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The theoretical study of the bimetallic Ni/Pd, Ni/Pt and Pt/Pd catalysts for hydrogen spillover on penta-graphene

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ABSTRACT

The catalytic property of the bimetallic Ni/Pd, Ni/Pt and Pt/Pd particles for hydrogen spillover on penta-graphene (PG) are studied by using the first-principles and kinetic Monte Carlo (KMC) calculations. The bimetallic Ni/Pd, Ni/Pt and Pt/Pd particles can be stably decorated on PG surface with binding energies in the range of 4.15–5.52 eV. The adsorption enthalpies of H₂ molecules on bimetallic particles are in the range of –11.56––15.35 kcal/mol. The H atom can migrate from the bimetallic particles to PG with the migration barriers range from 0.67 to 0.95 eV. The KMC simulations show that the hydrogen spillover reactions can occur at a suitable temperature (260–361 K), which meet DOE target for on-board hydrogen storage systems applied to light-duty vehicles. In the study, the highest occupied molecular orbital and electric field analysis shows that the bimetal mixing can reduce the hydrogen adsorption enthalpy, and thereby reduce the H migration barrier, which displays a synergistic effect for hydrogen spillover.

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Introduction

In recent years, the rapid development of hydrogen fuel cell technologies has vigorously promoted the progress in the research of hydrogen energy. Unlike other fuel, hydrogen is gaseous at ambient temperature and pressure, how to store and transport hydrogen safely at reasonable temperature and pressure is a bottleneck of practical application. Carbon-based nanoporous materials are an appealing and well-studied

material class within hydrogen sorbents, and it has been demonstrated that both high surface area and an appropriate pore size distribution are necessary for their high sorption capacities [1]. However, experimental studies show that the H₂ storage uptakes of these nanoporous materials lower than 1 wt% at 298 K [2–4].

The hydrogen spillover effect (activation or dissociation of H₂ molecules on catalytic metal and subsequent migration of atomic hydrogen onto receptor surface) has been utilized as a potential mechanism for achieving high-density hydrogen

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storage at near-ambient condition in lightweight, solid-state materials. In experiment, the inelastic neutron scattering (INS) and X-ray photoelectron spectroscopy (XPS) measurements provide definite evidence that the H atoms can diffuse to the carbon surface in the spillover process [5,6]. Hydrogen spillover has been studied using many carbon materials, such as carbon nanotubes [6,7], carbon aerogel [8,9] and graphene [2] et al. For example, by chemical doping 5.6 wt% Pt catalyst on AX-21 (a superactivated carbon), Yang et al. reported that the hydrogen uptake was increased up to 1.2 wt% at 298 K and 10 MPa [10]. Further work are performed on a series of template carbons with various surface areas, and the results showed 0.4 wt % (70% enhancement) $H_2/1000\text{ m}^2/\text{g}$ of carbon sorbent at 298 K and 100 atm [11]. Yang group also reported significant enhancements (from 1.17 wt% to 1.74 wt%) in hydrogen storage on oxygen plasma treated carbon via spillover [12].

Addition of pre-reduced Pt supported on activated carbon (Pt/AC) to metal-organic frameworks (MOFs) via physical mixing or a 'pre-bridge' technique can generate a secondary spillover process, where MOFs can receive active hydrogen species as secondary spillover receptors [13,14]. Zhou et al. reported that the hydrogen uptakes of MOF/graphene oxide composites can enhance by a factor of 3.6 or 4.1 by hydrogen spillover mechanism [15]. Li et al. announced that the measured hydrogen uptake of IRMOF-8 can be increased from 0.5 wt% to 4 wt% by doping bridged Pt/AC catalyst at 100 bar and 298 K [14], and their results have been verified by the Tsao group [16]. Lueking et al. test the stability of MOF supports after various doping techniques (direct doping, physical mixing and pre-bridge catalytic doping), they reported that addition of Pt/AC via a 'pre-bridge' technique led to high MOF stability [17].

In theoretical research, the hydrogen spillover mechanism on Pt-doped graphite are studied by density-functional theory (DFT), and the results reveal that the migration of H from Pt to the graphite substrate is the rate-limiting step in the overall spillover [18]. How to reduce the migration barrier in the rate-limiting step becomes one of the crucial points in hydrogen spillover research. A series of methods on graphite surface, including boron substitution and oxygen-group decoration, are put forward in theory, and the migration barrier can be reduced from 2.6 eV to 0.40–0.65 eV [19–21]. Exploring the effective substrate for hydrogen spillover is also an important issue. The saturation storage density of several MOFs and covalent-organic frameworks (COFs) were accurately predicted by DFT calculations, and the results showed that the MOFs and COFs have the potential to be good hydrogen storage materials by spillover [22–24]. Meanwhile, hole doping method was proposed by Zhang et al. in MOFs to enable spillover at ambient conditions [25].

The hydrogen uptake capacity by spillover is not only relative to the texture of porous materials, but also depends on metal catalyst, which is also a crucial factor for hydrogen storage. A variety of transition metals (such as platinum, palladium, ruthenium, nickel and titanium et al.) can be doped onto the receptor as hydrogen spillover catalyst [1,26–29]. Wang and Yang doped three different metals (Ru, Pt, and Ni) on AX-21 and templated carbon, and found that the hydrogen storage capacity followed the sequence of $Ru/C > Pt/C > Ni/C$ [29]. They explain that the difference in storage

capacity was related to the equilibrium amount adsorbed on the metal. Recently, bimetallic or polymetallic nanoparticles are reported as highly efficient catalysts for hydrogen generation and storage [30–32]. Gu et al. reported that Au–Pd nanoparticle immobilized in the MIL-101 have a much higher catalytic activity than monometallic Au and Pd counterparts [32]. Gang et al. has demonstrated that the 2.5% Pt and 2.5% Pd hybrid doping is more beneficial to the diffusion of dissociated atomic hydrogen than pure Pt doping [30]. Ostrom et al. explored the synergistic effects of Pd, Ag, and Cd on hydrogen storage, and showed that the trimetallic alloy $PdAg_{10}Cd_{10}$ significantly enhances hydrogen sorption capabilities of Pd-based dissociation catalysts [33]. Catalytic effects of bimetallic nanoparticles have been theoretically studied in gas purification [34], N_2O decomposition [35] and dry reforming of methane [36] et al. However, the theoretical study of the bimetallic catalysts in hydrogen spillover is rarely reported.

In this paper, the catalytic property of bimetallic Ni/Pd, Ni/Pt and Pt/Pd particles on hydrogen spillover is explored. The penta-graphene (PG) is used as the substrate material for hydrogen chemisorption. PG material was proposed in theory by Wang et al. in 2015, which constructed from a mixture of sp^3 - and sp^2 -coordinated carbon atoms [37]. At present, though PG has not been experimentally synthesized, an analogous 2D material—pentagonal $PdSe_2$ has been successfully fabricated, which provide a confidence for PG synthesis in the future [38]. Our previous work has revealed that the atomic H can be adsorbed on sp^2 carbons, and the saturation H_2 storage uptake of PG is estimated to be 5.3 wt% [39]. However, using Pt_4 , Pd_4 , and Ni_4 clusters as the catalyst, the spillover reaction cannot occur under the appropriate temperature (the optimal reaction temperatures $> 390\text{ K}$) [39]. The purpose of this work is to explore whether hydrogen spillover can occur at appropriate temperature by using the bimetallic catalyst.

Computational details

All calculations were performed using the VASP package [40] based on DFT with PBE [41] for exchange and correlation potential, and the core electrons were described by projector augmented wave [42]. The plane wave energy cut-off was set to 500 eV, and a $2 \times 2 \times 1$ grid for k-point sampling was used in the calculations. The forces converged criterion for the structural optimizations was 0.03 eV/Å. We use the nudged elastic band (NEB) method [43] to find the minimum energy path for the spillover reactions. Combining with the DFT calculations, the kinetic Monte Carlo (KMC) simulations were carried out to study the hydrogen spillover process. The detailed algorithm and scheme of KMC can be seen in [Supplementary Information](#).

Results and discussion

The bimetallic Ni/Pd, Ni/Pt and Pt/Pd particles supported on PG

The supporting PG structure (3×3 supercell) was optimized using DFT. The PG model consists of 54 carbon atoms in the

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