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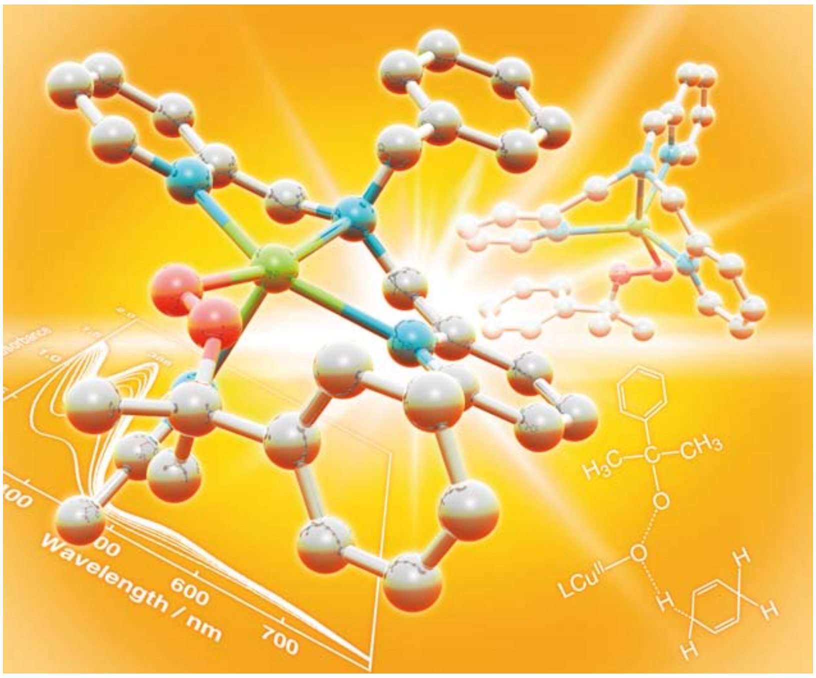

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PAPER

Intracrystalline diffusion in Metal Organic Framework during heterogeneous catalysis: Influence of particle size on the activity of MIL-100 (Fe) for oxidation reactions

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Three MIL-100 (Fe) samples differing in average crystal size (from 60–70 to >400 nm) have been synthesized by microwave heating using three HF/Fe^{3+} ratios. Oxidation of diphenylmethane with *tert*-butylhydroperoxide (TBHP) and thiophenol with oxygen are catalyzed by three MIL-100 (Fe) samples with similar reaction rates regardless of its average particle size. In contrast, the activity of the three MIL-100 (Fe) samples for the oxidation of bulky triphenylmethane by TBHP largely depends on the average crystal size of the sample: the smaller the average particle size, the larger the initial reaction rate of triphenylmethane oxidation. These results show that diffusion limitation takes place on MOF catalysis depending on the substrate size and provides indirect evidence that these reactions take place inside the intracrystalline space of the porous catalysts.

Introduction

Crystalline microporous materials, in particular, zeolites have opened many possibilities as shape selective, environmentally friendly catalysts. Their potential has been widen with the synthesis of new structures with extra large pores[1–4] as well as structures containing 10 and 12 ring pores in the same structure.[5] The possibilities of crystalline microporous materials have also been expanded with the use of metal organic frameworks (MOFs) materials. In this sense there is much current interest in exploiting the positive features of MOFs in catalysis.[6–20] For liquid phase reactions under conditions that do not compromise their crystal structure,[21] MOFs as heterogeneous catalysts offer the advantage of large pores, high surface area and porosity together with a high number of potential active sites.[22–24] One important aspect of crystalline microporous materials is their potential to act as molecular sieves and to select by size and polarity the molecules that can diffuse inside of the channels and cavities to react. These shape selective effects have been well established for the case of the more rigid inorganic structures of the zeolite, but less so for the more flexible MOF structures whose catalytic activity could also be influenced by potential metal leaching and structure stability.

While diffusion limitations in microporous systems could be used positively to select and react a given molecule present in a mixture, there are other occasions where severe restrictions for molecular diffusion within the channels result in low turnover frequencies since only the active sites at the external or close to the external surface, are accessible to reactants.[25–29]

One classical methodology to address diffusion limitations in zeolites has been to study the catalytic activity of a given zeolite for substrates with the same functionality but different molecular dimensions. Then the larger the diffusion limitations, the smaller the TOF should be. In the limiting situation when the reactant is practically excluded from the internal voids of the microporous material, the reaction is restricted to the external surface of the crystallites. Then, catalyst activity improvement can be achieved by either increasing the dimensions of the pores or by increasing the external surface area of the zeolite crystallites. It is clear that the second solution could be achieved by decreasing the size of the crystallites. Therefore, while the use of a zeolite with different crystallite sizes has been frequently applied to ascertain that the reaction mainly occurs inside the pores, maximizing catalyst activity in diffusion limited reactions, similar studies have not been yet been undertaken, as far as we know, using MOFs as catalysts.

In the present manuscript, we will show that MIL-100 (Fe) is able to carry out selective oxidations using TBHP as an oxidating agent. Then, we have selected two reactions involving substrates with one, two and three phenyl rings: these substrates provide a wide range of molecular dimensions for the reactants, and their catalytic behaviour has been studied with three MIL-100 (Fe) having the same crystal structure, similar chemical compositions but different average crystallite size. The results

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obtained have shown that all the MOF samples were highly selective oxidation catalysts. However, when bulky molecules are used as substrates, then, a remarkable effect of diffusion control on the catalytic activity arises. In those cases, catalytic activity has been improved by synthesizing the MOF with smaller crystallite sizes. Interestingly, the use of smaller crystallites did not affect the stability of the catalyst. The results also indicate not only that MOF can act as stable molecular sieves for catalysis, but also that despite being more flexible than zeolites, diffusion is impeded when the size of the molecule approaches that of the pores.

Experimental

1. Materials

Full details of the preparation of the MIL-100 (Fe) samples differing in average particle size will be reported separately and is based on the protocol of MIL-100 (Fe) synthesis using microwaves (already published).[30–32] The samples used in the present study were prepared by Prof. Jong-San Chang from the Catalysis Center for Molecular Engineering, Korea Research Institute of Chemical Technology (KRICT), Daejeon, Korea. In summary the procedure for the synthesis of the MIL-100 (Fe) samples consists of hydrothermal crystallization under microwave irradiation. A typical synthesis was carried out at 200 °C under acidic conditions. In a general synthesis, 0.4 g of metallic iron and 1.1 g of 1,3,5-benzenetricarboxylic acid (BTC) were added in an aqueous solution of x M HF and 1 M HNO_3. Then, the solution was loaded in a 100-mL Teflon autoclave, which was sealed and placed in a microwave oven (Mars-5, CEM, maximum power of 1600 W). The reaction mixture was heated from room temperature to 200 °C for 2 min (microwave power: 800 W) and then maintained at the same temperature for an additional period of 2 min. The molar composition of reactants was $1.0Fe/0.67BTC/x HF/0.60HNO_3/309H_2O$ ($x = 0.125, 0.5, 1.5$). The light orange solid product was recovered by filtration and washed with deionized water. The as-synthesized MIL-100 (Fe) was further purified by two-step processes using hot water and ethanol.

The size of the nanometric particles was determined by counting a statistically relevant number (60–80) of particles by transmission electron microscopy (TEM) using a Philips CM300 FEG system with an operating voltage of 100 kV. TEM samples were prepared by placing microdrops of the corresponding MIL-100 (Fe) samples suspended in acetonitrile solution directly onto a copper grid coated with carbon film (200 mesh).

Powder X-ray diffraction patterns of the as-synthesized MIL-100 (Fe) samples were obtained by a Rigaku diffractometer (D/MAX IIIB, 2 kW) using Ni-filtered Cu-Kα-radiation (40 kV, 30 mA, $\lambda = 1.5406$ Å) and a graphite crystal monochromator. The BET surface area measurements were performed with N_2 adsorption–desorption isotherms under liquid nitrogen (−196 °C) after dehydration under vacuum at 150 °C for 12 h, using a volumetric sorption analyzer (Micromeritics Tristar 3000). The specific surface areas were evaluated using the Brunauer–Emmett–Teller (BET) method in the p/p_0 range 0.05–0.3. The particle morphology and crystal size were analyzed by a scanning electron microscope (Philips, XL30S FEG).

Microwave synthesis of MIL-100 (Fe). Fig. 1 provides a powder XRD pattern of MIL-100 (Fe) prepared using different HF/Fe ratios. It can be concluded that variation of the HF/Fe ratio does not significantly influence their crystallinity, the three MIL-100 (Fe) exhibiting the same XRD pattern with similar intensities.

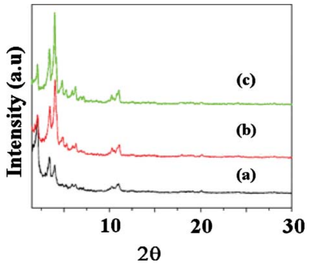


Fig. 1 Powder XRD pattern of MIL-100 (Fe) with HF/Fe ratio of 0.125 (a), 0.5 (b) and 1.5 (c).

The BET surface area of MIL-100 (Fe) samples with different F^- content was measured from the corresponding nitrogen isotherms provided in Fig. 2. The measured surface area of these three catalysts and the corresponding pore volume values are given in Table 1. As shown in Table 1, the three samples exhibit similar BET surface areas.

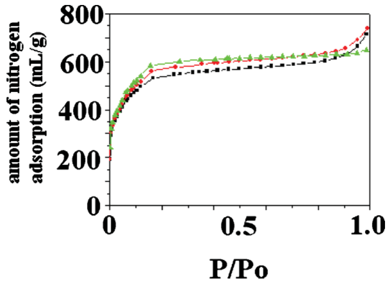


Fig. 2 Nitrogen adsorption–desorption plots of MIL-100 (Fe) with different fluorine content: HF/Fe 0.125 (square), 0.5 (circle) and 1.5 (triangle).

Fig. 3 provides the SEM analysis of MIL-100 (Fe) with different fluorine content showing the textural properties and morphology of these catalysts. It is clear that SSC MIL-100 (Fe) exhibited a smaller crystallite size than SMC and SLC. A similar observation was noticed in the TEM analysis.

2. Typical reaction procedure

25 mg of MIL-100 catalyst was activated according to the conditions described in Fig. 4 and 5. After activation, the catalyst was suspended in 4 mL of acetonitrile followed by addition of

Table 1 Textural properties of MIL-100 (Fe) with different fluorine content

Properties	MIL-100 (Fe)		
Sample Name	SLC	SMC	SSC
HF/Fe ratio	1.5	0.5	0.125
S_{BET} (m^2 g^{-1})	1950	1920	1830
V_{pore} (ml g^{-1})	1.00	1.14	1.10
Average particle size (nm)	400	120–130	60–70

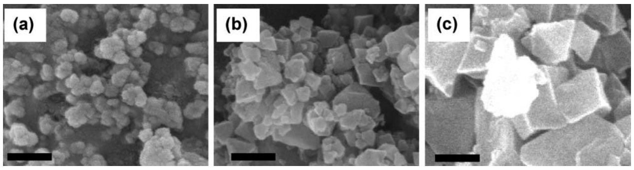


Fig. 3 SEM images of MIL-100 (Fe) synthesized by different molar ratios of HF/Fe in the reactant solutions: (a) 0.125, (b) 0.5, and (c) 1.5. The scale bar in the images corresponds to 0.2 μm.

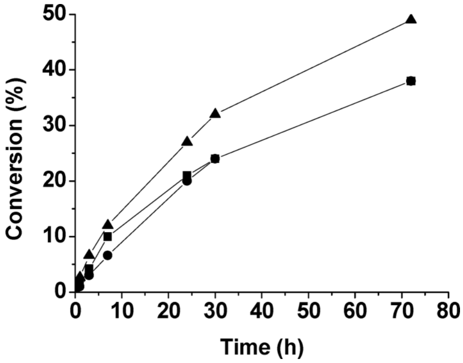


Fig. 4 Time-conversion plot for the oxidation of DPM to benzophenone using MIL-100 (Fe) with different HF/Fe ratio as catalyst and TBHP as oxidant. Square, circle and triangle represents MIL-100 (Fe) prepared using HF/Fe ratios of 0.125, 0.5 and 1.5, respectively. Reaction conditions: DPM (0.1 mL), MIL-100 (Fe) (25 mg) preactivated at 150 °C for 3 h under vacuum, acetonitrile (4 mL), TBHP in decane (0.1 mL).

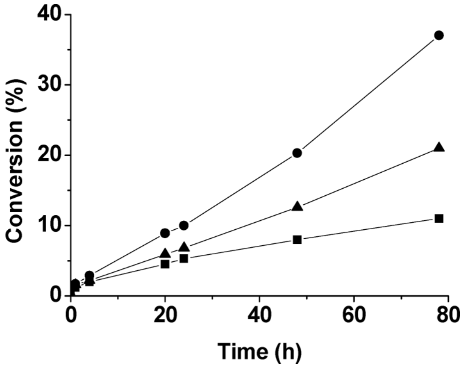


Fig. 5 Oxidation of TPM to triphenylmethanol using MIL-100 with different HF/Fe ratio as catalyst and TBHP as oxidant. Circle, triangle and square represent MIL-100 (Fe) prepared using HF/Fe ratios of 0.125, 0.5 and 1.5, respectively. Reaction conditions: TPM (0.1 g), MIL-100 (Fe) (25 mg) preactivated at 150 °C for 3 h under vacuum, acetonitrile (4 mL), TBHP in decane (0.1 mL).

0.1 g of diphenylmethane (DPM) or triphenylmethane (TPM). To this mixture, 0.1 mL of *tert*-butylhydroperoxide (TBHP) in decane was added and the reaction mixture was stirred at 70 °C. The reaction was monitored at different time intervals and the reaction mixture was analyzed by GC and the products identified by GC-MS analysis. Experiments of DPM and TPM oxidation were carried out in duplicate. A control reaction was carried out under nitrogen atmosphere at 80 °C in *tert*-butanol (5 ml) using $Fe(NO_3)_3$ as catalyst and an excess of TBPH (10 mmol, a solution in water) respect to DPM or TPM (1 mmol), whereby about 80% conversion was achieved for both substrate at 90 min. Aerobic oxidation of thiophenol was performed similarly except no TBHP was used and oxygen was purged into the reaction mixture.

Conversion, and yields were determined using Hewlett Packard 5890 series II gas chromatograph with FID detector and high purity helium as carrier gas. The products were identified by comparing their GC retention times with authentic samples and by comparing the corresponding mass spectra obtained using a GC-MS Hewlett Packard 6890 series

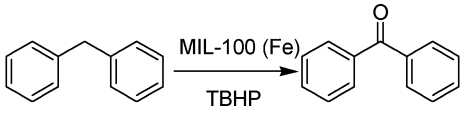
Results and discussion

The catalytic use of porous crystalline MOFs is increasing largely due to: their wide range of compositions and structure types with low framework densities, their tunability in terms of metal and ligands, and the possibility to generate accessible active sites thorough coordinatively unsaturated metal sites (CUS).[21] Furthermore, the generation of CUS by thermal activation of MOFs before performing catalytic tests can strongly influence the activity of these solids.[33,34]

MIL-100 (Fe) is a crystalline three-dimensional Fe(III) trimesate, which is based on μ_3-oxo-centered trimers of octahedral Fe^{III}.[9] It has two sets of large cages with 2.5 and 2.9 nm diameter that are accessible through windows of 0.5 and 0.9 nm diameter, generating a large surface area and pore volume (see Table 1). In the as-synthesized form, the ligands of two of the three octahedral irons are H_2O molecules and, depending on the synthesis conditions, the third iron is coordinated to either F^- or OH^- anions. It has been established that the activation temperature can determine the oxidation state of the metal present in the MOFs, by removing only the coordinated water molecules at 150 °C or, if the temperature is increased at 260 °C, by also removing an anionic ligand (F^- or OH^-) with the simultaneous reduction of the oxidation state of the corresponding Fe from +3 to +2.[9]

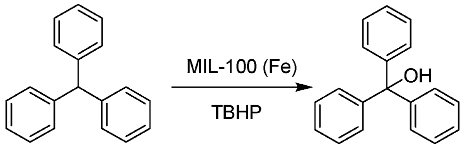
It is then apparent that activated MIL-100 (Fe) could be used to catalyze oxidation reactions using organic peroxides,[10] and we have attempted here the oxidation of diphenyl- (DPM) and triphenylmethane (TPM) to benzophenone and triphenylmethanol respectively, with *t*-butyl hydroperoxide (TBHP). Also we have performed the aerobic oxidation of thiophenol to phenyldisulfide. These reactions were selected because we have earlier reported that they can be promoted by commercial Fe(BTC) that has the same organic linker and similar Fe content to our synthetic MIL-100 (Fe).[10] However, the use of synthetic MIL-100 (Fe) offers us the possibility to prepare a consistent set of samples in which a parameter is varied in a controlled manner. In particular, in our case we have varied the average particle size maintaining a high crystallinity and very similar specific surface area.

When DPM was reacted with TBHP in the presence of MIL-100 (Fe) prepared with a ratio HF/Fe of 1.5, and which results in a well crystallized sample (Fig. 1) with high surface area and micropore volume (Fig. 2, Fig. 3 and Table 1), oxidation occurs (Fig. 4) and the only product observed was benzophenone (Scheme 1). It is



Scheme 1 Oxidation of DPM to benzophenone using TBHP as oxidant with MIL-100 (Fe).

then possible to say that MIL-100 (Fe) is a very selective catalyst for the above mentioned oxidation. However, when the same oxidation was carried out with TPM, while triphenylmethanol was the only product (see Scheme 2), the rate of formation was much lower than for DPM oxidation. This difference is not due to an intrinsic chemical effect but, most probably, due to the larger size of TPM that impedes its diffusion through the smaller size windows (0.5 nm) in MIL-100(Fe) (see Fig. 5) therefore decreasing the rate of diffusion. If this is the case, one would have to conclude that diffusion limitations would be much less severe for DPM than for TMP in MIL-100(Fe). To check the relative reactivity of DPM and TPM in the homogeneous phase a control was carried out at 80 °C using *t*-BuOH as solvent and $Fe(NO_3)_3$ as homogenous catalyst, whereby about 80% conversion was achieved for DPM and TPM at 90 min reaction.



Scheme 2 Oxidation of TPM to triphenylmethanol using TBHP as oxidant with MIL-100 (Fe).

In order to check the above hypothesis, MIL-100 (Fe) was prepared with different crystal sizes by changing the HF/Fe ratio in the synthesis (see Table 1). In the range of HF/Fe presented here, the three MIL-100 (Fe) samples under study do not exhibit significant changes in the crystallinity nor in the BET surface area (Table 1 and Fig. 1 and 2). It is worth noting that the high crystallinity of the three samples rules out the presence of amorphous material in the samples. Therefore, it is unlikely that these two parameters play any role in explaining the differences in the relative catalytic performance of the three MIL-100 (Fe) samples when the substrate is DPM or TPM. However, SEM clearly shows that a decrease in the HF/Fe ratio produces samples with smaller crystallite size (Table 1 and Fig. 3). When the two new samples with smaller crystallite sizes, *i.e.* SMC and SSC, were tested for the oxidation of DPM, the results presented in Fig. 4 indicate that when decreasing the crystallite size of the catalyst there is not an increase but, a small decrease in activity. Therefore we can conclude that there are not diffusion limitations for DPM and the oxidation reaction is probably taking place inside the cavities of the MOF. The higher activity observed with the sample with larger crystallites (SLC) could be explained considering the presumably higher percentage of F^- coordinated to tetra iron clusters as the concentration of F^- in the synthesis increases. The higher content of F^- as ligand should somewhat increase the Lewis acidity of the CUS that takes part in the oxidation reaction.

In the case of TPM oxidation, we related the lower activity of the SLC MOF to diffusion limitations of this larger molecule within the pore system. If this hypothesis was true, one could expect an increase of catalyst activity when decreasing the crystallite size of the MOF. Indeed, when TPM was oxidized with TBHP on SLC, SMC and SSC, there is a clear increase in activity when decreasing the crystallite size (see Fig. 5). The results not only confirm the diffusion limitations of MIL-100 (Fe) to oxidize TPM with TBHP, but at the same time, indicate that the process with DPM is dominated by the reaction occurring within the cavities of the MOF.

The above rationalization of the different relative catalytic behavior of the three MIL-100 (Fe) samples depending on the molecular dimensions of the substrate is in good agreement with molecular modeling that shows that TPM is larger than the available pore dimensions of MIL-100 (Fe). Fig. 6 provides some views of the outcome of the modeling.

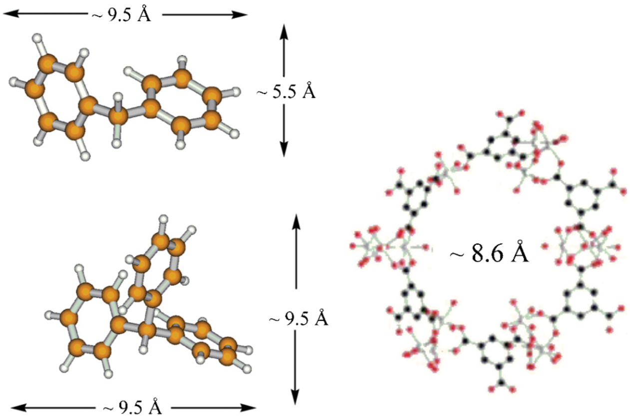
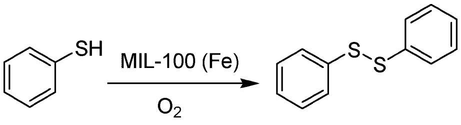


Fig. 6 Modeling of DPM (top left) and TPM (bottom left) indicating the molecular dimensions and an illustration of the pore opening of MIL-100. The calculations suggest that while DPM can cross the pores, TPM is too large to enter inside the MIL-100 pores.

Since MOF-100 (Fe) appears to be an active and selective catalyst for oxidations, we have expanded the study to the aerobic oxidation of thiophenol to diphenysulfide in acetonitrile as solvent (Scheme 3). Taking into account the results presented above with DPM, we should expect that this aerobic oxidation of thiophenol would not be controlled by intracrystalline diffusion. Indeed the kinetic results presented in Fig. 7 show a high activity of the MOF for the aerobic oxidation with an excellent selectivity for disulfide that was the only product observed. Furthermore, the influence of the crystallite size on conversion, was qualitatively the same as the one observed before with DPM, *i.e.*, SLC gives higher activity than the other two samples. Since the size of thiophenol is smaller than DPM, the catalytic results obtained with the former also confirm that the reaction for DPM oxidation was not controlled by intracrystalline diffusion.



Scheme 3 Aerobic oxidation of thiophenol to diphenyldisulfide using MIL-100 (Fe).

Stability of MOF-100 (Fe)

We said before that all the available data indicates that the catalytic process is probably heterogeneous. Nevertheless, we have studied the possibility that some metal leaching occurs and consequently an homogeneous catalytic reaction may also occur. To check that possibility, the aerobic oxidation of thiophenol was carried out under the experimental conditions described in Fig. 7 and with the

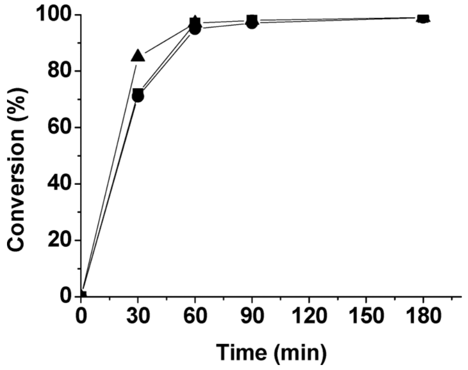


Fig. 7 Aerobic oxidation of thiophenol to diphenyldisulfide using the catalyst MIL-100 (Fe) with three different HF/Fe ratios. Square, circle and triangle represent MIL-100 with HF/Fe ratios of 0.125, 0.5 and 1.5 respectively. Reaction conditions: thiophenol (0.1 mL), MIL-100 (Fe) (25 mg) preactivated at 150 °C for 3 h under vacuum, acetonitrile (4 mL), 70 °C, oxygen purged.

MOF with smaller crystallites (SmC) as catalyst. When conversion reached 35%, the catalyst was separated by filtration and the remaining solution was allowed to further react with oxygen. After 2 h of reaction time the conversion increased from 35 to 47%. However, this conversion increase was not catalytic but thermal, since the blank experiment showed 11% conversion in a 2 h period. Hence, it can be concluded that besides some thermal reactions, most of the oxidation of thiophenol to the disulfide (see Fig. 7) corresponds to an heterogeneous catalytic in where the oxidation occurs within the cavities of MIL-100 (Fe).

The remaining catalyst was reused three times. After each run, the catalyst was washed with acetonitrile and the solid was activated as per the conditions described in Fig. 7 before performing the next run. As can be seen in Fig. 8 the catalyst remains stable after recycling and no deactivation was observed. Also, crystallinity remains very high and no significant variations were observed upon catalyst recycling and activation.

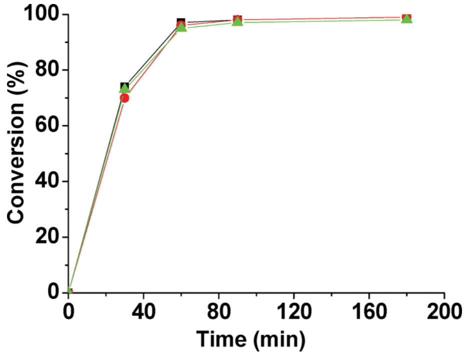


Fig. 8 Reusability of MIL-100 (Fe) (0.125) for the aerobic oxidation of thiophenol to diphenyldisulfide in acetonitrile medium. Square, circle and triangle represents MIL-100 (Fe) (0.125) catalyst used for first, second and third reuse. See Fig. 7 for reaction conditions.

Conclusions

MIL-100 (Fe) is an active and selective catalyst for oxidation of DPM and TPM with TBHP, as well as for the aerobic oxidation of thiophenol. The catalyst is stable, can be recycled and no deactivation was observed. The oxidations studied here correspond to an heterogeneous catalytic process, where the reaction occurs within the pores of the MOF, provided that the reactant molecules can diffuse through. This has been demonstrated by performing the reaction with MIL-100 (Fe) with different crystallite sizes. Then, the aerobic oxidation of thiophenol and the oxidation of DPM with TBHP are not controlled by intracrystalline diffusion, while the oxidation of TPM occurs mainly at the external surface of the catalyst. Then, catalyst activity can be improved by preparing a MOF catalyst with smaller crystals.

Acknowledgements

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