Adsorption and Dissociation of CO on Body Centered Cubic Transition Metals and Alloys: Effect of Coverage and Scaling Laws

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Introduction

With the decrease in crude oil supplies, Fischer-Tropsch synthesis (FTS) on coal- and biomass-derived synthesis gas is becoming an increasingly attractive route for producing chemicals and fuels. Catalysts for coal-derived Fischer-Tropsch are based on iron, and alloys with other bcc metals are presently being explored for optimization of the selectivity of the process. CO dissociation is the first step in the reaction mechanism. However, very little information is available on the interaction of CO (and in fact all other relevant gases) on the surfaces of bcc metals other than iron. Hence, we calculated the adsorption and dissociation of CO on Fe(100), Cr(100), Mo(100) and W(100) using density functional theory (DFT). The calculations were performed for CO surface coverages of 0.25 ML and 0.5 ML.

Materials and Methods

We have used the Vienna ab-initio simulation package (VASP) [1,2], which performs an iterative solution of the Kohn-Sham equations in a plane-wave basis set. Plane-waves with a kinetic energy below or equal to 400 eV have been included in the calculation. The exchange-correlation energy has been calculated within the generalized gradient approximation (GGA) using the revised form of the Perdew, Burke and Ernzerhof exchange-correlation functional [3] proposed by Hammer et al. [4]. The electron-ion interactions for C, O, Mo, W, Cr, and Fe are described by the projector-augmented wave (PAW) method developed by Blöchl [5]. The metal surfaces have been modeled within the slab model approximation using a five-metal layer slab model and six vacuum layers (>10 Å). The reciprocal space of the p(2x2) and c(2x2) unit cells have been sampled with a (5x5x1) and (7x7x1) k-points grid, respectively, automatically generated using the Monkhorst-Pack method [6]. To verify whether the calculated states are either true minima or transition state structures on the potential energy surface, a full analysis of the vibrational frequencies was made.

Results and Discussion

On all four metals CO is the most stable at these coverages at four-fold hollow sites with the C-O axis tilted away from the surface normal by 47-58°. Our results show that the adsorption energies of CO on the four BCC metals are comparable at both surface coverages. The CO stretching frequencies, on the other hand, do change. Increasing the surface coverage from 0.25 to 0.5 ML leads to higher CO stretching frequencies for both the Fe and Cr(100) metal, whereas to a lower CO stretch for both Mo and W(100). The latter is a striking result as it is against the general observed trend.

For the dissociation of CO at both surface coverages, we will show a complete energy scheme (as displayed in Figure 1 for 0.25 ML CO on Mo(100)) of each metal in which all the transition states and stable geometries will be presented. Next, we will compare the energy schemes of all the metals with each other.

Moreover, we will show that the recently introduced scaling laws by Nørksov and coworkers [7,8] hold for tilted CO on Fe, Mo, W, Cr, and on the alloys Fe₃Mo and Fe₃Cr. Both the heat of adsorption and the activation energy for dissociation of CO depends linearly on the heat of adsorption of the carbon atoms.

Significance

Tuning of especially the iron catalyst in FTS is of great importance, as this metal is inexpensive and able to work under low H_2/CO ratios due to its water-gas shift capability, making it valuable to use in coal FTS. The calculations, and hence, the use of the scaling model help to find for example an iron alloy which selectivity toward certain olefins is much better than the iron catalyst itself in a much faster, easier, and cheaper way than could be done before with experiments only.
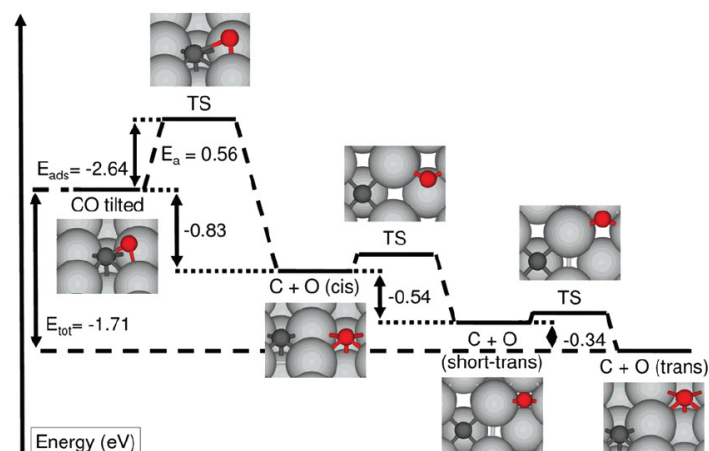
Figure 1. Energy diagram of 0.25 ML CO on Mo(100). [9]

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