Evaluation of Ni metallic states in Ni/Al_2O_3 catalysts obtained by chemical routes and magnetron sputtering

Laboratory of Surface Treatments

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INTRODUCTION: Supported-metal catalysts are commonly used in the chemical industry from fine chemical production to petrochemicals and generally consist of metallic particles, known as active phase, dispersed on the surface of a metallic oxide support with different geometrical formats[1,2]. They are usually produced by chemical routes that involve processes like thermal sintering in air, leading to decreasing of the catalyst activity due to the increase of metal oxides on its surface[1,2], where the production of catalysts in vacuum or inert environment such as those in magnetron sputtering systems (MS) may be an alternative to solve this issue[2]. Thus, the concentration of Ni metal states in Ni/Al_2O_3 catalysts produced by washcoating and MS was evaluated by X-ray photoelectron spectroscopy in this work.

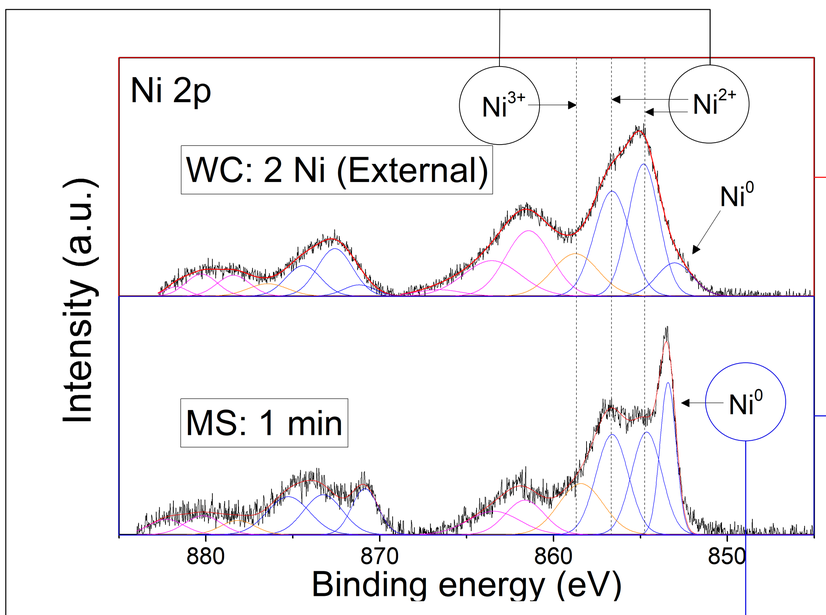
MATERIALS AND METHODS

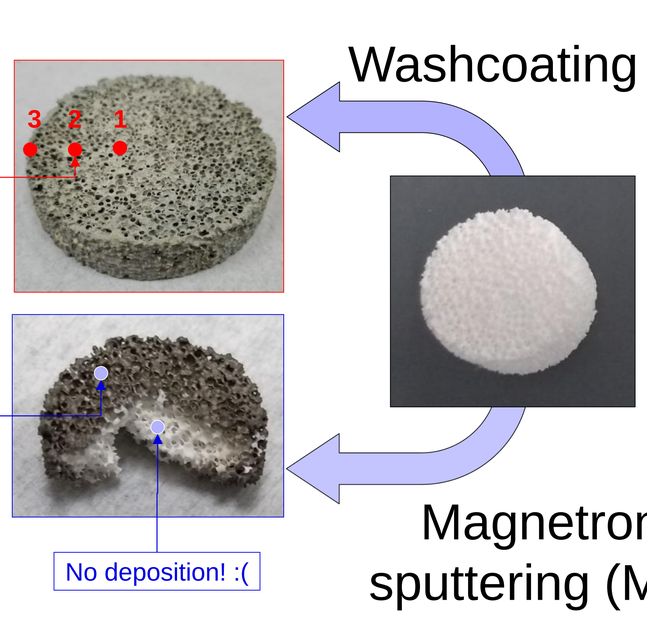
Ni/Al_2O_3 catalysts produced by magnetron sputtering: Al_2O_3 foams with 26 pores/cm, 12.7 mm thick, 15 mm in diameter and mean pore size of 0.4 mm. Ni films were made on both sides of alumina foams by magnetron sputtering using a DC Pinnacle Plus power supply as function of the deposition time (1, 3 and 5 min) with only one sample produced in each condition. The working pressure, Ar mass flow rate, target-to-substrate distance, target current and applied voltage was kept at 3.0 mTorr (0.4 Pa), 2.5 sccm, 7.0 cm, 1.0 A and 600 V, respectively, resulting in a Ni deposition rate of 120 nm/min.

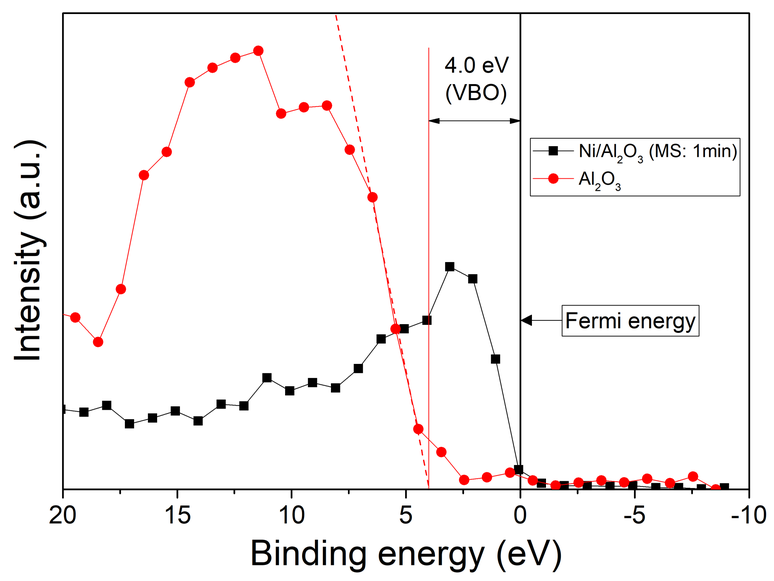
Ni/Al_2O_3 catalysts produced by magnetron sputtering: Al_2O_3 foams with 26 pores/cm, 12.7 mm thickness and 80 mm diameter were used. Samples were dried at 110 ºC for 1 h and immersed for 1 min in a paste composed of 40% Al_2O_3, 1% Na_2SiO_3, 1% HNO_3, and 58% distilled water. Monoliths were dried at 110 ºC for 1.5 h and calcinated at 600 ºC for 2 h and Ni particles were impregnated using aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$ with a concentration of 2.5 M for 16 h, dried at 150 °C for 12 h and calcinated for 2 h at 600 °C. Two samples were prepared with one and two layers of Ni impregnated by washcoating (before drying) being designated as 1Ni and 2Ni samples, respectively. XPS analyses were done on three different surface points in either external or internal parts of the monoliths to evaluate the uniformity of the chemical states.

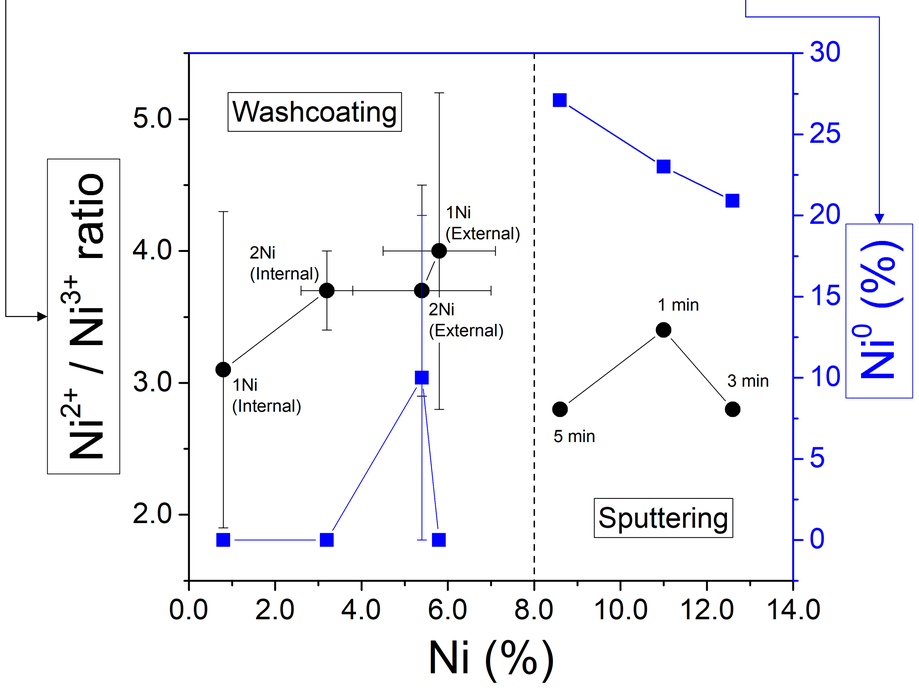
Investigations by XPS: The chemical composition and electronic structure was evaluated by X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha) from measurements of high-resolution spectra for the Ni2p, Al2p, O1s and C1s orbitals. The valence band was also investigated from the density of states measured between –10 and 30 eV.

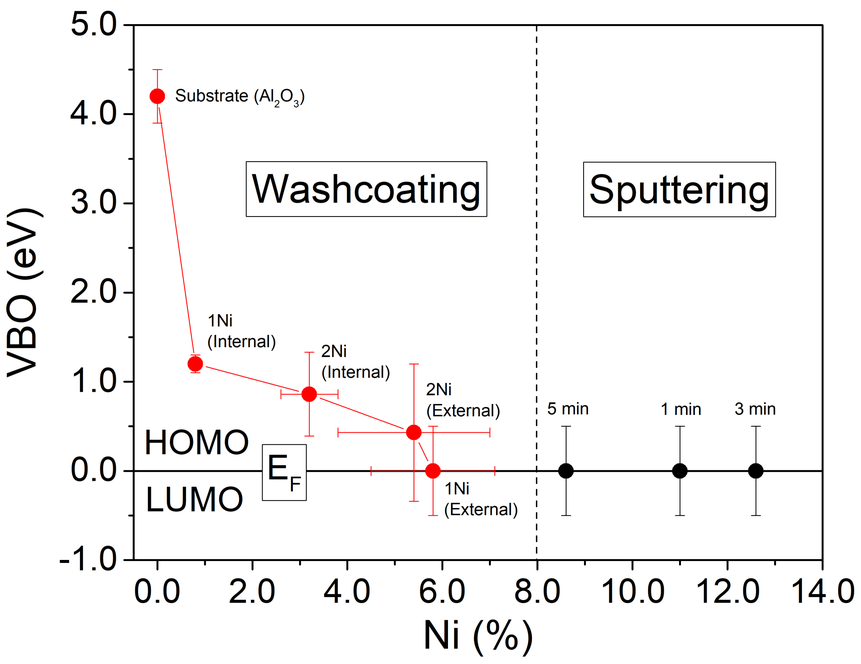
RESULTS AND DISCUSSIONS











VBO decreasing is assigned with the increase of the metallic behavior

* Ni^0 = metal; Ni^{2+} = Ni-O and $Ni(OH)_2$; Ni^{3+} = NiOOH

General comments:

- Catalysts produced by MS present:
  - high concentration of Ni^0 states;
  - metallic surface;
  - negligible concentration of Ni inside the catalyst.
- Catalysts produced by WC present:
  - low concentration of Ni^0 states ;
  - reduced gradient of Ni between external and internal parts of the catalyst after two impregnations;
  - increase of the metallic behavior after two impregnations.

REFERENCES
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2. A. M. Santos et al., Vacuum 200, 111042 (2022)