Development of a new volumetric gravimetric device of H_2 sorption for the analysis of zeolites under equilibrium conditions

B. Weinberger[1]*, F. D. Lamari*[1]*, S. Kayiran*[1] *and S. Moreau*[2]
[1]CNRS LIMHP UPR1311, 99 Avenue J.B. Clément, 93430 Villetaneuse, France.
[2]Air Liquide CRCD, 1 chemin de la Porte des Loges, 78354 Jouy en Josas, France.

For the H_2 production, realized by reformation or partially oxidation of hydrocarbons using the Pressure Swing Adsorption (PSA) as key method, the knowledge of thermodynamic parameters of the used adsorbents like selectivity, heat of adsorption and desorption are magnitudes for the efficiency of the process. For the separation of gas mixtures using zeolites is very interesting because of the surface charges of this material. The aim of this work is the determination of the thermodynamic data obtained from sorption measurements of gases on different zeolites under equilibrium conditions. So, a new experimental setup for the measurement of adsorption by the gravimetric-volumetric method was built. Intended for the study of thermodynamic gas equilibriums in adsorbents, either in the powder shapes or of pellets, it allows also the study of their equations of state. The device is designed to operate with pure gases until a maximum pressure of 5 MPa and temperatures ranging between 273.15K and 333.15K. As well the regeneration process is integrated up to 673.15K and secondary vacuum. The reliability of this device was established by comparison with results obtained in the Claude-Delorme Research Center at *Air Liquide* (France) and those referred in National Institute of Standards and Technology databases (USA). With our experimental device, we determined isotherms of adsorption of pure gases (H_2, CH_4, CO_2 and N_2) at several temperatures. The analysis of the results enables to conclude that the capacity of adsorption of a material is evaluated in a reliable way only if its true density were determined by helium displacement at high temperature. The considerable influence of the ratio of exchanged cations on hydrogen gas adsorption was highlighted for Na-LSX exchanged at the rates of: 78%, 83% and 99%. Among the considered zeolites, our research study leads to the selection of the best adapted to an effective use for the H_2 purification by PSA process.

Introduction

Hydrogen production by the reforming of natural gas followed by a purification using pressure swing adsorption (PSA) as key method is now the cheapest production way. The main advantage of the PSA in comparison to cryogenic and a permeation processes is the high product purity of up to 99.9999%. This is a quite important argument because proton exchange membrane fuel cells need hydrogen of high purity to prevent the degradation of cell membrane efficiency. Indeed, the world production of hydrogen currently rises approximately to 500 billions Nm^3/year but only 4.2% of this production is marketed, the major part of the production of hydrogen being used like produces intermediate in the synthesis of ammonia. In addition, with 14.4 $10^{15} \cdot$J/year, the share of hydrogen is negligible compared to the consumption of total primary energy. So it seems useful to make investigations for the optimisation of technologies like PSA to get clean and cheap hydrogen from natural gas or biomass in large amount.

In this paper we debate new framework materials of aluminosilicate able to lower the price of hydrogen production using the PSA engineering. The significant criteria of the performance of an adsorbent for the application in a PSA process are the capacity of adsorption of the components in the mixture containing H_2, CO_2, CO, N_2 and H_2O, the selectivity between the components to be adsorbed and those to let pass, the heat of adsorption and the desorbability of the components in the used range of pressure. Surely the price of the adsorbent is also a very important criteria. A successful way to get the needful information about the performance of a material is to measure its thermodynamical equilibrium at a fixed temperature and various pressures. The measurement of hydrogen equilibrium is quite difficult because the interactions between this gas and the surface of the material are weak. The principal problems during measurements of isotherms of adsorption of hydrogen are its high volatility and its weak adsorption. Consequently, we chose a procedure, which makes it possible to detect the escapes in the system, and were the systematic errors are negligible. The chosen experimental setup called gravimetric–volumetric measurement has got otherwise the advantages that there is no lifting force, like in the case of the gravimetric measurements and that there is no accumulation of the error like it is the case with the volumetric measurements. A scheme of the experimental setup is shown in figure 1.

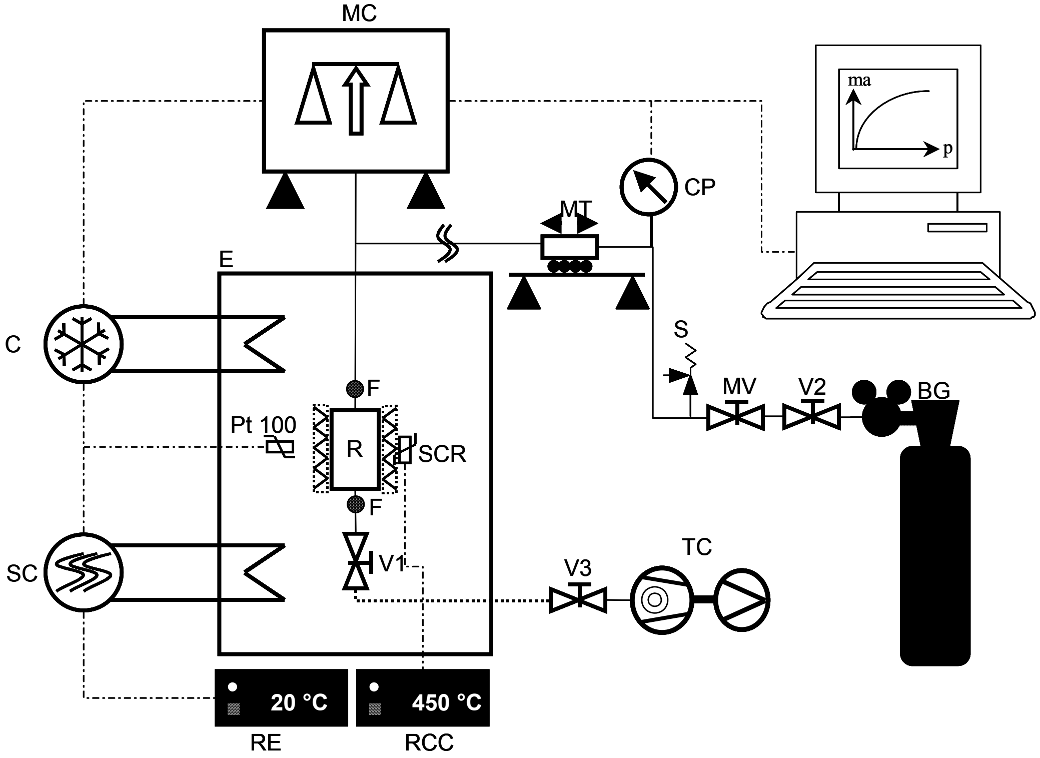

Figure 1: **MC**, Mass Comparator (Mettler Toledo, PR2004); **E**, Incubator (S.P.A.M.E.); **C**, Unichiller (Huber, 7006A-H); **SC**, Heating System; **Pt 100**, Platinum temperature sensor; **R**, Pressure Vessel; **SCR**, Heating system of the pressure vessel; **F**, Micro filters; **v**, Valves (Autoclave); **RE**, Regulation of the incubator (Eurotherm 2404), **RCC**; Regulation of the SCR (Watlow Série 93) ; **TM**, Micrometric table (Micro Controle); **CP**, Pressure gauge of reference (DH Budenberg DPM1); **S**, Security valve (Air Liquide) ; **VM**, Micrometric valve (Autoclave); **BG** Gas bottle (Air Liquide) ; **TC**, Turbo pump (Pfeiffer Vacuum TSH 071).

We obtained results for different, very promising zeolites type faujasite exchanged at different degree of cations in the view of application as adsorbents for PSA engineering. These materials are compared under the aspect of capacity of adsorption, the heat of adsorption and pressure range applicability for hydrogen. For the considered gas hydrogen adsorption selectivity of the Li-LSX exchanged molecular sieves at the rates of 78%, 83% and 99% have been performed up to a pressure of 5 MPa at a temperature of 293.15 K (see figure 2).

Adsorption properties of adsorbed species in faujasite zeolites are known to be strongly correlated to the nature and amount of cations in the structure. Adsorption as well as diffusion is in relation with the location of the cations. Therefore, we modified the chemical nature of the zeolites by exchanging the cations and as well the pore entry diameter which influences gas diffusion inside the exchanged zeolites.

The Na LSX sample was prepared hydrothermally according to the procedure described by Kühl from a gel with the molar composition : 1 Al_2O_3 : 2 SiO_2 : 4.9 Na_2O : 1.6 K_2O : 110 H_2O. Ionic exchange of the zeolite by lithium is realized by percolation technique. Different structural characterization techniques were performed on these crystals like X ray diffraction and scanning electronic microscopy for help to discuss the effect of the exchange on crystal morphology and structure and the influence of these adsorbent parameters for the PSA process.

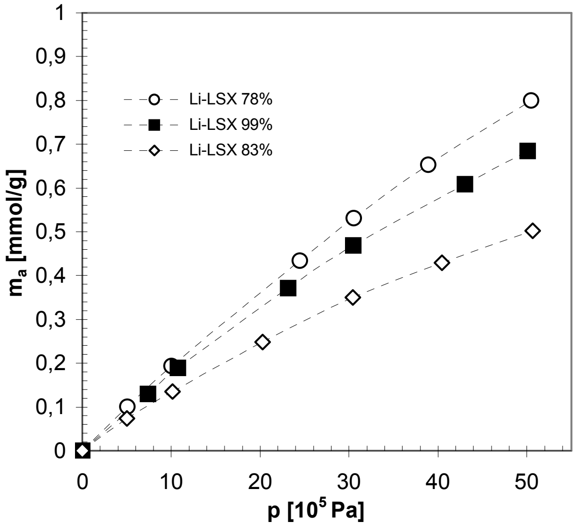

Figure 2: Adsorption equilibrium of the zeolites Li-LSX exchanged 78%, 83% and 99% with hydrogen at 293.15K.