

IV.C.1g Hydrogen Storage by Spillover

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Objectives

- To achieve the 28 g/L volumetric storage target at room temperature by 2010 by using nanostructured sorbents aided by hydrogen spillover.
- To develop a mechanistic understanding for hydrogen spillover that leads to hydrogen storage.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

- To develop hydrogen storage materials with capacities in excess of 28 g/L volumetric storage and 4.5 wt% at room temperature.
- To increase the rates of spillover.
- To develop direct metal doping technique on carbons or zeolites for maximum spillover storage.

Accomplishments

We have developed two metal-doped zeolites that showed 20 and 21 g/L volumetric capacity at 298 K and 100 atm. Unlike metal organic frameworks (MOFs), zeolites are highly stable and low-cost. The Ni-doped zeolites, in particular, are most promising for practical applications after further development [1].



Introduction

Because of the high bulk densities of zeolites which are substantially higher (2-3 times higher) than that of carbons and metal organic frameworks, plus the high densities of cation sites on a variety of zeolites, zeolites are promising sorbents for achieving high volumetric storage capacities.

Approach and Results

Hydrogen adsorption properties of low-silica type-X zeolites (LSX, Si/Al = 1) [1,2] containing alkali or alkali-earth metal cations (Li⁺, Ca²⁺, and Mg²⁺) have been studied in this project. Li-LSX is commercially used for air separation. It was found that the hydrogen adsorption capacities of LSX zeolites at 77 K were determined mainly by the porosity of the zeolite, while at 298 K, the storage capacities depended on both the H₂-cation interactions and the porosity. Among the three exchanged zeolites, Li-LSX had the highest H₂ capacity of 1.5 wt% at 77 K and 1 atm, and Ca-LSX had the highest capacity of 0.50 wt% at 298 K and 10 MPa.

Hydrogen storage in LSX zeolites via spillover was also investigated [1]. Three methods including bridge building with a catalyst, metal doping via incipient wetness impregnation and metal doping via chemical vapor deposition (CVD) were employed to induce hydrogen spillover and enhance the storage capacities. Thus, the storage capacities were increased to 0.96-1.2 wt% on the Pt-doped zeolites at 298 K and 10 MPa. The differences between the three methods were compared and discussed [1]. Furthermore, 5 and 10 wt% Ni were doped on Ca-LSX zeolite. The 10 wt% Ni-doped Ca-LSX zeolite showed a storage capacity of 1.15 wt% at 100 atm and 298 K. The important volumetric storage capacities of these zeolites were also estimated based on the densities of the densified zeolites. 21 g/L was obtained for Pt-doped Ca-LSX and 20 g/L was obtained for Ni-doped Ca-LSX, both at 298 K and 10 MPa. The high volumetric capacities were obtained because of the high densities of zeolites which are substantially higher (2-3 times higher) than that of carbons and MOFs.

CVD-Pt/Ca-LSX

In the present study, 5 wt% Pt was doped on Ca-LSX zeolite by CVD of the platinum precursor (Trimethyl) methylcyclopentadienyl platinum (IV) and subsequent reduction in a hydrogen atmosphere. The transmission electron microscope (TEM) image of CVD-Pt/Ca-LSX showed nanosized Pt (~1-3 nm) were well dispersed on the particles of LSX. The hydrogen adsorption isotherm at 298 K (Figure 1) showed that CVD-Pt/Ca-LSX had a storage capacity of 1.20 wt% at 10 MPa, enhanced by a factor of 2.4 compared with that of plain Ca-LSX (0.5 wt%). Reversibility was evaluated by measuring the desorption branch down to 1 atm. The desorption branch nearly followed the adsorption branch although there appeared to be a slight hysteresis. The second adsorption isotherm was in agreement with the first adsorption isotherm. These results indicated that hydrogen adsorption in the CVD-Pt/Ca-LSX was reversible at 298 K.

Ni/Ca-LSX

5 wt% Ni was doped on Ca-LSX by incipient wetness impregnation of an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and subsequent reduction in a hydrogen atmosphere at 723 K. The TEM image showed that black Ni particles were dispersed on the LSX zeolites with sizes around 4-10 nm. The loading amount of Ni on Ca-LSX was further increased from 5 to 10 wt% to increase the dissociation sites. As shown in Figure 2, the 10 wt% Ni/Ca-LSX had a storage capacity of 1.15 wt%. Although the loading amount of Ni was doubled, the storage capacity was not increased much.

The volumetric storage capacity of Ni/Ca-LSX was estimated to be 20 g/L (Figure 2), based on the pellet density of 1.7 g/cm^3 . This indicates Ni/Ca-LSX is a promising sorbent for onboard hydrogen storage.

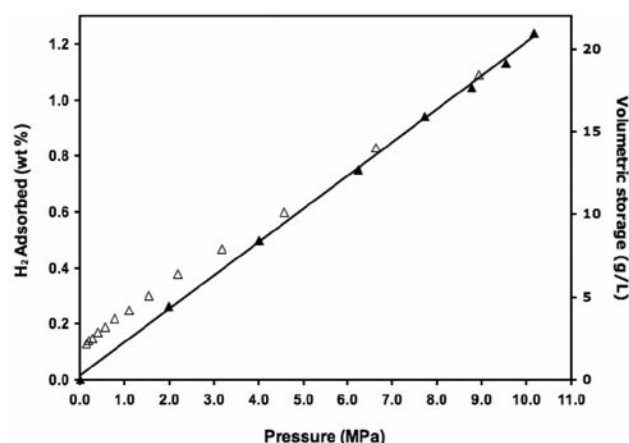


FIGURE 1. High-Pressure Hydrogen Isotherms on CVD-Pt/Li-LSX (adsorption: ▲; desorption: △) at 298 K and 10 MPa [1]

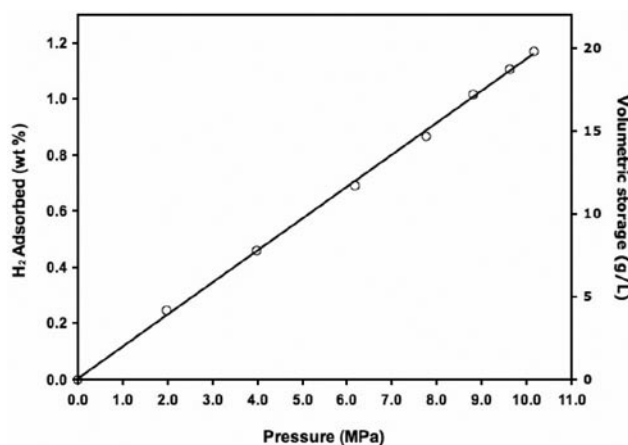


FIGURE 2. High-Pressure Hydrogen Isotherms on 10 wt% Ni/Ca-LSX (○) at 298 K and 10 MPa [1]

Conclusion

The updated DOE volumetric target for onboard storage is 28 g/L at near ambient temperature and 100 atm. The two metal-doped zeolites reported here showed 20 and 21 g/L. Unlike MOFs, zeolites are highly stable and low-cost. The Ni-doped zeolites, in particular, are most promising for practical applications after further development.

References

1. L.F. Wang and R.T. Yang, *Ind. Eng. Chem. Res.*, 2010, DOI:10.1021/ie1003152.
2. R.T. Yang, *Adsorbents: Fundamentals and Applications*, Wiley, Hoboken, NJ, 2003, Ch. 7.

Highlights of 2005-2010

- Developed a bridge-building technique for spillover storage, and obtained up to 4 wt% storage with MOFs at 298 K and 100 atm (U.S. and foreign patents pending).
- Achieved 1.2 wt% hydrogen storage on a Pt-doped superactivated carbon (AX-21) at 100 atm and 298K. Capacities of 1.6 wt% was obtained on Ru/carbon, and 1.1 wt% on Ni/carbon.
- The spillover storage process is reversible at 298 K, i.e., full storage capacity is obtained after degassing at 298 K.
- Developed a simple isotherm equation that is applicable to all spillover sorbents.
- For all spillover sorbents, the rates of discharge at 298 K exceeded the DOE target of 0.02 g/s/kW.
- Developed catalysts that could increase the rates of both charge and discharge for spillover storage.

- Increased spillover storage capacities on carbon by 10-40% by each of the following techniques: introducing surface oxygen groups, doping nitrogen and/or boron, plasma treatments, and dosing H₂ with hydrocarbon impurities.
- Using deuterium isotope tracer, direct evidence for dissociation/spillover and reverse spillover was obtained.

FY 2010 Publications

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