

## Nanostructured Ni/SiO<sub>2</sub> Catalyst and its Activity for Non-Oxidative Methane Activation

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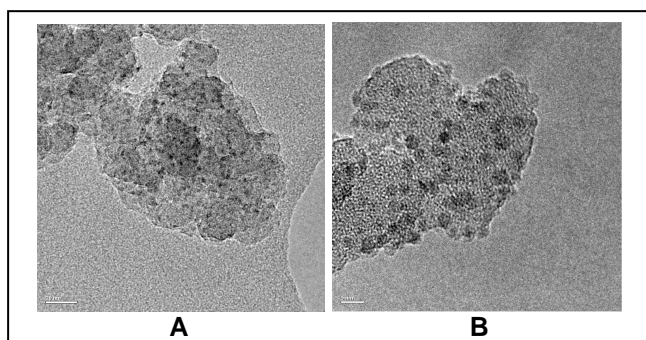
**Abstract** – In this work we describe the synthesis and characterization of highly dispersed nanophase nickel supported catalyst and its activity for non-oxidative methane activation. The catalyst was prepared using impregnation of nickel acetate on silica, followed by reduction with sodium borohydride and a thermal-oxidizing treatment for redispersion of nickel phase. After reduction of metallic phase with H<sub>2</sub> the catalyst presented a narrow size distribution with mean diameter of 3,5 nm. Experiments of methane activation with the oxidized and later reduced catalyst presented ten times more activity than the reduced precursor.

From the point of view of chemical utilization of natural gas, methane conversion into valuable products such as hydrogen, synthesis gas and higher hydrocarbons has been extensively examined in the last three decades. Methane dissociation, activation, is considered the determinant step in natural gas processing. As most of the previous work in the field of methane activation was performed on model catalyst surfaces, here we intend to study the behavior of real catalyst based on nickel nanoparticles over methane activation process in non-oxidative conditions. In this work we describe the synthesis and characterization of a highly disperse nanophase nickel supported catalyst and its activity in non-oxidative methane activation.

The Ni/SiO<sub>2</sub> catalyst was first prepared by impregnation of nickel acetate on silica, followed by reduction with sodium borohydride in aqueous solution. This precursor was then subjected to a mild oxidation process consisting of a thermal treatment at 383 K associated to homogenization procedure. The catalyst (Ni/SiO<sub>2</sub>) and precursor (NiB/SiO<sub>2</sub>) were characterized by X ray diffraction, transmission electron microscopy. The catalytic activity in non-oxidative methane activation was evaluated by chemisorption of CH<sub>4</sub> in the temperature range of 200 C – 500 C, followed by hydrogenation of adsorbed species. The adsorbed methane was quantified using mass spectrometry analysis of the products evolved during hydrogenation.

The reduction of the silica support impregnated with nickel acetate, a green solid, with sodium borohydride led to a black solid consisting of amorphous phase of nickel and boron over silica (NiB/SiO<sub>2</sub>), characterized by the absence of diffraction pattern. After thermal treatment the solid turned to a green color again. XRD analysis showed the presence of reflections associated to the formation of an incipient structure of lamellar nickel hydroxide and lamellar nickel hydrossilicate on silica surface as described by Leroy et. al [1] on the hydrothermal synthesis of nickel hydrossilicate with antigorite-like structure. Activation of metal phase with H<sub>2</sub> at 500 C is required before the catalytic evaluation. TEM images of reduced catalyst show (Figure 1) a highly dispersed catalyst with mean particle size of 3,5 nm, while its precursor (NiB/SiO<sub>2</sub>) presented wide range of diameters and bigger particles, with mean size diameter of 15 nm barely dispersed over the support.

The evaluation of catalytic activity on non-oxidative methane activation with the oxidized and then reduced catalyst presented ten times more activity than its precursor reduced with borohydride.



**Figure 1:** TEM images of the catalyst Ni/SiO<sub>2</sub> after oxidizing treatment and reduction with H<sub>2</sub> at 500 C: A) Scale bar: 20 nm; B) Scale bar: 5 nm.

### References

[1] P. Leroy, F. J. C. S. Aires, T. G. de Monsabert, H. Dijon, J. L. Rousset, J. C. Bertolini Appl. Catal. A. 294 (2005) 131-140.