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Copper-based MOF-74 material as effective acid catalyst in Friedel–Crafts acylation of anisole

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ABSTRACT

Metal organic frameworks (MOFs) are emerging potential materials for catalytic applications. Among them, the honeycomb M_2(dhtp) family, also known as MOF-74 or CPO-27 materials, are characterized by remarkable textural properties and accessible unsaturated metal sites (M). This work has been focused on the catalytic properties of novel Cu-MOF-74 material for the Friedel–Crafts acylation of anisole, as acid-catalyzed reaction test. The influence of reaction variables such as the type of acylating agent and solvent, and the reaction temperature have been studied. Additionally, the stability of Cu-MOF-74 was evaluated under different reaction conditions. Cu-MOF-74 achieved a remarkable catalytic performance in terms of anisole conversion and p-MAP yield. Additionally, the structural MOF-74 phase was preserved when using diluted concentrations of acetyl chloride as acylating agent. The relative acylating agent concentration was demonstrated to be crucial in the collapse of the crystalline MOF-74 phase. The catalytic activity of Cu-MOF-74, in terms of anisole conversion and selectivity to p-MAP product, was also superior to other Cu-containing MOF materials (HKUST-1) and conventional inorganic acid catalysts, such as aluminum-containing microporous zeolites (H-ZSM-5 and BETA) and mesoporous ordered materials (Al-MCM-41). Cu-MOF-74 also showed high stability and remarkable catalytic performance for seven consecutive reaction cycles when this MOF material was used in the best reaction conditions.

1. Introduction

Metal organic frameworks (MOFs) are a class of materials constituted by metal or metal clusters bounded to multifunctionalized organic molecules, such as amines, pyridines, carboxylates, sulphonates, and phosphonates. The combination of both parts provides a wide variety of crystalline materials with one-, two-, or three-dimensional porous structures ranging from microporous (smaller than 2 nm) to mesoporous (between 2 and 40 nm). Additionally, the extensive reactivity of metal species and organic compounds allow the design of a remarkable large number of MOF structures with a broad diversity of physicochemical properties [1].

Although MOF materials have been originally used in several applications such as gas storage, they are especially suitable for catalysis. MOF materials have been proposed as active and selective catalysts for a wide range of reactions, from acid–base to redox catalysis [2–6]. In MOF compounds, both the metallic component and the organic ligand can play an important role in the catalytic reaction mechanism. Regarding the inorganic metallic moiety, they can act as electron-pair acceptor, i.e. Lewis acid, in particular when uncoordinated metal sites are generated as result of the removal of coordinated solvent molecules that remain after the MOF synthesis [7]. In other cases, catalytic groups can be included directly into the bridging ligands of the organic building blocks of MOFs. The number of MOFs belonging to this category with demonstrated catalytic activity is very limited. This is because the reactive groups have to be accessible to interact with the catalytic substrates and therefore not being coordinated to the metal ions of the MOF. Therefore, the difficulty in preparing MOFs containing organic reactive groups lies in the natural tendency of metals to interact with all the available functional groups of the ligand.

Several studies on catalytic activity of MOFs with active metal sites have shown their potential application to reactions like hydrogenation/isomerization [8–11], cyanosilylation of aldehydes [12–14], oxidation of organic substrates [15–17], photocatalysis [18,19], acylation/alkylation of aromatics [20–23], and condensation reactions [24–26].

The Friedel–Crafts acylation reaction essentially consists of the production of an aromatic ketone by reacting an aromatic substrate with an acyl component in the presence of a catalyst [27].

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Main reaction products constitute fundamental intermediates in the pharmaceutical, fragrance, flavor, dye, and agrochemical industries [28]. Conventionally, the electrophilic acylations are catalyzed by Lewis acids (such as $ZnCl_2$, $AlCl_3$, $FeCl_3$, $SnCl_4$, and $TiCl_4$) or strong protic acids (such as HF and H_2SO_4). In particular, the use of metal halides causes some problems associated with the strong complex formed between the ketone product and the metal halide itself which requires the use of more than stoichiometric amounts of catalyst, and in general a large amount of waste. Therefore, there is a strong incentive to replace homogeneous processes by green and efficient heterogeneous processes for economic and environmental reasons. The separation of reaction products also becomes easier and the catalyst can be reused due to less leaching problems contrasting with homogeneous catalysts. Solid catalysts used have been almost exclusively inorganic materials up to now, particularly micropore zeolites [29,30].

According to the large number of publications about MOFs for catalytic applications during last years, these materials are considered promising candidates as heterogeneous catalysts [26,31,32]. Properties like well-ordered size and shape of the pores, flexible activity in response to guest molecules, designable channel surface functionalities, high metal content and high crystallinity make MOFs unique between porous solids.

Another important point to be evaluated when a given MOF structure is tested as heterogeneous catalyst is its stability to certain solvents and reaction conditions. Particularly, MOF materials with unsaturated metal sites have shown a better performance when using low polarity solvents, which minimize dissolution of the catalyst [13]. In contrast, donor type solvents, such as tetrahydrofuran and other ethers, compete against the reaction substrates for the metal Lewis acid sites, so that they can block the catalytic active centers or even react with them destroying the MOF structure.

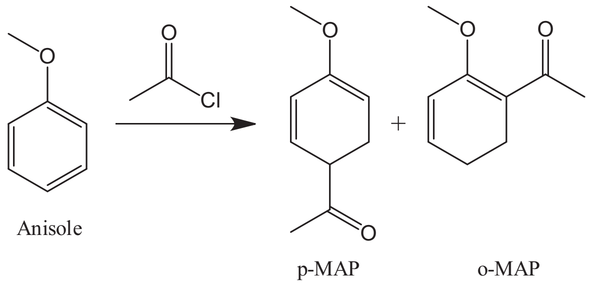
In our previous work [33] a new Cu-based MOF material was developed, Cu_2(dhtp), structurally homologous to the honeycomb-like MOF-74/CPO-27 series, with unsaturated and accessible metal sites. Herein we report the catalytic performance of this MOF material as a Lewis acid catalyst in the Friedel–Crafts acylation of anisole, studying its structural stability at different reaction conditions.

2. Experimental

2.1. Catalysts preparation

The synthesis procedure of Cu-MOF-74 was slightly modified from literature [33]. In a typical synthesis, a mixture of 2.2 g of 2,5-dihydroxyterephthalic acid (H_2dhtp, 11.2 mmol, Aldrich) and trihydrated copper nitrate(II) (5.9 g, 24.6 mmol, Aldrich) were added over a 20:1 (v/v) solution of N,N-dimethylformamide (DMF) and 2-propanol (250 mL) in a 500 mL screw cap bottle. The suspension was stirred until homogeneous solution. Then, the resultant solution was placed in an oven at 80 °C for 18 h. Thereafter, the sample was cooled down to room temperature and the mother liquor was separated from reddish needle-shaped crystals by vacuum filtration. Thereafter, the crystalline solid sample was washed with DMF. Afterwards, the crystals were immersed in 100 mL of methanol for four 4 days, renewing it by fresh methanol every 24 h. Finally, the sample was dried at 150 °C under vacuum (10^{-3} bar) for 5 h and stored under inert atmosphere.

Other catalyst materials used in this work with the purpose of comparison like HKUST-1, H-ZSM-5 and BETA were purchased to Sigma–Aldrich Química S.L., Sud Chemie Iberia S.L. and Zeolyst International, respectively. Al-MCM-41 was synthesized in our laboratory following the procedure described in the Supporting Information.



Scheme 1. Simplified reaction scheme for the acylation of anisole with acetyl chloride.

2.2. Catalyst characterization

Nitrogen adsorption–desorption isotherms at −196 °C were measured using an AutoSorb equipment (Quantachrome Instruments). The micropore surface area was calculated by using the Brunauer–Emmett–Teller (BET) model [34]. The pore volume and diameter were estimated by non-local DFT calculations, assuming a kernel model of N_2 at -196 °C on carbon (cylindrical pores, NLDFT equilibrium model) [35]. X-ray powder diffraction (XRD) patterns were acquired on a PHILIPS X'PERT diffractometer using Cu Kα radiation. The data were recorded from 5 to 50° (2θ) with a resolution of 0.01°. Scanning electron microscopy (SEM) micrographs were obtained on a PHILIPS XL30 ESEM electronic microscope operating at 200 kV. Simultaneous thermogravimetry and derivative thermogravimetry analyses (TGA/DTG) were carried out under a nitrogen atmosphere with an N_2 flow of 100 mL min^{-1} at a heating rate of 5 °C/min up to 700 °C, using a TA Instruments SDT 2860 apparatus.

2.3. Reaction procedure

In order to evaluate the catalytic performance of Cu-containing MOF with open metal sites, the acylation of anisole with acetyl chloride to form methoxyacetophenones (MAPs) was studied as a reference acid catalyzed reaction (Scheme 1). All the catalytic experiments were carried out in a round bottom flask placed in a silicone bath under N_2 atmosphere. Reactants and catalyst were charged at room temperature, and then heated up to the reaction temperature. Stirring was fixed for all runs at 700 rpm in order to avoid diffusional limitations. The influence of reaction solvent, acylating agent, temperature, acylating agent/anisole molar ratio and molar catalyst concentration (always referred to the acylating agent) was studied according to previous operation conditions found in the literature [36]. Samples were withdrawn at selected reaction times ranging from 0 to 5 h. Anisole and o- and p-MAPs were identified and quantified by gas chromatography, using a GC-3900 Varian chromatograph equipped with a CPSIL 8 CB capillary column (30 m × 0.25 mm, film thickness 0.25 μm) and a flame ionization detector (FID). GC temperatures were as follows: injector 250 °C; FID 330 °C; program for the oven, 50 °C for 1 min; 100 °C/min to 175 °C and hold for 4.25 min; then 40 °C/min to 270 °C. Sulfolane was used as an internal standard and all samples were analyzed twice.

The relative anisole conversion and p-MAP yield were monitored along the reaction time. Relative anisole conversion (χ) was calculated taking into account the maximum theoretical anisole conversion, which depends on the particular anisole/acylating agent ratio of each catalytic run. Relative p-MAP yield (Y) was estimated as the product of the relative maximum theoretical anisole conversion and the p-MAP selectivity (S). The p-MAP selectivity (S) was calculated as mol of p-MAP obtained per mol of anisole converted.

Table 1
Characteristics of MOFs and other inorganic catalysts used in this study.

Catalyst	Structure	Channel structure	Channel diameter (Å)	Surface area (m^2/g)	Cu content (mmol/g)	Si/Al molar ratio
Cu-MOF-74	MOF	1D	10–12	1126	6.2	–
HKUST-1	MOF	3D	10	708	5.0	–
H-ZSM-5	Zeolitic material	3D	5.1–5.6	429	–	30
BETA	Zeolitic material	3D	6.6	710	–	19
Al-MCM-41	Mesoporous material	1D	27	894	–	29

In order to assess the activity of copper leached as homogeneous catalyst, a typical test was performed evaluating the anisole conversion once the catalyst was removed from the reaction medium by hot filtration after 1 h.

3. Results and discussion

3.1. Characterization of Cu-MOF-74

The most relevant characterization data of the Cu-MOF-74 synthesized by solvothermal method is depicted in the supporting information (Figs. S1–S5). The porosity of the Cu-based MOF material was measured by nitrogen adsorption at −196 °C (SI, Fig. 1). The basically type I adsorption/desorption isotherm revealed a permanent microporosity with a BET specific surface area of 1126 m^2/g, a pore volume of 0.57 cm^3/g and an average pore diameter of ca. 11 Å. Powder X-ray diffraction pattern showed the typical reflections of MOF-74/CPO-27 phase [37], characteristic of a three-dimensional coordination polymer with a honeycomb topology that contains 1-D broad channels (SI, Fig. 1). SEM micrographs (SI, Fig. 3) revealed large needle-shaped crystals, similar to those shown by crystalline MOF-74/CPO-27 in literature [37,38]. The thermogravimetric analysis (TGA/DTG) in N_2 atmosphere (SI, Fig. 4) indicates the decomposition of the organic moiety of the sample about 375 °C. This fact is a clear evidence of the thermal stability of the Cu-MOF-74 framework. This thermal stability is very similar to that shown by the copper terephthalate MOF (Cu-tp) reported by Tannenbaum and co-workers [39], and slightly lower than the pure Zn-MOF-74/CPO-27, which is stable up to 400 °C [37]. Additionally, a significant loss of weight was determined at lower temperature (centered at 85 °C) which was attributed to the methanol used for the removal of original DMF solvent, either physisorbed on the porous MOF structure or coordinated into the open metal sites of its structure. Note that final thermal treatment of Cu-MOF-74 at 150 °C under vacuum for 5 h assured the activation of the material by evaporation of coordinated methanol and generation of free coordinated metal sites with Lewis acid properties. Fig. 5 of the SI illustrates a simplified scheme of the activation method for the exchange of the synthesis solvent and final extraction of methanol over a bidimensional view of the honeycomb structure of Cu-MOF-74. Previous characterization by single crystal X-ray diffraction analysis confirmed this isostructural framework, typical of MOF-74 and CPO-27 family [33]. Table 1 summarizes the most important characteristics of Cu-MOF-74 as well as other catalysts used in this work with the purpose of comparison: (i) HKUST-1 as another Cu-containing MOF and (ii) H-ZSM-5 and Al-MCM-41 materials as conventional inorganic catalysts.

3.1.1. Influence of the reaction solvent

As mentioned before, the design of MOFs containing unsaturated metal centers is of key importance for catalytic applications, since they strongly favor the direct interaction between metal and substrates (reactants or even the solvent molecules present in the reaction) and the potential activity of metal as Lewis acid sites. In this sense, the affinity of the solvent molecules for uncoordinated metal sites and their chemisorption on them may affect the catalytic performance, hindering the access of reactants, and subsequently decreasing the catalytic activity. In our particular reaction of anisole acylation, a series of solvents with different polarity have been studied in order to assess their effect on the catalytic activity of Cu-MOF-74 material. Fig. 1 shows the influence of various solvents (nitrobenzene, acetonitrile and dimethylformamide) when using acetyl chloride as acylating agent. The initial reaction conditions were 120 °C, a equimolar anisole/acetyl chloride ratio and 1.5 molar% of catalyst according to operation conditions of a previous work [36]. Nitrobenzene, being the less polar solvent, achieves

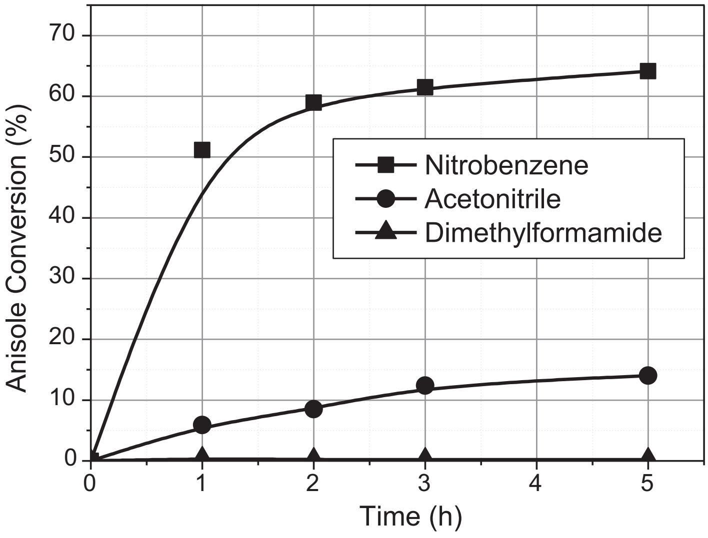


Fig. 1. Influence of solvent in the acylation of anisole with acetyl chloride using, Cu-MOF-74.

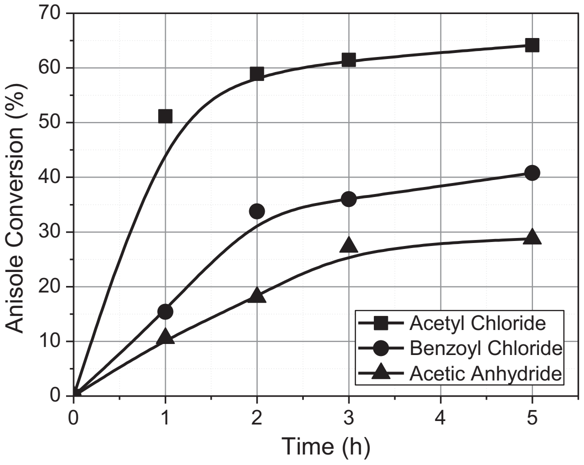


Fig. 2. Influence of acylating agent in the acylation of anisole using Cu-MOF-74.

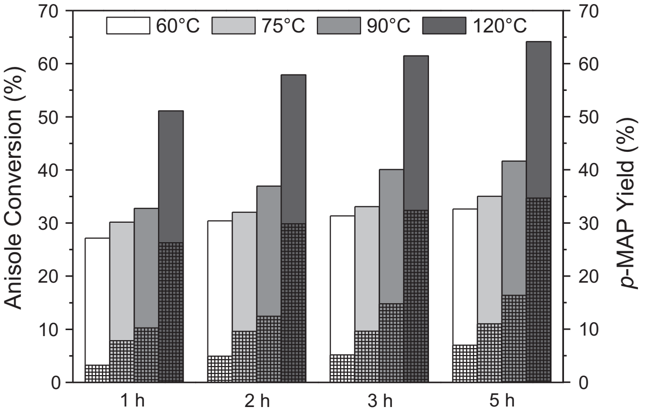


Fig. 3. Influence of reaction temperature in the acylation of anisole using Cu-MOF-74. Normal columns indicate anisole conversion; dense fill columns indicate p-MAP yield.

64% anisole conversion after 5 h of reaction, whereas DMF, with the highest polarity, shows a negligible anisole conversion. These results indicate that the lower solvent polarity, the better performance of Cu-MOF-74 catalysts. Thus, the affinity of polar solvent molecules for uncoordinated metal sites seems to have a significant influence in the Friedel–Crafts acylation reaction, being detrimental to access substrate molecules to the active acid centers. These results prove that the selection of solvent is crucial, not only in terms of favoring the diffusion of reactants and products in the catalytic system, but also to increase the availability of unsaturated metal sites of MOFs for catalytic applications. These results are in agreement with other studies reported in the literature with other catalysts like MCM-41 and borate zirconia type-acid catalyst [40,41].

3.1.2. *Influence of the acylating agent*

The effect of different acylation reagents on the Friedel–Crafts acylation of anisole with Cu-MOF-74 has been also studied using acetyl chloride, benzoyl chloride and acetic anhydride. Fig. 2 illustrates the anisole conversion for the three acylation reagents at 120 °C, equimolar anisole/acylating agent ratio and 1.5 molar% of catalyst. As it is well-known, Lewis acid catalysts are able to form electrophilic acylium ions ($R{-}C^{+}{=}O$) from acyl halides or acid anhydrides, which can be attacked by π-electrons of the $C{=}C$ aromatic rings following a typical nucleophilic addition to the acylium ions. In general, the more electrophilic is the acylium ion, the more favored is the nucleophilic attack of the aromatic ring. In the case of acetyl chloride and benzoyl chloride, the acylium ions generated from the benzoyl chloride are less electrophilic due to the resonance stabilization of the aromatic ring. The anisole conversion using acetyl chloride was remarkably much higher than that obtained with benzoyl chloride. These results seem to confirm the higher catalytic performance by the more electrophilic character of the acylium ions. Nevertheless, it must be noted that benzoyl chloride as acylating agent produces more bulky acylated products which could be also affecting the activity of Cu-MOF-74 due to diffusion constraints.

In the case of acetyl chloride and acetic anhydride, both of them generate the same acylium ion ($CH_3{-}C^{+}{=}O$), but the catalytic performance of Cu-MOF-74 was also significantly different. This fact can be explained by the weakness of the $C{-}Cl$ bond in acetyl chloride, which contributes to the higher activity of this acylating agent as compared to the acetic anhydride. This behavior of both acylating agents have been also reported in the literature for zeolitic H-ZSM-5 catalyst [29,36]. Regarding these results, acetyl chloride was considered the best acylating agent for Cu-MOF-74 in the Friedel–Crafts acylation reaction of anisole.

3.1.3. *Influence of reaction temperature*

The influence of the reaction temperature in the catalytic performance of the Cu-MOF-74 was also evaluated in the range of 60–120 °C for the acylation of anisole with acetyl chloride and nitrobenzene as solvent. In this part of the study, both relative anisole conversion and p-methoxyacetophenone (p-MAP) yield were monitored along the reaction time. The results shown in Fig. 3 revealed the increase of the anisole conversion with the temperature. A slight increase of anisole conversion was observed from 60 to 90 °C. However, the increase of temperature until 120 °C yields a remarkable enhancement of the anisole conversion. Moreover, this increase of activity in terms of anisole conversion was also accompanied by an increase of p-MAP yield. Concerning the reaction kinetics, high initial reaction rates can be estimated for the first hour following a remarkable decrease for the next four hours, regardless the reaction temperature. Similar results have been also found in the literature for the acylation of anisole using zeolitic materials as Lewis acid catalysts [42] or perfluorosulphonic mesoporous materials as Brønsted acid catalysts [43]. The main reason of this loss of activity is attributed to chemisorbed reactants and acylated products on the acidic sites of the materials [44]. Cu-MOF-74 achieved a 65% of anisole conversion with a relative p-MAP yield of ca. 35%. Ruling out the selectivity to o-MAP, which was negligible according to quantitative analysis in the liquid phase of reaction, the formation of other polyacylated byproducts or the partial chemisorption of the target p-MAP into the microporous structure of Cu-MOF-74 cannot be discarded. Several studies reported in literature for microporous zeolitic and mesoporous materials have confirmed these hypotheses, although the p-MAP yields were higher for that materials [36,44,45].

3.2. *Stability of Cu-MOF-74 for the acylation of anisole*

3.2.1. *Catalytic stability of Cu-MOF-74*

For liquid-phase reactions where solid metal-based catalysts are used, the dissolution of some active metal species of the solid phase into the solution during the reaction is considered a serious problem. In the case of partial solubility of metal species, the reaction could proceed under homogeneous or partially homogeneous catalysis conditions [31]. Moreover, in the case of MOF materials, leaching of metal species can also produce a partial or total collapse of the MOF structure, since the metal is forming an essential part of the material structure.

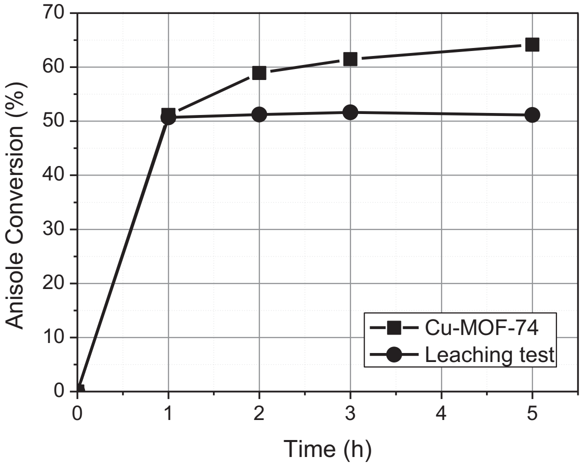


Fig. 4. Influence of the homogeneous contribution from the copper leaching of Cu-MOF-74.

In order to confirm the influence of Cu-leaching from Cu-MOF-74 catalyst in acylation reaction of anisole, a typical experiment was performed at 120 °C, equimolar anisole/acetyl chloride molar ratio, 1.5 molar% of catalyst and nitrobenzene as solvent, but after 1 h of reaction the solid Cu-MOF-74 was removed from the reaction medium by hot filtration. The liquid mixture after filtration was maintained at 120 °C for another 4 h in the same reaction system. Fig. 4 shows anisole conversion profiles for the typical experiment using the solid catalyst and the new experiment being the solid catalyst removed after 1 h of reaction. As observed, the anisole conversion did not continue after the solid catalyst separation, which evidenced a low contribution of homogeneous catalysis to the anisole acylation. Thus, the active role of the solid Cu-MOF-74 in the acylation of anisole is clearly proven when comparing the anisole conversion after the first hour of reaction for both experiments. Moreover, it must be noted that similar activity was achieved by trihydrated copper nitrate(II) when this homogeneous catalytic system was used with the same copper content (data not shown). Although the catalytic performance of the homogeneous catalyst was also remarkable, this reaction has the environmental drawback of the metal presence in the liquid phase. However, novel heterogeneous materials as the described here avoid these environmental impacts.

Although the contribution of active leached species of Cu-MOF-74 was ruled out, additional characterization of fresh and used catalyst after reaction by XRD was performed. These difractograms evidenced the complete disappearance of the typical Cu-MOF-74 phase (Fig. 5). A secondary crystalline phase was detected by intense diffraction peaks located at 29, 47.5 and 56 degrees, which clearly match up with typical XRD pattern of copper(I) chloride. These facts indicated the collapse of microporous Cu-MOF-74 crystalline phase accompanied to the formation of a new copper(I) chloride phase, possibly due to the acidic conditions of the media. A similar collapse phenomenon of Cu-based MOF has been described recently for Opanasenko et al. [24] In order to know the possible catalytic activity of Cu(I)Cl in the acylation of anisole, a new experiment using Cu(I)Cl with the same copper content was performed. This experiment achieved a 28% of conversion after 1 h of reaction, which was significantly lower than the 55% obtained by Cu-MOF-74 when its structure was partially degraded (Fig. 6). So, these results suggest that the catalytic activity, cannot only come from the Cu(I)Cl formed, but also from the MOF structure, evidenced by an important extra contribution in the anisole conversion.

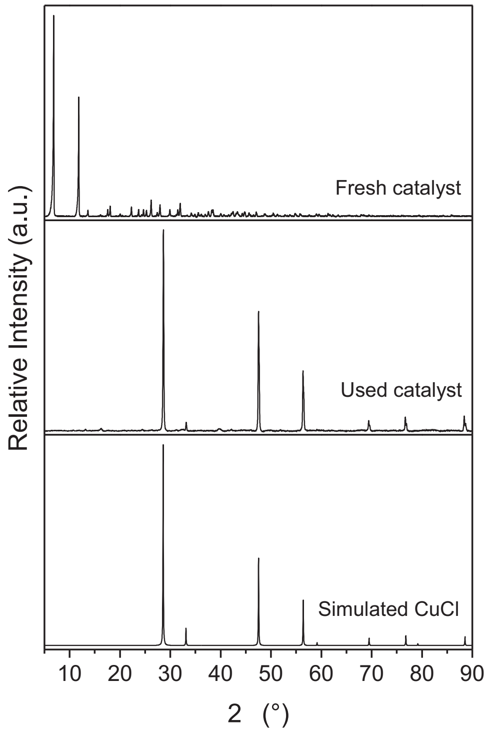


Fig. 5. X-ray diffraction patterns of fresh and used solid catalyst.

3.2.2. *Influence of catalyst concentration and anisole/acetyl chloride ratio*

Previous stability tests of Cu-MOF-74 in nitrobenzene at 120 °C and presence of the reagents used for the acylation reaction evidenced that acetyl chloride affected dramatically the stability of the Cu-MOF-74 phase. According to the typical mechanism of acylation reactions [46], the preliminary formation of acylium ions over uncoordinated Lewis acid centers, in this case uncoordinated copper sites, can alter the coordination sphere of copper producing the collapse of Cu-MOF-74 phase.

Taking into account the stability tests, the catalyst concentration was increased from 1.5 to 15 molar% in order to get a higher catalyst/acetyl chloride ratio and after that, the influence of the acylating agent concentration was explored by increasing of anisole/acetyl chloride molar ratio (MR) from 1/1 to 5/1. Fig. 6 shows the catalytic performance using 15 molar% of catalyst and different anisole/acetyl chloride molar ratios. The catalysts were recovered after methanol washing and vacuum drying, being

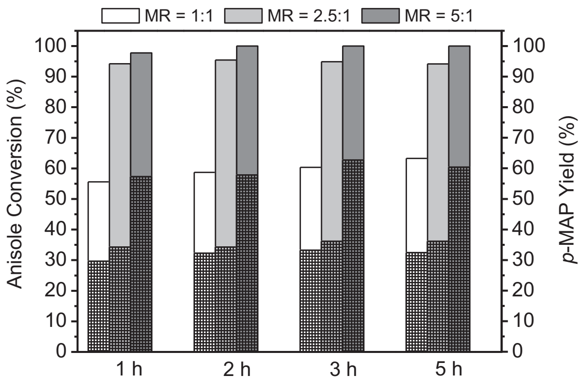


Fig. 6. Influence of the anisole/acetyl chloride ratio for the acylation of anisole using, a Cu-MOF-74 catalyst concentration of 15 molar%. Normal columns indicate anisole, conversion; dense fill columns indicate p-MAP yield.

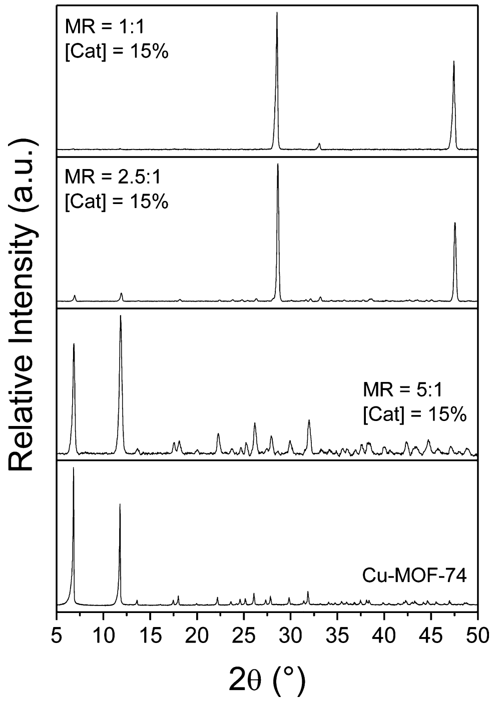


Fig. 7. X-ray diffraction patterns of fresh and used Cu-MOF-74 catalyst for different, anisole/acetyl chloride ratios and a Cu-MOF-74 catalyst concentration of 15 molar%.

characterized by XRD (Fig. 7). The catalytic activity of Cu-MOF-74 was slightly improved with the increase of the catalyst loading as compared to previous results (anisole conversion and p-MAP yield obtained for equimolar anisole/acetyl chloride ratio and 1.5 molar% of catalyst). The increase of the anisole/acetyl chloride ratio allowed enhancing the relative anisole conversion above 90% with respect to the maximum conversion achievable with the initial acetyl chloride concentration. Moreover, the p-MAP yield also increased as the relative acetyl chloride concentration was reduced. In terms of Cu-MOF-74 stability, it was observed that the increase of the catalyst concentration, which meant an increase of the catalyst/acetyl chloride ratio, was not effective to preserve the crystalline MOF-74 phase. However the combination of decreasing the acylating agent concentration by increased the anisole/acetyl chloride ratio and the increase of catalyst concentration allowed keeping the crystalline MOF-74 phase, as observed in the recovered catalyst after reaction. These results confirm the negative effect of the acylating agent concentration on the stability of Cu-MOF-74.

3.3. *Catalytic performance of hybrid Cu-MOF-74 versus other inorganic catalysts*

The catalytic performance of Cu-MOF-74 was assessed in comparison to other different acid catalysts: (i) HKUST-1 as another Cu-containing MOF and (ii) other conventional inorganic catalysts typically used in acid catalyzed reaction such as H-ZSM-5 and BETA zeolitic materials and Al-MCM-41 mesoporous materials. Fig. 8 displays the catalytic performance of all the catalysts studied in terms of relative anisole conversion and p-MAP yield. All the experiments were carried out at 120 °C, anisole/acetyl chloride molar ratio of 5/1 and 15 molar% of catalyst, using nitrobenzene as solvent.

The copper-based MOF material, HKUST-1, is characterized by a 3-D porous channel system, with a pore diameter ca. 1 nm, as a result of the linkage between well-known paddle-wheel metallic clusters and tritopic linkers (trimesic acid). In contrast, Cu-MOF-74 material is built up from infinitive rod-like metallic clusters joined together by tetratopic linkers (2,5-dihydroxiterephthalic acid) giving rise a 3-D framework with a unique 1-D honeycomb like porous channel system with a diameter of about 1.1–1.2 nm. The higher interconnectivity of the HKUST-1 porous network did not enhance its catalytic performance. The higher activity of Cu-MOF-74 as compared to this material was attributed to its higher surface area and metal content (see Table 1).

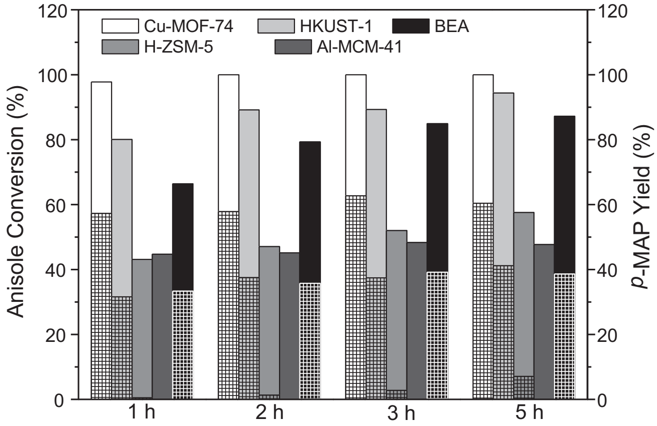


Fig. 8. Comparison of different types of acid catalysts for the acylation of anisole., Normal columns indicate anisole conversion; dense fill columns indicate p-MAP yield.

Regarding the inorganic catalysts, both materials are considered potential acid Lewis catalysts. Zeolitic H-ZSM-5 material is an aluminosilicate with crystalline MFI-type microporous structure, whereas Al-MCM-41 is an amorphous aluminosilicate mesoporous material with hexagonal arrangement. Both inorganic materials led to lower anisole conversions as well as lower p-MAP yields. Superior behavior of MOF materials over zeolites has been also shown in the Pechmann reaction of naphthol and Prins condensation reaction of β-pinene [24,26]. Taking into account the similar Al/Si ratio for both materials, the slight improved activity of microporous H-ZSM-5 is associated to better accessibility of Al centers in the crystalline microporous structure of H-ZSM-5 material as compared to the amorphous pore walls of Al-MCM-41. In addition, microporous BETA zeolitic material with a larger pore size than ZSM-5 (6.6 vs 5.5 Å) showed a better catalytic performance than its aluminosilicate homologues, but still below Cu-MOF-74. These results could be explained not only due to the large pore size of BETA, but also because the higher acidity (Si/Al = 19) respect to the other aluminosilicate materials used (Si/Al ~ 30). So, the Cu-MOF-74 exhibited the best anisole conversion and higher p-MAP yield. Regarding other zeolitic materials reported in literature for the same reaction, such as hierarchical ZSM-5 zeolites and hybrid zeolitic-ordered mesoporous materials [30], the anisole conversion of Cu-MOF-74 was still higher than theses inorganic materials. Therefore, the acid capacity of copper atoms located into the hybrid MOF-74 phase as well as its remarkable surface area makes Cu-MOF-74 a promising material for acid catalyzed reactions, in particular for the acylation of anisole.

3.4. *Reusability of Cu-MOF-74*

The reusability of the catalyst was also studied in the acylation of anisole. In this particular case, since most of the anisole conversion was normally achieved after 1 h of reaction, the reutilization of the catalyst was carried out for reactions performed at 1 h of time. Likewise, in order to assure enough amount of catalyst for several consecutive cycles, the catalyst concentration was increased from 15% to 37.5% respect to the acylating agent. The anisole/acylating agent ratio was also set to 2.5:1 with the purpose of increasing the overall production of p-MAP product. The results displayed in Fig. 9

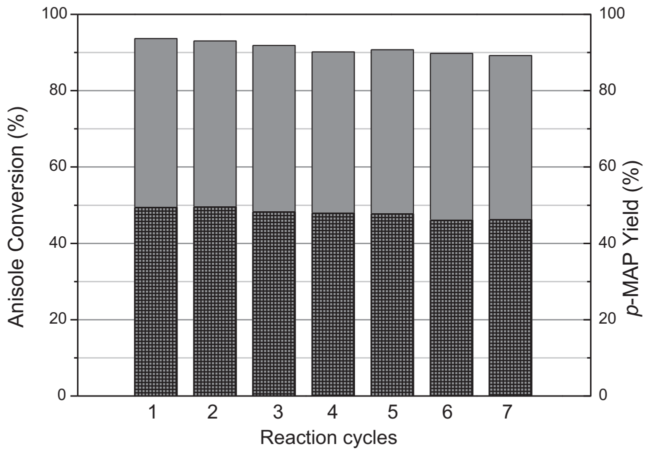


Fig. 9. Cyclability of Cu-MOF-74 in the acylation reaction of anisole. Normal columns indicate anisole conversion; dense fill columns indicate p-MAP yield.

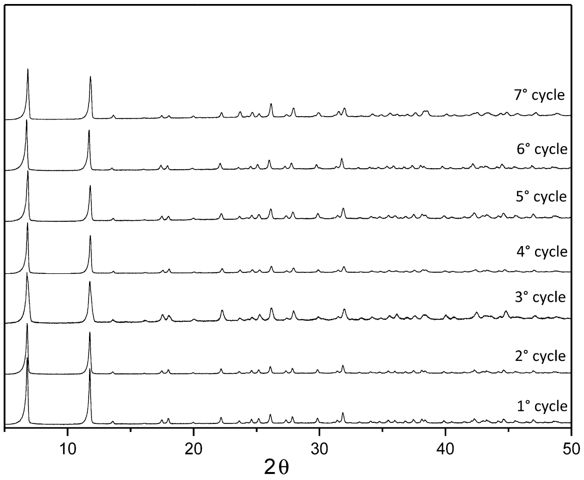


Fig. 10. X-ray diffraction patterns of fresh and used Cu-MOF-74 catalyst after several reaction cycles.

evidence a catalytic activity practically constant in terms of relative anisole conversion and p-MAP yield after seven cycles. Additionally, XRD patterns of the catalyst after each reaction cycle (Fig. 10) confirm the stability of Cu-MOF-74 phase, suggesting this material arises as an interesting catalyst for acylation reactions.

4. Conclusions

The activity of Cu-MOF-74 for acid catalyzed reactions, in particular the Friedel–Craft acylation of anisole using acetyl chloride, has been proven. The polarity of the solvent molecule was considered a crucial factor for the use of Cu-MOF-74 as a catalyst, due to the affinity of polar molecules to uncoordinated metal sites, which decrease the accessibility of reactants and subsequently the loss of activity. High concentrations of the acylating agent in the catalytic system promoted the degradation of the crystalline Cu-MOF-74 phase. The structural stability of the material was maintained by increasing of catalyst concentration and the anisole/acylating agent ratio. Under these reaction conditions, Cu-MOF-74 exhibited a better catalytic performance than HKUST-1 as representative of other Cu-MOF, and conventional zeolitic and mesoporous inorganic materials (H-ZSM-5 BETA and Al-MCM-41). Moreover, the catalytic performance of Cu-MOF-74 was maintained quite constant for seven catalytic cycles, showing very promising results for its application in acid catalyzed reactions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2013.11.062.

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