

Theoretical study of the methane decomposition catalyzed by niobium doped nickel oxide: thermodynamic profile and reaction mechanism

Authors: Maíra dos Santos Pires⁽¹⁾, Livia Clara Tavares Lacerda⁽¹⁾, Telles Cardoso Silva⁽¹⁾, Silviana Corrêa⁽¹⁾, Francisco Guilherme Esteves Nogueira⁽²⁾, Alexandre Alves de Castro⁽¹⁾, Teodorico de Castro Ramalho⁽¹⁾.

Address: ⁽¹⁾ *Laboratory of Molecular Modeling, Department of Chemistry, Federal University of Lavras, CEP 37200-000, Lavras-MG, Brazil.*

⁽²⁾ *Department of Chemistry, University of São Paulo, Institute of Chemistry of São Carlos, São Carlos Campus. CEP 13566-590, São Carlos-SP, Brazil.*

Abstract:

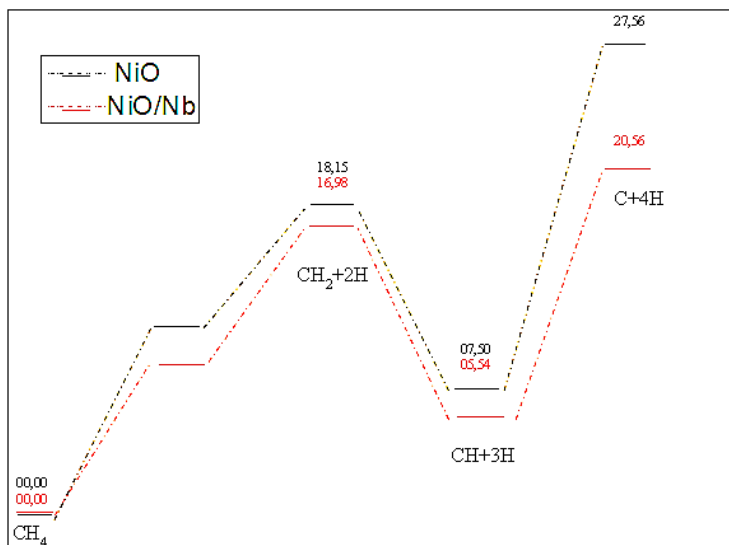
The formation of carbon nanofibers (CNF) and carbon nanotubes (CNT) can be attributed to the ability of NiO to decompose hydrocarbons, mainly methane (CH₄). This process includes the activation and the CH₄ decomposition in the crystallographic Ni (100) and Ni (110) planes, and the CNF germination in the Ni (111) plane [1]. According to experimental studies, the addition of Nb₂O₅ in these catalysts can increase the intensity of the active planes, favoring the CH₄ decomposition [2]. In this context, the goal of this work is to investigate, through theoretical calculations, the properties of the material after doping with Nb. All calculations were performed using the ADF-BAND package, with application of the DFT method at the GGA-PBE level and TZP basis set. The structures of the pure and niobium doped NiO catalysts were indexed in the (100), (110) and (111) planes. The addition of Nb conferred greater stability to the compound in all analyzed planes. This variation was of 186.15, 186.20 and 167.70 kcal/mol to lower energy values, in the (100), (110) and (111) planes, respectively. For the adsorption study, the methane molecule was optimized in contact with the (111) plane of the NiO and NiO/Nb catalysts at different distances. The methane adsorption begins to take place on the surfaces at a distance of approximately 4 Å and reaches the minimum energy at 3 Å. However, on the Nb doped catalyst, the equilibrium geometry occurs at an adsorption energy of 9.92 kcal/mol larger than on pure NiO. As for the proposed mechanism, the study suggests that the carbon deposition on the catalyst starts with adsorption, followed by a series of steps of methane dissociation on the metal surface, leading to the formation of several adsorbed species and, finally, carbon and hydrogen. From now on, it takes place the growth of the crystalline carbon. The potential energy surface of the dissociation catalyzed by NiO, in black, and by NiO/Nb, in red, is then obtained.



XIX SBQT

Simpósio Brasileiro de Química Teórica 2017

12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil



It is found that the CH₄ dissociation into carbon and hydrogen by the modified surface is favored thermodynamically with respect to the pure catalyst at all stages. This behavior may be related to the existence of a synergistic effect between Ni and Nb, which results in improved catalytic performance of the modified structure throughout the dissociation. Thus, the theoretical results indicate that the modification of the NiO structure caused by the presence of Nb can bring about improvements in the activity of this material in methane decomposition reactions and subsequent formation of CNF and CNT.

Key-words: *DFT, Nickel oxide, Methane decomposition, CNF, CNT.*

Support: This work has been supported by FAPEMIG and FAPESP.

References:

- [1] K. P. De Jong; J. W. Geus Catal. Rev.-Sci Eng. **2000**, 42, 481
- [2] Li, J. Z.; Lu, G. X.; Li, K. Chemistry Letters **2004**, 33, 652.