In situ polymerization of the metal-organic framework 5 (MOF-5) by the use of maghnite-H+ as a green solid catalyst

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ABSTRACT

Metal-organic framework MOF-5 [$Zn_4O(BDC)_3$, BDC : 1,4 benzenedicarboxylic] is a microporous material with a large specific surface area and high porosity formed by benzenedicaroboxylic acid as organic ligand and zinc nitrate hexahydrate as metal ion . This material is mainly used in the field of automobile industry as a container for storing hydrogen (alternative fuel) and for the environmental preservation by trapping CO_2 (greenhouse gas emissions). The present study shows the synthesis of this material using a clay called Maghnite-H+ as catalytic support in order to enhance the yield which increases from 35% to 63% and improve the thermal stability of MOF-5. Maghnite-H+ is a montmorillonite sheet silicate clay, exchanged with protons, it is an efficient catalyst for polymerization of many vinylic and heterocyclic monomers. The structure of resulting products is characterized and established by Magic Angle Spinning Nuclear Magnetic Resonance (^{13}C MAS NMR). ^{27}Al MAS NMR and ^{29}Si MAS NMR results show that there are interactions between the chains of MOF-5 and the silicate surface or aluminum of Maghnite-H+. Fourier Transform Infrared spectroscopy (FTIR) is also used to confirm the structure of these products showing that there is a complete deprotonation of benzenedicaroboxylic acid. The X-Ray Diffraction (XRD) allows to study the morphology of the obtained compounds and reveals the formation of a partially exfoliated/partially intercalated structure. Thermal stability is studied by Thermogravimetric Analysis (TGA) and shows an enhanced thermal stability for MOF-5/Mag-H+ with a gain of 40°C. Copyright © 2015 VBRI press.

Keywords: Maghnite-H+; green catalyst; MOF-5; *in situ* polymerization; thermal properties.

Souad Bennabi is currently pursuing her studies PhD at the polymer chemistry laboratory, in the chemistry department at the University of Oran, Algeria. She received her Magister degree in polymer chemistry in 2010 at the University of Oran, Algeria. Actually, her active areas of research interest include the synthesis and characterization of MOF (Metal-Organic Framework) or nanocontainers molecular and their use for CO_2 capture and storage of Hydrogen.

Mohammed Belbachir is Professor of Chemistry at the University of Oran, Algeria. He is director of the Laboratory of Polymers Chemistry that he created in 2000. He is at the head of a research team that focuses on the synthesis of catalysts, their characterization and their activity. Moreover, he developed an ecological catalyst including a new nanoreactor extracted from natural clay from the region of Maghnia (Tlemcen, Algeria) which the reserves are estimated at 1 million tons, named "Maghnite". This research resulted in globally recognized patents and filed in the United States of America. He has authored several scientific articles in high impact and reputed scientific journals and he has delivered numerous invited talks in national and international conferences. Therefore, he was one of the 12 Algerian laureates in the 3rd edition of "Scopus Awards" in 2013 organized in partnership with Elsevier Dutch company dedicated to the celebration of science and rewarding researchers who have published scientific articles in line with international visibility. He was awarded the (first) National Award for the environment from the President of the Republic of Algeria in 2005 for "all of his work in green chemistry and nonpolluting". He initiated a number of CNEPRU and CMEP projects in partnership with European universities. His areas of research interest include the research for other clays and derivatives for their use and recovery as green materials, the production of new decontamination membranes (ultrafiltration and osmosis), the Development of polymeric membranes for "Fuel Cells", the synthesis and characterization of hybrid nanocomposite (Maghnite/polymer), the development of new green polymers (e.g., The pinene) as plasticizers for various polymers or common plastics and the production of new photovoltaic films (Solar Panels).

Introduction

In the last decade, a porous coordination polymer (PCP) with infinite structures has been intensively studied. These compounds are MOFs (Metal-Organic Frameworks). Their syntheses are based on the use of a vast variety of metal ions (clusters), i.e. inorganic nodal points, interconnected

by organic ligands to form rigid and oriented Metal-Oxygen-carbon (M-O-C) groups [1]. MOFs offer potential applications in catalysis, ion exchange, separation and polymerization due to their extremely large surface area, diverse means available for functionalization and well-ordered porous structures with various geometries: one-dimensional 1D (channels), two-dimensional 2D (layers) and three-dimensional 3D (networks) [2]. MOFs have also attracted considerable attention in the field of adsorption as a means of storage of fuel gases, such as hydrogen and methane in order to promote utilization of adsorbed natural gas (ANG), as well as trapping CO_2 which is a greenhouse gas [3-5].

One of the most representative MOFs is MOF-5. It is a structure which is formed by groups of $(Zn_4O)^{6+}$ and extended in a 3D network with BDC (1,4-benzenedicaroboxylic acid) to produce a simple cubic lattice, with BET surface area from 260 m^2/g to 4400 m^2/g based on the synthetic method and good thermal stability up to 400 °C [6]. The amount of methane absorbed in the different zeolites is proportional to their specific surface areas, therefore, MOF-5 is a transporter of fuel more convenient due to the properties of its cavities that easily adapt by creating linkages (Van Der Waals forces, hydrogen bonds) [7].

In this work, we propose a new approach for the synthesis of MOF-5. It consists in the use of a clay called Maghnite-H$^+$. It is natural, more efficient, less expensive and less polluting to the environment with the aim to respect the principles of green chemistry [8]. It has a lamellar structure and shows remarkable catalytic capacities towards various polymerization reactions. Maghnite-H$^+$ is going to play the role of a catalytic support to improve the yield of MOF-5 obtained but especially to increase its temperature stability.

Experimental

Materials

Maghnite used in this work comes from a quarry located in Maghnia (North West of Algeria) and was supplied by company "ENOF" (Algerian manufacture specialized in the production of nonferric products and useful substances). Terephthalic acid (BDC: 1,4-benzenedicaroboxylic acid) (Aldrich, 98%), Zinc nitrate Hexa-hydrate $[Zn(NO_3)_2.6H_2O]$ (Aldrich, 98%) and N,N-Dimethylformamide (DMF) (Aldrich, 99.8%) were used as received without further purification.

Preparation of the maghnite-H$^+$

The preparation of Maghnite-H$^+$ was carried out by using a method similar to that described by BELBACHIR and coworkers [9]. In an Erlenmeyer flask of 500 ml, 30 g of crushed and dried raw-maghnite are dispersed in 120 ml of distilled water; the mixture is stirred for 2 hours. After this time, 100 ml of 2.5M sulfuric acid solution is added, the solution thus obtained is kept under stirring for two days at room temperature. Then, the product is filtered and washed with distilled water until complete disappearance of traces of acid. Once purified clay, it is dried overnight in an oven

at 105°C, and then stored in vials well saddled against moisture and any impurity.

Synthesis of MOF-5

MOF-5 is prepared according to the method of Yaghi and co-workers [10]. A typical synthesis of MOF-5 is performed by simply heating in a closed vessel at 100°C a solution of zinc nitrate in dimethylformamide (DMF) and the acid form of 1,4-benzenedicarboxylate (BDC). White crystals are observed after heating the reaction mixture for 18h. During filtration, the crystals are washed several times with fresh solvent. The solid is stored under dry dimethylformamide. The yield is 35.17%. **Fig. 1** summarizes the synthesis conditions:
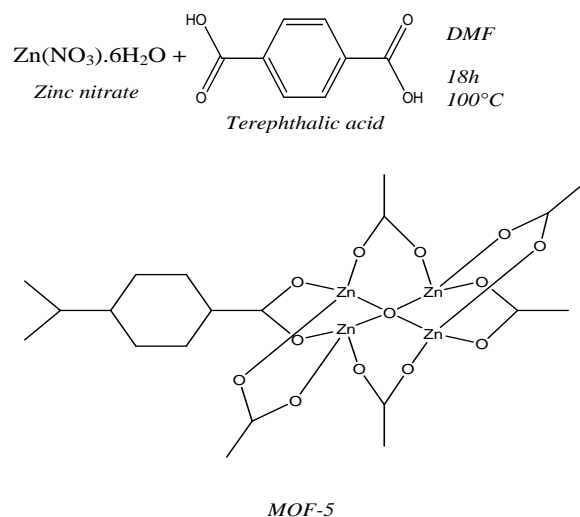

Fig. 1. Synthesis conditions of MOF-5

Synthesis of MOF-5 with maghnite-H$^+$

MOF-5/Mag-H$^+$ is synthesized by in-situ polymerization of zinc nitrate and 1,4-benzendicarboxylic acid (BDC) with an amount of Maghnite-H$^+$ in dimethylformamide (DMF). The mixture is kept in thermostat (100 °C) for 18 hours. The product is collected by filtration and washed several times with fresh solvant and stored under dry dimethylformamide. **Fig. 2** summarizes the synthesis conditions:
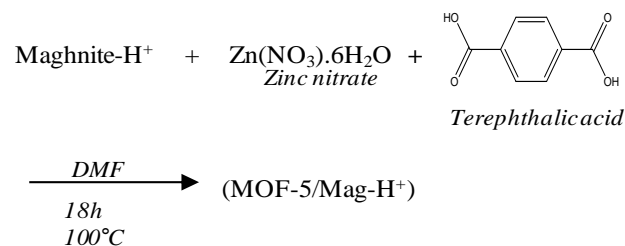

Fig. 2. Synthesis conditions of MOF-5/Mag-H$^+$.

Effect of the amount of maghnite-H$^+$ on the polymerization

Table 1 shows the effect of the amount of Maghnite-H$^+$ on the polymerization yield. Indeed, using various amounts of Maghnite-H$^+$: 5, 10, 25, 40, 50 and 60% by weight, the

polymerization is carried out in solution at 100°C for 18 hours. The increased yield with the amount of Mag-H⁺ is observed, this is mainly due to the number of active sites in the catalyst responsible for the initiation of the polymerization reaction until a maximum amount of the catalyst (25wt% of Maghnite-H⁺) from which the yield remains unchanged, in this case, the catalyst acts as a co-monomer participating in the reaction.

Table 1. Effect of the amount of Maghnite-H⁺ on the polymerization of MOF-5.

Maghnite-H⁺ (% by weight)	Yield (%) of MOF-5/Mag-H⁺
5	42.13
10	54.76
25	63.03
40	63.65
50	63.20
60	63.34

Characterizations

Solid State ^{13}C, ^{27}Al and ^{29}Si MAS NMR spectra are recorded with a Bruker spectrometer (Avance III 400WB). The sample spinning frequency is 10 kHz for 13C, 5 kHz for ^{29}Si and 12 kHz for ^{27}Al. FT-IR absorption spectra are recorded on an MATTSON GENESIS II FT-IR spectrometer using the KBr pressed disc technique. Powder X-ray diffraction (DRX) patterns are collected on an AXIOS spectrometer in transmission mode in the form of powder supported between two foils, which are then clamped in the PW1818/40 sample holder for as-prepared samples, the foil used is Mylar 3.6 microns. Thermogravimetric analyzes (ATG) are recorded on a SETARAM Labsys TG-DTA/DSC (room temperature - 1600°C) with a nitrogen sweep of 200 mL/min. The temperature ramp is 10°C/min.

Results and discussion

Structure determination of MOF-5 and MOF-5/Mag-H⁺

The present study examines the catalytic activity of an Algerian proton exchanged montmorillonite clay called ''Maghnite'' via MOF-5 polymerization. The aim of this research is to improve the thermal stability of MOF-5 and the yield of the obtained products.

Magic angle spinning nuclear magnetic resonance (MAS NMR)

The analysis by MAS NMR can reveal the structure of the chain.

^{13}C MAS NMR

The different signals observed in the spectra of **Fig. 3** and which are summarized in **Table 2**, correspond to the groups shown in the structural formulas of MOF-5 and MOF-5/Mag-H⁺ containing 01%, 25% and 50% by weight of Maghnite-H⁺. The spectra show also the peaks corresponding to DMF trapped in MOF-5 and MOF-

5/Mag-H⁺. ^{13}C MAS NMR spectra of MOF-5 and MOF-5/Mag-H⁺ are obtained nearly identical. In fact, the chemical shifts of different groups confirm the structure of these products. The spectra show particularly that the structure of MOF-5 is not altered by the addition of Maghnite-H⁺.
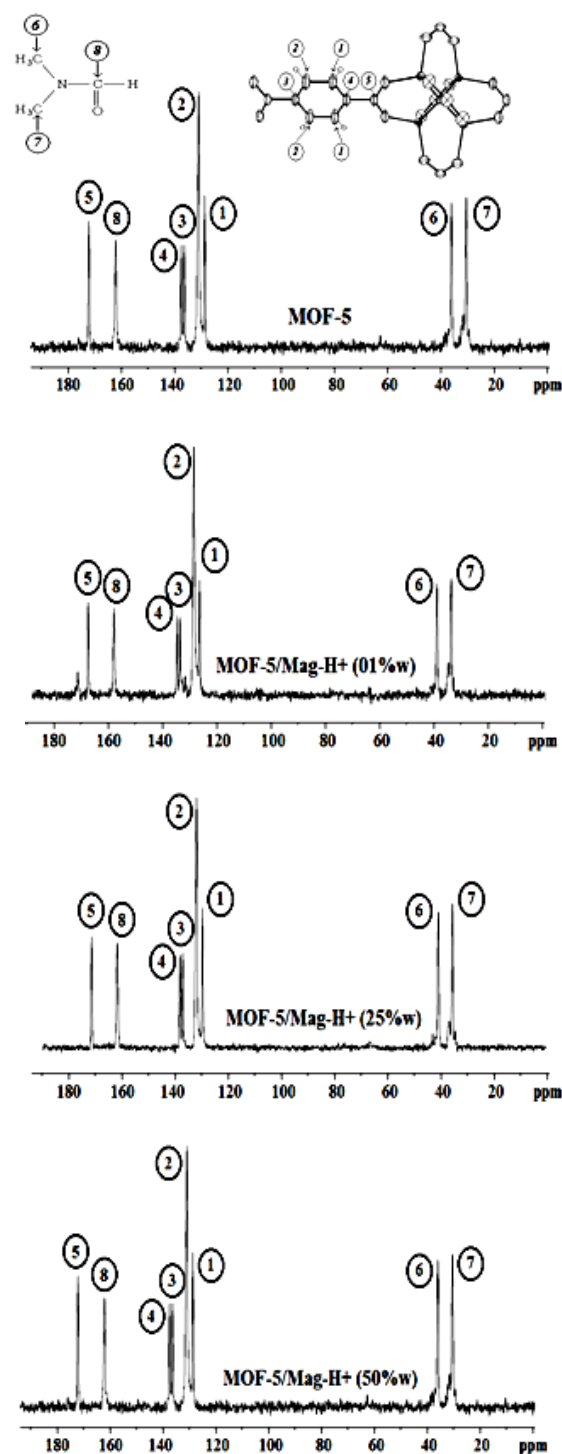

Fig. 3. ^{13}C MAS NMR spectra of MOF-5, MOF-5/Mag-H⁺ and DMF.

^{27}Al MAS NMR

The ability of ^{27}Al MAS NMR to distinguish between AlO_4 and AlO_6 units is very informative for structural

characterization. Because [27]Al nucleus has a very high natural sensitivity and reasonably short relaxation time, NMR spectra with good signal to noise ratio can be obtained easily [11]. **Fig. 4** shows the [27]Al MAS spectra of Maghnite-H^{+} and MOF-5/Mag-H^{+} containing 01%, 25% and 50% by weight of Maghnite-H^{+}.

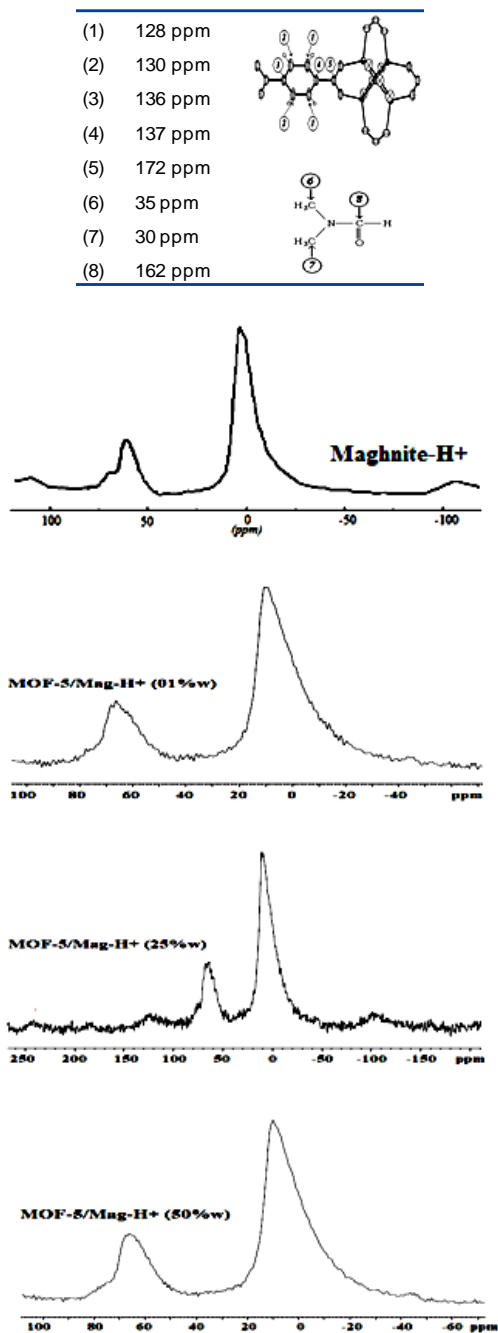**Table 2.** Different signals of Carbons of MOF-5, MOF-5/Mag-H^{+} and Dimethylformamide (DMF).

(1)	128 ppm
(2)	130 ppm
(3)	136 ppm
(4)	137 ppm
(5)	172 ppm
(6)	35 ppm
(7)	30 ppm
(8)	162 ppm

Fig. 4. ^{27}Al MAS NMR spectra of Maghnite-H^{+} and MOF-5/Mag-H^{+}

The spectra provide information about the local environment of the aluminum sites in Maghnite-H^{+} and MOF-5/Mag-H^{+}. On all the spectra, two small bands can be distinguished at apparent chemical shifts of 58–60 ppm and 68–71 ppm, and another dominant asymmetric line at apparent chemical shifts of 3-4 ppm. The former

resonances (60–70 ppm) can be assigned to AlO_4 octaedric sites in the Maghnite structure as a consequence of isomorphic ions substitution within the silicate layers, whereas the later one to AlO_6 sites within the octahedral sheets of the clay [12-15]. All spectra are similar, indicating that the aluminosilicate layers of the clay are not chemically modified by their incorporation in MOF-5 during the polymerization process.

^{29}Si MAS NMR

^{29}Si MAS NMR spectra provide supporting evidence for no change occurring on silicate sites of the clay. **Fig. 5** shows the ^{29}Si MAS NMR spectra of Maghnite-H^{+} and MOF-5/Mag-H^{+} containing 01%, 25% and 50% by weight of Maghnite-H^{+}. The ^{29}Si MAS NMR spectra of Maghnite-H^{+} shows an intense signal Si Q^3 (OAl) at -93 ppm corresponding to tetrahedral silicon Si^{4+} where each ion is surrounded by three silicon ions. The same signal is observed at -88 ppm for MOF-5/Mag-H^{+} at different percentage by weight of Maghnite-H^{+}. Resonance at -110 ppm is assigned to the amorphous silica SiO_2 Q^4 (OAl) [16, 17]. It was noticed that a small change of about 5 ppm is observed between the ^{29}Si MAS NMR spectra of Maghnite-H^{+} and that of MOF-5/Mag-H^{+}. This change could be induced either by interactions of the polymer chains with the silicate surface or local environmental changes on neighboring aluminum sites upon grafting.
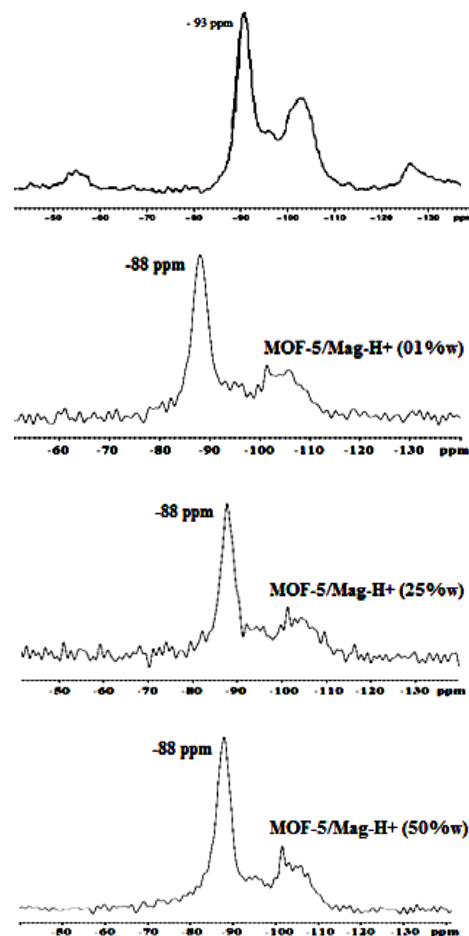

Fig. 5. ^{29}Si MAS NMR spectra of Maghnite-H^{+} and MOF-5/Mag-H^{+}.

Fourier transform tnfrared spectroscopy (FTIR)

FT-IR spectrum of terephthalic acid is given in **Fig. 6**. **Fig. 7** shows FT-IR spectra of MOF-5 and MOF-5/Mag-H$^+$ containing 01%, 25% and 50% by weight of Maghnite-H$^+$. FT-IR measurements of products are in a good agreement with MOf-5 and MOF-5/Mag-H$^+$ structures and by comparing the different frequencies of characteristic groups, we find that there is disappearance of the intense and large characteristic band of O-H which is between 2500 and 3340 cm^{-1} in FT-IR spectra of MOF-5 and MOF-5/Mag-H$^+$ confirming that there is a complete deprotonation of terephthalic acid and that the polymerization has occurred. In FT-IR spectra of MOF-5/Mag-H$^+$, we find the usual characteristic frequencies of Maghnite-H$^+$, in particular a broad band which represents the vibration of Si-O at 1039 cm^{-1}, and a band of deformation Si-O-Si at 465 cm^{-1}.
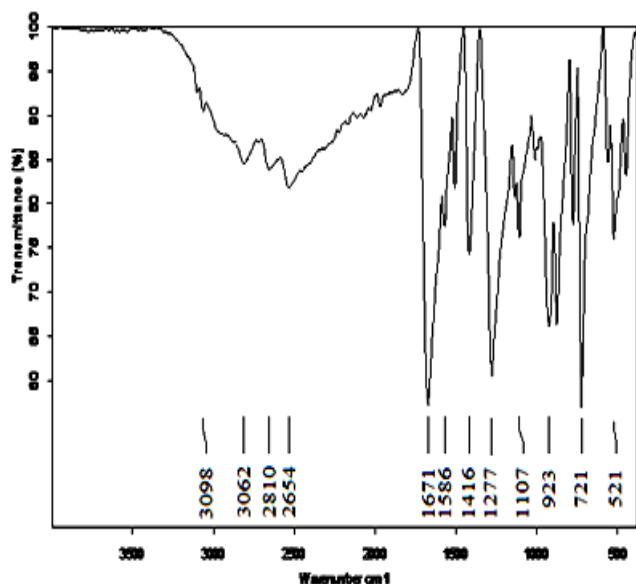
Fig. 6. FT-IR spectra of terephthalic acid.

Morphology of the resulting MOF-5 and MOF-5/Mag-H$^+$

The morphology of MOF-5 and MOF-5/Mag-H$^+$ structures is studied by X-ray diffraction (XRD). **Fig. 9** shows that there is a broad peak in the area of small angles which confirms the presence of the clay in the structure of MOF-5/Mag-H$^+$ (25 wt %). This peak is not present in XRD patterns of MOF-5 which does not contain Maghnite-H$^+$ (**Fig. 8**). The intense peak below 10 ° (2Θ = 9.8 ° corresponding to d = 9.1 Å) is observed in samples of MOF-5 and MOF-5/Mag-H$^+$. This peak is the result of a distortion of the cubic symmetry in the structure of MOF-5 [18]. The broad peak at 2Θ = 5.8° (**Fig. 10**) allows to conclude that there is formation of a partially exfoliated/partially intercalated structure. The increase in the interlayer distance from 13.3 Å to 15.6 Å suggests intercalation of some chains of MOF-5 between the layers of clay. The exfoliated part of the structure is caused by the high molecular weight of MOF-5. This exfoliation is confirmed by FT-IR spectrum of MOF-5/Mag-H$^+$ (25%wt) which have a characteristic band at 465 cm^{-1} attributed to the Si-O-Si.
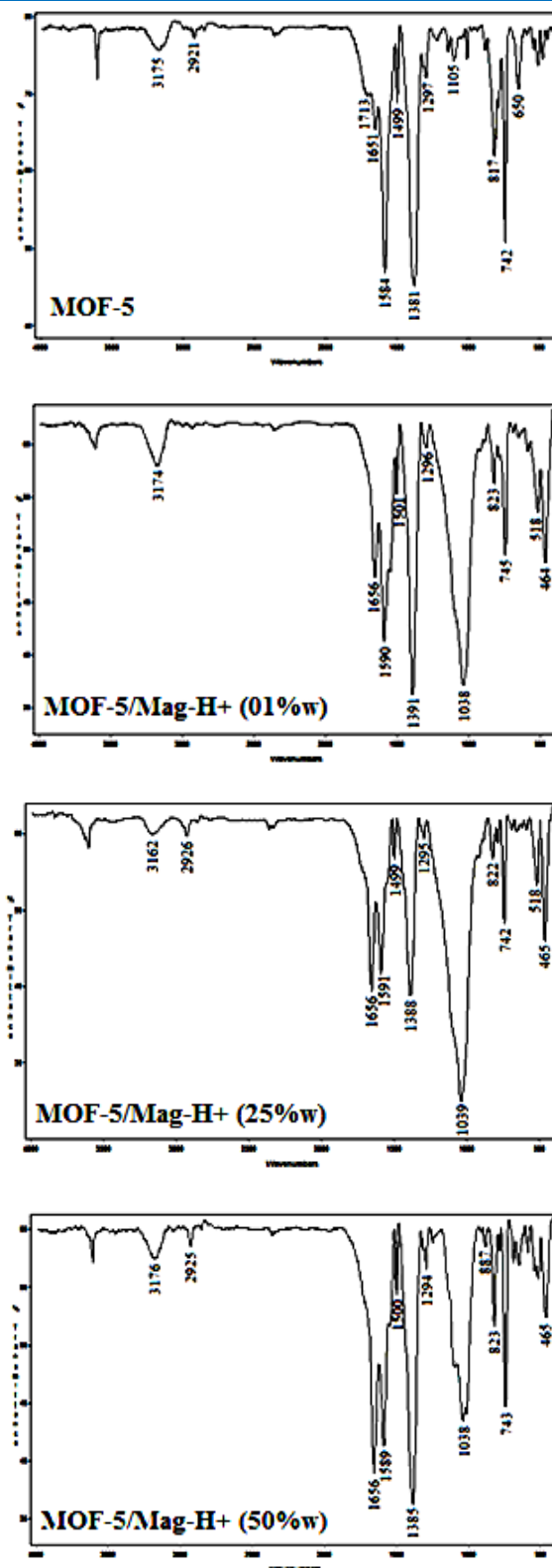

Fig. 7. FT-IR spectra of MOF-5 and MOF-5/Mag-H$^+$.

Thermal properties of MOF-5 and MOF-5/Mag-H$^+$

The thermal stability of MOF-5 and MOF-5/Mag-H$^+$ prepared by in situ polymerization process is studied by TGA (Thermogravimetric Analysis). **Fig. 11** shows the thermograms of MOF-5 pure and MOF-5/Mag-H$^+$ that contain 5 wt%, 25 wt% and 50 wt% of Maghnite-H$^+$. The

thermograms of MOF-5/Mag-H$^+$ containing 5 wt%, 25 wt% and 50wt% of Maghnite-H$^+$ record a first weight loss at 100°C caused by the removal of water and also a second mass loss from 160 °C which is the result of the removal of DMF. MOF-5/Mag-H$^+$ at different weight percentages of Maghnite-H$^+$ show high thermal stability up to 465 °C for MOF-5 containing 5 wt% of Maghnite-H$^+$ and up to 478 °C for MOF-5 containing 50 wt% of Maghnite-H$^+$, while that of pure MOF-5 is about 440°C. Thermal stability increases proportionally with the increasing the amount of the clay (**Fig. 11**), a gain of 40 °C which is reached at 50 wt% of Maghnite-H$^+$. This stability is mainly due to the fine dispersion of exfoliated or intercalated particles of Maghnite-H$^+$ playing an inorganic support for MOF-5.
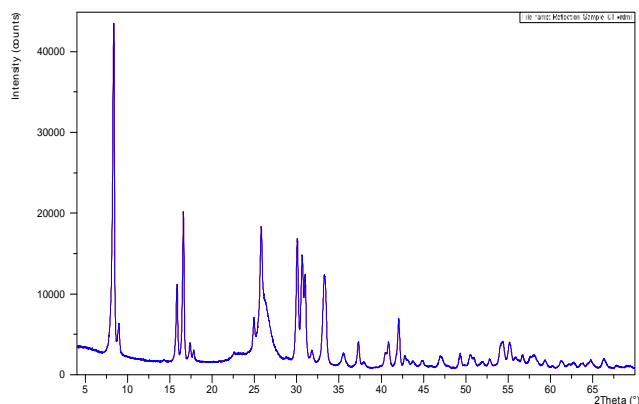
Fig. 8. XRD patterns of MOF-5.
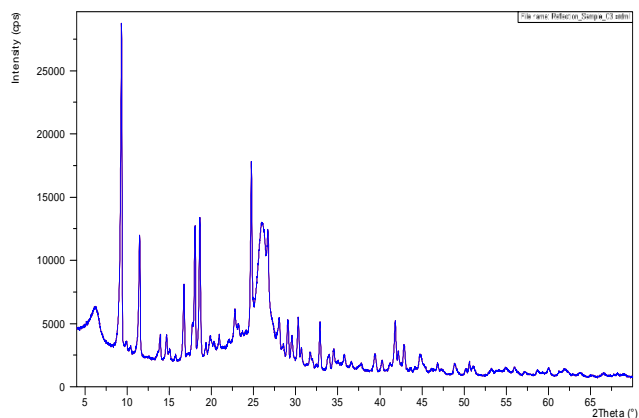
Fig. 9. XRD patterns of MOF-5/Mag-H$^+$ (25wt%).
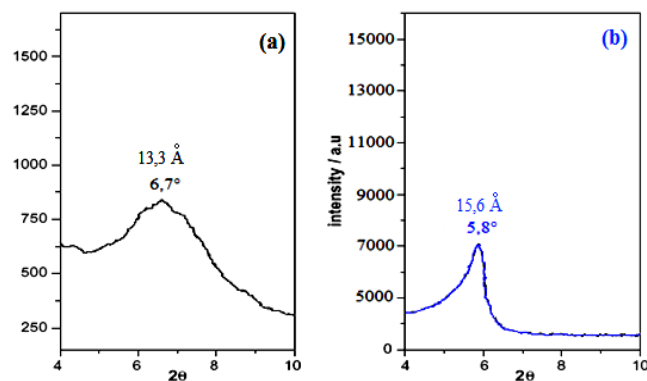
Fig. 10. XRD patterns of (a) Mag-H$^+$ and (b) MOF-5/Mag-H$^+$ (25wt%).
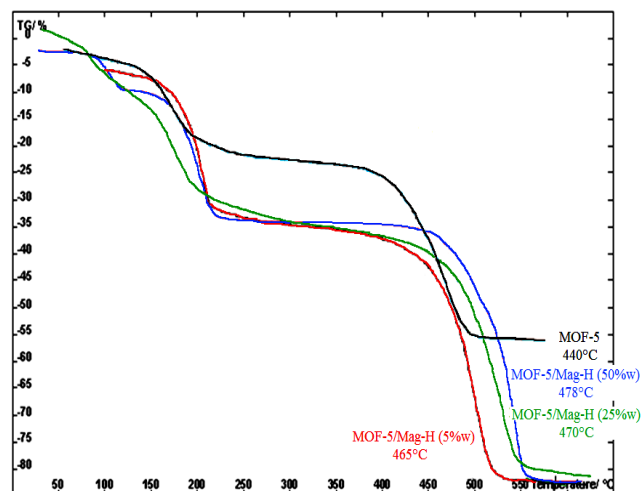
Fig. 11. Thermograms of MOF-5 and MOF-5/Mag-H$^+$ (05 wt%, 25 wt%, 50 wt%).

Conclusion

The objective of this work is to develop an efficient method which is the use of Maghnite activated by sulfuric acid H_2SO_4 (Maghnite-H$^+$) in the synthesis of MOF-5. ^{27}Al and ^{29}Si MAS NMR spectra show that during the in situ polymerization of MOF-5/Mag-H$^+$, the grafting of the polymer onto the layered silicates is achieved on specific tetracoordinated Al sites without significant chemical change on the aluminosilicate layers of the clay. The study of the morphology of these materials by X-ray diffraction (XRD) shows that exfoliated/intercalated structures are obtained. The thermal stability of the resulted MOF-5/Mag-H$^+$ is much higher than pure MOF-5. The synthesis of MOF-5 using Maghnite-H$^+$ is very efficient and led to polymerizations with higher yields and better thermal stability which will allow its use in optimal conditions i.e. a degradation temperature which exceeds 450 °C without deterioration of the product structure.

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