**Catalytic activity of Si-modified Ni/Al2O3 catalysts for CO2 hydrogenation to methane**

Elena Spennati1, Paola Riani\*2, Guido Busca1, Gabriella Garbarino1\*

*1 Department of Civil, Chemical and Environmental Engineering, University of Genoa, Via Opera Pia 15, 16145 Genoa, Italy*

*2 Department of Chemistry and Industrial Chemistry, University of Genoa, via Dodecaneso 31, 16146, Genoa, Italy*

*\*Corresponding authors E-Mail: gabriella.garbarino@unige.it, paola.riani@unige.it*

**1. Introduction**

Nowadays, environmental pollution represents one of the main international concerns. In this context, CO2 emissions achieved the remarkable value of 31.5 Gt in 2021, increasing greenhouse gases concentration and correlated global warming [1]. A possible strategy to mitigate this environmental problem is the conversion of CO2 into methane by the Sabatier reaction using green hydrogen i.e., arising from renewables. Conventional catalysts for this application are based on Ru- and Ni- [2-6]. Thanks to their high activity and robustness, the low cost of Ni and its remarkable natural abundance, Ni-based catalysts represent a suitable choice for Sabatier reaction. Several supports have been investigated to enhance the catalytic performances i.e., Al2O3, SiO2 [7], TiO2, zeolites etc [8]. However, Ni-based catalysts showed low activity at low temperature, low dispersion of the active phase and, high deactivation mainly due to particles sintering or coking. For these reasons, the study for the possible industrial application of nickel-based catalysts requires further efforts in order to make them more efficient and competitive than noble metals-based catalysts. In this work [9], a series of Ni-based catalysts (from 1 to 33 wt. % NiO) was prepared and the influence of the addition of SiO2 to Al2O3 supports was investigated.

**2. Methods**

The series of Ni-based catalysts with NiO content ranging from 1 to 33 wt.% were prepared by incipient wetness impregnation over commercial silica-alumina with different silica content, 1 and 20 wt.% (SA01 and SA20, respectively) and pure silica (S100), by relying on comparison with Ni/Al2O3 [10]. Ni(NO3)2·6H2O was used as precursor salt. The precursor solution was added to the support and dried at 353 K for 12 hours, then the catalysts were calcinated at 1023 K for 5 hours with a heating ramp of 2 K/min. Fresh and exhaust catalysts were characterized by means of XRD, FE-SEM, FT-IR, and UV-Vis techniques. Before the catalytic test, 88 mg of catalyst was mixed with 700 mg of quartz sand, placed into a fixed-bed silica glass reactor, and reduced in situ at 1023 K for 30 minutes in a reducing environment (20% v/v of H2 in N2, total flow 80 NmL/min) with a heating ramp of 25 K/min. The catalytic tests were performed in N2 diluted flow with an H2/CO2 ratio of 5. The reaction temperature was increased from 523 to 773 K (ascending temperature test) and decreased from 773 to 523 K (descending temperature test), in order to assess stability and eventual deactivation effects. The products composition was analyzed online by means of a FT-IR spectrophotometer.

**3. Results and discussion**

The addition of silica to the support led to a reduction of catalytic activity at all the investigated NiO loading, as observed in Figure 1, where the CH4 yields obtained using the catalysts with 16 wt.% of NiO over the investigated supports are reported. Above 673 K, all catalysts approached the forecasted thermodynamic equilibrium evaluated in the chosen experimental conditions by using a Gibbs reactor and Redlich- Kwong-Soave equation of state.

It is possible to observe that, at low temperature (T<623 K), only the catalyst with the lowest SiO2 content produced a remarkable methane yield (23% at 573 K). Moreover, only at high temperature (673 K, around the thermodynamic equilibrium) it was obtained a sufficient amount of CH4 yield using Ni/S100 (27%), even if its performances are significantly lower than that one obtained by using SA01 and SA20 (73 and 66%, respectively). On the other hand, an increase of Ni loading in the catalysts enhanced the catalytic activity with a positive effect towards methanation reaction and a negative effect on reverse water gas shift reaction, leading to the production of CO. The CH4 yield obtained at 623 K using SA01 was increased from 1 to 74% by increasing the NiO content from 1 to 33%. This effect has been further investigated by kinetic measures carried out in differential reactor conditions together with the determination of apparent activation energies.



**Figure 1.** Methane yield obtained using the catalyst with 16 wt.% of NiO load over SA01, SA20 and S100.

**4. Conclusions**

Silica addition is beneficial at very low loadings, but it reduces the catalytic activity towards carbon dioxide methanation. At the same time, it slightly enhances the production of carbon monoxide, thus leading to the careful determination in-between improved catalysts stability, optimum nickel loading, high CO2 conversion and methane selectivity. The best nickel loading for the CO2 methanation over all the investigated supports was the 16 wt.% NiO. Among tested catalytic materials, 16 wt.% NiO supported on SA01 resulted the best catalyst in terms of both catalytic and morphological point of view, by achieving a methane yield of 73% at 673 K at atmospheric pressure and at a GHSV of 55000 h-1.

**References**

1. Iea.org/reports/global-energy-review-2021/CO2-emissions
2. G. Garbarino, P. Riani, L. Magistri, G. Busca, Int. J. Hydrog 39 (2014) 11557-11565
3. G. Garbarino, D. Bellotti, P. Riani, L. Magistri, G. Busca, Int. J. Hydrog 40 (2015) 9171-9182
4. G. Garbarino, D. Bellotti, E. Finocchio, L. Magistri, G. Busca, Catal. 277 (2016) 21-28
5. G. Garbarino, F. Pugliese, T. Cavattoni, G. Busca, P. Costamagna, Energies 13 (2020) 2792
6. G. Garbarino, P. Kowalik, P. Riani, K. Antoniak-Jurak, P. Pieta, A. Lewalska-Graczyk, W. Lisowski, R. Nowakowski, G. Busca, I. S. Pieta, Ind. Eng. Chem. Res. 60 (2021) 6554-6564
7. F. Meirer, B.M. Weckhuysen, Nat. Catal. 1 (2018) 127–134.
8. W. Gac, W. Zawadzki, M. Rotko, M. Greluk, G. Słowik, G. Kolb, Catal. Today 357 (2020) 468–482.
9. P. Riani et al., Effect of Si- in the formulation of Ni-based catalysts for Sabatier reaction, Manuscript in preparation.
10. G. Garbarino, C. Wang, T. Cavattoni, E. Finocchio, P. Riani, M. Flytzani-Stephanopoulos, G. Busca, Appl. Catal. B 248 (2019) 286-297.