

ZEOLITE AS MATERIAL FOR HYDROGEN STORAGE
IN TRANSPORT APPLICATIONS

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For transport needs the hydrogen is mostly stored in a compressed (at 350–700 bars) form, while methods for its storage at lower pressures are rapidly developing. In particular, nanoporous oxides and zeolites, which do not normally absorb notable amount of hydrogen, with a small Pd additive or ion exchange demonstrate enhanced hydrogen adsorption properties. An original thermogravimetric method has been developed to study the hydrogen adsorption in zeolite, consisting of its heating in the inert gas (argon, nitrogen) flow and cooling in the hydrogen atmosphere. It is found that natural zeolite (clinoptilolite) with Mg-ion exchange possesses a high adsorption capacity for hydrogen – up to 6.2 wt%, which is explained by its encapsulation in zeolite pores. The FTIR spectra of the hydrogen-treated samples have shown new absorption bands at 2340 and 2360 cm^{-1} .

Key words: *hydrogen storage, zeolite, spillover effect, Pd/zeolite composite*

1. INTRODUCTION

Storing hydrogen molecules in porous media based on a physisorption mechanism is one of the approaches to reach the US Department of Energy (DOE) target for 2015: 9 wt% at on-board hydrogen storage [1]. Results on the hydrogen storage in zeolite reported in [2] show that the 2010 DOE target (6 wt%) can be reached using appropriate materials and low-temperature (77 K) treatment. Nowadays, as hydrogen storage materials the stable and metastable metal hydrides as well as different chemical hydrides [3–5] replacing tanks with compressed gas are being studied for commercialization in the transport sector and autonomous power supply systems. These materials are characterized with slow kinetics and, therefore, non-reversibility. Unfortunately, none of the metal hydrides meets the requirements – highly reversible storage capacity and fast kinetics at ambient temperature – for commercial use as hydrogen storage materials. Reversibility and fast kinetics could be expected in zeolite, since in the hydrogen physisorption (as a non-activated process [6]) weak van-der-Waals forces (dispersion, orientation and induction) are involved [7]. However, many researchers (see, e.g. [8–10]) do not consider practical applications of zeolites because of too small amount of hydrogen that could be absorbed.

In the case of Pd/oxide composites the hydrogen is adsorbed and dissociated by the so-called spillover effect [11]: in particular, such catalysts as Pd and Pt

enhance the hydrogen sorption capability through “spillover”, when nanoporous oxide surface serves as an inert oxide substrate for hydrogen transport. We have already reported gravimetric and volumetric hydrogen adsorption and desorption results for different Pd- (Pt-) activated porous oxides and zeolites [12, 13]; however, still opened is a question about the hydrogen adsorption centres. In this work, to study the hydrogen adsorption on natural zeolite the infrared spectroscopy was used.

2. EXPERIMENTAL

For our investigation the natural zeolite – clinoptilolite (from Ukraine deposits) was used. Before the experiments, zeolite samples were washed in deionized water 4–5 times. To exchange Mg^{2+} cations in zeolite, 1 ml/l MgCl_2 salt solution was prepared. Zeolite in the solution was mixed using magnetic stirring for 48 h at 40 °C. After the ion exchange procedure, the sample was washed with deionized water at least 3 times and dried in air at 100° C for 12 h.

The thermogravimetric hydrogen sorption method used in the work was elaborated in our laboratory [13] based on a commercial thermogravimeter *SHIMATZU TG-TDA* at constant gas flow 50 ml/min of two test gases: argon (or nitrogen) – for heating, and hydrogen – for cooling the samples (Fig. 1). As test material in this adsorption/desorption method we used commercial Pd powder (<75 μ , 99.9%, *Aldrich*). All experiments were performed in aluminium crucibles, with the sample mass about 35 mg. As seen in Fig. 1, the first stage of the proposed method is actually the sample cleaning from adsorbed gases, while the second stage – adsorption of the selected gas (in our case hydrogen) in the sample.

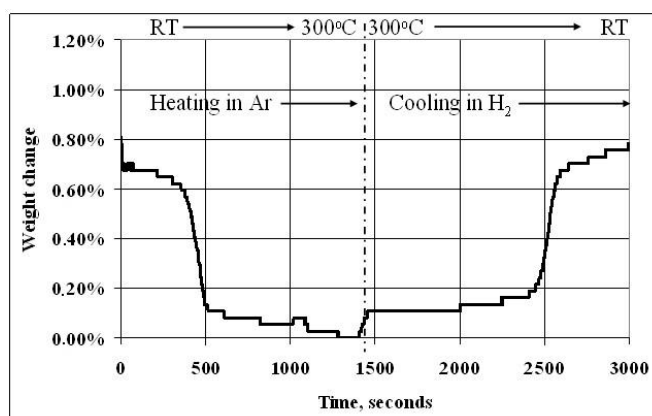


Fig. 1. Schematic of the thermogravimetric hydrogen desorption-adsorption for a palladium powder sample.

For FTIR (Fourier transform infrared spectroscopy) analysis a Bruker VERTEX 80v with a diffuse reflectance sphere was used in the wavelength region 500–7000 cm^{-1} .

3. RESULTS AND DISCUSSION

Ions of different metals are known to strongly promote the hydrogen adsorption in zeolites; therefore, we performed Mg-ion exchange in clinoptilolite.

The thermogravimetric method has shown the highest values of adsorbed hydrogen (up to 6.2 wt%) for zeolite (Mg-exchange), and a lower value (5.3 wt%) for the washed sample (Fig. 2). From our previous results it follows that the zeolite finely ground without activation has a marked hydrogen adsorption capacity – up to 7 wt% when heated in the nitrogen atmosphere [13]. Slightly lower adsorption capacity was observed for Pd-activated zeolite. In the mentioned work up to five desorption/adsorption cycles were realized, with recurrence of the results.

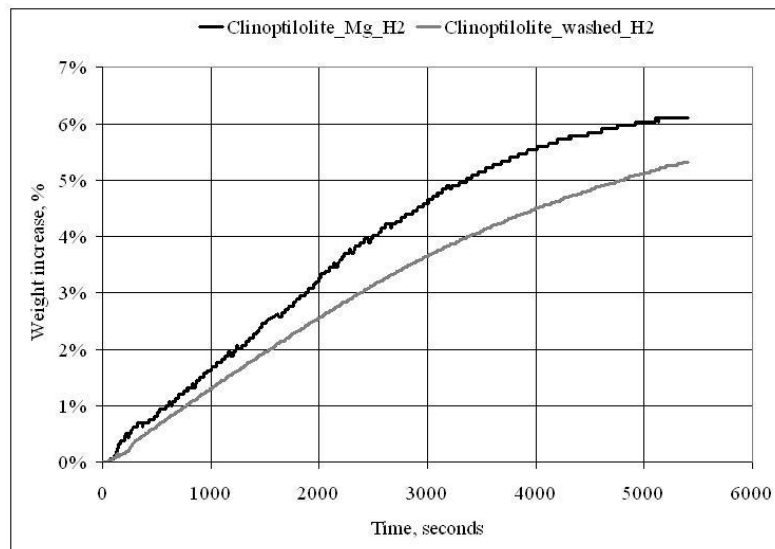


Fig. 2. Thermogravimetric hydrogen adsorption of Mg-exchanged and washed clinoptilolite sample.

The measurements were repeated several times for different fine and coarse zeolite samples activated with Pd nanoparticles and without activation, with similar results obtained. The results of thermogravimetric method could be explained by the hydrogen encapsulation mechanism in zeolite (proposed in [9, 10]). During the cleaning stage the inert gas flow at the atmosphere pressure leaves the zeolite pores in a slightly stressed state; small hydrogen molecules can easily enter the stressed pores while replacing the inert gas by hydrogen at higher temperature (150–200 °C). The following cooling to room temperature closes the pores or contracts their inlet channels, and, therefore, hydrogen remains in the pores.

FTIR spectra of the washed and Mg-exchanged clinoptilolite before and after the hydrogen treatment are shown in Fig. 3.

Typically, FTIR spectroscopy is used to specify the structure of zeolites and monitor the reactions in zeolite pores, at vibration frequencies mostly in the range 200–1500 cm^{-1} [14]. In the O-H stretching region (3000–5000 cm^{-1}) the infrared spectra of zeolites contain information on the hydroxyl groups attached to the zeolite structures. From five types of hydroxyl groups that are present in zeolites [14] in our samples only two (OH groups attached to extra framework alumina (EFAL) species, $\sim 3655 \text{ cm}^{-1}$, and bridging OH groups with Bronsted's acidity, ~ 3630 and 3560 cm^{-1}) were noticed (Fig. 3). New peaks at 2340 and 2360 cm^{-1}

(Fig. 3, inside) appear in the FTIR spectrum after the treatment in hydrogen, which can be explained rather by O–H stretching vibrations in a water molecule confined in a nanopore [14] than by those in a hydrogen molecule adsorbed in zeolite at 77 K ($\sim 4100\text{ cm}^{-1}$) [15].

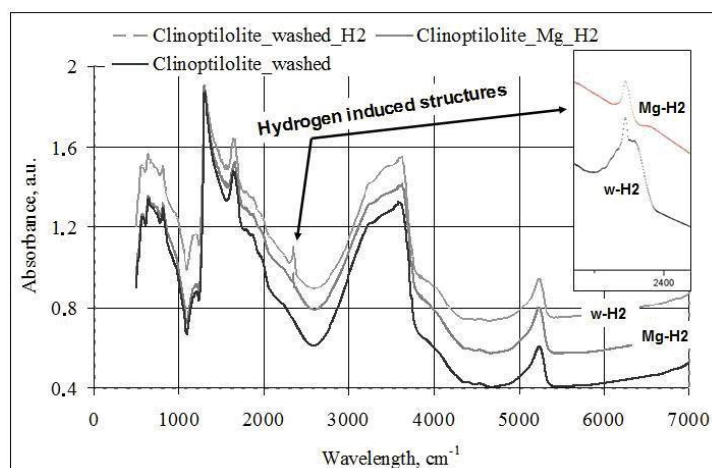


Fig. 3. FTIR spectra of washed and Mg-exchanged clinoptilolite samples before and after hydrogen treatment.

4. CONCLUSIONS

The method elaborated for measuring the hydrogen storage capacity in solid materials with a commercial thermogravimetric instrument has been successfully tested. It consists of three steps:

- 1) thermal and inert gas flow treatment to decontaminate the samples;
- 2) exposure of the samples to hydrogen gas flow at elevated temperature; and
- 3) cooling them down to room temperature in hydrogen atmosphere.

Using this method allowed us to obtain the hydrogen adsorption capacity of Mg – 6.2 wt% for exchanged zeolite (clinoptilolite). The mechanism of hydrogen encapsulation in the pores of zeolite has been adapted to explain such a high hydrogen uptake.

In the FTIR spectra of both clinoptilolite samples new absorption bands at 2340 and 2360 cm^{-1} are observable after hydrogen treatment.

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CEOLĪTA KĀ ŪDEŅRAŽA UZGLABĀŠANAS VIDES IZPĒTE

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Kopsavilkums

Mūsdienās transportlīdzekļos ūdeņradis pārsvarā tiek izmantots saspiestā veidā 350–700 bāros, taču intensīvi tiek attīstītas arī metodes uzglabāšanai zemākos spiedienos. Nanoporaini oksīdi un ceolīti parastos apstākļos absorbē nelielu ūdeņraža daudzumu, taču aktivācija ar nelielu pallādija daudzumu vai jonu apmaiņa šajos materiālos var nodrošināt ievērojamu ūdeņraža adsorbciju. Izstrādāta oriģināla termogravimetrijas metode, lai pētītu ūdeņraža adsorbciju ceolītos, kas sastāv no parauga iztīrīšanas stadijas, to sildot inertās gāzes (argona, slāpekļa)

plūsmā, un dzesēšanas stadijas ūdeņraža atmosfērā. Konstatēts, ka dabiskais ceolīts (klinoptilolīts) ar iemainītiem Mg joniem uzrāda augstu ūdeņraža adsorbcijas spēju – līdz 6,2 svara%, ko var skaidrot ar ūdeņraža ieslēgšanu ceolīta porās dzesēšanas procesā. Furje infrasarkanajos spektros ar ūdeņradi apstrādātos paraugos novērota jaunas joslas 2340 un 2360 cm^{-1} parādīšanās.

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