THEORETICAL STUDY OF HYDROGENATION ELEMENTARY REACTIONS OF DOPED ALUMINIDE CLUSTERS $Al_{12}X$, X = Al, B, C, Si, Ti

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Introduction

Computations of potential energy surfaces are performed within the density functional theory (B3LYP) with two basis sets 6-31G* and 6-31+G* (for negative ions) for elementary reactions of addition H_2 molucule to Ti-doped *closo*-aluminide cluster $Al@TiAl_{11}$ and its anion $Al@TiAl_{11}^-$ with dopant on periphery of 12-vertex $TiAl_{11}$ with inner Al atom, energies E and activation barriers h are estimated.

Results and discussions

Computations of these reactions are performed for both icosahedral and marquee isomers of $Al@TiAl_{11}$ and $Al@TiAl_{11}^-$, lying at short range by energy, and with different multiplicity. Results are compared with our previous computations ones by the same theory approximation for similar hydrogenation reactions of "bare" *closo*-aluminides Al_{13}, Al_{13}^- and its B- , C- and Si-doped derivatives. Varying of hydrogenation energies in range 15-23 kcal/mol depending from structure, charge and multiplicity of cluster $Al@TiAl_{11}$ was found. At the first stage of H_2 addition (chemisorption) μ-H_2-complex (intermediate) is arisen with ~4-10 kcal/mol energy goal and distance R (Ti-H_2) ~ 1.9-2.0 Å. H—H bond in μ-complex elongate by ~0.1 Å and valence oscillation frequency ν_{val}(H-H) decrease by ~700-1500 cm^{-1} and more, compared with along H_2 molecule characteristics. In transition state with imaginary frequency ~600i – 1000i molecule H_2 is coordinated to attacked edge Ti-Al_r usually, and its length R(HH) is increased to ~ 0.9 – 1.1 Å. Height of activation barrier counted from μ-H_2-complex varies from few kcal/mol to ~8-10 kcal/mol, and counted from dihydride product $Al@TiAl_{11}H_2$ in range ~ 18-22 kcal/mol.

Conclusions

The latter barrier is essentially above than barriers of H atoms migration around metallic framework of dihydrids $Al@TiAl_{11}H_2$. On base of computations we can conclude that hydrogenation elementary reactions (also dehydrogenation) of Ti-doped aluminides should progress match faster and in more soft conditions than of "bare" aluminides and its analogues, doped with non-transition elements atoms. Dependence of energies E and barriers h of hydrogenation reaction on structure, outer charge and multiplicity of cluster $Al@TiAl_{11}$ is traced.

References

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