Effect of the support on Ni catalytic performances in glycerol steam reforming

Valentina Nichele[a], Michela Signoretto[a], Federica Menegazzo[a], Francesco Pinna[a], Alessandro Gallo[b], Vladimiro Dal Santo[c], Giuseppina Cerrato[d]

[a] Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Dorsoduro 2137, 30123, Venice, Italy.
[b] Istituto di Scienze e Tecnologie Molecolari-CNR, via G. Fantoli 16/15, 20138, Milan, Italy.
[c] Istituto di Scienze e Tecnologie Molecolari-CNR, via C. Golgi 19, 20133, Milan, Italy.
[d] Dipartimento di Chimica IFM e NIS – Centro di Eccellenza,Università di Torino, via P. Giuria 7, 10125, Turin, Italy.
e-mail: valentina.nichele@gmail.com

In the last years, the use of hydrogen as new energy vector has been widely encouraged, because it is clean and carbon-free [1]. Nevertheless, an effective solution of environmental problems such as the greenhouse effect and the global warming, as well as the decrease of the dependence on fossil fuels, requires the use of renewable sources. In this context glycerol, the main by-product in biodiesel production, has emerged as a promising source of hydrogen, because of its high hydrogen content and renewability, safeness and non toxicity [2].

Several catalysts have been proposed for glycerol steam reforming. In this work we report the catalytic performances of Ni-based catalysts at two different reaction temperatures. Moreover, the effect of the support (*i. e.* TiO_2, SBA-15 and ZrO_2) on the selectivity to hydrogen was studied.

TiO_2 and ZrO_2 were synthesized by a conventional precipitation method [3], whereas SBA-15 was prepared through a template synthesis [4]. Catalysts were prepared by incipient wetness impregnation of the supports with an aqueous solution of the Ni precursor in order to obtain a 10 wt% Ni loading and they were finally calcined. The physico-chemical properties of the catalysts were determined by nitrogen physisorption analysis (BET), temperature programmed reduction (TPR) and high resolution transmission electron microscopy (HR-TEM). The activity tests were carried out in a fixed bed tubular quartz reactor at atmospheric pressure at two different temperatures (500°C and 650°C), after reduction of the samples in H_2 flow for 1 hour at either 500 or 700°C respectively. A water/glycerol solution was fed (10 wt% solution of glycerol in water) at the constant flow rate of 0.06 mL/min. Data were collected up to 20 hours on each sample.

The Ni/TiO_2 sample exhibits negligible activity at 650°C because of the collapse of the support. Concerning Ni/SBA-15, our results indicate the insufficient hydrothermal resistance of the support, which leads to the progressive deactivation of the catalyst. However this support is able to stabilize the active phase in a rather efficient way, thus preventing Ni sintering. Ni/ZrO_2 exhibits the best performances: a stable glycerol conversion of ~72% and a hydrogen yield of ~65% were obtained. This is due to the almost full preservation of the structure of the zirconia support even after 20 h in the SR conditions; moreover, also the dispersion of the Ni active phase remained unchanged.

The different behaviour of the three catalysts can be then ascribed (i) to the chemical, thermal and mechanical resistance of the support in the reaction conditions and (ii) to the intensity of the interactions between the support and the active phase, which affects in particular the stability of the Ni nanoparticles. Our results highlight the importance of the nature of the support, which plays a key role in designing the catalytic performance.

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