SILICA AND ZIRCONIA SUPPORTED CATALYSTS FOR THE LOW-TEMPERATURE ETHANOL STEAM REFORMING

I. Rossetti¹, J. Lasso¹, V. Nichele², M. Signoretto², E. Finocchio³, G. Ramis³, A. Di Michele⁴

¹ Dip. Chimica, Università degli Studi di Milano, INSTM Unit Milano-Università and CNR-ISTM, via C. Golgi, 19, I-20133 Milano, Italy

² Dip. di Scienze Molecolari e Nanosistemi, Università Cà Foscari Venezia, Calle Larga S. Marta, 2137, Venezia, Italy and INSTM Unit Venezia

³Dip. di Ingegneria Civile, Chimica e Ambientale, Università degli Studi di Genova, P.le J.F.

Kennedy 1, I-16129, Genova, Italy and INSTM Unit Genova

⁴Dip. di Fisica - Università degli Studi di Perugia, Via Pascoli, 06123 Perugia Corresponding author's email address: ilenia.rossetti@unimi.it

The steam reforming of ethanol raised interest for the production of H₂ from a renewable source. Broad efforts have been devoted to develop active and stable catalytic systems for this application. Differently prepared Ni-, Co- and Cu-based catalysts supported over TiO₂ have been recently tested for the steam reforming of ethanol. The results evidenced that the highest activity may be reached in general with Ni as active phase, but its tendency to form C filaments remains a key problem, besides coking due to support acidity [1,2]. It was also underlined that the interaction strength between the support and the active phase, tunable with the preparation procedure, determines the success of a formulation [3-5]. It was repeatedly shown that Ni is much more stable against coking when prepared in very dispersed form [6,7]. The possibility to disperse (and stabilize in dispersed way) the metal depends on the preparation method but also on the support. ZrO₂ and SiO₂ showed interesting supports for Ni, provided the right preparation route is chosen. Therefore, in this work we investigated different Ni-, Co- and Cu-based catalysts supported over ZrO₂ or over a mesoporous SiO₂ with SBA-15 structure. All the samples were calcined at 500°C in order to keep the active phase as dispersed as possible and we focused on low temperature activity testing in the temperature range 300-500°C. Complementary catalyst characterization by means of various techniques allowed to compare the main physical-chemical properties of the catalysts and to comment activity data.

The present data confirm Ni-based ones as the most promising catalyst for this reaction, especially at 500°C. Attention was particularly paid to the resistance to coking, possibly deriving from polymeric species forming mainly over acidic sites of the support or from the formation of carbon nanotubes (CNTs) over the active phase. Both Co and Ni led to the formation of CNTs, but in the latter case this phenomenon was tightly dependent on the support and its interaction with the active phase. The strongest the metal-support interaction, evidenced by a lower reducibility of the metal ions, the highest the resistance to coking, mainly due to smaller Ni particle size.

References. [1] Díaz Alvarado, F. & Gracia, F. (2010): *Chem. Eng. J.*, **165**, 649; [2] Lima da Silva, A., de Fraga Malfatti, C., Müller, I. (2009): *Int. J. Hydrogen Energy*, **34**, 4321; [3] Rossetti, I., Biffi, C., Bianchi, C.L., Nichele, V., Signoretto, M., Menegazzo, F., Finocchio, E., Ramis, G., Di Michele A. (2012): *Appl. Catal. B*, **117-118**, 84; [4] Rossetti, I., Gallo, A., Dal Santo, V., Bianchi, C.L., Nichele, V., Signoretto, F., Finocchio, E., Ramis, G., Di Michele A. (2013): *ChemCatChem*, **5**, 294; [5] Finocchio, E., Rossetti, I., Ramis, G., (2013): *Int. J. Hydrogen Energy*, **38**, 3213; [6] Centi, G., Perathoner, S. (2009): *Catal. Today*, **148**, 191; [7] Gonzalez-De la Cruz, V.M., Holgado, J.P., Pereniguez, R., Caballero, A. (2008): *J. Catal.*, **257**, 307.