Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2015

Supplementary Information

Metallic Ni Nanocatalyst *in situ* Formed from Metal-Organic-Framework by Mechanochemical Milling for Hydrogen Storage in Magnesium

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Experimental Section

Synthesis of Ni-MOF-74 as precursor

The synthesis details of Ni-MOF-74 (Ni₂C₈H₂O₆) can be referred to the published literature [1]. 1 g of 2,5-dihydroxyter-terephthalic acid (DHTA, purchased from Sigma-Aldrich) and 3 g of Ni(NO₃)₂•6H₂O were dissolved in 140 mL DMF, 140 mL ethanol, and 140 mL water under sonication. The solution was sealed in 100 mL autoclaves and heated to 100 °C for 3 days. After cooling to room temperature, the resultant product was filtered and washed with methanol. The solid product was immersed in methanol to exchange guest molecules for three times in three days. And then the filtered product was evacuated to 200 °C for 5 hours to dry and kept in argon filled glove box.

Mechanochemical synthesis of (Ni-NPs)@MgH₂ composites

Different amounts of the as-prepared Ni-MOF-74 precursor (5wt%, 20wt% and 50wt%) were mixed with commercial MgH₂ powder (hydrogen storage grade purchased from Sigma-Aldrich), respectively, and then milled under 1 bar Ar for 2 h in a high energy SPEX 8000 vibration ball mill (60 Hz model) in the sealed vial with ball-to-powder weight ratio of 40:1. All the sample handling was performed in an Ar-filled glovebox (MBraun), in which the water/oxygen levels were below 1ppm.

Synthesis of MgH₂+Ni/AC composite

The activated carbon (AC) supported Ni nanocatalyst (denoted as Ni/AC) was prepared by the wet impregnation method. Microporous AC with BET specific surface area of 1174 m² g⁻¹ was obtained from Calgon Carbon Company as Ni nanoparticle support. Before the impregnation procedure, AC was first dried under vacuum at 140 °C for 12 h in order to remove moisture and gaseous impurities from the porous structure. Afterwards, 10 mL Ni(NO₃)₂·6H₂O (0.34 M) solution was added drop-wise to AC and stirred for 48 h, followed by drying the slurry at 120 °C overnight and subsequently reducing in 5% H₂/N₂ gas mixture at 500 °C for 2 h. Base on the TGA analysis of Ni content in Ni-MOF-74, the Ni loading in Ni/AC was 40 wt% for comparison study. Afterwards, 5 wt% Ni/AC catalyst was mixed and ball milled with MgH₂ under the same condition.

Characterization and measurements

The synthesized samples were characterized by powder X-ray diffraction (XRD, Rigaku Miliflex) with Co Kα radiation, nitrogen physisorption measurement (Quadrasorb SI, Quantachrome), and X-ray photoelectron spectrometer (XPS, Kratos Axis ULTRA). The microstructure and composition of (Ni-NPs)@MgH₂ nanocomposite were analyzed by transmission electron microscope (TEM, FEI Tecnai 20) equipped with an energy dispersive X-ray spectroscopy (EDXs) analysis unit (AMETEK). The sample for TEM measurement was dispersed in heptane by ultrasonication and then deposited onto a holey carbon film on a copper grid. To determine the content of the Ni in as-synthesized Ni-MOF-74, the thermogravimetric analysis (TGA, Mettler Toledo) was carried out under air atmosphere with an air flow of 20 ml/min at a heating rate of 5 °C/min from room temperature to 800 °C.

Hydrogen storage properties that include thermodynamic change and kinetic studies of the composites were examined by an automated Sieverts' apparatus (Suzuki Shokan PCT H_2 Absorption Rig).

Computational methods

Magnesium (Mg) substrate is modelled by Mg(0001) surface with a (3×3) supercell. After it is optimized, Ni₄ cluster is introduced on the surface and fully relaxed, then H₂ is firstly introduced over the Ni₄ cluster and geometry optimization confirms it prefers to split as two hydrogen atoms, based on which NEB method is employed to calculate the energy profile for H-atom to diffuse from Ni₄ to Mg(0001). All geometry optimizations and energy calculations were carried out within the scheme of spin-polarized density functional theory, under the generalized gradient approximation method [2]. The Perdew-Burke-Ernzerhof functional has been employed for the exchange-correlation term, as embedded in the Vienna ab-initio Simulation Package (VASP) [3,4]. During the calculation, the projector augmented wave method [5] with a cutoff energy of

450 eV has been employed to achieve high computational efficiency. During the calculations, the k-spaced is sampled by the gamma point because more k-points do not result in remarkable improvements based on our tests.

Justification of the computational model

The calculation is to examine the diffusion of hydrogen from the edge of Ni-cluster to Mg matrix. A cluster with four Ni-atoms, indicated Ni₄, is employed to create edge site for this simulation. It is true that a larger cluster can be more close to real particles prepared in this work, but the calculation cost will be remarkably increased because the possible configurations for clusters increase exponentially. Moreover, a larger substrate needs to be employed to hold the cluster, which is very difficult for DFT calculations.

Compared with the traditional model with single-atom embedded into Mg-lattice [6], the Ni₄model has several edge positions, which is essential for studying H-diffusion from Ni-cluster to Mg-matrix. Generally, low-coordinated surface atoms are more active than those saturated or high-coordinated ones. Therefore, the barrier for H-diffusion calculated from Ni₄-model gives an uplimit, and real barriers should be smaller than the calculated data. Consequently, the conclusion made from Ni₄-model that H-diffusion from Ni-cluster to Mg-matrix only needs to get over a small barrier is convincing because the data from large clusters should even smaller than the value obtained from Ni₄.

As to the configurations of Ni₄, the original shape is a tetrahedron shape as optimized in the gas phase, and then introduced to Mg(0001). After full relax, it becomes to the current nearplanar shape, indicating strong Ni-Mg interaction. Similar phenomenon has been observed for Au clusters on active metal oxides [7]. This is the basis for the effective loading of Ni-cluster on Mg(0001).

As early calculations confirmed [6], the real challenge for H-diffusion comes from the strong H-Mg interaction, not from H-Ni breakage. As explained above, Ni₄ cluster is good enough to demonstrate this point. Being consistent with our calculations, small Ni-cluster can improve the

dehydrogenation performance of MgH₂, and the electron transfer associated with Mg-Ni interactions is the physical basis, just similarly with the nonmetal-doping to remove electrons from Mg to nonmetals [8].



Figure S1. Nitrogen sorption isotherms of as prepared Ni-MOF-74.



Figure S2. XRD patterns of (a) dehydrogenated sample of MgH₂+5%(Ni-MOF) at 300 °C, (b) hydrogenated sample of MgH₂+5%(Ni-MOF) at 100 °C.



Figure S3. TGA curve of the as-synthesized Ni-MOF-74 sample.



Figure S4. (a) TEM bright-field image of Ni/AC catalyst.



Figure S5. Determination of activation energies for absorption and desorption of hydrogen in (Ni-NPs)@MgH₂ nanocomposite derived from MgH₂+5%(Ni-MOF-74) by mechanochemical milling. Hydrogen absorption was measured at three different temperatures (T = 473, 423, and 373 K), desorption was measured at three different temperatures (T = 573, 553, and 533 K) and the activation energies were determined by plotting the log of the rate constant k versus 1000/T.

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