Trends underlying the Brønsted acidity and chemistry of zeolites

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Introduction

The formation of a bond between a molecule and a metal surface is an important phenomenon in a number of processes including heterogeneous catalysis [1], contact formation in molecular electronics [2], and anchoring of biomolecules to solids for sensors and other biomedical applications [3]. The adsorption energy is a key quantity describing the strength of the interaction of molecules with the surface. The adsorption energy can be measured by advanced surface science techniques [4-6]. Alternatively, density functional theory (DFT) offers the possibility of calculating adsorption energies with reasonable accuracy [7-11]. While both experiments and DFT calculations are feasible for a limited number of systems, they can hardly be performed in detail for all potentially interesting adsorption systems, thus complicating the search after for example new heterogeneous catalysts.

There is therefore a need for simple models with the ability to estimate bond energies in a first screening of interesting systems [12]. Such a model for hydrogen-containing molecules adsorbed on transition metal surfaces has recently been presented [13], and was shown to be useful in the design of transition metal-containing surface alloys for selective hydrogenation catalysis [14]. While linear energy relations thus are omnipresent and extremely useful in the field of transition metal catalysis, they have not historically played a significant role in the interpretation or oxide or zeolite catalysis.

Recently, it is shown that a number of linear energy relations rather surprisingly could be straight-forwardly generalized to the surfaces of more complex compounds such as oxides, sulphides, and nitrides [15]. We here address that observation in more detail, with a focus on the adsorption properties of zeolites.

Methods

Throughout we apply density functional theory calculations in a plane wave pseudopotential approach, as implemented in the DACAPO package. The full zeolite framework is represented in the calculation, and the exchange-correlation description is RPBE.

Results and Discussion

We show that adsorption scaling relations exist in transition metal substituted zeolites. For transition metal surfaces the scaling relations can be explained in terms of a generalized frontier orbital theory for transition metals called the d-band model [8]. We have thus investigated whether the scaling relations in zeolites should be the result of a similar frontier orbital activity variation. This leads us to define a frontier orbital theory for transition metal compounds such as oxides. We show in the case of transition metal substituted zeolites that variations in Brønsted acidity can be understood in terms of this model.

Significance

Understanding the trends underlying the adsorption of reactants and the Brønsted acid properties in zeolites is an important step towards designing zeolitic materials with desired properties. We consider this work to be one important step towards such an understanding.

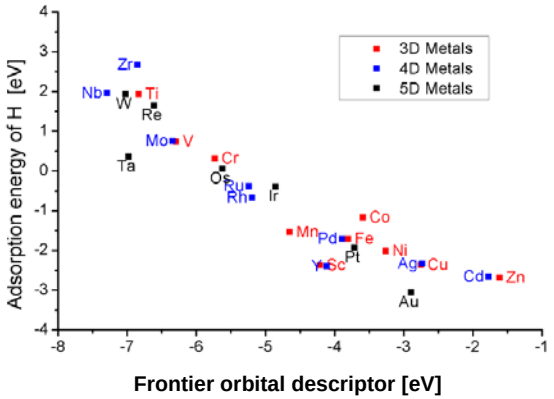

Figure 1. The binding strength of a hydrogen atom at the Brønsted acid site of a transition metal substituted zeolite as a function of the frontier orbital descriptor.

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