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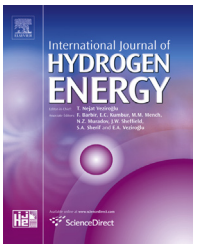

Kinetics of hydrogen adsorption in MIL-101 single pellets

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ABSTRACT

A new type of MIL-101: aluminum composites with improved thermal conductivity is reported and their hydrogen adsorption rate investigated in a systematic study of hydrogen adsorption/desorption kinetics of MIL-101 single pellets, filling the gap of data on hydrogen sorption kinetics by compressed monoliths in the cryo-adsorption storage conditions.

Kinetic curves were measured within a wide range of pressure in the temperature range 77–159 K and the hydrogen diffusivity were estimated from the rate constants obtained by fitting the fractional uptake with the kinetic equations. In order to compare MIL-101 with other metal-organic frameworks (MOFs), measurements on pellets of MIL-100(Fe) and HKUST-1 were also performed. As expected, the results, together with some data available in literature, reveal that the hydrogen diffusivity obtained from kinetic studies is strongly related to the pore diameter. The activation energy of hydrogen diffusion in MIL-101, calculated from the rate constants, is 1.6 kJ mol^{-1}, close to the literature values reported for other MOFs. Kinetic studies on composite pellets of MIL-101 with Al tapes (8–10%) with improved thermal conductivity (~0.5 W $m^{-1}K^{-1}$) are also reported. They show indeed higher uptake rates, consistent with the requirement of fast filling time (less than 3 min) required for applications. The adsorption/desorption rate at 77 K allows ~90% fractional uptake in about 40 s, promising for applications of cryo-adsorption storage. The results show that the time required to reach saturation and thermal equilibrium depends on pellet geometry and hydrogen diffusivity.

Introduction

The recent introduction of fuel cell electric vehicles on the market was noted as a demonstration of combined achievements in the technology of fuel cells, hydrogen production, delivery and storage [1]. For hydrogen storage, the near term is focused on compressed gas at 700 bar while cryo-compression, metal hydrides, physisorption on high surface area sorbents and chemical storage are considered for longer terms.

Metal-organic frameworks with their high surface area and large pore volume are considered the most promising adsorbents for hydrogen, methane, carbon dioxide, acetylene and other gases. High hydrogen storage density on MOFs can be obtained only at low temperatures, because of their low heat of adsorption. A comparative analysis of cryo-compression and cryo-adsorption, with focus on MOF-5 and MIL-101 as

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Nomenclature

F	fractional excess uptake
m_t	hydrogen mass (adsorbed at time t)
m_∞	hydrogen mass at equilibrium (adsorbed at time t_∞)
D_c	intra-crystalline diffusivity
r_c	crystal or particle radius
k_F	mass transfer coefficient for FD model
k_L	mass transfer coefficient for LDF model
α	parameter that describe the uptake in experiments at constant volume
Λ	the amount of hydrogen consumed (generated) in the system by adsorption (desorption), relative to the amount at start
ε	macroporosity (interparticle void)
ε_μ	microporosity (particle void)
ε_{tot}	total porosity
a	thermal diffusivity
e	thermal effusivity
k	thermal conductivity
C_v	volumetric heat capacity
τ	equilibrium time;
c_∞	excess uptake at equilibrium pressure P^∞ (identical with N_{ex} in wt.% H_2 units – in pcT curves) at a given temperature T
P^{**}	hydrogen pressure introduced in sample cell
$k_F{}^p$	corrected mass transfer coefficient for FD model
$k_L{}^p$	corrected mass transfer coefficient for LDF model
K_n	Knudsen number
D_t	transport diffusivity
D_o	corrected transport diffusivity
D_s	self-diffusivity
R_p	pellet radius
$F^{FD}{}_{calc}$	calculated fractional excess uptake by FD model
$F^{LDF}{}_{calc}$	calculated fractional excess uptake by LDF model
E_A	activation energy of the thermally activated diffusion
V_p	pore volume
S_{BET}	BET surface area

the most promising sorbents, concludes that "the cryogenic temperatures needed for both techniques could be viewed as problematic for application situations without access to liquid hydrogen or liquid nitrogen (for 80 K fueling), or as a complete non-issue for those scenarios with developed LH_2 or LN_2 infrastructure" [2]. The advantage of liquid hydrogen in cost, weight and specific storage capacity is of interest for the development of liquid hydrogen storage systems [3]. However, the car manufacturers are also interested in hydrogen storage on MOFs at cryogenic temperatures for new generations of vehicles [4].

For on-board applications, a high volumetric total storage capacity is essential in order to minimize the volume of the storage tank. Generally, the MOFs are materials with low crystal density and lower powder densities (0.15–0.20 g cm^{-3}). Their total storage capacity (the adsorbed amount plus compressed gas within pores and inter-grain voids) can be substantially increased by compression of powders in pellets form. Hydrogen adsorption was reported on MOF-5 pellets [5–7], MOF-177 [8,9] and MIL-101 pellets [10,11]. The pellets of MIL-101, a robust MOF resistant to water, show a total storage capacity that reaches DOE targets, though only in the cryo-adsorption range of interest (77.3–150 K) [12]. Experiments on MIL-101 pellets of bulk density (0.7–0.72 g cm^{-3}), higher than crystal density, show a significant decrease of storage capacity [13].

High storage capacity (gravimetric and volumetric), moderate pressure, cycling behavior-full reversibility, fast kinetics (refueling time 3 min) are required for applications [14]. The adsorption/desorption is an exothermal/endothermal process and the heat involved must be removed/supplied to the storage tank. Properties such as storage capacity, heat of adsorption, heat capacity and thermal conductivity are essential for thermal modeling of hydrogen storage tanks [15–18].

Studies of hydrogen adsorption kinetics by small amounts of powder have been reported on MOF-5 [19], MOF-177 [20] and MIL-101 [21] for which a very small temperature increase was observed on a few milligrams of sample. However, for high amounts of pelletized sorbent the situation is different and the heat management is crucial. Modeling of single MOF-5 pellet [6] shows that the heat released at rapid pressurization can increase the pellet temperature up to 160 K, so restoring to 80 K needs an adequate thermal conductivity material.

The rate of hydrogen adsorption/desorption can be increased only by improving the thermal conductivity of the pellets. MOF-5 pellets with 5–10% expanded natural graphite (ENG) with increased thermal conductivity were reported and their hydrogen storage capacity measured and modeled [21,22]. The thermal modeling of MOF-5:10%ENG cylindrical pellets (1 × 1 cm) with thermal conductivity 0.55 W m^{-1} K^{-1}predicts an almost complete adsorption at 80 K and 30 bar [16]. Although in a first stage, the pellets temperature increase, as a consequence of exothermal hydrogen adsorption, the equilibrium should be approached in about 40s because of their increased thermal conductivity [6].

Recently, the thermal conductivity and specific heat capacity of some MOFs were measured in conditions close to cryogenic hydrogen storage, pointing out to the implication of ortho-para hydrogen conversion to the extension of the dormancy time [23,24].

While the material engineering properties, such as the specific heat capacities and thermal conductivity, were recently reported for some MOFs [6,21,22,24–27], the adsorption/desorption kinetics is scarcely reported for compressed MOFs pellets, except for MOF-5 pellets of bulk density 0.39 g cm^{-3} at 77.3 K and high pressure [7].

The higher thermal conductivity of aluminum as compared to ENG [28] motivated us to investigate the effect of Al as additive to improve the rate of hydrogen adsorption. In the present study we explore the hydrogen adsorption/desorption kinetics of MIL-101 powder, pellets and composite pellets with Al. Some MIL-100(Fe) and HKUST-1 pellets have

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