Communication

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Tunable catalytic activity of solid solution MOFs in One Pot Multicomponent Reactions

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Abstract: The aim of this research is to establish how metal-organic frameworks (MOFs) composed of more than one metal in equivalent crystallographic sites (solid solution MOFs) exhibit catalytic activity, which is tunable by virtue of the metal ions ratio. New MOFs with general formula $[In_xGa_{1-x}(O_2C_2H_4)_{0.5}(hfipbb)]$ were prepared by the combination of Ga and In. They are isostructural with their mono-metal counterparts, synthesized with Al, Ga and In. Differences in their behavior as heterogeneous catalysts in the three-component, one pot Strecker reaction illustrate the potential of solid solution MOFs to provide the ability of addressing the various stages involved in the reaction mechanism.

Metal-organic frameworks, MOFs, are a class of crystalline materials formed by the linkage of metal ions or clusters (denoted secondary building units, SBUs) through organic ligands.[1] MOFs have many applications, including gas storage or separation,[2a] luminescence,[2b] drug delivery,[2c] or heterogeneous catalysis.[2d] Compared to traditional heterogeneous catalysts, MOFs exhibit the advantage of offering a wide range of different chemical compositions, as well as topological and structural features. Thus, MOFs can be prepared with different metal ions and in different coordination environments, suitable to be used as catalytic active sites in organic transformations.[3] In addition, it is possible to use different metal elements to obtain MOFs with the same framework type so that the properties of the materials vary depending on the selected metal atom while keeping the same structural features.[4] More recently, it has also been demonstrated that different metal atoms can be incorporated within the same MOF, occupying equivalent positions in the crystalline framework, which we denote solid solution MOFs.[5] Despite multi-metal systems offer great opportunities in the field of catalysis, thus far the only examples of multi-metal MOFs as heterogeneous catalysts are limited to materials where a second metal site is post-synthetically introduced within the framework, typically in the form of metal complexes or as nanoparticles em-

bedded in the MOF pores.[6] Thus, there are no examples yet where the catalytic activity of a MOF is modified with the introduction in the appropriate ratio of various metal atoms in the framework. Herein we report the synthesis and characterization of three new isostructural MOFs, AlPF-1, [Al(OH)(hfipbb)], GaPF-1, [Ga(OH)(hfipbb)], and InPF-11β, $[In(O_2C_2H_4)_{0.5}(hfipbb)]$ (H₂hfipbb = 4,4'-(hexafluoroisopropylidene) bis(benzoic acid), (scheme 1), which show catalytic activity in the solvent free, one pot Strecker reaction. These three materials showed different behavior in this catalytic reaction affording three different products. In case of AlPF-1 the expected α-aminonitrile product was obtained; however when using GaPF-1 and InPF-11β, the cyanosilylation and the imine formation products were respectively obtained. These differences are attributed to the various possible reaction pathways related to the reactant activation process for each catalyst. Thus, in order to probe whether the combination of both paths could reach the desired α-aminonitrile product, we have prepared solid solution MOFs with the combinations of gallium and indium cations. Our results demonstrate for the first time that it is possible to control the catalytic activity of the MOFs in a multicomponent reaction by using specifically selected metal ratios.

S*cheme 1*. The organic ligand H₂hfipbb reacts with aluminium, gallium, indium, and combination of gallium and indium to form a series of new MOFs.
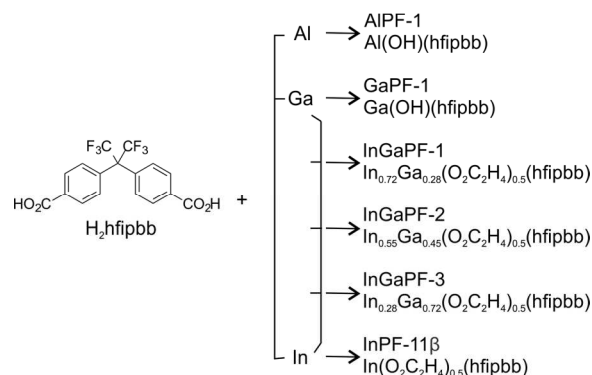
The Strecker reaction is a versatile way of preparing α-aminonitriles through the attack of a nitrile group to an imine group.[7] The resulting α-aminonitriles can be hydrolyzed to obtain α-aminoacids, or used as intermediates in the preparation of nitrogen-containing heterocycles (such as imidazoles and thiadiazoles) that are significant in organic synthesis.[8] In order to perform a highly selective and effective Strecker reaction, different catalysts and several reaction modifications have been studied.[9] These are mainly focused on homogenous systems, and there are only a few reports where heterogeneous catalysts were used.[10] In this three-component (A^3) reaction the imine group is typically prepared prior to the addition of the nitrile group following a cascade methodology.[11] However, a one pot methodology, which goes through the *in situ* imine formation by the addition of the three reactants (scheme 2a)[12] is desirable because of the atom economy impact and its simplistic execution cutting out several purification steps, minimizing chemical waste generation, and saving time.[13] Challenges are associated to the formation of by-products, arising from side reactions (scheme 2 b-d), or to the need of using multiple catalysts.

MOFs constructed with *p*-block elements as metal centers are less common than their transition metal counter parts despite some group 13 based MOFs[14] have already shown interesting properties in the storage of gases[15] or as catalyst.[16] The new materials were prepared under solvothermal conditions with the combination of the corresponding metal salts and the organic linker H_2hfipbb, and their structures were determined by means of single crystal X-ray diffraction. Purity of the samples was monitored by comparison of the experimental powder X-ray diffraction (PXRD) patterns with the ones calculated from the single crystal data.

***Scheme 2.* a) One pot Strecker reaction and its possible sub-products: b) imine formation, c) aniline silanes formation and d) cyanosilylation.**
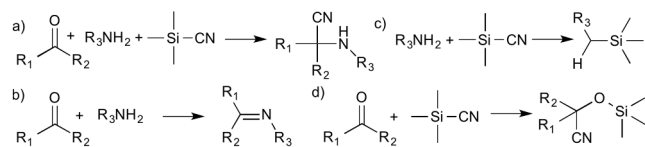

AlPF-1, GaPF-1 and InPF-11β are isostructural. Their structure consists of M^{3+} ions in octahedral $[MO_6]$ coordination environment. Two of the M-O bonds come from the μ-OH group in the case of AlPF-1 and GaPF-1, while in the case of InPF-11β these atoms belong to ethylene glycoxyde groups. It is worth noting that attempts to synthesize InPF-11β under the same conditions used for GaPF-1 and AlPF-1 resulted in the obtaining of a different polymorphic compound, previously reported.[3b] Only by using a solvent mixture of ethylene glycol and water it was possible to obtain InPF-11β. The crystal structure of this compound reveals the presence of eth-

ylene glycoxyde anions instead of the OH groups found in AlPF-1 and GaPF-1. Chains of sharing vertex octahedra that run along the *c* direction are formed. μ-O atoms from the OH or the ethylene glycoxyde groups occupy the shared vertexes. In all three cases the metal coordination sphere is completed with four oxygen atoms coming from the $\eta^2\mu_2$-$\eta^2\mu_2$ hfipbb^{-2} linker carboxylic groups. The resulting rod-shaped inorganic SBUs[17] are connected through the organic linkers giving rise to a three-dimensional framework (figure 1), which can be topologically simplified to a **dia** type network. N_2 adsorption isotherms showed no significant gas uptake by the new materials.

$[M(-O)(-CO_2)]_n$ (hfipbb)$^{2-}$

M(OH)(hfipbb), M = Al, Ga
M($O_2C_2H_4)_{0.5}$(hfipbb), M = In
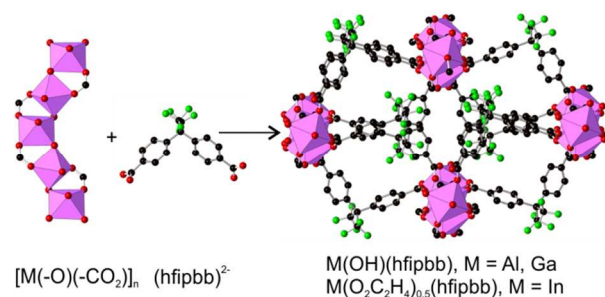
Figure 1 The structure of AlPF-1, GaPF-1 and InPF-11β consists of rod-shaped inorganic SBUs, which are linked by the hfipbb^{2-} anions to produce three-dimensional frameworks.

We started by testing the catalytic activity of these three new materials in the A^3 reaction between benzaldehyde, trimethylsilyl cyanide (TMSCN), and aniline. Catalytic amounts of the MOFs were placed in a Schlenk tube, followed by the addition of the three reactants. The reactions were performed without solvent at room temperature. The results of the reactions are summarized in table 1. When using AlPF-1 as catalyst, the reaction evolves to the quantitative formation of the α-aminonitrile. Assuming that the one pot Strecker reaction takes place following a mechanism as the one proposed in figure 2, the formation of the α-aminonitrile requires the activation of both the carbonyl and silyl groups to allow the imine formation, followed by the cleavage of the cyano group and its attack to the imine carbon atom.
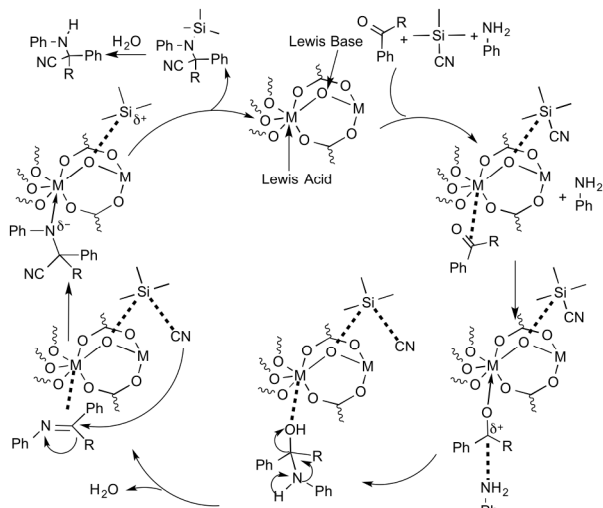
Figure 2. Proposed Mechanism for the M[+3]PF mediated A[3] Strecker reaction of carbonyl compounds. Lewis acid and base sites are proposed based on the MOFs structure.

It seems clear that with AlPF-1 as catalyst, these processes occur with the appropriate rate to yield the final Strecker product in a short time (Table 1, entry 7). On the other hand, when using InPF-11β as catalyst, the formation of the imine is the main product (Table 1, entry 5) indicating that the Lewis basic site required to activating the silyl group and complete the addition of the cyano group is hindered. Nevertheless, after long reaction times (22 h), the reaction between the imine and the cyano groups occur and the product of the Strecker reaction was observed. GaPF-1, gives only the product of the aldehyde cyanosilylation, indicating that both the carbonyl and the silyl groups are quickly activated and the TMSCN is fully consumed before any imine can be formed (Table 1, entry 4). At the view of these results, we thought that it would be possible to control the rates and selectivity of the different steps involved in the one pot Strecker reaction with a combination of Ga and In catalysts, which efficiently activate the silyl groups and produce the imine groups, respectively. Thus, we decided to start by using a physical mixture of both InPF-11β and GaPF-1 catalysts. Indeed, when using equimolar amounts of InPF-11β and GaPF-1 (named [In+Ga] from now on), the α-aminonitrile product was quantitatively formed (table 1, entry 6). Encouraged by these results, we then decided to prepare solid-state solution compounds where the two metals, In and Ga, are sharing the same crystallographic position in the framework.

Table 1: Catalysts performance in the A[3] Strecker reaction using benzaldehyde, aniline and TMSCN.[a]

Entry	Catalyst	t (h)	Yield (%)[b]			TON[c]
			a	b	c	
1	InGaPF-1	96	64	-	-	64
2	InGaPF-2	1.33	91	-	-	91
3	InGaPF-3	0.33	96	-	-	96
4	GaPF-1	0.08–8	-	99	-	-[d]
5	InPF-11β	0.17-8	-	-	99	-[d]
6	[In+Ga]	1	99	-	-	99
7	AlPF-1	0.08	99	-	-	99

[a]benzaldehyde (1mmol), aniline (1mmol) and TMSCN (1mmol), 1 mol% catalyst, r.t., no solvent; [b]Isolated yield; [c]mmol subs./mmol cat. [d]TON is calculated only when Strecker product is obtained.

Therefore, we prepared three new MOFs with general formula $[In_xGa_{1-x}(O_2C_4H_4)_{0.5}(hfipbb)]$, where x = 0.72, 0.55, and 0.28, for InGaPF-1, InGaPF-2, and InGaPF-3, respectively. Note that we formulate these compounds as including ethylene glycoxyde groups instead of OH groups, based on the absence of the typical OH vibration band and the presence of CH_2 bands in their IR spectra (SI, S9-S11). However, we cannot completely rule out the presence of both hydroxyl and ethylene glycoxyde anions in the structure. The metal content was determined with ICP and total X-ray fluorescence (TXRF) spectroscopies. The PXRD patterns of the solid solution MOFs indicate that the three compounds maintain the parent structure. The absence of peak splitting rules out the possibility of having a mixture of two separate phases. Furthermore, a full pattern profile refinement carried out for each one of the three compounds demonstrates that their unit cell parameters values are ranging between those of InPF-11β and GaPF-1 (SI, S3-S5). The mixed InGaPF compounds were subsequently used as catalysts for the A[3] Strecker reaction. InGaPF-1 leads to the product although at a very slow rate (96 h). This indicates that the cleavage of the cyano group is still hindered in a material with a large percentage of indium in the framework. In the case of InGaPF-2, where the metal ratio is close to 1, the Strecker reaction becomes much faster, reaching a 91% of conversion in 1.33 h. Finally, InGaPF-3 exhibits a rate of reaction comparable to that of AlPF-1, with a 96% of conversion to α-aminonitrile in only 0.33 h, thus indicating that the presence of a small amount of indium is enough to favor the imine formation over the aldehyde cyanosilylation. The TON values of AlPF-1 and InGaPF-3 are similar or higher than the ones showed by other reported heterogeneous catalysts under similar conditions (95 and 75 for ref. 10c and 10d, respectively).

Typically, ketones are more difficult to activate than aldehydes. Thus, there are few reports where heterogeneous catalysts are used in Strecker reactions with ketones, and in many cases elevated temperatures (50-60 ºC), use of solvents, and/or high catalytic loadings (4-50mol%) are required.[10] AlPF-1, InPF-11β and GaPF-1 demonstrate excellent activity in the A[3] Strecker reaction

using acetophenone as carbonyl compound with yields between 50-87% (Table S1). Interestingly, in all cases the Strecker product was obtained, with the highest yield for the cases of [In+Ga] (87%) and InGaPF-3 (80%) materials. The different results between aldehyde and ketone based reactions presumably indicate differences in the mechanistic pathway, possibly related to differences in the activation time of the carbonyl groups. Current work is being carried out to find out the origin of these differences.

In conclusion, this paper shows how the activity of a heterogeneous catalyst can be controlled by modulating the ratio of different metals occupying the same crystallographic position of the framework. This reveals a strategy to use solid solution MOFs in multicomponent catalytic reactions.

ASSOCIATED CONTENT

Complete synthesis and characterization details and crystallographic information (CIF files) can be found in the supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

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