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Llabrés I Xamena, FX.; García Cirujano, F.; Corma Canós, A. (2012). An unexpected bifunctional acid base catalysis in IRMOF-3 for Knoevenagel condensation reactions. *Microporous and Mesoporous Materials*. 157:112-117.
doi:10.1016/j.micromeso.2011.12.058



The final publication is available at

<https://doi.org/10.1016/j.micromeso.2011.12.058>

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Additional Information

**An unexpected bifunctional acid base catalysis in IRMOF-3 for Knoevenagel
condensation reactions**

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Abstract

In this work we have reexamined the catalytic properties of zinc aminoterephthalate IRMOF-3 for the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate. The active sites for this reaction were previously proposed to consist in the amino groups of the aminoterephthalate linkers [1]. We have now found that the reaction can also be catalyzed by MOF-5, which has the same crystalline structure than IRMOF-3, but in which the aminoterephthalate ligand is replaced by terephthalate, thus lacking the amino groups that are present in IRMOF-3. It has been found that the catalytic activity of MOF-5 is related with the presence of defects and/or occluded metal oxides. Different preparation routes of MOF-5 have been followed that result in different concentration of defects and different reactivity. These defects sites can also be present in IRMOF-3 and contribute to the catalytic activity. Therefore, depending on the preparation conditions and on the concentration of defects, in the case of IRMOF-3 we can pass from a simple, monofunctional base to a (unintentional) bifunctional catalyst.

Keywords: MOF catalysts; Knoevenagel condensation, bifunctional acid-base catalysts

1. Introduction

The zinc aminoterephthalate metal-organic framework IRMOF-3 has recently been found to be an active heterogeneous catalyst for the Knoevenagel condensation reaction between benzaldehyde and different activated methylene compounds [1]. When this work was published it was one of the few existing reports on MOFs whose catalytic activity was attributed to the functional groups of the organic ligand, being the number of materials with catalytically active functional groups (i.e., with active sites located at the organic molecule of the MOF and not at the metal ion) still very scarce. This is because, in order to have a catalytic material, the functional groups need to be free and accessible to the substrates and cannot be directly coordinated to the metal ions of the MOF. However, given the high tendency of the functional groups to coordinate to metal ions, this condition is seldom satisfied. Thus, IRMOF-3 constitutes, in principle, a very interesting and rare example of a MOF having accessible functional (amino) groups imparting basic character to the material.

Starting from the initial work by Gascon *et al.* [1], we have now reexamined the catalytic properties of IRMOF-3 for the Knoevenagel condensation reaction between aldehydes and activated methylene compounds, aiming at determining the actual origin of the outstanding catalytic performance of this material. It will be shown here that besides the amino groups presented as responsible active sites in the referenced work, the presence of structural defects and the presence of extraframework ZnO species can also be active for the Knoevenagel reaction. Then, we propose that the potential presence of those sites should also be considered when preparing the MOFs to be used for catalysis.

2. Materials and Methods

2.1 Samples preparation. All chemicals used in the preparation of MOFs ($\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, terephthalic acid, 2-aminoterephthalic acid, DMF and CH_2Cl_2) were purchased from Sigma-Aldrich and used without further purification. MOF-5 and IRMOF-3 samples were prepared by conventional solvothermal crystallization methods [1, 2]. For the synthesis of IRMOF-3, zinc nitrate hexahydrate (1.5 mmols) and 2-aminoterephthalic acid (0.5 mmols) were dissolved in DMF (50 mL) and placed inside an autoclave. The mixture was heated at 373 K for 24 h, and the resulting solid was recovered by filtration, washed twice with DMF, and finally covered twice with CH_2Cl_2 for 12 h to displace DMF from the pores. The synthesis of MOF-5 and all the washing procedure was identical, but replacing the 2-aminoterephthalic acid by terephthalic acid. Alternatively, MOF-5 and IRMOF-3 samples containing high concentrations of defects (MOF-5_{def} and IRMOF-3_{def}, see text for details) were prepared by the fast precipitation method with triethylamine following a synthesis procedure described by Huang et al. [3]. Briefly, zinc nitrate hexahydrate (4 mmols) and either terephthalic acid or 2-aminoterephthalic acid (2 mmols) were dissolved in DMF (40 mL) and 16 mmol of triethylamine were added at room temperature under vigorous stirring for 4 h. The recovered solid was washed with DMF and treated with CH_2Cl_2 as described above for the other two MOF samples. All the samples prepared were characterized by powder X-ray diffraction and were found to be MOF-5 and IRMOF-3 (see Fig. S1 in the Supporting Information). Higher values of surface area (S_{BET}) were obtained for the samples prepared by solvothermal methods (2185 and 2325 $\text{m}^2 \text{g}^{-1}$ for IRMOF-3 and MOF-5, respectively) than for those prepared by the fast precipitation method (750 and 785 $\text{m}^2 \text{g}^{-1}$ for IRMOF-3_{def} and MOF-5_{def}, respectively).

2.2 General procedure for the Knoevenagel condensation reaction. In order to avoid structural changes and/or defect creation during prolonged storage of the MOFs, the samples used in this study were freshly prepared and CH_2Cl_2 washed MOFs. In a typical catalytic experiment, 60 mg of IRMOF-3 (corresponding to *ca.* 0.2 mmols of $-\text{NH}_2$ groups) were placed inside a round bottom flask connected to a reflux condenser, containing 5 ml of an ethanolic solution of benzaldehyde (8 mmol) and ethyl cyanoacetate (7 mmol) under an inert (N_2) atmosphere. The reaction was performed at 333 K, and the course of the reaction was followed by GC analysis using *n*-hexadecane as external standard. When comparisons were made between different catalysts, the amount of solids were calculated to have the same molar amounts of $-\text{NH}_2$ groups (for aniline, dimethyl aminoterephthalate and the two different IRMOF-3 samples) or the same amount of Zn^{2+} (when comparing IRMOF-3 and MOF-5 and/or ZnO nanopowder).

3. Results and discussion

Preliminary experiments were performed to find the conditions in where the reaction is not controlled by external diffusion. Then, three experiments were performed at 333 K while the reactor was stirred at 500, 1000 and 1500 rpm. No differences in the initial reaction rate were observed, indicating that for stirring speeds of 500 rpm the reaction is not controlled by external diffusion. Therefore, the experiments have always been performed at 500 rpm.

Fig. 1 shows the results obtained for the Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate in ethanol at 333 K in the presence of IRMOF-3. A maximum conversion of about 90% and 100% selectivity was obtained after 4 h of reaction. A blank experiment, in absence of catalyst, gave a maximum conversion of ca. 7% after 4 h. The reaction was also performed without added solvent, but in this case the maximum conversion achieved was only of about 50%. Hot filtration tests showed that the catalytic process was heterogeneous. All these results are in line to those reported by Gascon *et al.* under similar conditions, and variations can be attributed to small differences in catalyst preparation (*vide infra*). We then performed an additional blank experiment, in which IRMOF-3 was substituted by MOF-5 [4]. MOF-5 is a MOF having the same crystalline structure than IRMOF-3, but in which the aminoterephthalate ligand is replaced by terephthalate, thus lacking the amino groups that are present in IRMOF-3. In our hands, MOF-5 also catalyzes the Knoevenagel condensation (ca. 65% conversion after 4 h, see Fig. 1), albeit with a lower activity than IRMOF-3. These results clearly demonstrate that there are other active sites, besides the amino groups, that can catalyze the condensation reaction when using that MOF structure. Then, at this point we have to answer the following questions: 1) What are the active sites in MOF-5?; and 2) Are these sites also present and operate in IRMOF-3?.

<Insert Fig 1 here>

Do the amino groups of IRMOF-3 catalyze the Knoevenagel condensation reaction?

Since aniline is well known to catalyze the Knoevenagel reaction, the answer to this question seems straightforward. Nevertheless, we have also repeated the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate in the presence of aniline at 333 K, using the same substrate to -NH_2 molar ratio than with IRMOF-3 and the results are compared in Figure 2.

<Insert Fig.2 here>

It can be seen there that with aniline the initial rate, as well as the conversion after 4 h is sensibly lower than over IRMOF-3. These results are also in line with those obtained by Gascon

et al.[1], who attributed the higher activity of IRMOF-3, as compared to aniline, to an enhancement of the basicity of the amino groups of the ligand when incorporated in the MOF structure. This enhancement would be due to hydrogen bond interactions between the amino groups and an electron donating carboxylate oxygen (see Scheme 1) [1, 5]. To support or refute this hypothesis, we have carried out the Knoevenagel reaction in the presence of dimethyl aminoterephthalate (DMAT) as catalyst, in which such hydrogen bond interactions should also be possible and should also enhance the basicity of the amino groups (see Scheme 1). However, we did not observe any significant differences in the initial reaction rates with aniline or DMAT as catalysts (see Fig 2). If any, aniline was even a better catalyst than DMAT at long reaction times. Therefore, although we cannot exclude that the higher activity of IRMOF-3 is due to an enhancement of the basicity of the amino groups upon incorporation into the framework, the results presented above justify a further investigation and to search if there is another reason that can explain the enhanced activity of IRMOF-3 with respect to aniline. To do that, we decided firstly to find if MOF-5, which has the same structure than IRMOF-3 but without the amino group, was active for the reaction and, if this is so, to find which are the catalytic active sites in this amino-free MOF.

<Insert Scheme 1 here>

Catalytic activity of MOF-5

The Knoevenagel condensation reaction has usually been considered as a test reaction to evaluate the basicity of a material. If the reaction is performed with different methylenic groups and different acceptors, it is then possible to evaluate the concentration and strength of the basic sites of a catalyst [6, 7]. Besides the base catalyzed mechanism of the Knoevenagel condensation reaction, acid catalysts such as zeolites or mesoporous and amorphous silica alumina, are also known to catalyze the Knoevenagel reaction [8]. In these materials, the acid sites interact with the carbonyl group of the acceptor molecule (benzaldehyde), producing a polarization of this group and thus enhancing the electrophilic character of the carbonylic carbon atom. This polarization favors the attack from the methylenic compound (ethyl cyanoacetate). Though it appears that base as well as acid sites can catalyze the Knoevenagel reaction, it has been shown that bifunctional catalysts with adequate acid-base pairs are more active than either purely acid or base catalysts [8-10]. Indeed, if the acid and basic sites of these bifunctional catalysts are well balanced, a concerted and synergic action can take place, in which the acid sites activate the acceptor carbonyl compound, while the basic sites abstract the proton from the methylenic compound to form the corresponding enolate species. In this way, the following mechanism was proposed for the condensation between benzaldehyde and ethyl cyanoacetate on bifunctional acid-base aluminophosphate catalysts [8]:

<Insert Scheme 2 here>

When MOF-5, that does not contain amino groups, was tested as a catalyst for the Knoevenagel reaction, the results obtained (see Fig. 1) showed that its activity is not negligible, being the initial reaction rate with MOF-5 approximately half that for IRMOF-3 that contains the active basic sites. It is now well established that MOF-5 has acidic properties and thus, this material can act as a solid acid catalyst [11-13]. The acid sites in MOF-5 can have different origins, but all of them are associated to the presence of defects. These defects originate because partial hydrolysis of the Zn-carboxylate oxygen bonds in the MOF-5 structure can occur and lead to the formation of Zn-OH species with the concomitant generation of carboxylic acid protons [3] (see Scheme 3). The occurrence of such a process is reflected, for instance, by the presence of a sharp IR absorption band at *ca.* 3600 cm^{-1} , assigned to the $\nu(\text{O-H})$ stretching mode of Zn-OH groups, together with a $\nu(\text{OCO})$ band at 1715-1680 cm^{-1} , due to protonated terephthalic acid (see Fig. S3) [3]. Note that this hydrolytic process would introduce two potential acid centers: carboxylic acid protons and Zn-OH groups. Both of them could in principle be responsible for the observed catalytic activity of MOF-5 for the Knoevenagel reaction.

<Insert Scheme 3 here>

At this point, it should be taken into account that Zn-OH groups in MOF-5 can also have another origin than the hydrolysis presented in Scheme 3. There are experimental evidences indicating that, depending on the preparation procedure, MOF-5 may contain variable amounts of ZnO impurities either as segregated crystallites or nanoparticles entrapped inside the pore cavities [14, 15]. The termination of these (nano) particles would lead to Zn-OH groups that would saturate dangling bonds of surface Zn ions.

Finally, Zn^{2+} ions having coordinative unsaturation might also be formed from a defective origin and to be present in MOF-5. These coordinatively unsaturated zinc sites would act as Lewis acid sites and could also activate the carbonyl substrates of the Knoevenagel condensation, thus acting as catalysts (or co-catalysts) for the reaction. Indeed, Neogi et al. have reported on the activity of a MOF containing coordinatively unsaturated Zn^{2+} sites as catalyst for Knoevenagel condensation and aldehyde cyanosilylation reactions [16]. However, in our case the contribution of coordinatively unsaturated Zn^{2+} ions in framework positions to the activity of MOF-5 can probably be ruled out since the reaction was carried out in ethanol as solvent and this could eventually coordinate to the vacancies of Zn^{2+} and neutralize its Lewis acidity. Nevertheless, as we said above, Lewis acid Zn^{2+} sites belonging to ZnO (nano)particles formed during the synthesis of the MOF could also be present, and this possibility should be certainly tested.

Summarizing, the active sites responsible for the observed catalytic activity of MOF-5 could be: i) carboxylic acid protons; ii) Zn-OH groups in framework position and/or associated with ZnO particles; and iii) coordinatively unsaturated Zn²⁺, either in framework positions or belonging to ZnO particles, or a combination of the above.

In order to investigate the potential catalytic role of carboxylic acid protons (coming from the partial hydrolysis of Zn-carboxylate oxygen bonds of MOF-5), we have repeated the Knoevenagel condensation reaction under the same conditions as before, but using terephthalic acid as the sole catalyst. The results obtained are shown in Fig 3, in which a comparison is made with MOF-5 under the same reaction conditions. Note that the amount of terephthalic acid used in this reaction was calculated to be the same mols of ligand than those present in MOF-5. Interestingly, even with this very large excess of free H₂BDC, our results clearly demonstrate that the contribution of carboxylic acid protons to the observed activity of MOF-5 is negligible for the Knoevenagel reaction (see Fig. 3)

<Insert Fig.3 here>

The remaining potential catalytic centers in MOF-5 will be Zn-OH groups and coordinatively unsaturated Zn²⁺ sites, which may come from partial hydrolysis of the framework or from the inclusion of ZnO particles during the synthesis of the MOF. As we have already mentioned above, the amount of ZnO (or Zn(OH)₂) impurities present in the MOF sample will depend on the synthesis procedure [14, 15]. Thus, when MOF-5 samples are prepared with the fast precipitation method with triethylamine reported by Huang et al.[3], the ZnO content of the resulting MOF-5 is not negligible. On the contrary, when slow (solvothermal) crystallization methods are used, as in the case of the MOF-5 sample used in this study (see Experimental Section), the material contains less ZnO impurities. Therefore, we have prepared an additional MOF-5 sample, following the method proposed by Huang et al., which is expected to yield a sample with a higher amount of occluded ZnO nanoparticles. Indeed, from the corresponding TGA, it can be estimated that this defective sample contains 24 wt% of ZnO impurities, while the highly crystalline MOF-5 sample prepared solvothermally contains 11 wt%. Then, when the highly defective sample was used as catalyst for the Knoevenagel reaction, the observed activity increased with respect to that of the highly crystalline sample (see Fig. 4). In a first approximation, we attribute this increase in activity to a higher content of ZnO impurities in the former sample, since nanocrystalline ZnO has been reported to be active for the Knoevenagel condensation reaction [17, 18].

<Insert Fig.4 here>

To check the hypothesis, the activity of the MOF-5 sample containing the highest level of ZnO impurities was compared with the catalytic activity of ZnO nanoparticles (~ 100 nm size). We have also considered that the MOF sample contained ZnO nanoparticles of about 15-20 nm in diameter, as suggested by Calleja et al.[15]. Due to the larger particle size of the commercial ZnO sample, this has a surface-to-volume ratio which is about 6 times lower than in the ZnO nanoparticles in MOF-5, as calculated by simple geometric considerations and assuming spherical particles in both cases. Therefore, the amount of commercial ZnO catalyst used for comparison in the reaction was larger in this same proportion in order to keep the same amount of surface Zn²⁺ ions in both materials. Thus, the catalytic activity of 100 mg of defective MOF-5 (containing 24 mg ZnO nanoparticles according to the TGA) was compared with 144 mg (24 x 6 = 144 mg) of commercial ZnO nanopowder (with particles of 100 nm in diameter), and the results are shown in Fig. 5. According to those, the initial reaction rates obtained for ZnO and MOF-5 are very similar, although for long reaction times the performance of ZnO was some better. These results clearly demonstrate that pure ZnO nanoparticles can catalyze the Knoevenagel reaction, and consequently the occluded ZnO nanoparticles in MOF-5 could also contribute to the observed catalytic activity. Moreover, the similar initial reaction rates obtained for the two materials (having the same amount of unsaturated Zn²⁺ ions at the surface of ZnO nanoparticles), suggests that occluded ZnO nanoparticles are the most likely origin of the overall catalytic activity of the MOF-5 sample. These results do not exclude the participation of eventual Zn(OH)₂ sites that could also be present in the MOF sample.

<Insert Fig.5 here>

Summarizing, our results on MOF-5 as catalysts for the Knoevenagel condensation reaction indicate that: i) the observed catalytic activity is associated with the existence of defects, either generated by the partial hydrolysis of the framework or by the inclusion of ZnO particles during the synthesis of MOF-5; ii) samples prepared by different synthesis methods may contain variable amounts of defects, which results in a different catalytic activity; and iii) contribution of carboxylic acid protons to the overall catalytic activity can be ruled out.

Active sites in IRMOF-3

At the light of the results discussed above, it remains to determine whether the defects responsible for the catalytic activity of MOF-5 could also be present in IRMOF-3 and, more importantly, if they could also contribute to the observed catalytic activity. The IR spectrum of IRMOF-3 does not show any IR absorption band at 3600 cm⁻¹ characteristic of Zn-OH groups (see Fig. S3), nor diffraction peaks that could indicate the presence of ZnO particles. Although this indicates that the concentration of defects in IRMOF-3 is certainly lower than in the case of

MOF-5, these findings do not completely rule out the presence of some defects, which could escape detection by these techniques. Actually, the TGA analysis of the sample reveals a content of ~3 wt% excess of ZnO residue. A clear clue that the catalytic activity of IRMOF-3 could have a certain contribution from defect sites comes from the comparison of two IRMOF-3 samples prepared by different methods, as shown in Fig.6. When IRMOF-3 was prepared by a fast precipitation method, adapted from the synthesis of Huang et al. using triethylamine [3], the resulting material showed a higher catalytic activity than the sample prepared by a solvothermal synthesis route. Note that the fast precipitation procedure would lead in principle to less crystalline samples containing more defects (~5 wt% ZnO according to TGA), in analogy with the case of MOF-5. Obviously, the comparison of the two materials shown in Fig.6 was made using the same amount of catalyst (and so, the same amount of $-NH_2$ groups). It appears then that the difference in the catalytic activity of the two IRMOF-3 samples can be related with the different concentration of defects in both solids, as a consequence of the different preparation procedures used. It appears then that, at least for this reaction, a better crystallinity of the material does not necessarily result in a better catalyst, but the presence of defects and/or occluded metal oxides can also play a positive role for catalysis. Therefore, we can conclude that in IRMOF-3, and more specifically in IRMOF-3 prepared by a fast precipitation method, the presence of Zn-OH and/or ZnO may contribute with the amino groups to the final observed activity. This contribution can occur through an independent catalytic route and/or by means of a synergetic effect in where the amino groups would be the basic sites, while the acid sites would come from the presence of Zn-OH or ZnO defects.

<Insert Fig.6 here>

We have also evaluated the contribution to the overall catalytic activity of the small amount (~5 wt% according to TGA) of ZnO impurities that are present in the defective IRMOF-3, following an analogous procedure to that employed in the case of MOF-5. Thus, the catalytic activity of 100 mg of defective IRMOF-3 (containing 5 mg ZnO nanoparticles according to the TGA) was compared with 30 mg ($5 \times 6 = 30$ mg) of commercial ZnO nanopowder (with particles of 100 nm in diameter), and the results are shown in Fig. 7. Note that in order to establish the comparison we have assumed that the ZnO nanoparticles which are present as impurities in IRMOF-3 have the same average size (i.e., 15-20 nm) than those in MOF-5. Nevertheless, our experiments revealed that even this small amount of ZnO could account for (at least) 25% of the overall catalytic activity observed for the defective IRMOF-3 sample. Therefore, the data shown in Fig.7 clearly reveals that the ZnO defects (even when present in such a small amount as in the case of IRMOF-3) can play a significant role in the catalytic process.

<Insert Fig. 7 here>

Very recently, Vermoortele et al. have reported on the preparation of bifunctional acid-base MOFs catalysts for aldol condensations [19]. The materials were prepared by controlled thermal treatment of Zr-aminoterephthalate UiO-66(NH₂), leading to bifunctional catalysts containing simultaneously basic sites (amino groups of the ligand) and Zr Lewis acid sites formed in situ upon dehydroxylation of the solid. The close proximity of the two types of centers improve the catalytic performance of the material, since Zr sites can activate benzaldehyde, while the amino groups can activate the methylenic group in the aliphatic aldehyde [19].

In the case of IRMOF-3, a similar synergic process may also occur, which would explain the excellent catalytic performance of this material for the Knoevenagel condensation reaction. However, contrary to UiO-66(NH₂) in which the acid sites are intentionally created upon controlled dehydroxylation of the material, in IRMOF-3 the acid sites would come from a defective origin, either as Zn-OH groups formed upon partial hydrolysis of the framework or by the inclusion of ZnO particles during the synthesis. This would be in line with the observed dependence of the catalytic activity on the synthesis conditions (see Fig 6). The Knoevenagel condensation reaction is probably the first example in which the accidental presence of structural defects imparting acidity to the solid is not detrimental, but it is rather beneficial for the overall performance of the material. Therefore, attention should be paid to the possible (unintentional) presence of catalytic defect sites in MOFs, which could influence the final catalytic results.

Conclusions

The present study on the Knoevenagel condensation reaction using IRMOF-3 and MOF-5 illustrates the relevance of the synthesis procedures used to prepare the MOFs. Depending on the synthesis conditions, we can pass from a simple, monofunctional base to an (unintentional) bifunctional catalyst. Although the introduction of a (defective) second catalytic functionality to the material may seem advantageous for certain reactions, such as the Knoevenagel condensation reaction, we must take this into account when dealing with other reactions in where the Lewis sites can activate unwanted side reactions. In this latter case, preparation procedures and manipulation of the MOFs have to be carefully considered to generate or to avoid this second type of sites.

Acknowledgements

Financial support by Ministerio de Educación y Ciencia e Innovación (Project MIYCIN, CSD2009-00050; PROGRAMA CONSOLIDER.INGENIO 2009), Generalidad Valenciana (GV PROMETEO/2008/130) and the CSIC (Proyectos Intramurales Especiales 201080I020) is gratefully acknowledged.

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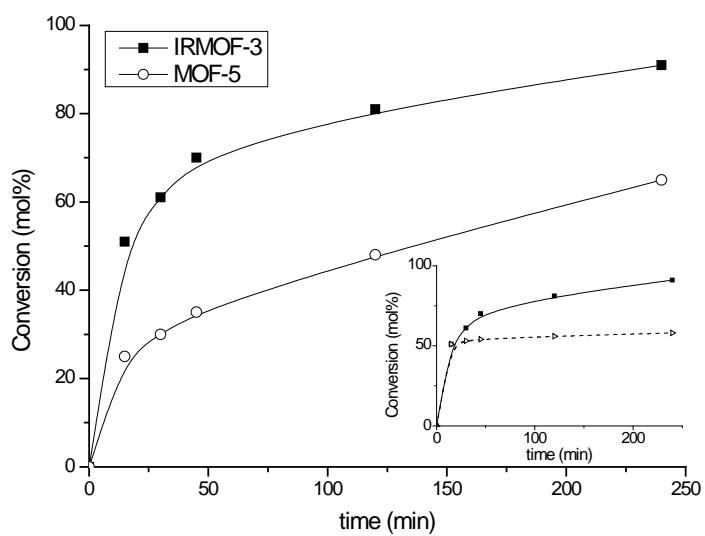


Fig 1. Conversion of ethyl cyanoacetate over IRMOF-3 and MOF-5 at 333 K. The inset shows the results obtained for a hot filtration experiment for IRMOF-3 (dotted line).

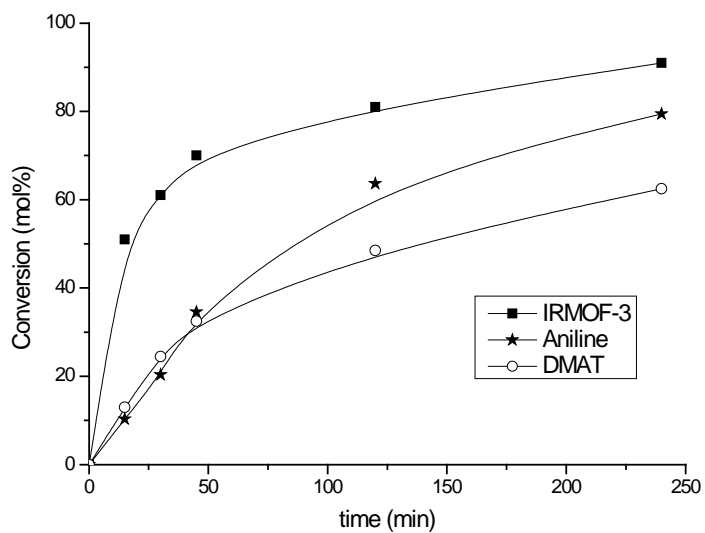


Fig 2. Conversion of ethyl cyanoacetate over IRMOF-3, aniline and dimethyl aminoterephthalate. The comparison was made using the same substrate to $-NH_2$ molar ratio in all three catalysts.

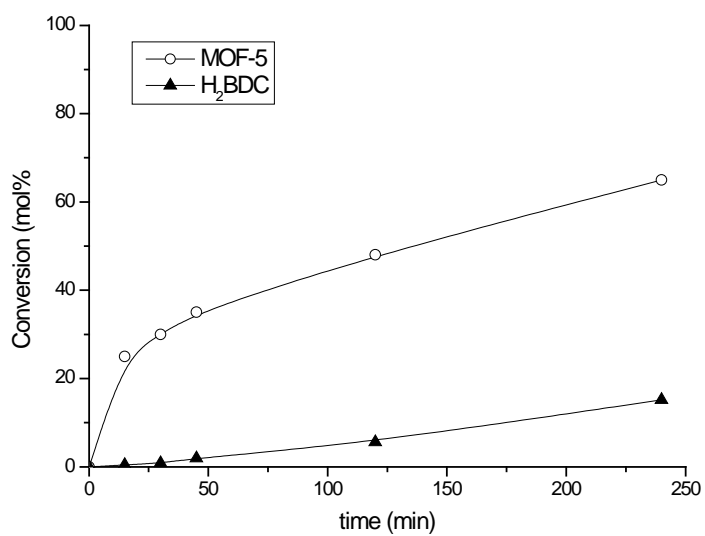


Fig 3. Conversion of ethyl cyanoacetate over MOF-5 and terphthalic acid (H₂BDC). To make the comparison, the amount of BDC used in MOF-5 and H₂BDC was kept constant.

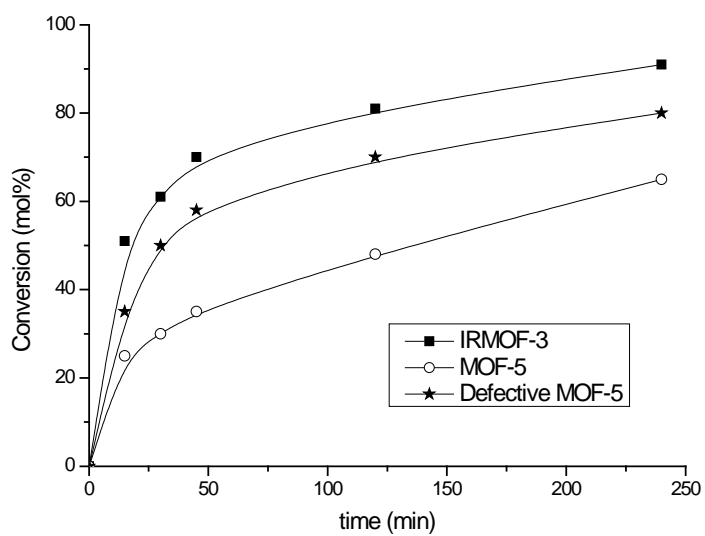


Fig 4. Conversion of ethyl cyanoacetate over two MOF-5 samples prepared by different methods (see text for details). The conversion attained over IRMOF-3 is also included for comparison.

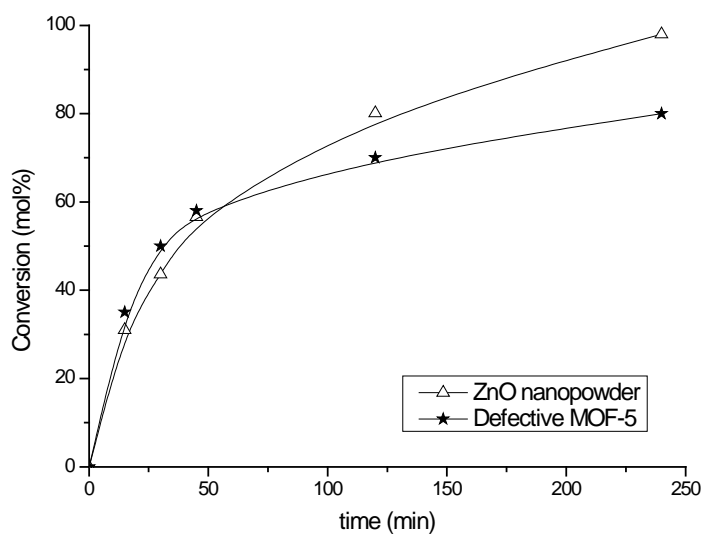


Fig 5. Conversion of ethyl cyanoacetate over a highly defective MOF-5 and a commercial ZnO nanopowder samples (see text for details).

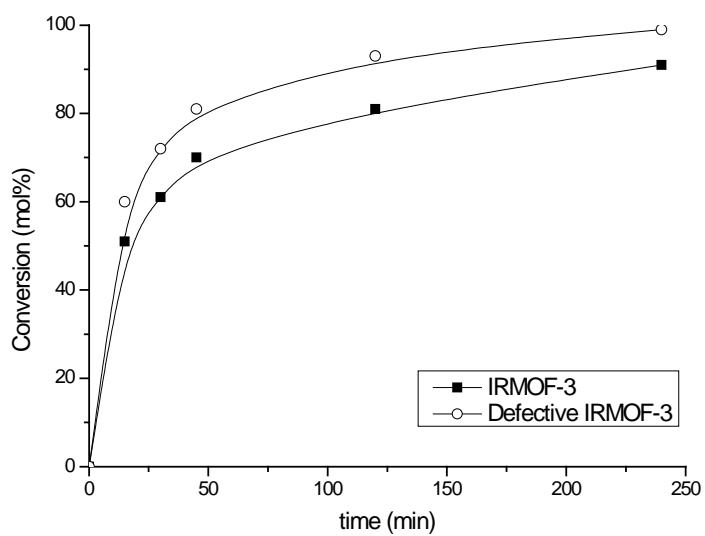


Fig 6. Conversion of ethyl cyanoacetate over two IRMOF-3 samples prepared by different methods (see text for details).

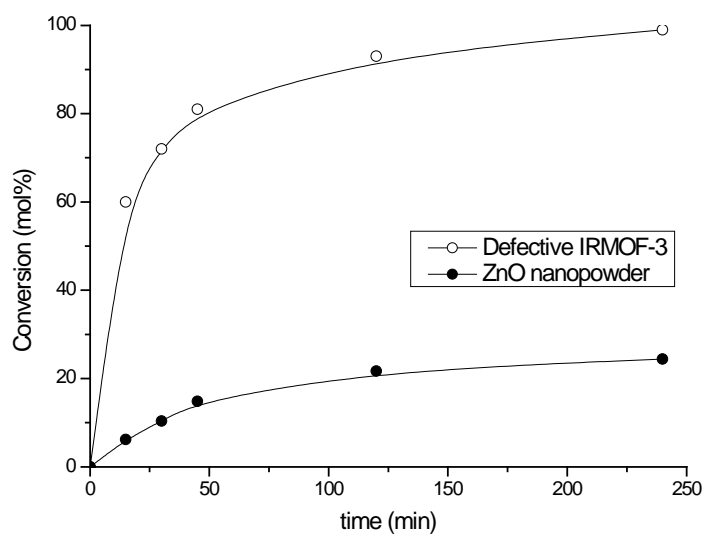
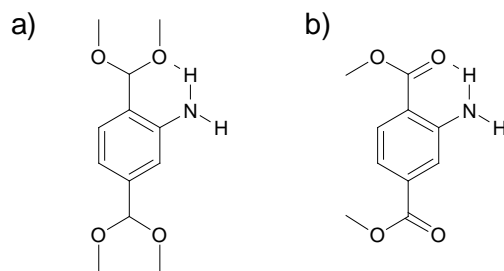
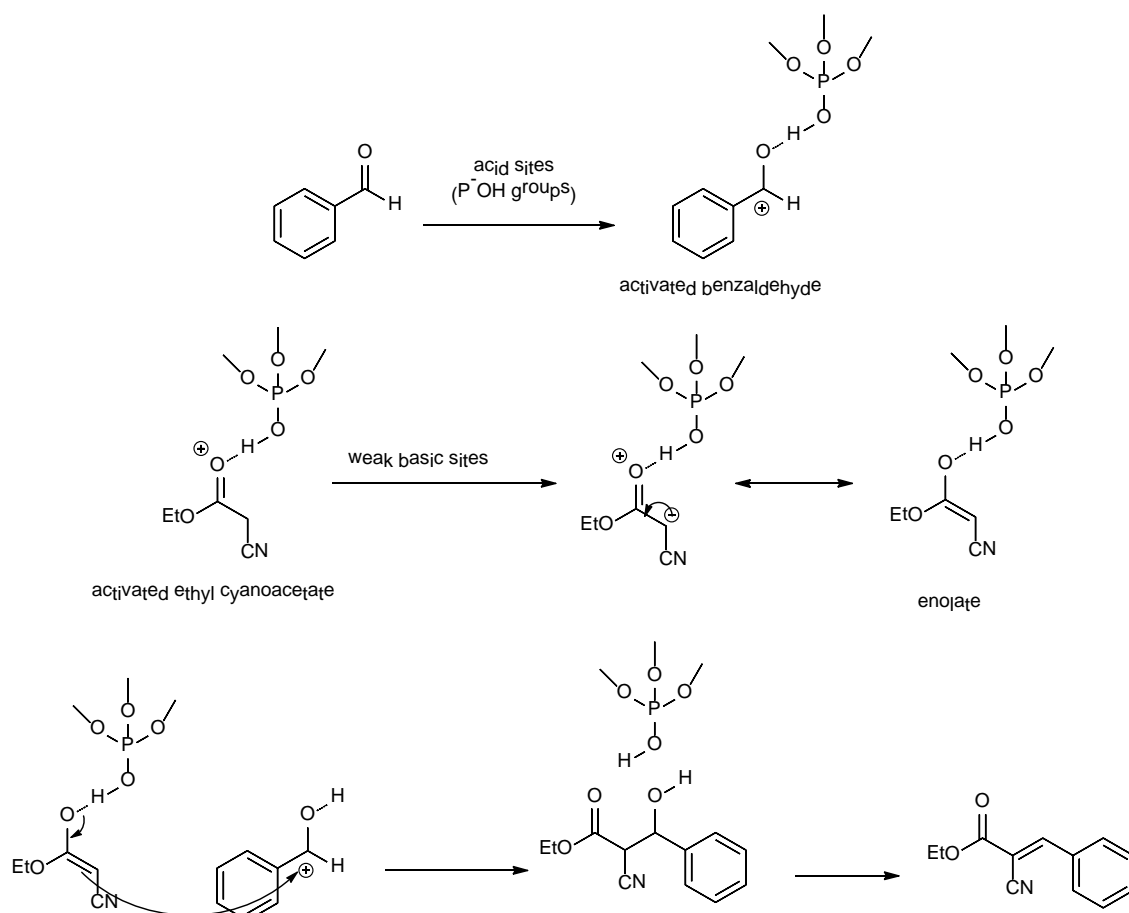


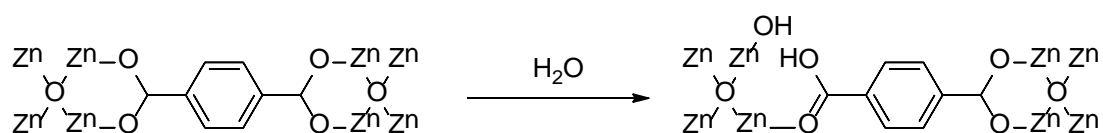
Fig 7. Conversion of ethyl cyanoacetate over a defective IRMOF-3 and a commercial ZnO nanopowder samples (see text for details).



Scheme 1. a) Hydrogen bond interactions between amino groups and carboxylate oxygen atoms in IRMOF-3. b) The same type of interactions is also possible in dimethylaminoterephthalate.



Scheme 2. Proposed Knoevenagel mechanism operating in aluminumphosphate acid-base bifunctional catalysts [8].



Scheme 3. Hydrolysis of the Zn-carboxylate oxygen bonds as possible origin for the formation of Zn-OH groups and carboxylic acid protons.