

Oxidative insertion and activation of the C-H bond of methane by niobium oxides NbO_m^{n+} ($m=1, 2$; $n=0, 1, 2$)

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Abstract: Transition metal oxides are considered as prototype models of reactions involving oxidative processes [1]. In this way, the detailed understanding of their electronic and molecular structure is of great interest in the prediction of their catalytic behavior and chemical reactivity toward inert organic molecules which are of industrial interest. In particular, it is possible to highlight the selective oxidation of methane to methanol by transition metal oxides in the gas phase [2]. Therefore, the present computational study intends to evaluate the efficiency of niobium oxides in the methane activation process. Optimization and frequencies calculations were performed using relativistic effective pseudopotentials (ECPs) for transition metals at B3LYP and CCSD (T) levels. For the oxygen and carbon atoms, an extended polarized basis set of 6-311++G(d, p) type was employed. Binding analyzes were performed using the Bader's Theory of Atoms in Molecules (AIM) and Natural Bond Orbitals (NBO) calculations. All calculations were performed in the Gaussian 09 program, with the exception of the AIM calculations that were performed in the AIM2000 program. Posteriorly, the oxidative insertion mechanism of the niobium oxides for the methane binding was investigated; analyzing all the possibilities of molecular precursors, transition state and reaction products. The reaction intermediates and transition states were characterized by vibrational frequency calculations. According to our results, there is a decrease in bonding lengths over the series of monoxides and dioxides. The calculated vibrational frequencies are in good agreement with the experimental values for the Niobium oxides [3]. According to the NBO calculations, a greater contribution is observed for the 4d orbital in the chemical bonds of the monoxide and 5s for the dioxide. According to the AIM calculations, the Bond Critical Point (BCP) is located at the center of the niobium oxides binding; the AIM parameters found point to an ionic and partial covalent character of the bonds of these oxides. The initial electrostatic interaction between methane and niobium oxides based on binding energy values is favored by the increase of oxo-coordinated ligands at the metal center and by the increase of their charge. The oxidative insertion energies of the niobium oxides at the C-H bond of methane are shown in Table 1.



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Table 1. Activation barriers (ΔE_{act}) and reaction energies ($\Delta E_{\text{reaction}}$) in kcal/mol for the oxidative insertion of niobium oxides at the C-H bond of methane.

| Species | ΔE_{act} | | $\Delta E_{\text{reaction}}$ | |
|--------------------------------|-------------------------|---------|------------------------------|---------|
| | B3LYP | CCSD(T) | B3LYP | CCSD(T) |
| NbO | 23.68 | 25.81 | -28.12 | -27.41 |
| NbO ⁺ | 37.86 | 40.55 | -15.62 | -17.76 |
| NbO ²⁺ | 50.20 | 50.61 | -10.11 | -13.27 |
| NbO ₂ | 31.80 | 33.01 | -29.85 | -32.62 |
| NbO ₂ ⁺ | 49.96 | 51.13 | -21.68 | -22.98 |
| NbO ₂ ²⁺ | 63.96 | 65.18 | -13.59 | -15.01 |

The activation barrier results indicate that the increase in the number of oxo-coordinated ligands at the metal center does not favor the kinetics of the methane activation. As regards the thermodynamics of the reaction, it can be observed that the reaction of niobium oxides with methane is exothermic. The theoretical results indicate that the kinetics of the methane activation processes is not favored due to the increase of oxo-coordinated ligands to the metal. Among the oxides investigated, NbO²⁺ shows better thermodynamic and kinetic conditions to react with methane in the gas phase.

Key-words: Niobium Oxides, Methane, Theoretical Calculations, Catalytic Effects

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