Natuurlike diatomiet gewysig om te dien as waterstof-stoormedium

Jiao Jin, Chenghui Zheng en Huaming Yang\*

Navorssentrum vir Mineraalmateriaal

Skool van Mineraleverwerking en Bio-ingenieurswese,

Sentraal-Suidelike Universiteit, Changsha 410083, Volksrepubliek, Sjina

[\*hmyang@csu.edu.cn](mailto:*hmyang@csu.edu.cn)

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Natuurlike diatomiet, onderworpe aan verskillende wysigings, is ondersoek vir waterstofadsorpsie-vermoëns by kamertemperatuur. 'n

Effektiewe metaal-aangepaste strategie is ontwikkel om platinum (Pt) en palladium (Pd) nanopartikels te versprei op die oppervlak van

diatomiet. Waterstofadsorpsievermoë van ongerepte diatomiet (diatomiet) is 0.463 gewig% teen 2.63MPa en 298 K, onder die hoogste

van die bekende sorbente, terwyl dié van suur-termies geaktiveerde diatomiet (A-diatomiet) tot 0.833 gewig% kan bereik as gevolg van die

gepaste porie-eienskappe by aktivering. Deur inkorporasie met 'n klein hoeveelheid Pt en Pd (\_0.5 gew.%), waterstofadsorpsie word die vermoëns verhoog tot 0,696 gewig% en 0,980 gewig% onderskeidelik, wat aandui dat geaktiveerde diatomiet interessante toepassing toon.

op die gebied van waterstofopberging by kamertemperatuur.

Sleutelwoorde: Diatomiet; suur-termiese aktivering; platinum- en palladiummodifikasie; waterstofadsorpsiekapasiteit.

Waterstofenergie is voorgestel as 'n alternatiewe brandstof vir die eienskappe van skoon en hoȅkalorieverbranding. Benutting van waterstof vereis die bemeestering van waterstofproduksie-, vervoer- en bergingstegnologie.1 Waterstofberging is besonder uitdagend aangesien die vestiging van 'n veilige en doeltreffende waterstofopbergstelsel moeilik is by kamertemperatuur en onder atmosferiese druk. Groot pogings is die afgelope tyd aangewend tot die ontwikkeling van materiale vir waterstofberging. Waterstofberging deur adsorpsie verteenwoordig een potensiële strategie vir effektiewe en relatief veilige tegnologie.2-4 Fisisorpsie op substrate lyk baie aanpasbaar aangesien die geadsorbeerde gas omkeerbaar vrygestel kan word.5 Natuurlike onlangs minerale is onlangs ontwikkel tot waterstofbergingsmateriaal.6 Onder minerale materiale is poreuse minerale aantreklike keuses, weens hulle lae koste, lang lewensiklusse, hoë duursaamheid,7 en waterstofadsorpsie / vrystelling by kamertemperatuur vergeleke met ander materiale.6 Diatomiet is 'n organiese sedimentêre gesteente met 'n unieke kombinasie van fisiese en chemiese eienskappe. Weens sy spesifieke eienskappe, word diatomiet wyd aangewend as filterhulpmiddel, vulstof, katalisator, adsorbent, verpakkingsmateriaal vir gaschromatografie of hoëprestasie- vloeistofchromatografie.8-10 Die hoë porositeit met 'n groot oppervlak, sterk adsorbeerbaarheid en uitstekende termiese stabiliteit maak diatomiet 'n perfekte kandidaat vir waterstofberging. In hierdie verhandeling is natuurlike diatomiet minerale gekies vir die toepassing van waterstofberging. Platinum- (Pt) en palladium- (Pd) nanopartikels is suksesvol op die oppervlak van diatomiet gemonteer. Die gevolge van suur-termiese aktivering en edelmetaalverandering op waterstofadsorpsievermoëns word bespreek.

Moreover, the effects of high-pressure hydrogen on the physical and chemical properties of the samples were also

investigated in detail. Raw diatomite clay was collected from Jilin, China. All of the chemicals were analytical grade and used without further purification. A 10 g of diatomite was dispersed into 80 mL of 2.0M hydrochloric acid solution for 4 h at room temperature. The acid-thermal activated diatomite (A-diatomite) was collected via filtering the solution, washing several times with distilled water, drying at 333K for 6 h and heat treatment at 573K for 4 h. Pt modified diatomite (Pt-diatomite) was synthesized as follows: 1 g of diatomite was dispersed in 100 mL distilled water and stirred for 0.5 h. 50mL water solution containing 13 mg chloroplatinic acid (H2PtCl6) was slowly added dropwise into the above solution under vigorous agitation for 20 min. The beaker containing the slurry was subjected into ultrasonic dispersion (110W, 30 kHz) for 1 h and then magnetically stirred at room temperature for

24 h. After being dried at 333K to evaporate the solvent, H2PtCl6 impregnated diatomite was calcined at 573K under

hydrogen flow for 2 h to obtain Pt-diatomite. Pd-modified diatomite (Pd-diatomite) was prepared according to the same procedures, except that the palladium source was palladium chloride (PdCl2 \*Corresponding author.) with the solvent of methanol.

X-ray diffraction (XRD) patterns were recorded on Rigaku D/max 2550 with Cu Kα radiation (λ ¼ 0:15406 nm)

over the scanning range 2θ ¼ 5–80○ with a step width of 0:02○. Scanning electron microscopy (SEM) was carried out on a JMS-6360LV electron microscope equipped with an energy-dispersive X-ray spectrometer (EDX) analyzer. Nitrogen adsorption-desorption isotherms were measured by a Micromeritics ASAP 2020 equipment at 77 K. All the samples were vacuum-dried at 423K for 6 h prior to the experiments.

Specific surface areas (SBET) were calculated from the isotherms by the Brunauer–Emmet–Teller (BET) method.

Pore size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method using the adsorption branch.

Fourier transform infrared (FTIR) absorption spectra of thesamples were measured by a Nicolet NEX-US 670 IR

spectroscopy with the range of 400–4000 cm\_1.

Hydrogen adsorption isotherms were measured using a static volumetric technique with a specially designed

Sievert*'*s apparatus at 298 K,11 which was previously tested to be leak-free and proven for accuracy through calibration at 298 K. The sample cell loaded with well-dried sample was completely degassed in vacuum at 513K (less than 4.0 Pa). Hydrogen activation was taken out at 1.2 MPa and 413K to remove other gases adsorbed in the samples. Then the samples were degassed for another time before measurements. After the cell cooled down to 298 K, pure hydrogen at different pressure was injected into the test system for measuring the hydrogen adsorption capacity.

Natural diatomite is regarded as a mineral of organic origin, where silica of fossilized diatom skeleton resembles

opal or hydrous silica in composition (SiO2 \_ nH2O). All the XRD patterns (Fig. 1) show reflections which are typical for amorphous silica (a broad reflection centered at 2θ ¼ 20–25○) and well-crystallized quartz (sharp reflection peak centered nearly at 2θ ¼ 27○). Meanwhile, three new reflections centered at 2θ ¼ 40:1○, 46:6○, 68:1○ (JCPDS 65-2867) corresponding to the lattice planes of Pd (111), Pd (200), and Pd (220) can be observed for Pd-diatomite sample. Three new reflections centered at 2θ ¼ 39:7○, 46:2○, 67:4○ (JCPDS 65-2868) corresponding to the lattice planes of the Pt (111), Pt (200), and Pt (220) can be observed for Pt-diatomite sample. The intensities of the above peaks are broadened and not very obvious due to the low incorporation of Pd and Pt (\_0.5 wt.%).

Figure 2 shows the SEM images of all the diatomite samples and EDX spectra of Pd-diatomite and Pt-diatomite.

The three different treatments did not affect the surface morphology of natural diatomite. All the samples feature a

disc-like morphology which mainly consists of the centric diatomite particles having two disks attached to each other by a circular girdle. Numerous skeletal pores and chambers make up the microfossil skeleton of diatomite particles. The centric diatoms particles have a diameter of about 30–40 μm and a thickness of several microns. Lots of pores with a diameter less than 0.4 μm regular array inside the centric diatomite particles, but small pores with a diameter between 0.1 μm and 0.25 μm outside the disc edge.

Compared with diatomite, A-diatomite shows more smooth surface, which is attributed to the removal of impurities and the dredging of pore channels after acid-thermal activation. The diatomite shows obvious lengthways edge, possessing plenty of surface hydroxyl groups confirmed in the following FTIR spectra.

The hydroxyl groups are potential reaction sites for surface modification. Surface edges and defects can bring higher specific surface energy and serve as nucleation sites for deposition.12 After loaded with Pt and Pd, small agglomerates of Pt and Pd nanoparticles were deposited on the surface of diatomite (bright spots on the surface of diatomite marked in black cycles). These make the surface of Pd-diatomite and Pt-diatomite much coarser. The corresponding EDX spectra indicate that Pd-diatomite is composed of the elements Si, O, Al, Pd and elements Si, O, Al, Pt for Pt-diatomite.

The results clearly confirm the existence of Pd and Pt on the surface of diatomite.

Nitrogen adsorption–desorption isotherms of all samples and corresponding BJH pore size distributions (Fig. 3) exhibit a type H3 hysteresis loop in the relative pressure (p=p0) range of 0.4–1.0. Hysteresis loop is the representative of capillary condensation occurred among the ordered porous channels or interspaces of particles.13 The type H3 hysteresis loop does not have any adsorption plateau at high relative pressure close to unity, which is an evidence of macropores existing in the samples which are clearly shown in the SEM images (Fig. 2).

However, the middle sections of the isotherms in the relative pressure range of 0.4–0.8 are due to capillary condensation caused by mesoporous adsorption and the pore sizes center at 2–4 nm (Fig. 3(b)). This indicates that the textural mesopores do exist in all the samples. The diatomite samples are constituted by multiple pores. After the acid-thermal activation, the pore size distribution of A-diatomite is relatively concentrated when compared with that of other samples. Owing to the thermal treatment, A-diatomite exhibited some structural shrinkage that led to a reduced BET surface area, pore volume, and average pore size when compared with that of diatomite sample (Table 1). In contrast, Pd-diatomite and Pt-diatomite samples display the reduced BET surface area, low pore volume, and large average pore size, caused by the deposition of the Pd and Pt nanoparticles in the samples.

Figure 4 shows the hydrogen adsorption isotherms measured at 298 K. All the hydrogen adsorption isotherms are

typically the physical adsorption. Hydrogen adsorption amounts increase with the increase of pressure. Hydrogen adsorption amounts of A-diatomite are slightly higher than those of diatomite at each pressure, which indicates that acidthermal activation could efficiently promote the hydrogen adsorption capacity. Removal of impurities, dredging of channels and shrinkage of pore diameter caused by acidthermal activation are beneficial to the improvement of the hydrogen adsorption capacity.14,15 Hydrogen adsorption amounts at different pressure (*x* MPa) are defined as Wx. W1:70 of A-diatomite (0.403 wt.%) is 0.6 time higher than that of diatomite (0.251 wt.%), while W2:63 of A-diatomite (0.833 wt.%) is 0.8 time higher than that of diatomite (0.463 wt.%). Large surface area favors hydrogen adsorption according to physisorption mechanism.12 SBET of diatomite is a little higher than that of A-diatomite. So for diatomite samples, specific surface area is not the primary factor for hydrogen adsorption. Appropriate pore volume and small pore size with intensive distribution also benefits hydrogen adsorption.

Despite the low surface areas, the metal-modified diatomite shows greatly enhanced hydrogen adsorption capacity, especially the Pd-diatomite sample. The noble metal nanoparticles in the sample are capable of efficiently

promoting the hydrogen adsorption capacities via a chemisorption or spillover mechanism.16 W2:63 of Pt-diatomite (0.696 wt.%) is 0.5 time higher than that of Diatomite. Hydrogen adsorption amount of Pd-diatomite is among the

highest of the diatomite samples. W1:70 of Pd-diatomite (0.417 wt.%) is 0.66 time higher than that of diatomite while

W2:63 of Pd-diatomite (0.98 wt.%) is 1.1 times higher than that of diatomite. Doping of transition metal (Pd, Pt, Ni, etc.) could enhance the storage capacity via a hydrogen spillover mechanism for the physisorption-based material, which was experimentally demonstrated by other researchers.17 Transition metals have strong ability in storage and dissociation of hydrogen. However, Pd is the most effective as hydrogen storage metal at room temperature, especially, the hydrogen adsorption capacity of Pd-diatomite is better than that of Pt-diatomite at different pressures. The maximum hydrogen-storage value of carbon nanomaterial, determined by thermal desorption spectroscopy, was found to be 1.5 wt.%, while the hydrogen adsorption properties of MOF-5 was 0.28 wt.% (at room temperature and 65 bar), 0.9wt.% (at 200K and 60 bar), and 5.1 wt.% (at 77 K).18,19 Comparison with the properties of above nanomaterials shows that modified diatomite materials could also be applied as hydrogen storage materials at room

temperature.

XRD patterns, FTIR spectra (Fig. 5) and SEM images (Fig. 6) were adopted for investigating the effect of high

pressure hydrogen on the composition, structure and surface characteristics of the resultant samples after hydrogen adsorption measurements. Both the XRD patterns and FTIR spectra of diatomite and A-diatomite after hydrogen adsorption (named as H-diatomite and H–A-diatomite) are almost the same as diatomite and A-diatomite which confirms that high-pressure hydrogen did not change composition and surface characteristics. The SEM images are basically consistent with the samples before hydrogen adsorption tests, indicating that high-pressure hydrogen did not have influences on the morphology and porous structure. XRD pattern of Pd-diatomite after hydrogen adsorption (H-Pd-diatomite) features the same characteristics as Pd-diatomite (Fig. 7(a)). The SEM image of H-Pd-diatomite remains similar to that of Pd-Diatomite (Fig. 7(b)), Pd nanoparticles (bright spot) are still anchored on the surface of diatomite, indicating that hydrogen adsorption does not change the composition and structure of diatomite.

Diatomite mineral is the promising physisorption-based material for hydrogen storage at room temperature. The hydrogen adsorption isotherms are typical of physical adsorption and the hydrogen adsorption capacity strongly depends on the natural pore characteristics of diatomite. Large surface area, appropriate pore volume and small pore size with intensive distribution benefits hydrogen adsorption. Meanwhile, the structure and composition of diatomite will not be damaged after hydrogen adsorption. An effective metal-modified method has been developed to disperse Pd and Pt nanoparticles on diatomite. The hydrogen adsorption capacity could be enhanced after the incorporation of noble metal.

Incorporation of \_0.5 wt.% Pt and Pd can markedly increase the hydrogen adsorption capacities (0.5–1.1 times higher). The diatomite mineral materials would lead to be novel ones in the performance of hydrogen storage.

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