

Experimental studies and DFT modeling of hydrogen sorption behaviour of Mg-based nanostructured composites and nanosized clusters

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Magnesium as a material for reversible hydrogen storage attracts a lot of attention from researchers over many decades due to the high mass content of hydrogen in the hydride MgH₂ (7.6%). Yet, its wide practical application is hindered by several drawbacks, the main of which is the slow kinetics of hydrogen sorption and desorption (s/d).

An effective way to solve this problem is to create Mg-based materials, in which the improvement of hydrogen s/d kinetics is achieved by introducing catalytic additives (3d metals) and simultaneous reduction of the grains of the magnesium phase to submicro- and nanosizes (nanoconfinement) [1]. Since experimental studies of subnano- and nanosized magnesium particles often face practical difficulties, quantum chemical (mostly DFT) calculations can provide valuable information for a purposeful development of advanced Mg-based hydrogen storage nanomaterials [2].

This report summarizes results of recent R&D activities [1–5] of the research teams from FRC PCP&MC RAS on the creation of novel Mg-based materials with improved hydrogen s/d kinetics. These R&Ds are featured by original approach lying in the combination of experimental studies and quantum chemical calculations, the objects of which, respectively, are nanostructured Mg-based materials and subnanosized Mg clusters, as well as in the search for correlation between the results obtained on studying those objects that are quite different in size and morphology.

Mg-based materials with enhanced hydrogen s/d behavior are powder composites of Mg-Ni alloys with nanocarbon additives prepared by high-energy ball milling under hydrogen. The particle morphology and microstructure of thus prepared composites allows achieving the nanostructured state of Mg phases and increasing the area of interphase boundaries; Ni-containing phases effectively serve as catalysts of H₂ molecules scission and H atoms transfer; nanocarbon additives make it possible to stabilize the nanostructured state during the hydrogen s/d processes and improve heat transfer in the powder composites.

The DFT calculations of the potential energy surfaces elementary hydrogenation reactions of Mg₁₈ and 3d-metals doped Mg₁₇L (L = Ti, V, Cr, Mn, Fe, Co, Ni) clusters were performed within the BP86 approximation using the

GAUSSIAN-09 program with the 6-31G* basis set. The geometric, vibrational, energy, and electronic characteristics of the intermediates and transition states along the minimum energy pathways of these reactions were determined, the activation barriers and energy changes at their key stages were evaluated, and the effect of the dopant nature on these characteristics as L varied along the 3d-period was analyzed.

Further comparison of the results of DFT modeling and qualitative conclusions for small Mg clusters with those for families of larger ones [4] suggests the validity of extending DFT approaches to even larger nanosized clusters with a higher content of dopant atoms. In this regard, the results of experimental studies correlate with the data obtained in DFT modeling, which show that the rate-limiting step of the Mg₁₇L + H₂ → Mg₁₇LH₂ catalytic cycle for all 3d dopants is the stage of “dopant cleaning” with the restoration of its catalytic activity by the beginning of each next hydrogenation cycle. The energy barriers of the rate-limiting step for Ni are the lowest, and the catalytic activity of the dopant decreases with decreasing atomic number L.

The reported R&Ds made it possible to reveal the features of hydrogen s/d behavior of the studied objects, to perform a purposeful search for advanced Mg-based hydrogen storage materials, as well as to develop devices with improved hydrogen storage performances. The obtained results were ranked high by both The Federal Service for Intellectual Property and The American Chemical Society.

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