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Hydrothermal and microwave synthesis of SAPO (CHA) zeolites on aluminium foams for heat pumping applications

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Dedicated to Prof. Carmine Colella on the occasion of his 70th birthday.

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ABSTRACT

In this paper, a study on direct growth of SAPO (CHA) zeolites on aluminium foamed supports is presented. A preliminary investigation on SAPO-34 and SAPO-44 syntheses was carried out by conventional hydrothermal and microwave route to select appropriate formulations for in situ growth on aluminium foams. Adsorption capacity of coated foams were evaluated by a McBain system and compared to adsorption isobars of pure zeolites measured by a Chan microbalance. Coated samples showed the typical behaviour of the corresponding zeolite, confirming that the interaction with aluminium support was not detrimental to the zeolite adsorption performances. SAPO-34 coatings grew ten times faster by microwaves than by hydrothermal route, while for SAPO-44 the microwave deposition was not feasible for the intense corrosion of aluminium foams.

1. Introduction

Since the beginning aluminosilicate zeolites have been the preferred adsorbent materials in adsorption heat pumps for their high water sorption capacity, mainly due to the high hydrophilic character of these porous materials [1,2]. However, such an elevated "water affinity" imposes to reach high temperatures during regeneration (desorption) phase so that high temperature heat sources are needed to drive the adsorption pump cycle. In mobile or residential applications of adsorption heat pumps, where such availability could represent a severe limitation, adsorption materials characterized by high water capacity and low regeneration temperatures have to be used [3]. More recently, SAPO zeotypes have been successfully proposed as possible alternative to alluminosilicate zeolites [4,5]. SAPO-34, for example, shows a water adsorption equilibrium curve with a typical "S-shaped" trend particularly suitable in the range of temperatures and pressures used in the thermodynamic cycle of adsorption heat pumps driven by low temperature sources [6].

The typical design of an adsorption pump is based on an "adsorbent bed" made of zeolite pellets or beads embedded into a heat exchanger [7]. However, the idea of replacing zeolite beads and pellets with zeolite coatings on the heat exchanger surfaces has recently gained interest among researchers for the increase in heat transfer and the consequent improvement of the adsorption pump efficiency [8–10]. Even if zeolite coatings can be deposited on a substrate by using binders (by dip coating, wash coating...) [11], direct synthesis on supports has the advantage of forming thin, well adherent layers of pure zeolite without extraneous components [7]. However, direct synthesis of SAPO coatings is a time-consuming process because the in situ growth is achieved by a conventional hydrothermal synthesis in presence of the support and SAPO syntheses take several hours, from 48 to 72 h (or more), at medium temperature and pressure ($T \sim 200\,^{\circ}\mathrm{C}$ and $P \sim 200$ atm) [12–15].

The aim of the present study was to investigate the feasibility of direct growth of SAPO zeolites with chabasite structure on aluminium foams for heat pumping applications. Aluminium foams could be the ideal support for the adsorption heat exchanger because of their high surface area and optimal thermal properties. Moreover, open cell foams have high surface area/mass ratio and high permeability therefore they can provide enough surfaces for coatings without hindering vapour flow [16]. SAPO zeolites were preliminary synthesized testing different formulations by varying raw material ratios and using two different organic templates. All syntheses were duplicated in a laboratory microwave oven. Next, selected formulations were used for direct growth of SAPO coatings on aluminium foams by conventional hydrothermal synthesis and by microwaves. Microwave synthesis of SAPO zeolites, indeed, is a well-established method as proved by numerous research papers reporting the successful preparation of various SAPO types [17–20]. However, few papers are available in literature concerning microwave synthesis of zeolites on supports [21–23], e.g. the synthesis of SAPO-34 membranes by microwaves was only recently reported by Chew et al. [24]. Our results demonstrated that

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microwaves can be profitably used for coating aluminium substrates with the typical advantages of microwave syntheses.

2. Experimental

2.1. Zeolite synthesis

In all formulations two different aluminium sources have been used, pseudo-boehmite (Pural SB1, 74 wt.% Al_2O_3–26 wt.% H_2O) and aluminium isopropoxide (98 wt.% $Al(OC_3H_7)_3$ Aldrich), and two different organic templates, tetraethylammonium hydroxide (35 wt.% TEAOH Fluka) and cyclohexylamine (99 wt.% $C_6H_{11}NH_2$ Aldrich). The silica source was an aqueous solution of colloidal silica (40 wt.% SiO_2 Aldrich). Principal parameters adopted in hydrothermal and microwave syntheses are resumed in Table 1. A typical precursor solution (formulation "A" in Table 1) was prepared as follows: 37.3 g of distilled water were mixed with 19.7 g of aluminium isopropoxide solution and 10.9 g of orthophosphoric acid (85 wt.% Aldrich) at room temperature in a 180 mL PP-bottle and stirred until homogeneous (30 min). 4.3 g of colloidal silica were then added to the mixture which was stirred for additional 30 min (10 min). Finally, 27.8 g of TEAOH were added and the precursor solution stirred for further 30 min at room temperature.

Concerning hydrothermal synthesis (HY), 50 g of this solution were poured in a stainless steel autoclave (ID = 38 mm; h = 90 mm; vol. = 0.10 L), PTFE lined, and heated at 200 °C in an oven for 72 h at autogenous pressure. After synthesis, the solid product was rinsed four times with distilled water, separated by centrifugation and dried overnight at 80 °C. In microwave syntheses (MW), 50 g of precursor solution were transferred in a microwave radiation transparent autoclave (PTFE, ID = 35 mm, h = 90 mm; vol. = 0.087 L) and irradiated in a laboratory microwave oven (Milestone FlowSYNTH), which has a multimode cavity of size (internal dimension) w = 345 mm × d = 345 mm × h = 340 mm. The solution was heated from room temperature to 200 °C at a rate of 6 °C/min and maintained at that temperature for 6 h. The microwave power (at 2.45 GHz) was pulsed with on/off sequence and output power directly controlled by the oven's computer. The temperature was measured by a fibre-optic temperature probe immersed in the solution. Microwave syntheses were not stirred.

2.2. Direct synthesis on aluminium foams

Rectangular pieces (20 × 10 × 5 mm) of an open-cell aluminium foam (GoodFellow, Al6101, bulk density = 0.2 g/cm^3, porosity = 93%, 16/cm pores) were cut from a larger bar, cleaned at room temperature with trichloroethylene in an ultrasonic bath for 15 min and then rinsed with distilled water. The zeolite growth was obtained by HY and MW in situ syntheses, placing one piece of aluminium foam on the autoclave bottom and then adding the reaction mixture. Reaction temperature and time were the same used in HY and MW syntheses of SAPO zeolites. After the reaction, the foam sample was accurately washed several times with distilled water to remove the excess material. Finally, the sample was dried overnight at 80 °C.

2.3. Zeolite characterization and coating evaluation

Phase identifications and crystallinity were obtained by X-ray diffraction analysis (XRD) using an ITALSTRUCTURE APD 2000 diffractometer (CuKα radiation, 40 kV and 30 mA). XRD analyses on coated foams were run on powders obtained by grinding coated samples and separating the base metal as much as possible. At the same time, XRD were run on zeolite powders co-precipitated in the reactor during the deposition. Coating morphology, zeolite-metal interface and surface covering grade were evaluated by scanning electron microscopy (JEOL 5600LV operated at 20 kV).

2.4. Zeolite and coating adsorption measurements

Adsorption properties of synthesised zeolites were evaluated by a thermogravimetric technique based on the use of a Cahn 2000 microbalance, in the typical range of pressures (P = 10–25.5 mbar) and temperatures (30 °C $\leqslant T \leqslant$ 150 °C) of a "low temperature" adsorption cycle. About 50 mg of zeolite were loaded in the vacuum-tight vessel of the balance and then degassed under vacuum (1×10^{-3} mbar) for 8 h at 150 °C. Afterwards, a constant water vapour pressure was imposed over the sample by connecting the vessel with a thermostated evaporator. Once fixed the isobaric conditions, a number of equilibrium points were taken by directly measuring the sample weight variation corresponding to stepwise temperature changes. A detailed description of the methodology can be found in [25].

To measure adsorption behaviour of coated foam samples the Cahn microbalance cannot be used because of the excessive size and weight of specimens and a thermogravimetric McBain adsorption apparatus was used. The McBain setup (in Fig. 1) consisted in a sample holder hung to a micro-load cell (range: 0–1 g ± 0.0002) inside a quartz tube that is connected to a vacuum pump and a thermostated evaporator by a 2-way valve. The sample temperature is controlled by a thermocouple placed in the sample holder and can be varied by an external ring heater separately controlled. A typical measurement of water uptake was carried out putting three samples of coated foam (for a total weight of ≈700 mg) in the sample holder for a preliminary activation at T = 150 °C in vacuum (P = 0.01 mbar) for 12 h. The samples were, then, cooled down (in vacuum) to a fixed temperature T_f and the quartz tube connected to the evaporator at P = 10 mbar of vapour pressure (absolute). The sample holder weight was let stabilize (not less than 4 h) then the weight value recorded to measure the adsorbed water (water uptake). The measurement was repeated for six different T_f values, i.e. 30, 40, 50, 60, 80 and 150. The water uptake is expressed as percentage weight increase of the total mass of

Table 1
Main parameters for SAPO (CHA) syntheses. R = template molar ratio.

Formulation	Gel molar ratio					Template	Al-source	Heating system
	Al_2O_3	SiO_2	P_2O_3	R	H_2O			
A	1.0	0.6	1.0	0.7	70	TEAOH	Al isop	HY, MW
B	1.0	0.6	1.0	0.5	70	TEAOH	Al isop	HY, MW
C	1.0	0.6	1.0	0.4	70	TEAOH	Al isop	HY, MW
D	1.0	0.6	1.0	0.5	70	TEAOH	Pseudo-b	HY, MW
E	1.0	1.0	1.0	1.9	63	Cyclohex	Pseudo-b	HY, MW
F	1.0	1.0	1.0	2.5	63	Cyclohex	Pseudo-b	HY, MW
G	1.0	1.0	1.0	1.9	63	Cyclohex	Al isop	HY, MW
H	1.0	1.0	1.0	2.5	63	Cyclohex	Al isop	HY, MW