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$H_3PMo_{12}O_{40}$@MOF as a New Catalytic System for Cycloxexanone Oxidation to Adipic Acid

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Abstract: Keggin-type phosphomolibdic acid ($H_3PMo_{12}O_{40}$, PMo_{12}) encapsulated in the mesocages of chromium-based terephthalate metal–organic framework (MIL-101), was established to be an active and new green catalyst for the adipic acid (AA) synthesis via cyclohexanone (-One) oxidation in free solvent conditions and hydrogen peroxide as green oxidant. In this paper, we wish to report the synthesis of MIL-101 with different high loadings of the PMo_{12} nanocrystals incorporated within the large pores of MIL-101. Two and five POMs per large cavity can be incorporated into the matrix of MIL-101 respectively, xH_3PMo_{12}@ MIL101 with x=0, 2 and 5, they were characterized by several physic-chemical technics, then investigated in the reaction oxidation with 30 mmol –One at 90 ° C for 20h. A sequenced addition of 0.5ml of H_2O_2 (30%) was made every 30 min. The catalysts have shown good activity and the purity of AA was invistigeted by ^{1}H and ^{13}C NMR.

Keywords: Heteropolysalts, Metal–organic framework, Catalytic oxidation, Hydrogen peroxide, Adipic acid

Introduction

Adipic acid (AA) is the raw material for the production of synthetic fibers, nylon 6,6, polyurethanes, plasticizers, and adiponitriles (Meng, 2015). Its industrial production is based on the oxidation of a mixture of cyclohexanone and cyclohexanol (known as KA oil) by nitric acid (40–60 %) using Cu/V catalyst (Vafaeezadeh, 2012). With a global annual production about 3.5 million tons, the HNO_3 use is the principal source of N_2O emissions (Penate, 2012). Its ability on the warming atmosphere is about 310 times higher than that of carbon dioxide (Vafaeezadeh, 2012). It is also the origin of ozone depletion as well as acid rain and smog (Lu, 2012). Despite of high adipic acid yields (>95 %) obtained with this process, the research of other industrial processes with an environmentally friendly is more than necessary (Mouanni, 2019).

On the other hand, the use of green oxidants like hydrogen peroxide can be one of the key technologies for synthesizing adipic acid, because of its low cost and abundance (Meng, 2015). Hydrogen peroxide can

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positively facilitate many oxidation processes for its manageably without any organic solvents, with water as the sole by-product (Amitouche, 2018). Polyoxometalates have also attracted much attention due to their diverse availabilities in electronic, magnetic, redox, medical and photonic field (Idrissou, 2019). Moreover, their non-toxicity makes them compatible with the environment. The most studied class of POMs is that of Keggin type (Mouanni, 2019). To further make POMs more stable and efficient, options and strategies have been attempted. Among them, the introduction of highly porous crystalline solids as MCM-41 (Jatupisarnpong, 2012) or SBA-15 (Meng, 2015) to support the POMs or Metal-organic frameworks (MOFs) to incorpore them (Haddadi, 2015). MOFs are a family of organic-inorganic hybrid materials containing nanometric pores and channels built from organic ligands bridging metal ions (Lik, 2014). It has been reported that POMs have successfully been incorporated into MOFs, some of them have shown their efficiency in many oxidation reactions (Saikia, 2015)

Within this context, we have used in this work MIL -101(Cr) MOFs (Material Institute Lavoisier-101), one of the archetypal MOFs constructed by chromium ion and terephthalate ligands to insert 2 or 5 Keggin units ($[PMo_{12}O_{40}]^{3-}$) noted $xPMo_{12}$@ MIL-101(x=0,2 or 5). MIL-101(Cr) exhibits strong hydrothermal stability, large surface area and high pore size. The size cages have diameters of 2.9 and 3.4 nm with two microporous windows of 1.2 and 1.6 nm respectively (Yu, 2017). These parameters make MOF an attractive host for the encapsulation of polyoxometalates. The incorporation of Keggin units in the MOF will allow a better distribution therefore to a better accessibility of active sites by organic substrate molecules (Saikia, 2015). The $xPMo_{12}$@MIL-101system was tested in the cyclohexanone oxidation to adipic acid in the presence of the hydrogen peroxide. AA purity was verified by ^{1}H and ^{13}C NMR. The characterization of the catalysts has been investigated using IR, Scanning Electron Microscopy (SEM-EDX), XRay diffraction and thermal analysis (TG).

Materials

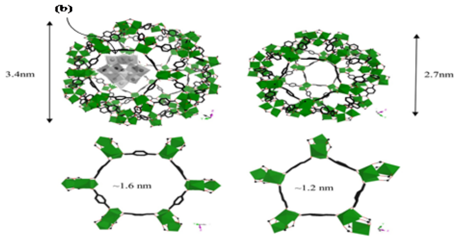
All reagents and solvents were used as received from Aldrich or from Fluka, without further purification. They included sodium molybdate $Na_2Mo_3·2H_2O$, chromium (III) nitrate nonahydrate ($(Cr(NO_3)_3.9H_2O)$), phosphoric H_3PO_4 (75%), perchlorique, $HClO_4$, hydrochloric HCl (37%), sulfuric H_2SO_4, acetic, $C_2H_4O_2$ and nitric, HNO_3 acids, diethyl ether, cyclohexanone, hydrogen peroxide (30%), 1, 4-benzenedicarboxylic acid (H_2BDC), ammonium fluoride (NH_4F), ether and acetone.

Catalyst Preparation

Preparation of MIL 101

MIL-101 (Cr) was synthesized hydrothermally (220 ° C, 10h, heating ramp: 1h) from a suspension containing chromium (III) $Cr(NO_3)_3.9H_2O$, terephthalic acid HO_2C- (C_6H_4) -CO_2H and H_2O, using a Teflon bomb body inserted in a metal bomb **[19]**. After a cooling ramp to room temperature for 3h, the MIL-101 powder was separated from the solution, washed with distilled water and then with acetone and finally dried at room temperature.

Incorporation



(a) **(c)**

Figure 1. (a) Super Tetrahedron of MIL101, (b) PMo12 incorporated into MIL101, (c) Metal Organic Frameworks MIL101 [MOF24-MOF30],

$H_3PMo_{12}O_{40}$ was prepared according to the literature (Amitouche, 2018). 0.2 g of MIL-101(Cr) are impregnated by 0.031g of $H_3PMo_{12}O_{40}$ dissolved in 5 ml of distilled water for 2 PMo_{12} @ MIL101 preparation and 0.2 g of

MIL-101(Cr) are impregnated by 0.077g of $H_3PMo_{12}O_{40}$ dissolved in 5 ml of distilled water for 5 PMo_{12} @ MIL101 preparation . The two resulting suspensions were stirred at room temperature for 8 hours to allow sedimentation. The solids were then recovered by centrifugation, washed several times with water and ethanol and then with ether and dried at 120 ° C for three days (Figure 1).

Characterizations

FT-IR spectra were recorded on a Nicolet 6700 FT-IR spectrophotometer, using the ATR diamond technique. X-ray diffraction patterns (XRD) were recorded with a Siemens D5000 diffractometer using Cu-Kα radiation (λ = 1.5418 Å). The indexing of the diffraction lines and the phase identification were carried out using the Highscore plus software. Thermal analysis was performed on TGA / DSC1, Star System Metlertoledo with a heating rate of 5 ° C / min up to 600 ° C under nitrogen flow. The number of POMs incorporated per large cavity was verified by EDX for the content of two POMs.

Catalytic procedure

The catalytic cyclohexanone oxidation was carried out in a 100 mL three-neck round-bottom flask equipped with a reflux condenser, a magnetic stirrer, and an adjusted temperature oil bath. The mixture of cyclohexanone (x mmol) and the target catalyst (y %) was heated with stirring (1000 rpm) at 90°C for 20 h to obtain complete AA crystals. 0.5 ml of hydrogen peroxide (30 %) was added every 30 min. After reaction, the mixture was cooled down directly at 0°C overnight. The resulting white precipitate was separated by filtration, and washed several times with small volume of cold water to afford pure adipic acid. Adipic acid was isolated as crystals and identified by ^1H and ^{13}C NMR.

Results and Discussion

Catalysts Characterizations

Infrared spectroscopy FTIR

Figure 2 shows both FTIR spectra of MIL101 and $xPMo_{12}$@MIL101 (x =2 or 5). The vibration bands observed at 1623, 1513 and 1397 cm^{-1} are attributed to carboxylate groups of the MOF and those at 1022 and 749 cm^{-1} assigned to δ (C-H) and γ (C-H) rings of the aromatic rings, respectively (Zhanga, 2017). The vibration bands, observed in 700-400 cm^{-1} range, are assigned to the plane and out-plane bending modes of the COO groups (Hassan, 2017). The FTIR spectra of $xPMo_{12}$ @ MIL101(Fig.1(2) and (3)) show, in addition to characteristic vibration bands of the MOF, those characteristic of Keggin anion as $P\text{-}O_a$ (1066 cm^{-1}), $Mo\text{-}O_d$ (960 cm^{-1}), $Mo\text{-}O_b\text{-}Mo$ (886 cm^{-1}) and $Mo\text{-}O_c\text{-}Mo$ (813 cm^{-1}) (Mouanni, 2019). These observations confirm that the MIL-101 (Cr) has incorporated the POM without modification of structure.

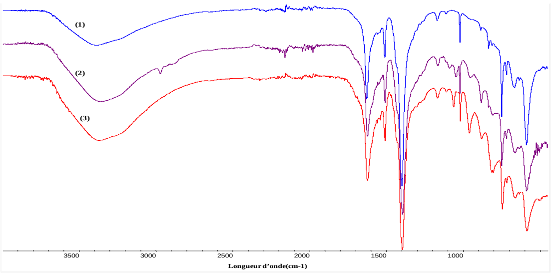


Figure 2. FTIR spectras of (1) –MIL 101, (2) -$2PMo_{12}$@MIL101, (3) – $5PMo_{12}$@MIL101

XRD diffraxion

The XRD diagrams of samples MIL101 and xPMo$_{12}$@MIL101 (x: 2 or 5) are given in figure. 3. The observed peaks at 2θ= 3.4, 8.5, 9.1, 10.4, 16.7 and 19.1° for MIL101 agree with those reported in the literature (Zhang, 2017). The XRD profiles of 2 PMo$_{12}$ @ MIL101 and 5 PMo$_{12}$ @ MIL101 are similar to that of parent MIL-101 (Cr) with a slight decrease in the intensity of the diffraction lines, indicating that the crystal structure of MIL-101 (Cr) remains unchanged after the phosphomolybdic acid introduction. These results confirm that the incorporation of POM in the cavities of MIL 101 does not modify the structure of the framework, results in according with those observed in IR spectroscopy.

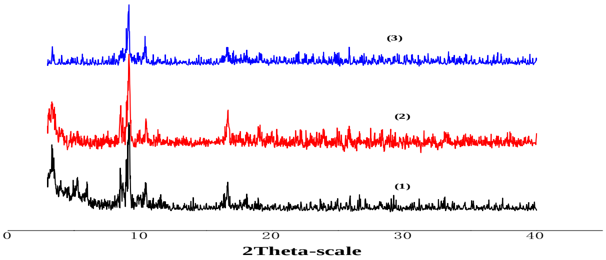


Figure 3. DRX xPMO$_{12}$ @ MIL101 diagrams *(1) – MIL 101, (2)- 2Pmo$_{12}$@MIL101, (3) – 5Pmo$_{12}$@MIL101*

Thermal Analysis TG

The thermal gravimetric analysis (Figure 4) of MIL101 and xPMO$_{12}$@MIL101 (x: 2 or 5) reavels a three-step weight loss. Below 150 ° C, the weight loss is due to the release of water molecules from the material cages. From 250 to 300 °C, the release of water molecules coordinated to the metal chromonium cluster takes place. The weight loss observed up to 350 °C is assigned to the organic linker degradation. The final decomposition of MIL101 is Cr_2O_3 while that of xPMo$_{12}$@MIL101 is $Cr_2O_{3,}$ P_2O_5 and MoO_3 **(**Benjamin, 2017). It should be noted that the decomposition temperature of 5PMo$_{12}$@MIL101 is slightly higher than that of MIL101 suggesting that the presence of five Keggin units in the framework slightly increases the stability of the MOF.

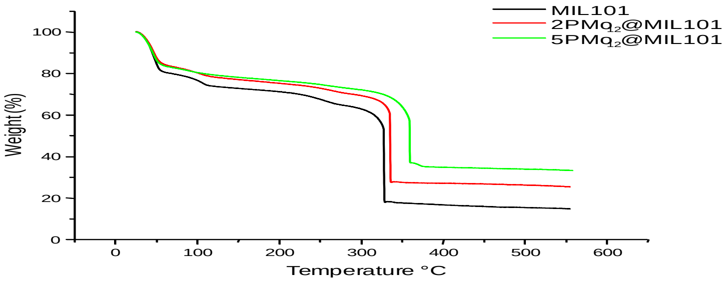


Figure 4. xPMO$_{12}$ @ MIL101 TG diagrams (x: 0, 2 or 5)

SEM-EDX Analysis

The figure.5 shows a spongy morphology with a smooth surface of the MIL101 material after incorporation of the POM. The obtained results from SEM-EDX spectra (Table. 1), show that the % atomics vary between 1.61 and 2.83, 74.48 and 79.06 and 19.33 and 22.99 for P, Cr and Mo respectively. From these results, the averages of % atomics are of 2.12, 75.85 and 22.02 for for P, Cr and Mo respectively. The results show also that cavity of MIL-101(Cr) sizes vary between 2.07 and 2.59 µm.

The particle size is 25 µm and the amount of POMs incorporated can be deduced from EDS analysis. The average molybdenum to chromonium ratio Mo/Cr= 0.29 corresponds to 2.47 POM per cavity of MIL-101(Cr), different expected value of 2. May be the amount of MOF introduced during the impregnation was overestimated. The dehydrated MOF can easily capture water and modify its weight.

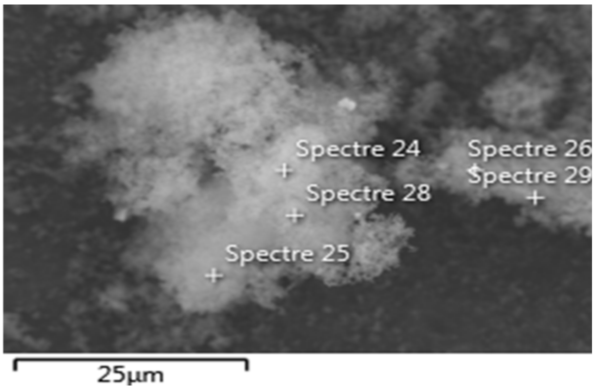


Figure 5. EDX-MEB images of $2PMo_{12}$@MIL101

Table 1. The results of the EDX-SEM analysis of precursor $2PMo_{12}$@MIL 101

Type of results	Atomic %		
Statistics	P	Cr	Mo
Maxi	02.83	79.06	22.99
Mini	01.62	74.48	19.33
Average	02.12	75.85	22.02
Standard deviation	00.47	01.82	01.52

Reactivity of POMs @ MOF

Recently, several researches on metal-organic frameworks MOFs have attracted a lot of attention. They are excellent candidates for catalytic applications since they offer multiple opportunities to create desirable active sites. The use of MOFs as catalyst or as supports for Keggin, can bring new opportunities in the development of more active catalysts for the oxidation of cyclohexanone to adipic acid. Two precursors $2PMo_{12}$@MIL101 and $5PMo_{12}$@MIL101 are prepared by the impregnation method. Their catalytic performances are studied via the oxidation reaction of cyclohexanone to adipic acid by hydrogen peroxide in the absence of solvent and in the same catalytic condition (30mmol, 20h, 90 ° C, 1% (30mg)). However, the characteristic color change of the reduced POMs was not very visible, as the MIL-101(Cr) presents a green color. As it happens, the sequenced addition of 0.5ml of H_2O_2 was made every 30 min.

Table 2. Reactivity of $xPMo_{12}$@ MIL101 systems (x = 0, 2 and 5)

Précurseur	R% AA	H_2O_2 (ml)
MIL101 (Cr)	10.34	10
$2PMo_{12}$@MIL101	11.45	10
$5PMo_{12}$@MIL101	24.05	10

The Lewis acid sites on Cr of metal-organic frameworks MIL-101(Cr) created by dehydration are known as active catalytic sites **[25]**, which must be considered in adipic acid yield and this explains the oxidative reactivity of the prestine MIL-101(Cr). The encapsulation of POM@MOF has some catalytic performance shown in table 2. The yield of adipic acid increase from 11.45 to 24.05% for $2PMo_{12}$@MIL101 and $5PMo_{12}$@MIL101 and show better performances compared to MIL101 (10% of AA yield). The encapsulation of more PMo_{12} units in the MIL-101 large cavity leads to a net amelioration in the AA formation. But the expected heterogeneous behavior of MOF was no longer achieved, as the system is homogeneous after twenty hours of reaction. Total degradation of MOF and POM structures occurred with increasing amount of H_2O_2 at 90°C. The same result has been observed with the insoluble ammonium salts $(NH_4)_3PMo_{12}O_{40}$ which become soluble at the end of the reaction, under the effect of a powerful oxidant such as hydrogen peroxide.

Adipic Acid Characterisation

The ^1H and ^{13}C NMR spectra of adipic acid for the same catalysts are shown in Figure 6 and 7 respectively. The analysis was carried out on a 300 MHz Bruker Avance spectrometer using standard NMR tubes and solubilizing 10 mg of AA in a volume of 0.5 ml of acetone C_6D_6.

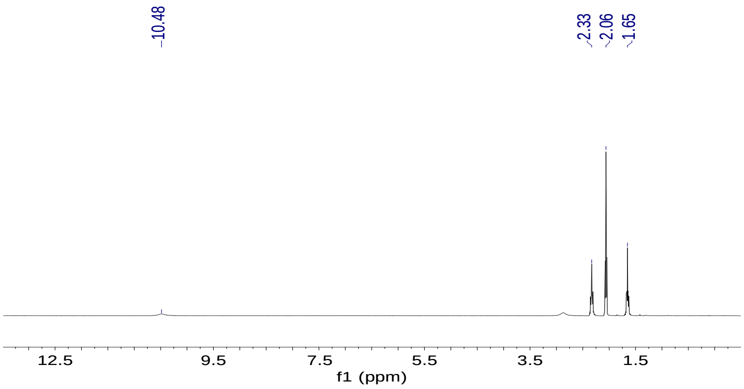


Figure 6. ^{1}H NMR spectrum of commercial Adipic acid

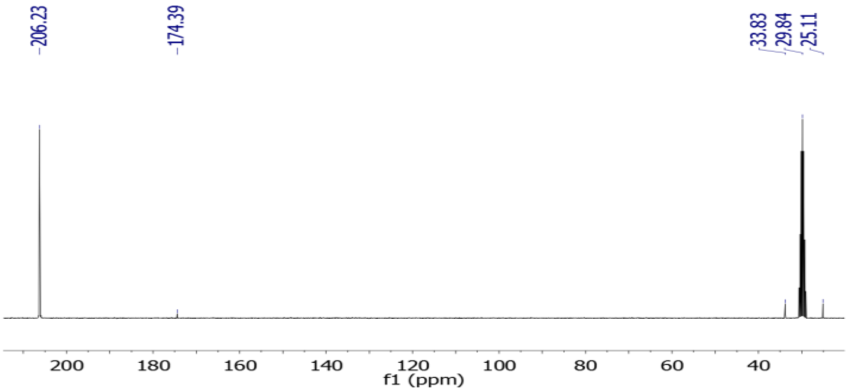


Figure 7. ^{1}H NMR spectrum of commercial Adipic acid

The NMR analysis results of obtained AA confirm its purity. Thus, COOH $(CH_2)_4$COOH presents three characteristic peaks in ^{1}H and ^{13}C NMR : two chemical shifts at 1.65 and 2.33 ppm corresponding to the two methyl groups $-CH_2-$ and that at 10.48 ppm corresponds to the carboxylic acid proton –COOH. In ^{13}C NMR too, 25.11 and 38.83 ppm correspond to the carbone atomes of the two methyl groups $-CH_2-$, and the carboxylic acid carbon corresponding to 174.39 ppm. The chemical shift of acetone solvent C_6D_6 appears around 2.06ppm in ^{1}H NMR, and 29.84, 206.23 ppm in ^{13}C NMR.

Conclusion

In this paper, new interesting POMs@MOF catalytic systems with the formula of xPMo12@ MIL101 (x=0, 2 and 5) were developed for clean AA production via the oxidation of cyclohexanone in the presence of hydrogen peroxide as a green oxidant without the use of solvent. Their catalytic properties showed that the AA yield is sensitive to the amount of POMs, with a higher AA yield of (24.05%) in the presence of 5 POMs@MIL101 under the optimised conditions; 20 hours reaction time, 30mmol substrate, 90°C and 10ml hydrogen peroxide. Thus, the use of a bifunctional catalyst (acid and oxidant) with low mass, a green oxidant (H_2O_2) with water as the only reduction product, and the non-use of solvent and co-catalyst are positive conditions for the production of adipic acid.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

Acknowledgements or Notes

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