**Effect of temperature on NiAl2O4 catalyst stability in the steam reforming of raw bio-oil**

Aingeru Remiro\*, Naiara García-Gómez, Beatriz Valle, Lide Oar-Arteta, Javier Bilbao, Ana G. Gayubo

*Dept. Chemical Engineering, University of the Basque Country, 48080 Bilbao, Spain*

*\*Corresponding author: aingeru.remiro@ehu.eus*

**Highlights**

* 600 and 700 ºC are suitable temperatures for enhancing NiAl2O4 catalyst stability
* Ni sintering is avoided at 600 ºC and coking is minimized at 700 ºC
* Temperature significantly affects the nature of the coke and its impact on catalyst porous structure
* Coke deposition affects more severely the porous structure at 650 ºC, thus causing a faster deactivation

**1. Introduction**

Among the alternatives for sustainable hydrogen production, the steam reforming (SR) of bio-oil obtained by pyrolysis of lignocellulosic biomass is a promising route with a low environmental impact because of neutral CO2 balance [1]. One of the main problems of bio-oil SR is the deposition of carbonaceous material that causes reaction equipment clogging and rapid catalyst deactivation. In order to improve its economic viability, research effort has been focused on the development of process strategies that improve the operability (minimizing clogging) and new catalysts with high resistance to deactivation and capability to be completely regenerated. In a previous work [2], the suitability of a bulk NiAl2O4 catalyst was highlighted, especially for its efficient regeneration at high temperature. The aim of this work is to establish an optimum reaction temperature for enhancing the H2 production and attenuating deactivation of bulk NiAl2O4 catalyst in the SR of bio-oil.

**2. Methods**

The raw bio-oil, obtained by flash pyrolysis of pine sawdust, was supplied by BTG Bioliquids BV (The Netherlands). The bulk NiAl2O4 catalyst (with 33 wt% Ni) was synthesized by the co-precipitation method, calcined at 850 ºC for 4 h and sieved between 150-250 µm. Fresh and deactivated catalysts have been characterized by N2 adsorption-desorption (porous structure), transmission electron microscopy (TEM) and X-ray diffraction (XRD) (metal properties) and temperature programmed oxidation (TPO) (amount and nature of the coke). The catalytic runs were performed in an automated reaction equipment (Microactivity Reference) provided with two steps (thermal +catalytic) in series [3]. The controlled deposition of pyrolytic lignin in the thermal step at 500 ºC minimizes operation problems and catalyst deactivation in the subsequent catalytic step. The latter has been carried out in a fluidized bed, with steam/carbon (S/C) molar ratio of 6 and space time of 0.15 gcatalyst/gbio-oil. Prior to each reaction, the catalyst is reduced *in situ* (with 10% v/v of H2 in N2) for 4 h at 850 ºC.

**3. Results and discussion**

The evolution with time on stream (TOS) of bio-oil conversion and H2 yield for different reaction temperatures (Figure 1a) show a slower and similar deactivation rate at 600 and 700 ºC, whereas the deactivation is faster at 650 ºC. This unusual result differs from that previously reported in bio-oil SR with Ni/La2O3-αAl2O3 supported catalyst [4], whose deactivation was attenuated by increasing temperature in the 600-700 ºC range. This different kinetic behavior suggests different deactivation mechanism for bulk NiAl2O4 catalyst and Ni/La2O3-αAl2O3 supported catalyst.

 

**Figure 1.** Effect of temperature on the evolution with TOS of conversion and H2 yield (a) and on the TPO profile of the deactivated catalyst (b). Reaction conditions: S/C = 6, space time of 0.15 gcatalyst/gbio-oil.

The XRD analysis of deactivated catalysts evidences that Ni sintering is incipient at 650 ºC and noticeable at 700 ºC. TPO analysis (Figure 1b) shows the formation of two different types of coke, which depends on the reaction temperature. An encapsulating coke that burns at low temperature is deposited at 600 ºC, whereas at 650 and 700 ºC a more condensed coke is deposited on the support, which partially blocks the porous structure. Both types of coke contribute to catalyst deactivation. The lower deactivation observed at 700 ºC compared to 650 ºC is explained by the promotion of coke gasification and a lower impact of coke on the porous structure of the catalyst.

**4. Conclusions**

The bulk NiAl2O4 catalyst undergoes greater deactivation during the SR of bio-oil at 650 ºC compared with that observed at 600 ºC and 700 ºC, because Ni sintering is avoided at 600 ºC, whereas coke deposition is attenuated at 700 ºC. It is concluded that 600 ºC is the optimum temperature for SR of bio-oil with bulk NiAl2O4 catalyst because it is suitable for attaining slightly higher H2 yield than at 700 ºC (because of WGS promotion), with lower energy requirement, and moreover, it is also suitable for strategies that enhance H2 selectivity (e.g., sorption enhanced steam reforming and membrane reactor).

**References**

1. W. Nagban, T.A.T. Abdullah, R. Mat, B. Nabgan, Y. Gambo, M. Ibrahim, A. Ahmad, A.A. Jalil, S. Triwahyono, I. Saeh, Renew. Sust. Energy Rev. 79 (2017) 347–357.
2. A. Remiro, A. Arandia, L. Oar-Arteta, J. Bilbao, A.G. Gayubo, Appl. Cat. B 237 (2018) 353–365.
3. A. Remiro, A. Arandia, J. Bilbao, A.G. Gayubo, Energy Fuels 31 (2017) 7147–7156.
4. B. Valle, B. Aramburu, M. Olazar, J. Bilbao, A.G. Gayubo, Fuel 216 (2018), 463–474