

DFT modelling of mixed oxide selective catalysts for oxidative dehydrogenation of ethane

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Introduction

Ethane oxidative dehydrogenation (E-ODH) catalysts having activity and selectivity which are high enough to compete satisfactorily with other ethylene production technologies available today are being actively sought worldwide. One of the systems proposed in recent years is based on NiO which, by incorporation of niobium and similar elements, improves largely selectivity while keeping high catalytic activity [1]. Basic understanding of this system is still scarce; here first principles calculations are undertaken to clarify the reasons for this improved performance. Ongoing modelling of other proposed systems like MoVNbTeO_x [2] will be presented as well.

Methods

Spin-polarized DFT-type calculations were carried out using program VASP, which expands the electronic density and orbitals in a plane wave basis and represents atomic cores with the PAW method. A standard PBE GGA functional, with on-site Hubbard correction for the Ni atoms (DFT+U method, U_{Ni}= 5.3 eV), was used together with periodic slab models to represent the catalyst surfaces. For the MoVNbTeO_x the M1 phase was studied through a model, developed in this laboratory, having half-sized crystalline cell but topologically equivalent structure

Results/Discussion

NiO tends to be nonstoichiometric, containing cation vacancies in the rocksalt structure (i.e. a Ni_{1-x}O description). The DFT+U calculations confirm that both Ni³⁺ and O⁻ species, known to promote combustion, result in this structure; but if Nb substitutes partially for Ni it is possible (for a given Nb:vacancy ratio) to suppress the formation of both Ni³⁺ and O⁻, which may explain the improved selectivity.

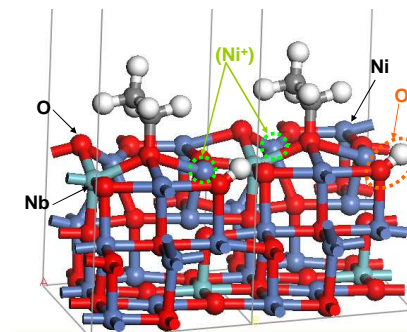


Fig. 1 Slab model of a (100) surface of (Nb,Ni)O_x, showing the optimized configurations of C₂H₅ (as ethoxy) and H (as OH) adsorbed species resulting from H atom abstraction from ethane.

Adsorption of ethyl + H species on a slab model of the (001) surface having Nb₂□₃Ni₁₃O₁₈ stoichiometry (□=cation vacancy) (Fig. 1) reveals a more favourable energetics for the rate controlling H abstraction step than on pure NiO; this difference seems to arise from both oxygen undercoordination (also effective in surface steps) and polarization/distortion by the Nb atoms. Still, adsorption is predicted to be highly endothermic in the absence of some excess oxidation degree; optimal behaviour seems thus to depend critically on the control by Nb of the residual amount of catalyst overoxidation in each experimental environment.

In the case of MoVNbTeO_x, a model has been developed having a Mo₁₅V₃Nb₂Te₂O₅₈ composition in the unit cell, the M=O bond orientations being optimized by molecular dynamics. It is shown that this stoichiometry keeps V and Nb fully in the V⁴⁺ and Nb⁵⁺ states respectively (in agreement with experiment), being accompanied by some Mo⁵⁺, and that these latter ions, not V⁴⁺, are first ones to be oxidized by O adsorption, as shown with a 160-atom two-layer periodic slab model. Work on the optimal configuration of adsorbed species is in progress.

References.

1. E. Heracleous and A. A. Lemonidou, *J. Catalysis*, **270**, 67 (2010) 67; and references therein.
2. P. Botella, A. Dejoz, M.C. Abello, M.I. Vázquez, L. Arrúa and J. M. López Nieto, *Catal. Today* **142**, 272 (2009)