Hydroxyl groups and undercoordinated aluminium sites at the external surface of ferrierite zeolite investigated by DFT and ML approaches

Emeline SOLA[1], Monika GEŠVANDTNEROVÁ[2,3], Adrien LEDUC[1], Katarina SKLADANOVÁ[3], Jerome REY[2], Thomas PIGEON[1], Tomáš BUČKO[3,4], Michael BADAWI[2], Céline CHIZALLET[1]

[1]IFP Energies nouvelles, Rond-Point de l'échangeur de Solaize, BP3 69360 Solaize (France)
[2]Université de Lorraine, CNRS L2CM, F-54000 Nancy (France)
[3]Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská Dolina, SK-84236 Bratislava (Slovakia)
[4]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská Cesta 9, SK-84236 Bratislava (Slovakia)

Dehydration of bio-sourced alcohols catalyzed by acidic zeolites is a key reaction in the synthesis of valuable alkene intermediates from renewable sources. However, notable variations in efficiency and selectivity were observed depending on the structure of the zeolite employed. In particular, ferrierite zeolites display remarkable selectivity towards linear butenes in the dehydration of isobutanol. [1, 2] This observation is all the more striking as this catalyst is well known for effectively catalyzing the isomerization of linear alkenes into isobutene. Moreover, experimental studies demonstrated that isobutanol cannot enter the pores of ferrierite and interacts only with its external surfaces. [2] Therefore, an in-depth study of the external surfaces of ferrierite is needed to understand this singular behavior.

In the present work, atomic-scale models of ferrierite (100), (010) and (001) external surfaces were built in order to study their reactivity regarding the dehydration of isobutanol. First, on each surface, the relative stability and acidity of both protonated Brønsted acid sites and dehydrated Al_{III} sites, behaving as Lewis acid sites, were assessed through static DFT computations (periodic calculations with VASP). It appeared that dehydration of Al-H_2O sites can lead to the formation of either three-coordinated (Al_{III}) or tetra-coordinated (Al_{IV}) aluminium atoms, with their stability depending on the hydrogen bonding network in presence on the surface considered. However, these results strongly depend on the thickness of the surface slabs considered, as static calculations are sensitive to small structural variations within slabs of varying thicknesses.

To gain a more comprehensive view and draw accurate conclusions, dynamic simulations are mandatory. Nevertheless, given the large cell sizes required to correctly describe external surfaces, ab initio molecular dynamics (AIMD) cannot be employed as such. Therefore, to address this at a reduced computational cost, a MACE-MPA foundation model [3] was fine-tuned on short AIMD data in order to obtain an accurate machine learned interatomic potential (MLIP). The model shows reasonable accuracy with respect to standard DFT for a set of validation data. It will be further tested on long dynamics of thick slabs, not doable with DFT, to determine more reliable estimation of the respective stability of hydrated and dehydrated sites, and in a second step to compute the reaction rate of key-steps of the dehydration of isobutanol.

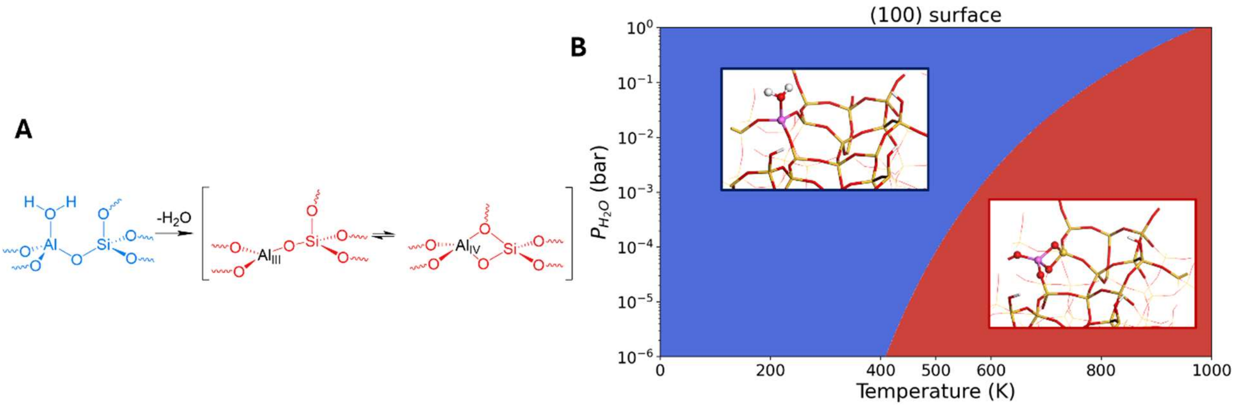

*Figure 1: **A)** Formation of Lewis acid sites at the external surface through dehydration of Brønsted acid sites Al-H_2O **B)** Phase diagram of the hydrated and dehydrated states depending on pressure and temperature for (100) surface*

References:

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