

Capture of Volatile Fission Products: Present Status and Future Perspectives – 15680

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ABSTRACT

The performance of some adsorbent materials for retention of volatile fission products has been assessed. Two different zeolites (Zeolite 4A and silver-coated mordenite) have been chosen owing to their known capacity to entrap cesium and iodine, respectively. To this purpose experiments have been made with a pilot plant termed OGATA (Off-GAs Treatment Apparatus), installed at ENEA laboratories. The tests have been carried out by heating the volatile species at 900°C and passing them through zeolite pellets with the help of argon as carrier gas. The products arising from the interaction with the zeolites have been analyzed mainly by X-rays diffractometry and scanning electron microscopy. The general conclusion from these experiments is that the retention of volatile elements, like cesium and iodine, occurs through a simple adsorption mechanism, which confirms the need to improve the trapping capacity of these materials, especially in view of the final disposal. Moreover, a metal-organic framework (MOF-5), as representative of the new class of materials proposed as adsorbents for volatile radionuclides has been taken into account. The metal-organic frameworks are a sub-family of the nanoporous crystals, characterized by metal-oxygen cages connected by organic bridges which currently attract intensive interest for their excellent potential for storing and separating gases. The synthesis of MOF-5 has been made according to a novel method reported in the literature. FTIR, XRD and Raman spectra, as well as SEM-EDS and thermal gravimetric analysis performed on the synthesized product are perfectly in agreement with current data and reveal the crystal structure of the MOF-5.

INTRODUCTION

Over the past two to three decades, a number of technologies have been developed to various stages of maturity for the off-gas treatment in a fuel reprocessing plant. Tritium, for instance, may be removed from the off-gas stream with molecular sieves or desiccants, like anhydrous calcium carbonate [1]; CO₂ can be treated with caustic scrubbing, molecular sieve adsorption, adsorbent bed fixation, and co-absorption/concentration in conjunction with ⁸⁵Kr recovery followed by fixation [2]; Krypton, on its own, can be trapped through cryogenic distillation and selective absorption in solvents [3]; numerous technologies have also been developed for the recovery of airborne ¹²⁹I based on scrubbing with caustic or acidic solutions and chemisorption on silver-coated or impregnated adsorbents [4]; in addition to the gaseous elements, a number of “semivolatile” species are released to the off-gas stream: these include oxides of ruthenium, cesium, technetium, tellurium, and antimony: of these, the most studied are ruthenium [5] and cesium [6], which also typically require the highest recovery factors. In spite of the job made up to now, issues remain about the effectiveness of the materials currently used as adsorbents. For example, referring to iodine, one of the most studied volatile fission products, the following items are of some concern:

- iodine diffusion inside the zeolite particles is very slow, and likely to limit the adsorption process
- the stability of silver-exchanged zeolite is also a concern:

- silver-exchanged faujasite (AgX) decomposes in the presence of NO_x and water vapor; it does not exhibit satisfactory thermal stability during regeneration
- the fibrous nature of mordenite may present an inhalation hazard
- silver-impregnated alumina and silica capture iodine by forming AgI along grain boundaries. The high iodine leaching rate of these materials can be a potential issue if they are directly used for disposal.

Studies have therefore been undertaken to design, synthesize and characterize new molecules for nuclear applications. The research efforts have been focused on nanoporous materials, thus bringing to the exploration of metal-organic frameworks (MOFs) for fission gas capture in reprocessing [7]. In particular, a well-known metal-organic framework (MOF-5) has been synthesized and studied for facile xenon capture and separation. Generally speaking, metal-organic frameworks (MOFs) have been found to have high sorption capacities and are tunable to different volatile elements. One very interesting area of technological expansion may be into the development of nanoporous materials for fission gas capture in the nuclear reactor plenum (the structural void/area located above the bundled fuel rods). The ability to develop a mechanically, thermally and radiologically stable separation material that can withstand the radiological load so close to the rods is of great interest as a method to favorably remove fission gases as they are forming.

Following up the previous considerations, this paper is devoted, on one hand, to assess the interaction between some adsorbent materials (typically zeolites) and volatile cesium [8] and iodine [9]; on the other hand, to the synthesis and characterization of nanoporous MOF-5, as one of the new materials proposed as adsorbents for volatile radionuclides.

METHODS

The interactions between volatile fission products and zeolites have been assessed by means of a pilot plant termed OGATA (Off-GAs Treatment Apparatus), assembled at ENEA laboratories (Figure 1). It consists of a little furnace where the volatile substances are generated, a second furnace containing the trapping agent at the operating temperature, and a final trap containing a proper solution for retention of residual gas effluent. Argon is used as carrier gas and tests can be performed by varying the main process parameters, like gas flow, initial temperature, material of piping, and test duration.

MOF-5 on its own has been synthesized according to a novel method reported in [10].



Fig. 1. General view of the OGATA pilot plant

Performance of Adsorbent Materials

Volatile fission products generated by many nuclear activities are prevented from contaminating the environment by passing them over trapping agents able to form nonvolatile and stable compounds. The stable compounds thus formed can then be easily isolated and contained during the period of maximum radioactive decay. From an engineering point of view, the removal of gaseous elements via adsorption onto a solid adsorbent has many advantages over other methods. Adsorption column operations are generally more simplistic in design, resulting in a more reliable system with lower maintenance costs. A properly designed adsorbent system should also yield higher removal efficiencies. Among solid adsorbents, activated carbon and zeolites (Figure 2) are often used as trapping agents. Activated charcoal performs very well in these applications, with some limitations lying in poor retention at high temperatures and in the relatively low ignition point. Moreover, the presence of nitrogen oxides in the gas stream adversely affects the media performance. Zeolites, on their own, are very effective in removal of volatile elements, especially if they contain metals in various forms. So, while cesium is retained by a surface adsorption mechanism, iodine is retained by silver impregnated zeolites, leading to the formation of stable silver iodide [9], while metals like ruthenium, molybdenum and technetium are effectively entrapped by a trapping agent selected from the group consisting of alkaline earth compounds, lanthanide compounds and lead compounds, with subsequent formation of nonvolatile ruthenates, molybdates and technetates. Such adsorbents all exhibit the following key characteristics:

- Effective retention of the volatile elements
- High loading capacity and removal efficiencies
- Non-flammability of the media.

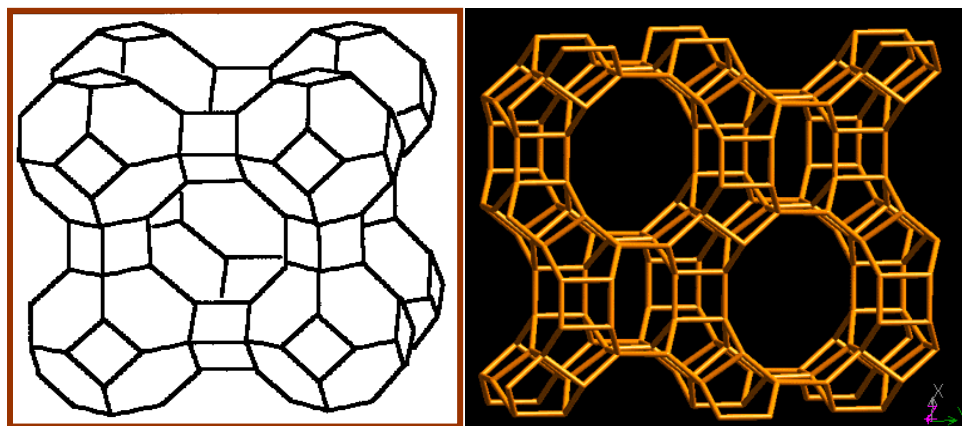


Fig. 2. Crystal structure of Zeolite 4A (*left*) and Mordenite (*right*)

Experiences have been made with OGATA plant, starting from cesium chloride and potassium iodide. To this purpose, 10.0 g of powdered CsCl have been heated up to 900 °C and transported by means of argon gas through 10.0 g of pelletized Zeolite 4A, previously dried under vacuum for 2 days and maintained at 520 °C. The effluent gas passed through a solution of 0.1M HNO₃ inside a Drechsel bottle. After 1 hour the weight loss of CsCl in the original crucible resulted of 0.37 g (3.7%), while Zeolite 4A showed a change in color, presumably due to the adsorption of cesium chloride. Figure 3 shows the XRD spectra of Zeolite 4A before and after the test: the spectrum before the test has been recognized as the phase 38-0241, Na₂Al₂Si_{1.85}O_{7.7}·5.1H₂O, while the spectrum after the test shows a slight shift with respect to the

matrix before the treatment, with the appearance of a new peak at 27.41°.

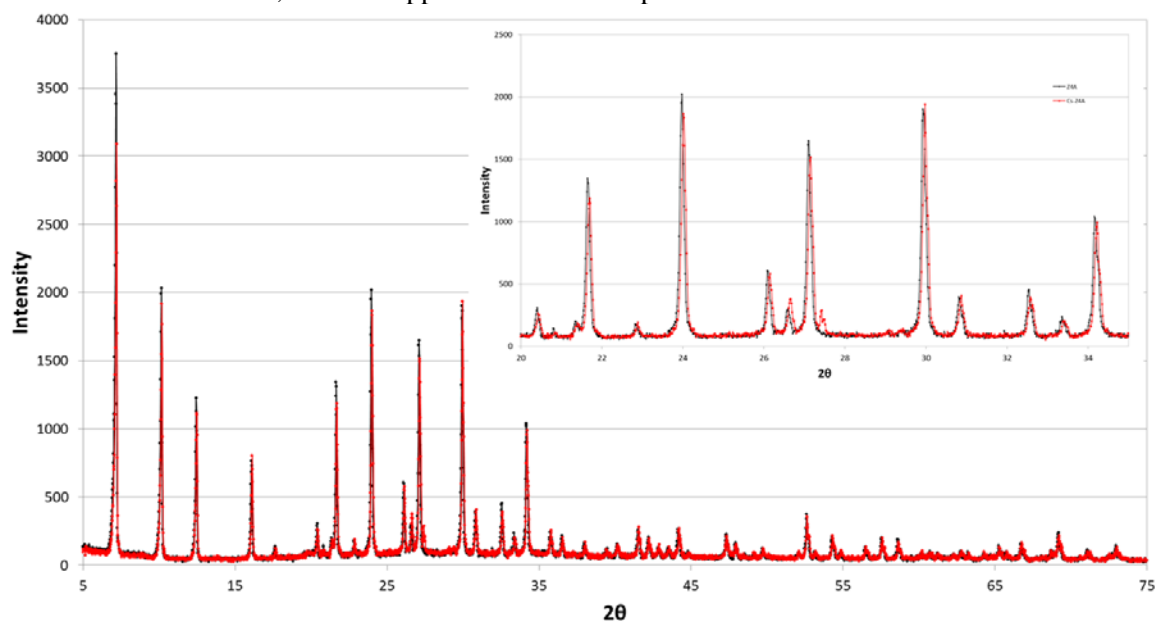


Fig. 3. XRD spectra of Zeolite 4A before (*black line*) and after (*red line*) the test with cesium chloride

A similar experience with KI has been made starting from 10.01 g of the salt heated at 900 °C and transferred under a flux of argon to a crucible containing pellets of silver-coated mordenite, previously dried at 300 °C under vacuum for 4 hours. During the experience Ag-MOR has been kept at 150 °C for 1 hour. The weight loss of potassium iodide resulted of 0.71 g (7.09 %). XRD spectra and thermal gravimetric analyses made on silver-mordenite are reported in Figures 4 and 5, while pictures of the zeolite obtained at both optical and electron microscope are shown in Figures 6 and 7.

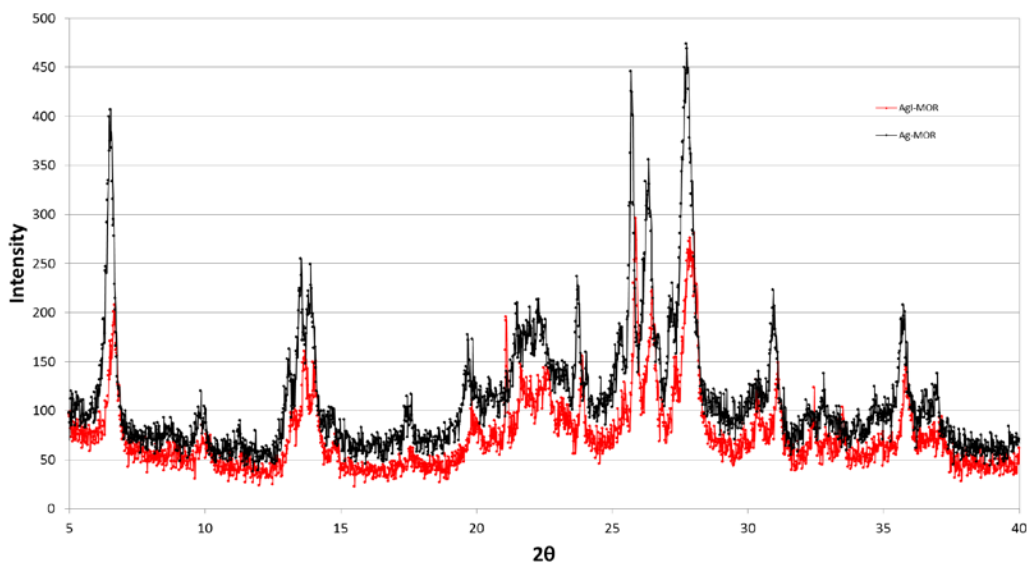


Fig. 4. XRD spectra of Ag-mordenite before (*black line*) and after (*red line*) the test with potassium iodide

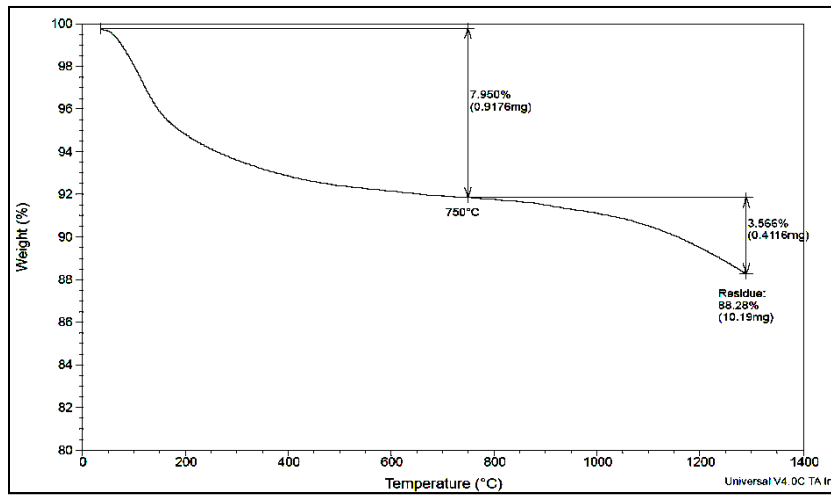


Fig. 5. Thermal analysis of Ag-MOR after the test with potassium iodide



Fig. 6. Pictures of Ag-mordenite pellets before (*left*) and after (*right*) the test with potassium iodide

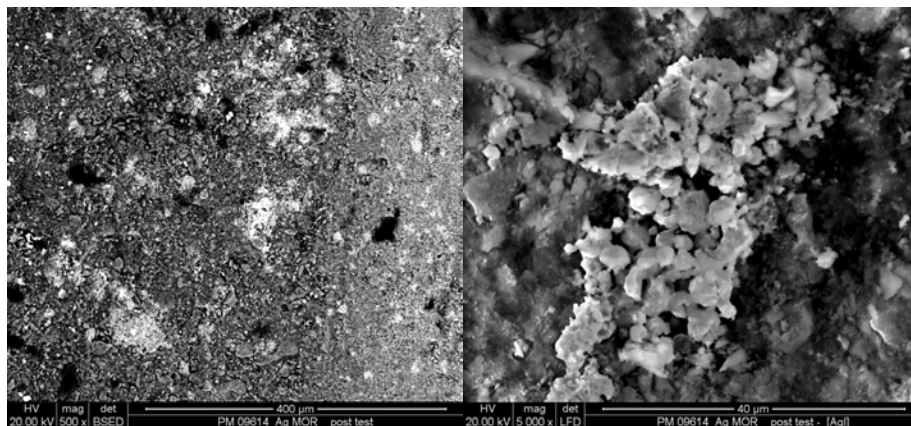


Fig. 7. Micrographs showing the formation of silver iodide onto the surface of silver-mordenite

Synthesis of MOF-5

The metal-organic frameworks (MOFs) are a sub-family of the nanoporous crystals, characterized by metal-oxygen cages (vertices) connected by organic bridges [11]. MOFs currently attract intensive interest for their excellent potential for storing and separating gases. Moreover, by changing the organic bridge and/or its functionalization, new MOFs can be designed and synthesized without changing the underlying topology. MOF-5 consists of ZnO_4 inorganic moiety, that acts as secondary building unit, coordinating to benzene 1,4-dicarboxylate, a bidentate ligand that acts as spacers, to form a three dimensional structure (Figure 8). It can be synthesized according to [10]. To this purpose, about 1.2 g of zinc nitrate hexahydrate and 0.334 g of benzene dicarboxylic acid (BDC) are dissolved in a solution containing 40 mL of dimethyl formamide (DMF) and 5 mL of chlorobenzene under constant stirring. Then 2.2 mL of triethyl amine (TEA) solution and 3–4 drops of Hydrogen Peroxide are added to the mixture. After agitation for 30–45 min a white precipitate is filtered off (Figure 9), washed with DMF and immersed in chloroform for 24 h to exchange DMF solution. Finally, it is dried in vacuum oven at 120 °C for 2 h and stored in vacuum desiccator. All the procedures are performed in a venting hood at ambient temperature (25 °C).

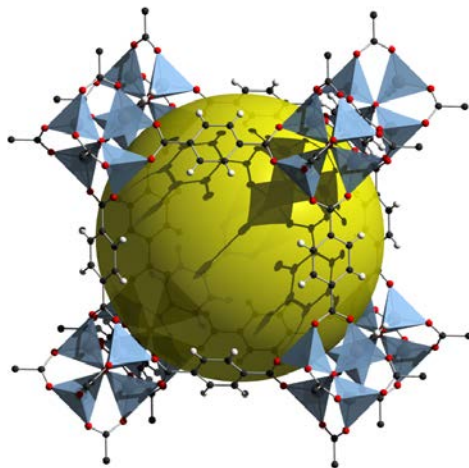


Fig. 8. The MOF-5 structure shown as ZnO_4 tetrahedra (blue polyhedra) joined by benzene dicarboxylate linkers (O, red and C, black) to give an extended 3D cubic framework with interconnected pores of 8 Å aperture width and 12 Å pore (yellow sphere) diameter. (Yellow sphere represents the largest sphere that can occupy the pores without coming within the van der Waals size of the framework) (after [12]).

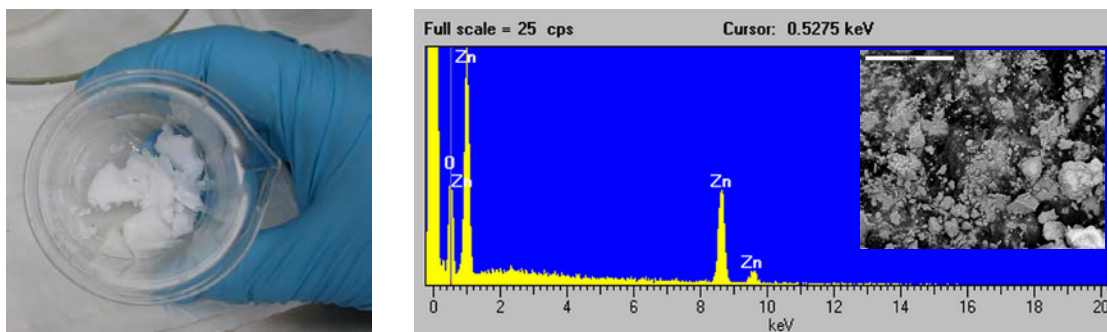


Fig. 9. Synthesized product after filtration (*left*) and SEM-EDS analysis of MOF-5 (*right*)

The product obtained has been characterized by means of SEM-EDS analysis (Figure 9), FTIR (Figure 10), XRD (Figure 11) and Raman (Figure 12) spectra, and thermal gravimetric analysis (Figure 13).

RESULTS

The XRD spectrum of Zeolite 4A before and after the test shows only a slight difference at 27.41° . XRD spectra of Ag-MOR before and after the test differ only slightly. More information are obtained by optical and electron micrographs, which reveal the presence of a precipitate onto the surface of the zeolite. The overall complex appears quite stable, as confirmed by the low weight loss up to 1300°C . The FTIR spectrum of MOF-5 (Figure 10) confirms the presence of the zinc-organic molecule in the sample. Two sharp peaks were obtained at 1579 and 1379 cm^{-1} . Several small peaks were seen in the range of 1294 to 900 cm^{-1} , while a sharp narrow peak at 3604 cm^{-1} was also seen. The X-rays diffractogram of MOF-5 is reported in Figure 10. The most significant peak is a sharp, intense peak shown at 8.81° .

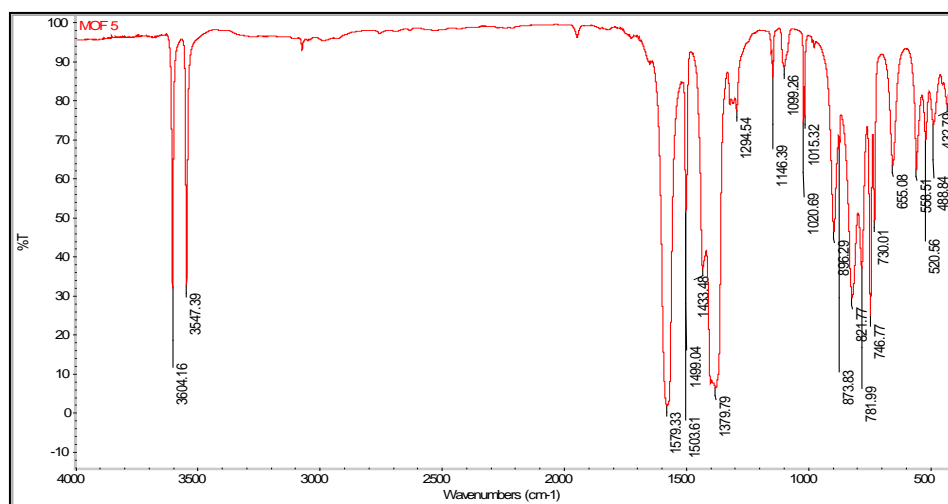


Fig. 10. FTIR spectrum of MOF-5

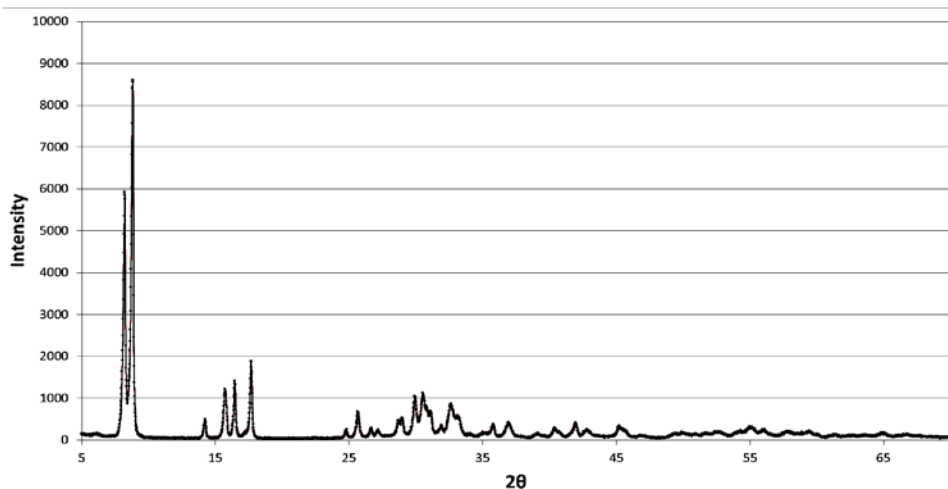


Fig. 11. XRD spectrum of MOF-5

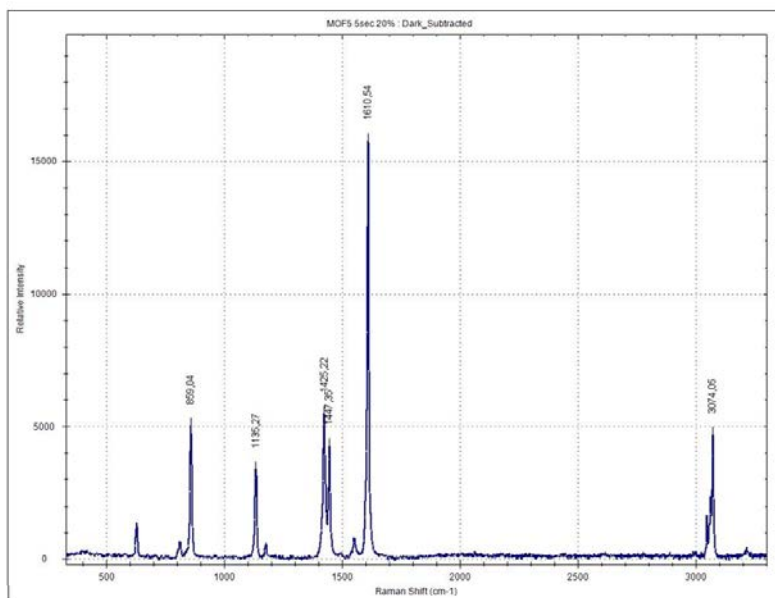


Fig. 12. Raman spectrum of MOF-5

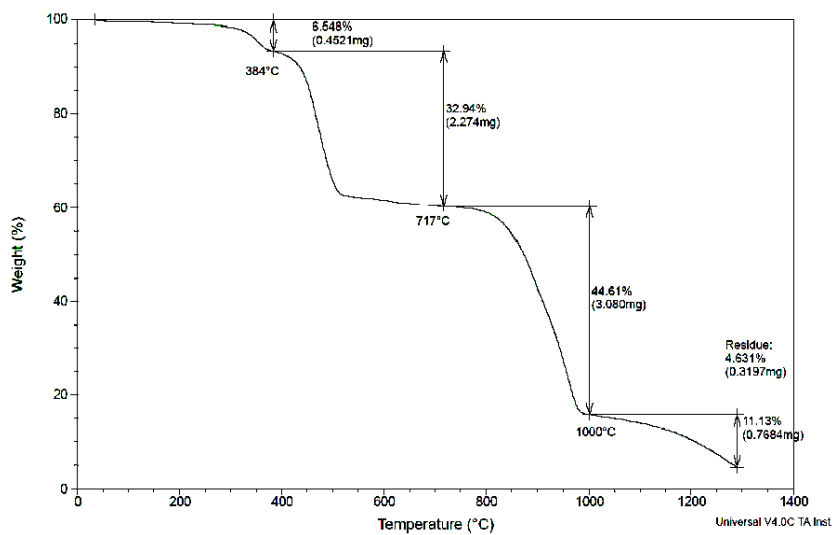


Fig. 13. Thermal gravimetric analysis of MOF-5

The Raman spectrum (Figure 12) presents five strong bands in the lower region, at 625, 859, 1135, 1425, and 1610 cm^{-1} , and a further band at 3074 cm^{-1} . The thermal gravimetric analysis is shown in Figure 13. The main weight losses occurred at around 384, 717, and 1000 $^{\circ}\text{C}$.

The scanning electron micrograph is shown in Figure 9, together with EDS analysis, confirming the presence of Zinc.

DISCUSSION

XRD spectrum of Zeolite 4A is practically unaffected by the presence of cesium chloride. The same holds for the X-rays diffractogram of silver-mordenite. Microscopy observation in this case reveals the formation of silver iodide, which is present as microscopic crystals onto the surface of the zeolite. Thus the conclusion can be drawn that both cesium and iodide are adsorbed by Zeolite 4A and Ag-mordenite respectively, which retain them owing to electrostatic and van der Waals forces, even if the formation of a compound with silver gives more stability against the release of iodine to the environment.

Referring to MOF-5, FTIR spectrum confirms the presence of all the functional groups present in this metal-organic molecule [10]. The two sharp peaks obtained at 1579 and 1379 cm^{-1} correspond to the symmetric and asymmetric stretching of C-O bonded to Zn, respectively. Several small peaks occurring in the range of 1294 to 900 cm^{-1} correspond to the in-plane bending of the C-H group present in the benzene ring of the benzene dicarboxylic acid (BDC) linker. Similarly, the small peaks occurring in the range of 900 to 655 cm^{-1} are because of the out of plane bending of the C-H group of the benzene ring of the BDC linker. Peaks occurring around 500 cm^{-1} are characteristic of the Zn-O stretching. The sharp narrow peak at 3604 cm^{-1} is because of the O-H stretching of the non-bonded hydroxy groups.

The X-rays diffractogram corresponds with that of the pattern obtained by other authors [10, 13, 14], and exhibits a cubic crystal structure, typical of MOF-5.

Two strong bands are the most interesting in Raman spectrum: the band at 1610 cm^{-1} associated with vibration stretching mode of organic benzene ring and the band at 1425 cm^{-1} associated with a complex stretching mode of carboxylate group [14].

Weight loss observed during thermal analysis can be attributed to the evaporation of nonvolatile adsorbed species, like dimethyl formamide, during the first stage and decomposition of the framework structure starting from 384 °C. The sample showed overall thermal stability up to about 350 °C.

Finally, it is evident from the SEM image the formation of crystals in the sample tested.

Generally speaking, the simplicity of synthesis of this complex molecule opens the route to exploration and commercialization of nanostructured materials. In order to effectively use the technologies based on these molecules, however, it is necessary to test the trapping systems in specific ranges of plant operations, by measuring entry and exit gas flow, even at a low level. Moreover, to assess the performance of these systems, specific experimental campaigns should be carried out by taking into account the influence of parameters like moisture, temperature, gas flow, and so on. In any case, a new front of fruitful research is open.

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