Recent advances in the field of nanoporous materials for energy and environmental applications

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Abstract

Advances in nanoscale science and engineering are providing unprecedented opportunities to develop more efficient and cost-effective materials and technologies for environmentally friendly processes.

Zeolites and related materials, such as functionalised mesoporous silicas and the more recent metal-organic frameworks (MOFs), represent a class of nanoporous materials characterised by very interesting and useful adsorption and/or ion exchange properties.

A brief overview on present and perspective utilizations of these materials in environmentally friendly processes, including solar and thermal energy storage, methane and hydrogen storage and CO2 capture, is here presented.

1. Introduction

The continued deterioration of environmental issues - from energy to water crisis, from climate change to deforestation - is a clear demonstration that the current model of development, based on an irrational exploitation of resources, a boundless energy consumption, an overproduction waste and pollution, is bringing humanity to a level never seen of environmental degradation and depletion of available natural resources.

Many of these problems can be connected precisely with the production of energy, whose currently adopted processes generate pollutant emissions that affect the whole geosphere, and particularly the atmosphere.

In this scenario, the scientific and technological research plays a critical role both through the exploitation of alternative energy sources with low environmental impact and the development of methods for the reduction of polluting emissions.

An important contribution in this area is provided by the science and technology of materials, especially through the synthesis of new materials. Among them, materials characterized by porous nanoscale structure (nanoporous materials) appear to be of enormous interest.

An important class of nanoporous materials is represented by zeolites and related materials, including the mesoporous silicas and the most recent hybrid materials based on a metal-organic structure (MOF, Metal-Organic Frameworks).

The porous structure results in a high specific surface area that, associated with the presence of chemically active sites, leading to the typical catalytic, adsorption and, in the case of zeolites, ion exchange properties.

There are many actual and potential applications of these materials in the field of energy and environment protection, some of which are described below.

2. Zeolites

Zeolites are, from a chemical point of view, hydrated aluminosilicates of alkaline and alkaline earth metals.

whose structure is constituted by a three-dimensional network of AlO_4^{5-} e SiO_4^{4-} tetrahedra linked through the sharing of oxygen atoms.

The spatial arrangement of these tetrahedra generates a network of cavities and interconnected channels having a diameter generally less than nanometer (nm, 1 nm = 10^{-9} m), the volume of which constitutes from 20% to 50% of the total volume of the zeolite crystals (Breck, 1974).

Under normal conditions, these cavities are occupied by water molecules and metal cations which, not being an integral part of the rigid aluminosilicate framework, can be, respectively, removed or exchanged without affecting the stability of the structure itself.

This justifies the extraordinary properties (adsorption, catalysis, and ion exchange) that characterize zeolites, both natural and synthetic, and on which are based on major industrial applications (Colella, 2002; Caputo and Pepe, 2007).

3. Ordered mesoporous silicas

In recent decades there have been many efforts for the synthesis of porous materials with pore sizes greater than those typically present in zeolitic structures (Davis, 2001). In 1992, researchers at Mobil Company have introduced a highly innovative synthesis technique, based on the possibility to use a supramolecular template constituted by surfactant micelles from which, by the following removal of the micelles, a porous solid is obtained (Kresge *et al.*, 1992; Beck *et al.*, 1992; Zhao *et al.*, 1998). By this technique, a class of mesoporous silica-based molecular sieves, called M41S, was produced: such materials (among which the most known terms are MCM-41, MCM-48 and SBA-15) show pore diameters between 15 and 100 Å. The development of these materials having well-defined, adaptable pore sizes, and functionalizable inner surface areas, has generated great interest in the chemical and petrochemical sector, due to their potential applications as catalysts and molecular sieves (Kresge *et al.*, 1992; Beck *et al.*, 1992). Recent progress in the techniques of internal functionalization of mesopores (Pasqua *et al.*, 2003; Gargiulo *et al.*, 2007; Gargiulo *et al.*, 2012) open new horizons for their use as adsorbents in gas separation processes.

4. Metal-organic frameworks (MOF)

Over the past decade considerable attention was paid to the definition of new approaches for the rational design and synthesis of zeolite-like materials with specific structures and functions. In this regard, the hybrid materials known as metal-organic frameworks (MOFs) can be considered the latest development of porous crystalline materials. Their structure is composed of individual units or small clusters of metal oxides joint by linking organic molecules (linkers) through strong covalent bonds. The final result consists in a framework similar to that of microporous zeolites (Li *et al.*, 1999). For this reason, MOFs are often labeled as "organic zeolites". The wide range of compounds useful as reagents for their synthesis allowed the production of numerous structures with specific surface area much higher (over 6000 m^2 / g) than what is usually detectable for active carbon and zeolitic materials. This characteristic, together with the detailed control of the size and chemical functionality of the pores, provides great freedom to design the structure more suited to a specific application.

5. Some application examples in the field of energy and environmental protection

5.1. Storage of solar and thermal energy

The sun, as a source of clean, free and renewable energy, is getting more and more attention among researchers.

However, the intensity of the solar radiation is subject to unavoidable fluctuations, due to the alternation of night and day, seasons and weather conditions, which in turn affect the efficiency of solar powered devices. The possibility to store the solar energy for a later use would represent a smart way to solve these problems.

Conventional methods to store thermal energy consist in varying the temperature of a suitable "reservoir device", or producing a phase change (usually solid-to-liquid or liquid-to-gas) of a fluid or also inducing an endothermic chemical reaction between two or more substances, but all these techniques involve some disadvantages, which practically limit the widespread availability of such technologies, and point out the importance of setting up alternative methods.

A method which use an adsorption-desorption cycle can be an interesting alternative. Generally speaking, the adsorption is the reversible process by which a solid (adsorbent) captures a liquid or a vapor (adsorbate) onto its surface. Being adsorption exothermic in nature, desorption is endothermic. It is so possible in principle to develop a device which allow to store energy by desorbing a fluid phase from an adsorbent substance, and to recover the same amount of energy simply by contacting again the adsorbent with the fluid. A critical aspect in the design of such a device would be the choice of the best adsorbent-adsorbate couple.

A common feature of many porous materials, such as zeolites, is the high affinity towards water molecules: zeolites are usually used as desiccants materials. Being the water adsorption a highly exothermic process, it is possible to store thermal energy using a cycle similar to that depicted in Figure 1, in which the thermal energy is: a) stored by heating the adsorbent (desorption step); b) used by contacting the anhydrous zeolite with water vapor (adsorption step).

This method would allow to store a higher energy density with respect than the conventional ones previously mentioned. Moreover, as far as the zeolite is held anhydrous, there is no loss of stored energy, allowing to virtually save it to infinity.

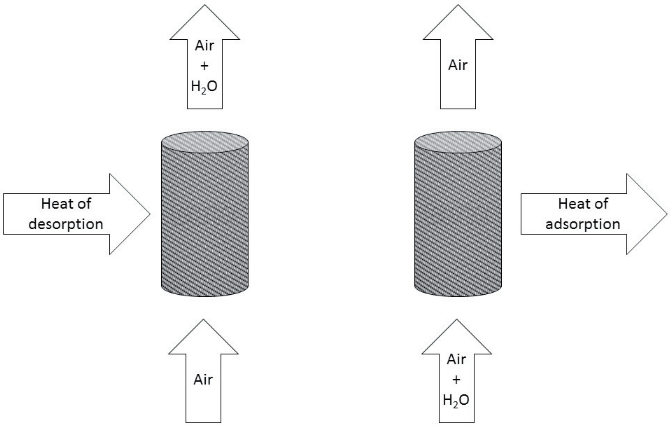

Figure 1 – Energy storage and reuse via a water vapor desorption-adsorption cycle.

Zeolitic materials are already used in "open heat pump" adsorption based devices, which are employed to store the thermal energy produced by conventional sources (Sizmann, 1989; Nan *et al.*, 1994; Hauer, 2002). These systems can assure high storage capacity, and can perform either heating or cooling tasks. In Munich, German (Hauer, 2002), devices are currently operating which combine a thermochemical energy storage system with a cogeneration module in order to recycle waste heat thus reduce the polluting emissions.

Solar thermal plants employing zeolitic materials can reach efficiency higher than 50% on average, much more than those of photovoltaic plants (12-15%). As an example, Vaillant recently put on the market a hot water heating system named Zeotherm, based on a zeolitic fixed bed and a solar energy heater (Vaillant Group, 2014).

This device basically consists of a condensation boiler and a zeolite bed under vacuum (see fig. 2 scheme). Its working cycle is composed by two steps:

I) Adsorption. It takes place in the lower part of the heating pump, where the water vapor in the vacuum reservoir is evaporated by the heat coming from the solar collector and carried to the zeolite bed, where is adsorbed and produces heat;

II) Desorption. It takes place in the zeolite bed, which is heated up by a burner, and frees the water vapor which is carried to the lower part of the heat pump where condenses, producing heat again.

This system can reach a per year efficiency higher than:

- 30% with respect to a conventional boiler
- 20% with respect to a modern boiler
- 10% with respect to a traditional boiler coupled with a solar energy system.

It also reduces the CO_2 emissions of about 30% at the same time.

Hauer and Fisher (2011) also proposed, in collaboration with Bosh Siemens Hausgeräte GmbH (BSH), a dishwasher which uses zeolites.

During a conventional dishwasher routine (fig. 3 – left), the water is heated twice: for the washing process (at about 50°C) and for the drying process (at about 60°C), which consists of the evaporation of the water from the dishes and its condensation on the dishwasher floor.

The dishwasher proposed by Hauer, recently put on the market, warms up and dries an air flow by means of adsorption on a zeolite bed in order to dry the dishes, and warms up the washing water by condensating the vapor desorbed from the same bed. In this way it is possible to perform just one heating instead of two, and, at the same

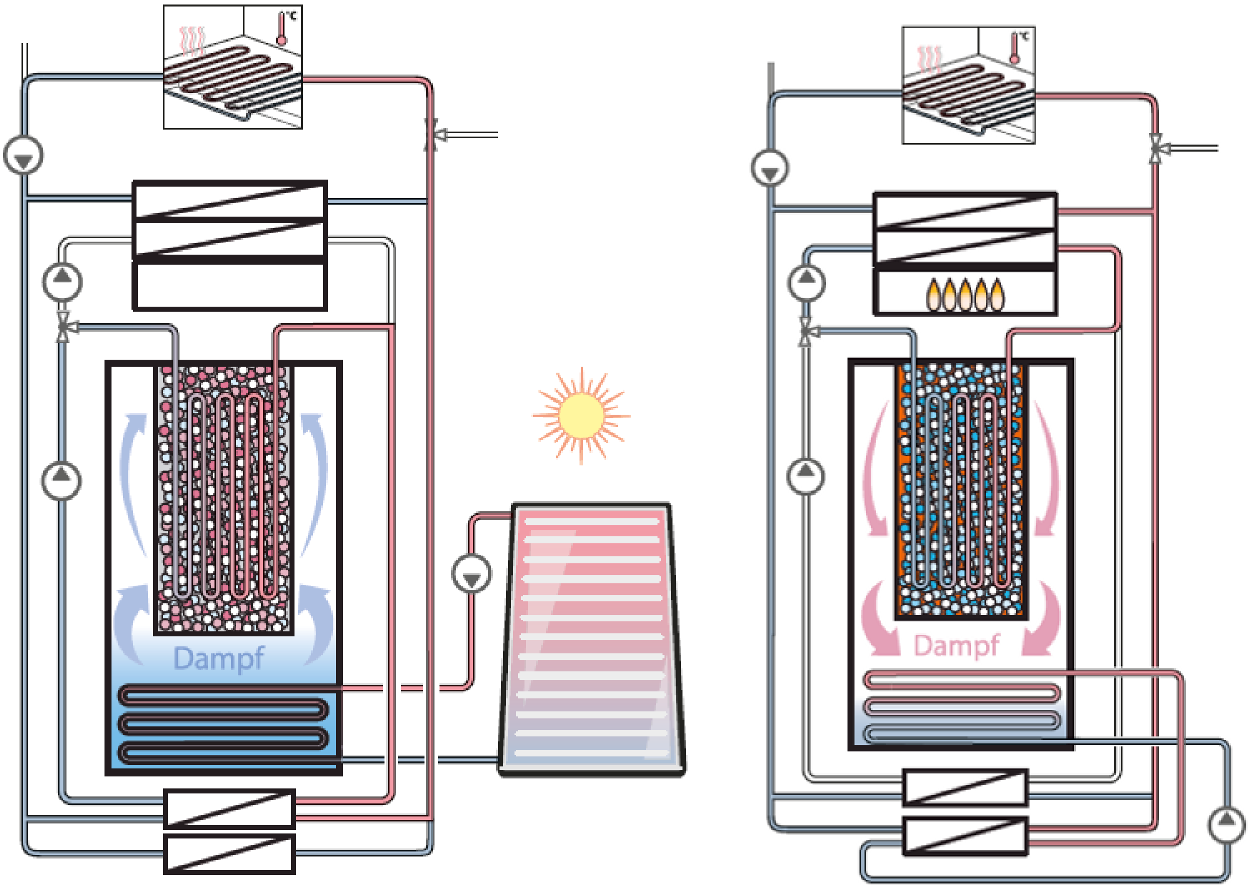

Figure 2 – Adsorption (left) and desorption (right) step in the Zeotherm appliace (Vaillant Group, 2014).

time, to reduce the power consumption of about the 25% with respect to a conventional appliance. In fat, during the washing process (Figure 3 – right), an electrical resistance at 250°C warms up an air flow which runs through the zeolitic bed and promote the water desorption. Such water vapor saturated flow, coming from the bed, is carried to a condenser where the vapor, becoming liquid, frees its latent heat and warms up the washing water. After the washing, the humid water coming from the dishes is carried to the zeolitic bed, still warm: the adsoption process dries and further warms the air flow, which can be used to dries the dishes in turn.

5.2. Storage of hydrogen and methane

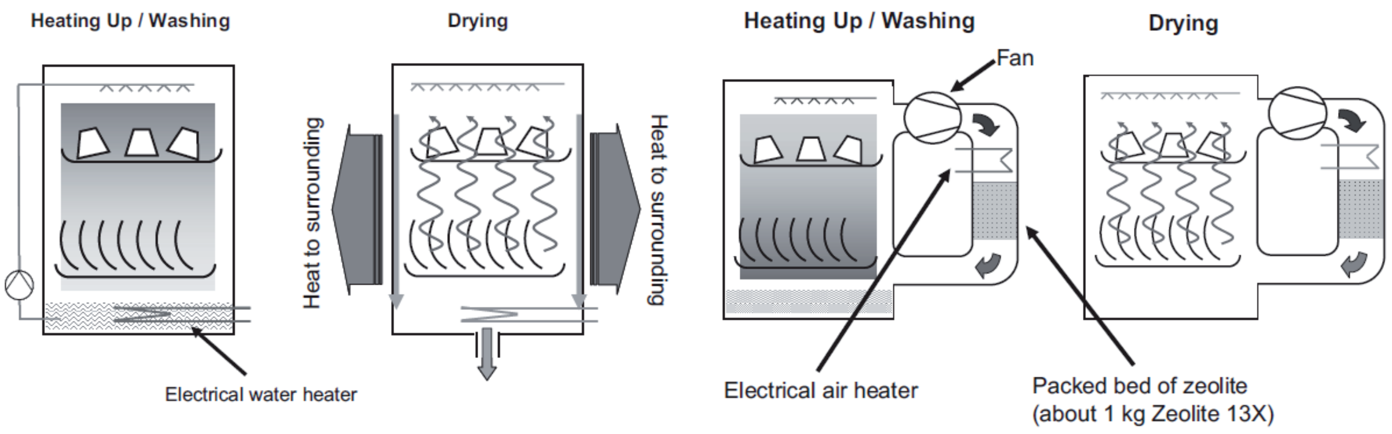

Figure 3 – Operation schema of a traditional dishwasher (left) and an integrated adsorption module dishwasher (right) (Hauer and Fisher, 2011).

It is well-known how many governments around the world declared the hydrogen economy as a target for future energy needs. In this respect, it seems that MOFs possess, or are close to own, hydrogen storage capacities high enough to significantly increase the performance of tanks operating at ambient temperature for automotive applications. On board hydrogen storage is the main problem to be overcome for a concrete perspective of use of fuel cells in the transport field. In the United States, in order to stimulate research in this area, the Department of Energy (DoE) set certain specifications that an effective storage system must have (Satyapal *et al.*, 2007; U.S. Department of Energy, 2014), including: (a) storage capacity; (b) working temperatures and pressures; (c) time for refueling / recharging. For these parameters, DoE set values to be considered as milestones to be achieved by 2010 and 2015, and a final target value. For example, as regards the storage capacity, the reviewed target values are 0.045, 0.055 and 0.075 kg of H2/Kg storage system (tank), respectively (U.S. Department of Energy, 2014).

The on-board storage systems so far considered for the creation of prototypes (Felderhoff *et al.*, 2007) envisaged the use of tanks containing (i) gaseous and high pressure-compressed hydrogen, (ii) liquid hydrogen at very low temperatures, (iii) solid-state hydrogen in the form of hydrides. None of them, however, fulfills all the criteria set by DoE, especially in terms of storage capacity, working temperatures and pressures, and costs (Thomas, 2007). One of the alternative methods to those described above, with excellent future prospectives, envisages hydrogen storage by adsorption in porous materials. The different types of adsorbent materials investigated so far (activated carbon, nanotubes, zeolites, etc..) showed very fast hydrogen adsorption / desorption kinetics, but storage capacities still very far from the targets set by DoE (Felderhoff *et al.*, 2007).

Metal-organic framework (MOFs) seem the most promising adsorbents, instead. Recently, the structure named MOF-210, consisting of [Zn4O (CO2) 6)] units connected by organic bridges, shoewd a BET specific surface area of 6240 m2 / g and a hydrogen adsorption capacity at 80 bar and 77 K equal to 0,086 kg H_2/Kg (Hirscher, 2011). Further imrpovements could be achieved by varying the chemical nature of both the metal and the organic linker. While waiting for hydrogen to become the next generation energy carrier, the use of nanoporous materials as adsorbents was also proposed for the on board storage of natural gas. The compressed natural gas (CNG) - powered vehicles entered the mass market several years ago. The tanks currently used contain compressed gas at about 200 atm, but the directions given by DoE to reduce the risk of explosions envisage a final target pressure of max 35 atm at near-ambient temperatures, with a minimum target for the storage capacity equal to 180 volumes (STP) / tank volume. MOFs seem to be most promising adsorbents also for methane storage. Very recently, a new metal-organic phase, called PCN-14, has been developed, showing a specific surface area of 2176 m2 / g and a methane adsorption capacity of 220 v (STP) / v at 35 bar and 290 K (Ma and Zhou, 2010), which is above the minimum target set by DoE. The high production cost is still one of the major limitations for the real world applications of MOFs.

5.3. CO_2 capture

Nanoporous materials can be also employed in the separation of gaseous mixtures, thanks to their peculiar properties of selective adsorption and molecular sieving. In particular, investigations about the use of such materials in the removal of toxic or environmentally hazardous gases mainly focused on CO_2 capture and separation. As particularly regards zeolites, through the appropriate choice of framework, Si / Al ratio and extra-framework cation content, it is possible, in certain cases, to tune the adsorption properties in order to achieve the selectivity required for a particular separation. 13X zeolite, characterized by a relatively high surface basicity, proved to be a very suitable adsorbent for CO_2 capture by means of Pressure Swing Adsorption (PSA) processes (Siriwardane *et al.*, 2001).

Despite the wide use of zeolites for CO_2 capture, in the last two decades, considerable efforts have been made in improving separation processes based on the adsorption of this gas and, more specifically, in the selection of new high-performance adsorbents, as the development of such materials is the key for improving the aforementioned processes. Recently, technological solutions based on the use of functionalized mesostructured silicas have been extensively studied, particularly focusing attention on the so-called “molecular baskets”, characterized by the use of polyethylenimine as functionalizing agent (Gargiulo *et al.*, 2007; Gargiulo *et al.*, 2012). These materials, however, have a marked tendency to reach the saturation capacity already at very low values of CO_2 partial pressure, and seem, therefore, particularly suitable only for separation processes in which the complete removal of CO_2 justifies the use of pressures in the order of magnitude of 10^{-6} bar for the regeneration of the adsorbent. Very recently, several materials belonging to the class of metal-organic frameworks (MOFs) have proved to be good candidates for improving the performance of adsorption-based CO2 capture processes. In particular, the copper 1,3,5-benzenetricarboxylate, mostly known to the scientific community by the acronym Cu-BTC, was compared in detail with a more traditional adsorbent, such as 13X zeolite. Selectivity level being the same, Cu-BTC showed a higher adsorption capacity at room temperature and developed less heat of adsorption during the process when compared to 13X zeolite: both these features are crucial for the improvement of fixed bed adsorption processes (Aprea *et al.*, 2010).

6. Conclusions

The results obtained so far in the application of nanoporous materials as adsorbents in the energy-environmental field appear to be very promising, especially with regard to metal-organic frameworks (MOFs). The ability to obtain new synthetic structures and the possibility to introduce chemical modifications in order to modulate the characteristics of the material to make it suitable for specific uses continue to stimulate research in this area. In particular, in the next few years, the attention will be focused on some parameters such as the volume of nanopores available to the adsorbate molecules and the adsorbent/adsorbate affinity, which seem to be more crucial than others for future developments in this field.

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