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Computational study of the adsorption of benzene and hydrogen on palladium–iridium nanoalloys

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ABSTRACT

The preferred chemisorption sites on a variety of palladium–iridium nanoalloys are determined for benzene and hydrogen molecules. Available sites on the surface of the nanoalloys are explored using a random-search method, directly at the density functional level of theory. These searches successfully reveal the site preference for benzene and significant nanosize effects in the chemisorption of hydrogen. It is hoped that through the study of the chemisorption properties of Pd–Ir nanoalloys, complex catalytic processes, such as tetralin hydroconversion and the preferential oxidation of CO, can be better understood.

Introduction

Nanoalloys (NAs) are a class of nanomaterials composed of two or more metallic elements. These include nanoparticles (NPs), 2D-like structures, such as nanogrids and sheets, and 1D-like structures, such as nanowires and nanotubes [1]. The combination of metals in a NP results in properties which are dependent not only on size and shape [2], but also on the composition and chemical ordering [3]. The presence of two or more metals introduces homotops, isomers differing in only the ordering of elements [4].

Palladium–iridium is a strongly demixing alloy system [5–7]. This is reflected in the structural characteristics of the corresponding nanoalloys [8,9]. Pd–Ir nanoalloys have been investigated previously for application in a number of catalytic processes [10–16], including tetralin hydroconversion through selective ring opening [14], a process which is key to understanding how to reduce particulate emissions from diesel fuel. Here it was hoped the catalytic properties of each metal would be combined in the nanoalloy catalyst. Ir has been shown to be active in C–C bond hydrogenolysis and Pd shows improved hydrogen activation and thioresistance over other noble metal catalysts. [17] Through alloying, depending on the relative proportions of the metals, increased activity and selectivity can be obtained [14].

Understanding the role of hydrogen in tetralin hydroconversion and other reactions, such as the preferential oxidation of CO (PROX), is vital [15,16]. Bulk Pd is the only metal at ambient temperature and hydrogen pressure to form a hydride [18,19]. Nanosize effects on the Pd–H system have been widely studied [19,20]. Nanosize Pd exhibits an increased hydrogen absorption rate and decreased absorption capacity [21,22]. Recently, the interaction of hydrogen with Pd, Ir and Pd–Ir was probed, with nanosized-induced hydrogen absorption being reported for Ir [23,16]. The sorption (adsorption + absorption) capacity of Pd–Ir nanoalloys was found to be strongly reduced compared with the pure NPs [16]. Furthermore, the addition of Ir to Pd inhibits the formation of Pd hydride. This is thought to be beneficial to the activity of Pd–Ir as a catalyst since the hydride is unselective in PROX.

Theoretical studies of the interaction of hydrogen with nanoalloys are limited. Pd, Pt and Pd–Pt nanoparticles (NPs) have been investigated previously using density functional theory (DFT) [24,25]. Kozlov and co-workers investigated the differences between the adsorption and absorption of hydrogen atoms on/in Pd and Pt NPs [25]. The work was found to be in agreement with

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