

Theoretical analysis of the adsorption of ammonia-borane and their dehydrogenation products on the (001) surface of TiC and ZrC

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The adsorption of ammonia-borane (AB) over the (001) surface of TiC and ZrC, has been studied systematically by means of periodic-boundary density functional calculations using slab models. We present evidence that a surface with an appreciable degree of polarity such as those used in this research, can simultaneously activate the N-H and B-H bonds of the AB molecule and its dimer AB-AB. The molecule is highly activated by both supports, and the N-H and B-H bonds are stretched long enough to release one or two hydrogens. Additionally, the bond distance B-N is shortened by 0.04 and 0.06 Å by TiC and ZrC supports respectively, which results in the strengthening of the bond, what seems convenient to avoid unwanted by-products (NH₃, BH₃, etc.). A systematic study for the adsorption of BH₂NH₂, which is isoelectronic with ethylene, was also done. The adsorption leads to a major elongation of the B-N bond with respect to the calculated value in the gas phase (0.17 and 0.18 Å for TiC and ZrC respectively). Both supports can activate the molecule, with the biggest impact being on the BH₂ fragment. On the other hand, the migration of hydrogen atoms on both supports is a thermodynamically favorable process. On the surface H prefers bonding to a C, which is in agreement with other studies for dissociative adsorption of H₂ on metallic carbides. Nevertheless, we show that the hydrogen molecule readily forms when both atoms sit on the transition metal of the surface. On the basis of this theoretical study, both supports are proposed as potential catalysts for the dehydrogenation of ammonia-borane. © 2018 Elsevier B.V.