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Switching acidic and basic catalysis through supramolecular functionalization in a porous 3D covalent imine-based material

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Non-covalent inclusion of small acid and base molecules (CH₃COOH and NET₃) in an imine structure based on micrometre COF-300 crystals and amorphous nanoparticles results on the facile modulation of its acid-base properties. Such strategy results in the triggering of acidic/basic catalytic activity of the otherwise inactive materials towards ring-opening epoxide and Knoevenagel condensation reactions. For both reactions, amorphous nanoparticles are better catalysts than micrometre crystals as they exhibit a higher external surface area. The found activities and stability of this supramolecular functionalization are modulated by confinement effects, which are rationalized with the help of DFT theoretical calculations. All results obtained suggests that reaction catalysed by these functionalized materials occur confined at pores closer to the material surface, which makes possible size-discrimination phenomena, and explains the major activity of the nanoparticulated material.

Introduction

The development of molecules and materials with catalytic cavities, inspired on biological systems, such as enzymes, has been a main topic in modern chemistry. For instance, different molecules known as molecular flasks4 are able to catalyse a variety of reactions in confined spaces. The outstanding performance of such molecular systems and other porous materials lays not only on the design of active catalytic centres, but also on the easy tuning of environment in a confined space, resulting on different regio-2 chemo-3 and stereo-selectivities4 in different reactions. In addition, the proximity between the different reactants in the confined space can result in an enhancement of the catalytic activity.5 Furthermore, confined catalysis offers the possibility to perform size-selective reactions, especially important when working with mixtures of compounds with similar chemical and physical properties. During the last years, confinement effects have been particularly studied in different porous materials such as zeolites,6 mesoporous silica7 and metal-organic frameworks (MOFs).8

In 2005, Yaghi and co-workers described a new concept on the reticular chemistry field: the covalent-organic frameworks (COFs).9 Their use as heterogeneous catalysts offers advantages compared to MOFs such as increased activity, durability and recyclability. COFs are based on the covalent linkage of organic subunits into two- or three-dimensional porous crystalline structures. Therefore, they show predictable composition, topology and porosity. As a consequence, COFs have been explored for applications related to gas storage and separation,10 ultrasensitive sensing,11 electronic applications,12 and clean energy technologies.13 However, only few recent studies initiated the exploration of their catalytic applications.14 In 2014, Yan et al. described the intrinsic basic property of a three-dimensional (3D) imine-based COF useful for the catalytic Knoevenagel reaction.15 After this achievement, other groups have employed two main covalent strategies in order to tune the catalytic activity of different COFs. The first one consisted in the post-functionalization of the material, attaching organic pending arms (top-left, Scheme 1)16 or metal nano-particles,14 which are both s irreversible functionalization processes. A second strategy relayed in the use of catalytic backbones, which often requires complex synthetic modifications of building blocks (top-right, Scheme

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Results and discussion

Preparation and characterization of a-3, c-3 and derivatized materials.

We have demonstrated that these porous materials can be reversibly functionalized (Figure 1) through supramolecular interactions. We selected the 3D COF-300\textsuperscript{20} made of terephthalaldehyde (1) and tetra-(4-anilyl)-methane (2) as it is stable up to 490 °C, in water and common organic solvents. COF-300 was synthesized by a well-known two-step process\textsuperscript{21,22} first, amorphous imine polymer nanoparticles (hereafter called amorphous-3 or a-3) were formed; and subsequently, these a-3 nanoparticles were further reacted to form micrometre COF-300 crystals (hereafter called crystalline-3 or c-3). In a first step, a room temperature synthesis in the presence of acetic acid allowed the formation of the amorphous imine-based polymer nanoparticles a-3, which contains CH\textsubscript{3}COOH molecules inside its structure.\textsuperscript{23} Then, in a second step, these nanoparticles were subjected to a dynamic covalent chemistry to crystallize them under similar conditions to those reported by Dichtel et al.\textsuperscript{21}

SEM images of the solid collected in the first step revealed the formation of amorphous-nanoparticles with diameters of nearly 100 nm (Figure 2; see S. I., Figures S1-3 for powder X-ray diffraction (PXRD) data). Solid-state MAS\textsuperscript{13}C-NMR and FT-IR spectra confirmed the chemical identity of the material (see S. I., Figures S6 and S9-12, respectively). The FT-IR spectrum of COF-300 showed the C=O stretching modes characteristic for imines at 1620 and 1202 cm\textsuperscript{-1}. The solid-state MAS\textsuperscript{13}C-NMR spectrum was also in agreement with the formation of the imine bonds. Thermogravimetric analysis (TGA) data revealed a 2.6 % of volatile molecules lost in the range of 50-400 °C, which was consistent with the presence of acetic acid even after numerous washing procedures with distinct solvents (see S. I., Figure S14). The presence of acetic acid was further confirmed by mass spectrometry coupled to TGA analysis, which showed peaks at m/z = 15 and 43 that can be assigned to [CH\textsubscript{3}COOH]\textsuperscript{-} and [CH\textsubscript{3}COO]\textsuperscript{-}, respectively. Further evidence of the presence of acetic acid molecules inside a-3 was acquired by solid-state MAS\textsuperscript{13}C-NMR. To this end, a-3 was synthesized in the presence of 13C isotopically labelled acetic acid. Solid-state MAS\textsuperscript{13}C-NMR of this newly synthesized a-3 gave a clear evidence of the presence of 13C-enriched acetic acid molecules by means of the CH\textsubscript{3} signal at 20 ppm (see S.I., Figure S8). Altogether, these observations confirmed the formation of CH\textsubscript{3}COOH@a-3.\textsuperscript{24}

The evacuation of all CH\textsubscript{3}COOH molecules in CH\textsubscript{3}COOH@a-3 was achieved by heating it at 80 °C during 12 hours under vacuum (1 mmHg). The resulting material showed the same morphology than its precursor (see S. I., Figure S5). First evidence of the evacuation of all acetic acid molecules was obtained by TGA analysis, from which no significant weight loss in the range of 50-400 °C was observed (see S. I., Figure S15). We also demonstrated the removal of acetic acid...
molecules by performing solid-state MAS-\textsuperscript{13}C-NMR of a sample of \textsuperscript{13}C enriched CH\textsubscript{3}COOH@a-3 exposed to identical activation conditions (see S. I., Figure S8).

In our quest of switching from acidic to basic properties of the material, a sample of CH\textsubscript{3}COOH@a-3 was treated with pure triethylamine (1 mL per 10 mg of CH\textsubscript{3}COOH@a-3) overnight at 80 °C. Again, SEM images confirmed the retention of the size and morphology of the nanoparticles after both amine treatments (see S. I., Figure S5). TGA analysis of CH\textsubscript{3}COOH···NEt\textsubscript{3}@a-3 showed a larger weight loss from 50 ºC to 400 ºC in comparison to CH\textsubscript{3}COOH@a-3 (4.6 % versus 2.6 %). Here, at this temperature range, mass spectrometry coupled to TGA revealed peaks at m/z = 43 and 51 in the ionization cell, which were assigned to [CH\textsubscript{3}CO]\textsuperscript{+} and [HNEt\textsubscript{3}]\textsuperscript{2+}, respectively, thereby confirming the presence of both acetic acid and triethylamine molecules (see S. I., Figure S17). The supramolecular interaction is strong enough to prevent leaching after 14 hours of stirring the material in toluene. Such stability is suggested by the fact that after such treatment no evidences of acetic acid nor NEt\textsubscript{3} were detected NMR measurements.

In order to determine the reversibility of the functionalization of this material, we performed vacuum in a sample of CH\textsubscript{3}COOH···NEt\textsubscript{3}@a-3, recovering the evacuated a-3, as revealed by TGA. It is worth mentioning that direct reaction of evacuated a-3 with pure Et\textsubscript{3}N results on a functionalized material in which the interactions between the imine structure and the guest molecules are very weak. Therefore, such functionalized material resulted in massive leaching of Et\textsubscript{3}N molecules under catalytic conditions (vide infra). Consequently, such strategy was not useful to achieve confined catalysis.

In a subsequent synthetic step, amorphous a-3 nanoparticles were converted to micrometre crystalline c-3 particles by heating them at 120 °C for 7 days in a mixture of dioxane, mesitylene and acetic acid. After exposing the treated solid under vacuum conditions, evacuated c-3 was obtained in the form of microcrystals with dimensions of nearly 1 µm in diameter (Figure 3a). PXRD showed the characteristic pattern of COF-300 (Figure 3b).\textsuperscript{20} Moreover, c-3 did not show significant spectroscopic changes in both FT-IR and solid-state \textsuperscript{13}C MAS NMR spectra in comparison to those seen for a-3 (see S. I. Figures S13 and S7, respectively). TGA analysis for the c-3 did not display any significant weight loss in the range of 50-400 °C, confirming the evacuation of guest molecules from its framework (see S. I., Figure S18). This observation was further corroborated by N\textsubscript{2} sorption measurements at 77 K. As shown in Figure 3c, evacuated c-3 showed to be porous after mild activation conditions (2 hours of primary vacuum at room temperature).
Then, **evacuated c-3** was functionalized with CH$_3$COOH or CH$_2$COOH···NEt$_3$ following the same methodology described for the amorphous materials (see S. I., section 1). It should be highlighted that N$_2$ sorption measurements in both CH$_3$COOH@c-3 and CH$_2$COOH···NEt$_3@c$-3 showed a dramatic loss of porosity, with total uptakes decreasing below 50 cm$^3$ g$^{-1}$ (49 cm$^3$ g$^{-1}$ for CH$_3$COOH@c-3, and 23 cm$^3$ g$^{-1}$ for CH$_2$COOH-NEt$_3@c$-3). Moreover, addition of CH$_3$COOH or CH$_2$COOH···NEt$_3$ adduct resulted on the change of the isotherms observed to Type III. These changes in the isotherm trend and uptake were indicative of the blocking of the pores by the post-synthetic inclusion of CH$_3$COOH and NEt$_3$ molecules.

### Catalysis of the materials.

**Comparison of the catalytic activity of amorphous a-3 and crystalline c-3 based materials.**

We started evaluating the catalytic activity of crystalline **evacuated c-3** and amorphous **evacuated a-3** and the corresponding functionalized materials in two model reactions: the ring-opening epoxide reaction of 4a with epoxide 5 obtaining product 6a under acidic conditions and the Knoevenagel reaction between malononitrile 7 and aldehyde 8a, obtaining product 9a under basic conditions. The results obtained are summarized in Scheme 2. The evacuated materials a-3 and c-3 showed a negligible catalytic activity for the two processes studied, being observed amounts of product similar to those obtained in control experiments without catalyst. On the contrary, crystalline acidic CH$_3$COOH@c-3 and basic CH$_2$COOH···NEt$_3@c$-3 materials showed a moderate catalytic performance for both ring opening epoxide and Knoevenagel reactions, respectively. We attributed this moderate activity to the fact that inclusion of these molecules dramatically reduces the porosity of c-3 (as confirmed by sorption N$_2$ measurements), thereby limiting the access of reagents to the internal parts of material. According to this hypothesis, we decided to study the catalytic activity of both amorphous CH$_3$COOH@a-3 and CH$_2$COOH···NEt$_3@a$-3, because they show a much higher external surface area due to their nanosized character. The higher dimension of the particle was 145±16 nm for amorphous materials and 1100±400 nm for crystalline COFs (see ESI). Indeed, amorphous materials, even though they show lower loadings of active molecules (see S. I. section 6), showed better catalytic performances for both acidic and basic catalytic systems.

We also studied the stability of such materials in the presence of the reagents used in both reactions (see section 12.3 in S.I. for more details). Overall, imine structures are sensitive to the nucleophilic attack that result in erosion of the organic framework as a consequence of the reversible nature of the imine bond. Such decomposition reactivity competes with the catalysed reaction. Consequently, imine structure reactivity limits the output of the catalytic reaction and the recyclability of the corresponding material.

### Acid catalysis: ring-opening epoxide reaction using CH$_3$COOH@a-3.

To generalize the use of CH$_3$COOH@a-3 to catalyse opening epoxide reactions, we performed different reactions with secondary amines (4b and 4c) following a solvent free procedure. Under these reaction conditions, CH$_3$COOH@a-3 catalysed the formation of product 6b with a 55 % yield (Scheme 3). Moreover, it could also catalysed the formation of 6c in low yields from Et$_3$NH (4c). Accordingly, while we observed a 20% of conversion that corresponds to the background reaction in the case of 4a and 4b, the uncatalyzed reaction did not generate a measurable amount of product when 4c was used as reagent. (see. S. I., section 7).

### Basic Catalysis: Knoevenagel Reaction using CH$_2$COOH···NEt$_3@a$-3.

We next expanded the scope of Knoevenagel reaction using different aldehydes 8b-g (Scheme 4). We found an excellent catalytic outcome, which was maintained with electron donating groups, such as methyl or methoxy groups (9b-c), alky groups (9d), and more sterically demanding aldehydes (9e and 9f). However, further increase of the steric hindrance
Knoevenagel reactions explored in this work between malononitrile and aldehydes catalysed by \( \text{CH}_3\text{COOH} \ldots \text{NEt}_3 \). [a] All the reactions were performed using 0.11 mmol of acetonitrile, 0.1 mmol of aldehyde and 5 mg of \( \text{CH}_3\text{COOH} \ldots \text{NEt}_3 \) in 0.6 mL of toluene at room temperature. [b] mol% obtained from TGA analysis (4.6 % of total mass). [c] A reaction was performed under homogeneous conditions (1.4 mol% of adduct \( \text{CH}_3\text{COOH} \ldots \text{NEt}_3 \)) in absence of the material, obtaining product 9a in 77% yield after 14h. [d] Full conversion to the product was obtained when free NEt\(_3\) was used instead of the porous material.

in reagent 8g resulted in null conversion to the Knoevenagel product 9g. This result is very interesting considering that product 9g could be obtained in homogenous catalysis using NEt\(_3\). Therefore, the null reactivity observed using \( \text{CH}_3\text{COOH} \ldots \text{NEt}_3 \) can be understood by a size discrimination effect that seems to point to a catalysis taking place inside the pores of the material. Moreover, the different catalytic activity showed by c-3 and a-3 materials in addition with \( \text{N}_2 \) adsorption experiments of the pre- and post-functionalized materials, led us to the hypothesis that catalysis using these materials, although confined, should be restricted to pores close to material surface. This hypothesis is also corroborated by DFT calculations (see below). We also discarded the possibility of significant leaching of molecular catalytic species (ie. CH\(_3\)COOH and NEt\(_3\)) from a-3. (see S.I., section 10), except for the case NEt\(_3\)@a-3 and NEt\(_3\)@c-3 materials. The weakness of the interaction between the amine molecule (Et\(_3\)N) and the porous material, either crystalline or amorphous, resulted in complete leaching of catalytic molecules.

DFT analysis.

DFT calculations for the imine structure-adsorbed molecules interactions.

With the aim of further characterizing these materials and supporting the experimental data, DFT calculations with periodic boundary conditions were used to evaluate the interaction between the imine structure of a-3/c-3 and CH\(_3\)COOH, NEt\(_3\) and CH\(_3\)COOH--NEt\(_3\) adduct (see S.I., section 12). Results are presented in Figure 4, showing the optimized geometries, selected geometrical parameters and the adsorption energies of these imine structures functionalized with CH\(_3\)COOH, NEt\(_3\) and CH\(_3\)COOH--NEt\(_3\) adducts. The interaction between acetic acid and the imine structure is stablished through hydrogen bonding between the acidic proton of the acetic acid and the imine group of the structure (Figure 4, top). The OH--N distance is 1.66 Å, which is indicative of a strong hydrogen bond. The associated adsorption energy is -79.4 kJ mol\(^{-1}\).

On the other hand, the imine of the structure and the adsorbed amine (NEt\(_3\)) are both basic and no hydrogen bonding is possible between them. In this context, the adsorption takes place only through Van der Waals interactions and the preferred structure presents the NEt\(_3\) close to the walls of the
ime material. The shortest distances between atoms of NEt₃ and those of the imine structure are smaller than 4 Å (Figure 4, middle). The resulting adsorption energy is -43.6 kJ mol⁻¹.

Finally, we studied the interaction of the CH₃COOH···NEt₃ mixture with the imine structure, considering a 1 to 1 relationship between CH₃COOH and NEt₃ (Figure 4, middle). Within these initial structures, two possibilities almost equally raised as the most favorable situations (see Figure 4 and S. I. Figure S21). The first one can be described as an CH₃COOH molecule interacting with the imine structure through hydrogen bonding, while the remaining NEt₃ molecule interacts with the imine structure and CH₃COOH through van der Waals interactions. The second one implies the formation of a neutral CH₃COOH···NEt₃ aggregate, interacting with the imine structure through van der Waals interactions. Therefore, the mixture CH₃COOH + NEt₃ in the imine structure shows a combination of intermolecular and molecule-imine structure interactions that enhance the adsorption of the base molecule.

**Analysis of Influence of Confinement of the Active Site by DFT Calculations.**

We next explored the Knoevenagel reaction considering two different aldehydes: benzaldehyde (8a) and anthracene-9-carbaldehyde (8g) (see S. I. section 12.2 for confinement DFT calculations for the ring-opening epoxide reaction). The reaction of 8a inside the cavity defined by the imine structure led to the formation of 9a with a 71% yield, but 8g did not react inside this cavity. Therefore, these two reactions are ideal examples to study the size selectivity.

Considering the homogenous system, molecular calculations in gas phase and solution showed that, regardless the reacting aldehyde, the nucleophilic attack to the carbonyl carbon directly leads to the formation of the alcohol product, resulting from the addition of the deprotonated malononitrile (see S. I.). In solution, the global process is energetically highly favourable (Figure 5, ΔE = -82.2 and -86.4 kJ mol⁻¹ for 8a and 8g respectively). The energy barrier with respect to the pre-complex are very low in these two cases (less than 26 kJ mol⁻¹). It is worth mentioning that the main difficulty to perform the reaction is to approach the three reactants (base, malononitrile and aldehyde). However, after thermal corrections, the global activation Gibbs energies are still consistent with a feasible process (ΔG‡ = 96.8 and 87.6 KJ mol⁻¹ for the 8a and 8g respectively, see Figure 5 and S. I., Figures S23-29). This is consistent with a relatively fast reaction, taking place at room temperature.

Several key features appeared when analysing the reactivity of 8a and 8g inside the cavity defined by the imine structure. In particular, aldehyde 8a is sufficiently small to be accommodated inside the cavity either with the phenyl ring placed along or perpendicular to the channels of the material. This is due to the fact that the width of the phenyl ring is less than half of the cavity section. In contrast, aldehyde 8g is significantly wider than 8a. Therefore, this imposes that the anthracene aldehyde 8g can only diffuse in the less hindered orientation. Moreover, although several arrangements of the transition state of 8a without steric hindrance from the cavity could be envisaged, we could only find two possibilities to settle the transition state associated to 8g, but with severe geometrical constrictions (S. I. Figures S23-29). Therefore, diffusion of the reactants and products along the material seems to be much more favourable for 8a/9a than for 8g/9g. Overall, although the best estimated energies of the transition states inside the cavity are similar to those in solution, computations suggest that the system involving 8g has much less flexibility inside the cavity and it would require a very specific orientation, which suggest that this would impose a high entropic penalization. This is especially relevant considering that the model used does not include neither the acetic acid needed to trap the triethylamine nor the solvent. Therefore, the diffusion of the resulting product 9g would be challenging if ever formed. All this data together suggest that while 8a and 8g should react similarly in solution, the reaction of 8g becomes more difficult inside the cavity. This reinforces the fact that the reaction takes place inside the material and that size selectivity would appear when the reactant is wider than 9 – 10 Å, such is the case of the three fused aromatic rings.

**Conclusions.**

In this work we successfully carried out the supramolecular functionalization of crystalline COF-300 and related amorphous imine polymer nanoparticles with CH₃COOH molecules and the adduct CH₃COOH···NEt₃. Gas adsorption experiments on crystalline samples corroborated that functionalization by inclusion of CH₃COOH molecules or CH₃COOH···NEt₃ adducts occurs inside the pores of material. Considering the accessibility of active centres, we increased the acid/base catalytic activity of these materials by using amorphous imine polymer nanoparticles. Despite that these nanoparticles are amorphous and non-porous, its functionalization with CH₃COOH molecules and CH₃COOH···NEt₃ adducts allowed to use them as efficient catalysts for acidic ring opening epoxide and basic Knoevenagel reactions, respectively. Moreover, this catalysis exhibited size.
selectivity in Knoevenagel transformations, suggesting that reactions must take place into cavities of the imine structure located close to the nanoparticle surface. Overall, this work presents a new alternative to modulate the catalytic properties of organic porous materials relying on non-covalent encapsulation of small acidic or basic molecules.

Conflicts of interest
There are no conflicts to declare.

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In order to verify the hydrogen bonding interaction with other species, we substituted acetic acid by Rhodamine 6G, which also contains an acidic proton in its structure. We synthesized the COF material in the presence of Rhodamine 6G. The resulting COF material contained a 1.8% in weight of Rhodamine 6G.

All the catalytic experiments were performed during a two weeks period from the synthesis of material, because we observed that storage of the materials for longer periods results in the decrease of catalytic activity, probably due to loss CH$_3$COOH and/or NEt$_3$ volatile molecules.
Non-covalent inclusion of small acid and base molecules in an imine structure based on COF-300 nanoparticles is presented.