higher stability, maintaining furfural conversion values higher than 75% after 5 h of time-on-stream at 170°C, and the main products detected were furfuryl alcohol (hydrogenation) and furan (decarbonylation) (Fig. 1). This would indicate that two types of active sites are present on the catalyst surface. It is noteworthy the high catalytic activity of this family of catalyst, since they exhibit a better performance than Cu-ZnO catalysts [6], but using a lower reaction temperature and H₂/furfural molar ratio, as well as a higher furfural concentration and WHSV values. The experimental conditions have been optimized in order to achieve the maximum yield in the target product, but preserving a high activity and stability. The fresh and spent catalysts have been characterized in order to elucidate structure-activity-stability relationships.

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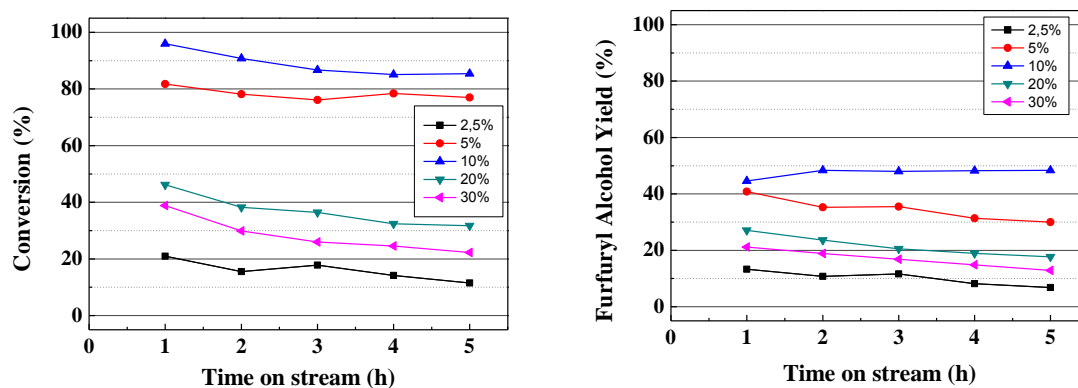


Figure 1. Furfural conversion (left) and furfuryl alcohol yield (right) of $\text{Ni}_3\text{N-SiO}_2$ catalysts with different Ni loading, as a function of the time-on-stream (Experimental conditions: $T_R = 170^\circ\text{C}$, $m_{\text{cat}} = 75 \text{ mg}$, $\text{H}_2 \text{ flow} = 10 \text{ ml min}^{-1}$, $\text{feed flow} = 4.6 \text{ mmol}_{\text{FUR}} \text{ h}^{-1}$)