Journal of Hazardous Materials 300 (2015) 711–717

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Capture of formaldehyde by adsorption on nanoporous materials

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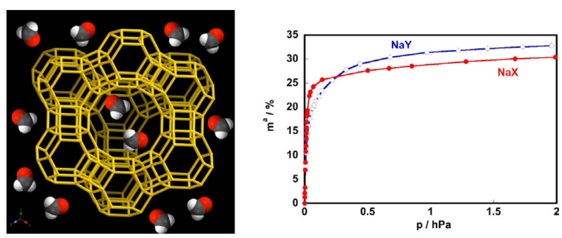
HIGHLIGHTS

- Adsorption of pure gaseous formaldehyde is studied on zeolites, silica, carbon and MOF.
- High-resolution adsorption–desorption isotherms are measured by TGA.
- Na or Cu FAU zeolites have the best adsorption affinities and capacities.
- These zeolites are very good candidates to capture or detect formaldehyde.

GRAPHICAL ABSTRACT



Cationic FAU zeolites: best adsorbents to trap formaldehyde?

ARTICLE INFO

Article history:
Received 29 May 2015
Received in revised form 20 July 2015
Accepted 30 July 2015
Available online 3 August 2015

Keywords:
Formaldehyde
Adsorption
Zeolites
Activated carbon
Silica
MOF

ABSTRACT

The aim of this work is to assess the capability of a series of nanoporous materials to capture gaseous formaldehyde by adsorption in order to develop air treatment process and gas detection in workspaces or housings. Adsorption–desorption isotherms have been accurately measured at room temperature by TGA under very low pressure ($p < 2$ hPa) on various adsorbents, such as zeolites, mesoporous silica (SBA15), activated carbon (AC NORIT RB3) and metal organic framework (MOF, Ga-MIL-53), exhibiting a wide range of pore sizes and surface properties. Results reveal that the NaX, NaY and CuX faujasite (FAU) zeolites are materials which show strong adsorption capacity and high affinity toward formaldehyde. In addition, these materials can be completely regenerated by heating at 200 °C under vacuum. These cationic zeolites are therefore promising candidates as adsorbents for the design of air depollution process or gas sensing applications.

1. Introduction

Formaldehyde is a volatile organic compound (VOC) well known in the medical sector for its disinfectant and biocide properties. This chemical is also used in many other industrial applications. For example, formaldehyde is a common precursor for the synthesis of various resins used in the textile industry, the automobile sector and more extensively the wood industry for the manufacture of wood-composites as plywood or chipboard. Formaldehyde is a highly toxic gaseous VOC. It is now admitted by all the medical authorities that the exposure of animals and humans to formaldehyde can lead to cancer [1]. In Europe, formaldehyde is recognized as carcinogen from 2015 and its domestic use is now forbidden. In a near future, this chemical will be probably prohibited in industry. Nevertheless, as no viable alternative to this compound has been found it will be still used in the coming years. Consequently, it is urgent for the safety of humans working with formaldehyde based materials to control the gaseous emission of formaldehyde and to develop gas sensors and air treatment processes able to completely eliminate this toxic chemical. As its occupational exposure limit

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http://dx.doi.org/10.1016/j.jhazmat.2015.07.078
0304-3894/

value is fixed at 0.5 ppm per 8 h [2], one needs to design materials able to trap this molecule at very low concentration levels.

Though formaldehyde is one of the most widespread VOCs, its removal by adsorption on solids has not been extensively studied. Most of studies quoted in the literature concern the adsorption of formaldehyde on activated carbons [3–10]. These works showed that the adsorption of formaldehyde depends on pore geometry and surface chemistry of the adsorbents. As we could expect, the adsorption of formaldehyde is favored by a small pore size, a high specific surface area and a high microporous volume of the adsorbent. Nevertheless, the chemical properties of the adsorbent surface are the most important parameters. The presence of functional groups such as hydroxyl groups, nitrogen oxides, pyridonic and pyridinic structures as well as aluminum-, silver- or copper coordinated metallic centers, enhances the adsorption affinity of the material for formaldehyde [11–14]. In addition, some experiences performed on activated carbons containing surface amino groups indicate that chemisorption of formaldehyde occurs on the surface [15]. Moreover, the adsorption properties of activated carbons for formaldehyde can be affected by the presence of water. Thus, Li et al. [16] have observed that the adsorbed amounts of formaldehyde significantly decreased in the presence of humidity. The adsorption of formaldehyde was also studied on various inorganic porous materials including silicas, phosphates and aluminosilicates. Furthermore, Srisuda and Virote [17] have investigated adsorption properties of amino group functionalized mesoporous silicas for formaldehyde. These materials have a high adsorption capacity (up to 1.2 g/g under 80 000 ppm of formaldehyde), which is significantly higher than those of activated carbons. As observed for activated carbons, the presence of surface amino groups on mesoporous silicas improves the adsorption capacity of formaldehyde. Nakayama et al. [18] and more recently Zhang et al. [19] have studied the adsorption of formaldehyde on zirconium phosphates. These materials can adsorb formaldehyde with adsorption capacity of about 0.20 g/g. However, adsorption kinetics seems to be extremely low (several days to reach the equilibrium). Moreover, a self-catalytic oxidation–reduction reaction of formaldehyde can occur, leading to the production of formic acid and methanol. Only a few works on the adsorption of formaldehyde on zeolites can be found in the literature [20–22]. These microporous solids in particular the cationic forms of LTA zeolites and faujasites (FAU) which have a strong adsorption affinity, are evidenced as promising adsorbents to capture formaldehyde at very low concentrations. However, the data published on all these systems are not detailed enough to draw solid conclusions about the real potentialities of these materials. In particular, no high-resolution adsorption–desorption isotherms are reported in the literature allowing to obtain a detailed understanding of the adsorption process of formaldehyde, and comparison with the properties of adsorbents of different nature is not available.

The objective of this work is to study different nanoporous adsorbents for the detection or capture of indoor formaldehyde by adsorption. In both applications, the role of the adsorbent that we look for is to concentrate formaldehyde, present in air at extremely low concentration, in order to allow its detection by gas sensors [23] or its efficient elimination by usual catalytic oxidation processes [24,25]. Thus, reversibility of the adsorption process, during the desorption step, is crucial to achieve a gas phase concentration of formaldehyde sufficiently high for carrying out a precise quantification or a complete oxidation. Consequently, only physisorption must take place in order to have a reversible adsorption–desorption process. This is the reason why a special attention has been paid to the measurements of high-resolution adsorption–desorption isotherms of pure gaseous formaldehyde, especially in the very low pressure range.

2. Experimental

2.1. Materials

Adsorption of formaldehyde was studied on four types of adsorbents: FAU and LTA zeolites, a mesoporous silica, an activated carbon and a metal organic framework. Their microporous volume (V_{micro}), mesoporous volume (V_{meso}) and specific surface area (S_{BET}) were determined by nitrogen adsorption at −196 °C, except for the LTA zeolite because nitrogen cannot enter the cavities of 3A zeolite. For this material the microporous volume has been determined by water adsorption at 25 °C and the specific surface

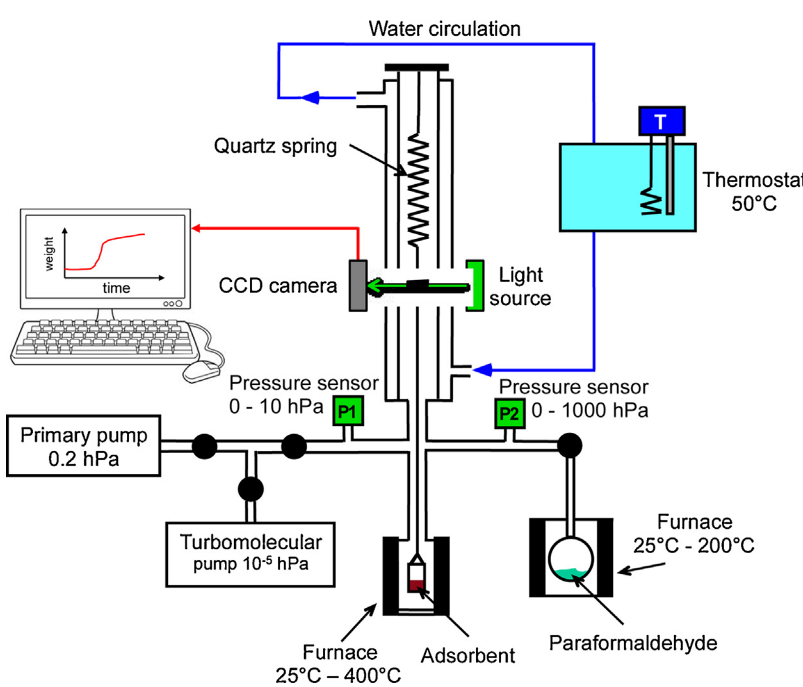

Fig. 1. Scheme of the McBain thermobalance used for measuring the adsorption isotherms of gaseous formaldehyde.