

Theoretical and experimental study of the CO₂ hydrogenation over Ni-Co catalyst

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Abstract Carbon dioxide is one of the most abundant pollutants at the industrial and domestic levels and has been pointed out as an important contributor to the global climate change and ocean acidification processes. However, provided the adequate catalyst and proper conditions, those pollutants serve as building blocks for more valuable compounds such as waxes, gasoline or methane, which is an efficient and environmentally friendly energy carrier. Now, since the overall performance of catalysts fundamentally depends on the structure and interactions at the molecular scale, an appropriate insight of the reaction mechanisms involved is required to screen and optimize catalysts.

In this work it is proposed that there is a synergistic effect in bimetallic Ni-Co alloy surfaces for the reaction of methanation of CO₂, i.e. enhanced performance in terms of activity, selectivity and stability compared to the monometallic Ni or Co catalyst. Emphasis is made on the theoretical description of reaction energetics along proposed mechanisms (current stage) employing periodic surface models under a density functional theory (DFT) treatment. Polarized DFT calculations using the revised PBE functional and dispersion corrections (rPBE-D3BJ) were considered as implemented in the VASP code.

Convergence of numerical and geometrical parameters has been considered. Dispersion corrections (needed for an appropriate description of chemisorbed *CO₂ species) led to systematic underestimation of lattice parameters. Model highly coordinated surfaces of fcc Ni, Co and ordered Ni-Co alloy (1:3, 1:1 and 3:1 proportions) were constructed. Site distributions were obtained from model clusters of different sizes constructed as Wulff polyhedral. Electronic and geometrical activity descriptors such as d-band center and generalized coordination numbers have been explored for future ponderation of the model surfaces contribution to global (experimentally observable) trends. Preferred adsorption sites and formation energetics of possible early intermediates (i.e. *COOH, *HCOO, *CO, *O) of the CO₂ methanation reaction at different coverages, as well as kinetics of surface *C diffusion and hydrogenation, have been studied on the most abundant surface ([111], according to Wulff constructions) for Ni, Co and the ordered equimolar Ni-Co surfaces.