Ni catalysts for hydrogen production through glycerol steam reforming: effect of the support

Michela Signoretto[1]*, Valentina Nichele[1], Federica Menegazzo[1], Francesco Pinna[1], Alessandro Gallo[2], Vladimiro Dal Santo[3], Giuseppina Cerrato[4]

[1]Università Ca' Foscari Venezia, Dorsoduro 2137, 30123, Italia. [2] Istituto di Scienze e Tecnologie Molecolari-CNR, Milano, via G. Fantoli 16/15, 20128, Italia. [3] Istituto di Scienze e Tecnologie Molecolari-CNR, Milano, via C. Golgi 19, 20133, Italia. [4] Università di Torino, via P. Giuria 7, 10125, Italia.

*e-mail: miky@unive.it

Introduction

Glycerol has recently emerged as a promising source of hydrogen, because it is cheap and renewable, so its employ for hydrogen production would be advantageous from both economical and environmental reasons [1, 2].
The steam reforming reaction of oxygenated compounds is usually affected by the formation of several by-products, that reduces the selectivity to hydrogen and leads to coke formation [3]: the design of a highly selective catalyst is then of primary importance. Several catalysts have been proposed for glycerol steam reforming; in this work we present the catalytic performances of Ni-based catalysts obtained at two different reaction temperatures, as well as the effect of the support (in particular TiO_2, SBA-15 and ZrO_2) on the selectivity to hydrogen.

Experimental

TiO_2 and ZrO_2 were synthesized by a conventional precipitation method, whereas SBA-15 was prepared through a template synthesis. Catalysts were prepared by incipient wetness impregnation of the supports with an aqueous solution of the metallic precursor, in the proper concentration in order to obtain a 10 wt% metal loading, and then calcined.
The physico-chemical properties of the catalysts were determined by nitrogen physisorption analysis (BET), O_2 chemisorption and transmission electron microscopy (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.

Results/Discussion

In Table 1 activity data in glycerol steam reforming for the Ni-based catalysts are reported.

	Time-on-stream / h					
	5		**10**		**20**	
	% Glycerol conversion	*% H_2 yield*	*% Glycerol conversion*	*% H_2 yield*	*% Glycerol conversion*	*% H_2 yield*
Ni/TiO$_2$ (500°C)	2.0	2.1	1.5	1.8	1.2	1.6
Ni/TiO$_2$ (650°C)	6.6	3.2	7.2	3.9	8.2	4.4
Ni/SBA-15 (500°C)	88.0	78.7	80.7	69.3	61.6	51.1
Ni/SBA-15 (650°C)	74.8	57.7	70.5	51.2	48.5	36.6
Ni/ZrO$_2$ (500°C)	91.4	82.9	87.6	78.7	82.2	67.5
Ni/ZrO$_2$ (650°C)	71.5	64.6	72.0	64.4	72.5	62.8

Table 1. Glycerol conversion and hydrogen yield for the three catalytic systems.

Ni/TiO_2 sample exhibits negligible activity at both temperatures. It has been ascertained that the high temperature reduction causes the collapse of the support, while the sample seems to be unstable under the reaction conditions: in fact, metallic Ni species are likely to transform into oxidic particles as a result of the reaction with glycerol/water (HRTEM evidences not reported for the sake of brevity). The SBA-15 sample, on the contrary, is highly active in glycerol steam reforming, especially at 500°C; nevertheless a significant activity decrease can be noted at both temperatures. TEM measurements revealed the total collapse of the ordered mesoporous structure of SBA-15, because of its relatively low hydrothermal stability. Ni/ZrO_2 sample shows the best catalytic performance: a little deactivation is detected at 500°C, whereas a stable glycerol conversion of ~72% and a hydrogen yield of 65% are obtained at 650°C. The characterization measurements we carried out revealed a high dispersion of the active phase on the surface of the support and a great stability of the catalyst in the reaction conditions as well.
These results evidence the key role of the support in directing the reaction towards hydrogen production, which can lead to a full exploitation of renewable resources in the perspective of a more green chemistry.

References.

1. M. Slinn, K. Kendall, C. Mallon, J. Andrews, *Biores. Technol.*, **99**, 5851 (2008).
2. F. Pompeo, G. Santori, N.N. Nichio, *Int. J. Hydr. En.*, **35**, 8912 (2010).
3. B. Zhang, X. Tang, Y. Li, Y. Xu, W. Shen, *Int. J. Hydr. En.*, **32**, 2367 (2007).