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Introduction

The development of multifunctional solid catalysts is currently of foremost relevance in the field of heterogeneous catalysis. The reason is that it is expected that bi/multi-functionalization can be used to promote cascade or tandem reactions in one single step, thus noticeably decreasing processing costs. In this context, metal–organic frameworks (MOFs) can be leading materials, given their chemically modulable nature and structural diversity, and their already proved suitable performance as solid heterogeneous catalysts for specific liquid phase chemical transformations.^{1–5} Multifunctional MOFs presenting different ligands and/or cations have already been used in catalysis,^{6–9} some of these materials being able to promote one-pot tandem reactions.^{10–14}

The real challenge in the synthesis of stable mixed-metal MOFs consists in the control of the metal stoichiometry particularly for cations with different oxidation states and therefore distinct chemical reactivities.^{15,16} In addition, most of

Exploring the catalytic performance of a series of bimetallic MIL-100(Fe, Ni) MOFs⁺

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A series of mixed-metal Fe^{III}/Ni^{II} metal–organic frameworks (MOFs) of the MIL-100 type containing different metal ratios have been synthesized *de novo*, following an approach that requires tuning of the Fe^{III}/Ni^{II} reactivity. The resulting heterometallic MIL-100(Fe, Ni) materials maintain thermal, chemical and structural stability with respect to the parent MIL-100(Fe) MOF as can be deduced from various techniques. The nature and the oxidation state of the accessible metal cations have been evaluated by *in situ* infrared spectroscopy and extended X-ray absorption fine structure measurements. The obtained mixed-metal MOFs and the parent material have been evaluated as heterogeneous catalysts in a model acid-catalyzed reaction, *i.e.*, the Prins reaction. It is found that the catalytic activity improves by more than one order of magnitude upon incorporation of Ni^{II}, with a complete selectivity for the formation of nopol. This increase in the catalytic activity upon incorporation of Ni^{II} correlates with the enhancement in the Lewis acidity of the material as determined by CO adsorption. The heterometallic MOF can be recycled without observation of metal leaching, while maintaining the crystal structure under the reaction conditions.

the new multimetallic MOFs present unsatisfactory chemical stability under catalytic conditions, an issue that has to be addressed before MOF catalysts can meet industrial applicability. Direct post-synthetic methods (PSMs) provide a convenient strategy for the preparation of mixed-metal MOFs, which has been widely explored recently.^{17,18} This PSM approach has been successfully applied to partially replace in MOFs some of the cations by ion metathesis, or to directly coordinate metal complexes in the framework.¹⁹⁻²¹

A more recently developed strategy consists in the direct synthesis of bi- or multi-metallic MOFs using a straightforward method with pre-designed mixed-metal subunits as starting materials. This approach has been denoted as the secondary building unit (SBU) approach.22 These SBU methods have been successfully used in the synthesis of porous pure cationic iron(m) dicarboxylate (MIL-88s)²³ (MIL stands for Materials of Institut Lavoisier) or zirconium(IV) dicarboxylate MOFs (UiO-66's)²⁴ (UiO stands for Universitetet i Oslo) and have been recently applied for the preparation of a mesoporous mixed-metal MIL-127 MOF or soc-MOF,25 as well as for the preparation of different ironcontaining robust MOFs with a preserved Fe^{III}₂M^{II}O metal cluster core ($M^{II} = Co^{2+}$, Ni^{2+} , or Mg^{2+}).^{26,27} These latter examples considered the use of mixed-metal acetate building blocks, i.e. the trimeric oxocentered bimetallic Fe^{III}/M^{II} acetate system [Fe₂M(µ₃-O)(CH₃COO)₆] (M = Co²⁺, Ni²⁺, Mn²⁺, Zn²⁺...)²⁸ obtained from the pure iron(m) oxo acetate cluster.29 In this context, we have devoted particular efforts to the preparation of the archetypal mesoporous mixed-metal MIL-100(Fe₂M) material using the pre-defined

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mixed-metal acetate building blocks. The main reason to select MIL-100(Fe₂M) is the ability of its parent MIL-100(Fe) solid to perform as a heterogeneous catalyst in a large variety of reactions, leading in many cases to large conversions and selectivity. The advantage in obtaining this particular MOF lies in its valuable features: (i) MIL-100(Fe) exhibits a very high surface area and pore volume, allowing easy diffusion of substrates and products of molecular dimensions smaller than the pore windows; (ii) it can be synthesized on a large scale following green methodologies and at low temperature; and (iii) its robust porous structure possesses a suitable chemical and thermal stability. Following the rational mixed-metal building block approach, we could obtain MIL-100(Fe₂Ni) with an appropriate crystallinity, although with several drawbacks: (i) the formation of undesired iron oxides during the synthesis, which considerably affect the properties of the material with regard to its use as a catalyst; and (ii) a dramatic reduction of chemical stability with respect to the parent robust MIL-100(Fe). These inconveniences prevented the practical application of the obtained MIL-100(Fe2Ni) material and prompted us to explore alternative synthetic routes leading to the incorporation of low Ni content in heterometallic MIL-100(Fe, Ni) materials. So far, to our knowledge, only mixed metal(III) MIL-100 (Sc combined with Al, Fe, or Cr) materials¹² and MIL-100(Fe, Mn)³⁰ have been obtained.

Herein we present the direct synthesis of a series of mixedmetal MIL-100(Fe^{III}, Ni^{II}) MOFs containing different proportions of Ni^{II}. The method follows a synthetic route previously developed by some of us,³¹ in which the preparation of a mixedmetal MIL-53(Cr^{III}, Fe^{III}) required the adjustment of the metal reactivity to permit the more inert Cr^{III} cation to enter into the framework. The mixed-metal MIL-100(Fe, Ni) MOFs obtained here are compared with their parent MIL-100(Fe) materials as heterogeneous catalysts in the Prins reaction between β -pinene and paraformaldehyde.³²

Results and discussion

Synthesis and characterization of mixed-metal MIL-100(Fe, Ni) MOFs

The synthesis of a series of heterometallic MIL-100(Fe^{III}, Ni^{II}) (1–3) MOFs with three different Fe/Ni ratios was carried out by directly mixing Fe^0 with trimesic acid in the presence of

aqueous solutions of HNO₃ and Ni^{II} salt. Similarly, pure MIL-100(Fe^{III}) was obtained using Fe⁰ as the only metal precursor. All materials were obtained in stoichiometric metal-to-ligand amounts, using water as the solvent and stirring for 24 h at relatively low temperatures (80 °C), avoiding in this case the addition of HF.³³ Under these conditions, the Fe^{III} cations are very slowly released in the reaction media, permitting to some extent the incorporation into the framework of the less favoured acidic Ni^{II} cation that is 100% available since the early stage of the reaction, in large Ni to Fe excess. Three different Fe^{III}/Ni^{II} metal ratios were considered, obtaining the bimetallic MIL-100(Fe, Ni) (1–3) MOF materials whose analytical data are summarized in Table 1.

Further attempts to obtain mixed-metal MIL-100 including post-synthetic ion metathesis of MIL-100(Fe) by soaking the crystalline material in concentrated aqueous Ni^{II} salt solutions, as well as direct mixture of the corresponding inorganic Fe^{III} and Ni^{II} salts with trimesic acid, were carried out. In all cases, the single metal MIL-100(Fe) material was obtained regardless of the M^{II} concentration and the immersion time. This failure to obtain the mixed-metal MIL-100(Fe, Ni) under these conditions is likely due to the preferential interaction of Fe^{III} hard cations with carboxylates with respect to soft cations (*i.e.* Ni^{II}).

The obtained heterometallic MIL-100(Fe, Ni) MOFs 1–3 and the corresponding homometallic MIL-100(Fe) were characterized by powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), N₂ sorption measurements, scanning electron microscopy (SEM) and extended X-ray absorption fine structure (EXAFS). As seen by PXRD, all powder diffraction patterns of the as-synthesized MIL-100(Fe) and mixed-metal MIL-100(Fe, Ni) (1–3) samples match that of the simulated MIL-100(Fe) material, confirming the formation of an isostructural single-phase MIL-100 material (Fig. 1).

The metal content of the mixed-metal MOFs was determined by ICP-OES analysis and revealed increasing amounts of Ni in the range of 1 to 5%, respectively, for samples 1–3. These metal compositions differ from the initial metal stoichiometry used under the synthetic conditions (see the Experimental section), evidencing the difficulty in incorporating a divalent cation into the metal nodes of MIL-100. This

Table 1 Summary of the Ni content, specific surface area and metal composition of the obtained heterometallic MOFs

			$a_{BET}\left(m^2 \; g^{-1}\right)$	% TGA based	
		% Ni ^{IIa}		Inorganic	Organic
MIL-100(Fe), M.W. 659.77 g mol $^{-1}$,	Theoretical		_	37.2	62.8
$Fe_3O(NO_3)[(CO_2)_3(C_6H_3)]_2$	Experimental		1600	36.7	63.3
MIL-100(Fe ₂ Ni), M.W. 597.77 g mol ⁻¹ , Fe ₂ NiO[(CO ₂) ₃ (C ₆ H ₃)] ₂	Theoretical			30.7	69.3
1	Experimental	1.0 ± 0.3	1545	33.5	66.5
2		3.1 ± 0.2	1525	33.7	66.3
3		5.0 ± 0.2	1570	34.1	65.9

^{*a*} ICP based. Standard deviation based on 3 independent syntheses. Normalisation of the samples was performed by considering 100% weight at 200 °C corresponding to the dried samples.



Fig. 1 (a) Structure of the heterometallic MIL-100(Fe, Ni) and trimeric heterometallic unit. Iron and nickel octahedra, and carbon and oxygen atoms are in orange, blue, grey and red, respectively. (b) Powder X-ray diffraction patterns of mixed-metal MIL-100(Fe, Ni) 1–3 materials as compared with the bare MIL-100(Fe) material.

fact can be attributed to the structural instability generated in the MIL-100(Fe) framework when the larger divalent Ni^{II} cation is incorporated leading to a neutral trimeric oxocluster unit (Fig. 1). In an effort to increase the percentage of incorporated divalent Ni, a synthetic route based on the SBU approach was followed using the preformed mixedmetal Fe₂Ni(μ_3 -O) (CH₃COO)₆ oxo-acetate trimer as the metal source, as previously reported by some of us.²⁴ MIL-100(Fe^{III}, Ni^{II}) containing 33% Ni was synthesized, leading to the formation of an amorphous gel-like material with a much lower specific surface area ($S_{BET} = 700 \text{ m}^2 \text{ g}^{-1}$). Similar results have been recently obtained in a series of acetatebased MOFs using in this case the acetate of the trimeric Cr₃(μ_3 -O) building block and biphenyl-4,4-dicarboxylic acid (H₂-BPDC).³⁴

Thermogravimetric analysis performed on the solids revealed comparable thermal stability up to 300 °C with weight losses of the mixed-metal MOFs in agreement with the expected range: about 66% ligand loss for MIL-100(Fe, Ni) 1-3 (63% and 69% calc. for the Fe₃O and Fe₂NiO ratio, respectively) (see Table 1 and Fig. S1-S4[†]). FT-IR analysis of MOFs 1-3 also confirmed the formation of the MIL-100 structure. All materials exhibited the characteristic asymmetric and symmetric stretching bands of the carboxylate anions at 1630-1576 cm⁻¹ and 1450-1382 cm⁻¹, respectively. The metal-oxygen bands of the $M_3(\mu_3$ -O) group were identified at 624 cm⁻¹ in MIL-100(Fe) corresponding to the Fe₃O trimeric unit, while the appearance of a new band at 569 cm⁻¹ in 1-3 attributed to the Fe₂NiO unit was recorded for the mixed metal samples (see Fig. S5[†]). The chemical stability of the obtained MIL-100(Fe, Ni) 1-3 materials was evaluated in water as compared to the bare MIL-100(Fe) material. After 24 h of stirring at room temperature, none of the materials presented leaching of Ni or Fe metals (<1%) and maintained their crystallinity (Fig. S6[†]). Upon water treatment at 80 °C a leaching of ca. 15-20% of the total Ni content was observed for materials 1-3, while no Fe leaching was detected. Similar studies conducted in MeCN at 80 °C revealed negligible Ni or Fe metal leaching (<1%).

The porosity of the solids was characterised by N_2 sorption analysis. Fig. 2 shows the isotherms of MIL-100(Fe) and MIL-100(Fe, Ni) 1–3 revealing characteristic type I isotherms expected for the MIL-100 microporous system with preservation of



Fig. 2 (a) N₂ sorption isotherms for MIL-100(Fe) and heterometallic MIL-100(Fe, Ni) **1–3** materials at 77 K. (b) Chemisorption of CO in MIL-100(Fe) and MIL-100(Fe, Ni) **3** at 303 K. Solids were activated at 423 K for 12 h under vacuum. Chemisorption is presented as a relative value of the total sorption isotherm.

the porosity (see the logarithmic scale of the pressure range in Fig. S3[†]). The obtained accessible surface area values calculated using the Brunauer–Emmett–Teller (BET) model are summarized in Table 1. The minor differences encountered in BET areas (1600–1521 m² g⁻¹) are in the range of possible experimental error in mass calculation. It is important to mention that a substantial drop in the BET surface area from 1600 to 1180 m² g⁻¹ is detected upon further insertion of the Ni^{II} cation (10–15% metal substitution) (Fig. S7 and S8[†]). This decrease in surface area may be related to the presence of occluded metal oxides, which is supported with a larger inorganic percentage detected in thermogravimetric studies.

CO adsorption experiments were performed to evaluate the effect of the nature and proportion of the different Lewis acid sites present in the framework as compared to the single cationic material.

Heterometallic material 3 was selected for these CO adsorption measurements considering its larger Ni^{II} content (5%) and preserved porosity. Fig. 2 (right) depicts the CO chemisorption isotherm for sample 3 compared to that of pure MIL-100(Fe) after activation at 423 K for 12 hours under vacuum. It is important to note that under these conditions, it has been shown previously that Fe metal sites remain in the +3 oxidation state, meaning that the presence of reduced Fe^{II} species is negligible.^{22,35} A noticeably lower CO chemisorption capacity is observed in this pressure range for the pure iron solid, while an increase in the chemisorption capacity of approximately 10% is measured for the mixed metal MIL-100(Fe, Ni) solid activated under the same conditions. This is consistent with previous studies carried out by some of us on MIL-127(Fe, Ni) materials.²⁴ These results point out the effective impact of mixed-metal cations on the Lewis acidity of the material and, therefore, also presumably on its catalytic activity as will be described below.

SEM and energy dispersive X-ray spectroscopy (EDS) elemental mapping of heterometallic MIL-100(Fe, Ni) material 3 confirmed the mixed-metal composition revealed by ICP-OES but also endorsed the regular Fe and Ni distribution in the material at submicrometric resolution, ruling out the presence of large aggregates of independent Ni or Fe nanoparticles (Fig. S9†). This elemental mapping is compatible with the homogeneous spatial distribution at the micrometric scale of Ni^{II} cations in the heterometallic MIL-100 material. Further

evidence of the structural composition was provided by analysis of the EXAFS spectra of the materials at the ROCK beamline of the SOLEIL synchrotron radiation laboratory. At the Fe K edge, iron is confirmed at the oxidation state +3. Least squares fittings of EXAFS spectra recorded for sample MIL-100(Fe) (without Ni) and heterometallic sample MIL-100(Fe, Ni) 3 (containing 5% Ni) are fully consistent with the MIL-100 reported structure (see Table S1 and Fig. S10–S17†). At the Ni K edge, Ni is confirmed at the oxidation state +2 with a rising edge position at the same energy position as that of the NiO or Ni(OH)₂ references. This conclusion concerning the oxidation state of the metals is similar regardless of the Ni loading of the sample.

Least squares fittings of EXAFS spectra recorded for materials MIL-100(Fe, Ni) 2 (3% Ni) and 3 (5% Ni) have been performed with the substitution of one iron atom by Ni. Very similar structural parameters were found for second neighbours (carbon) and iron second neighbours compared to those for characterizing the materials at the Fe K edge. The first Ni–O coordination shell is described with longer distances than that of Fe–O, which is consistent with the Ni(2+) oxidation state. Debye Waller factors are larger for Ni data than for Fe data likely due to the presence of local distortion upon substitution of Fe^{III} by Ni^{II} in the structure. Therefore, it is established that Ni^{II} atoms likely replace Fe^{III} positions in the trimeric units of the crystal and they are distributed homogeneously throughout the network.

In situ IR spectroscopy. Analysis of the accessible metal sites

To gain further insights into the nature and the oxidation state of the accessible cations in the framework, *in situ* IR analysis was carried out on mixed-metal MOF MIL-100(Fe, Ni) **3**, comparing the results with those of the pure iron-based MIL-100(Fe) material. Adsorption of NO as a molecular probe was monitored by *in situ* IR spectroscopy, given the well-known ν (NO) bands of adsorbed nitrosyls in the related MIL-127(Fe, Ni) material.²⁴ The infrared spectra were recorded at low temperature (-125 °C) after NO adsorption on MIL-100(Fe, Ni) and MIL-100(Fe) activated under vacuum at two different temperatures, 150 and 230 °C (Fig. 3). The addition of small NO doses on the activated materials causes the appearance of new absorption bands in the spectra, which are assigned to the



Fig. 3 IR spectra of MIL-100(Fe, Ni) **3** (a) and MIL-100(Fe) (b) recorded after introduction of an equilibrium pressure of NO (300 Pa) at low temperature (150 K). Spectra after activation of the solid at 423 K are represented with a black line while spectra after activation of the solid at 503 K are represented with a dashed red line. The assignment of the bands has been indicated in the drawings.

Table 2 Summary of the main NO bands attributed to the different $M^{\rm III}{-}{\rm NO}$ and $M^{\rm II}{-}{\rm NO}$ nitrosyls compounds formed

	Fe ³⁺ NO	ν (NO) cm ⁻¹ Ni ²⁺ ···NO	Fe ²⁺ NO
MIL-100(Fe, Ni) _{423K} (3)	1894	1868	_
MIL-100(Fe, Ni) _{503K} (3)	1895	1865	1805
MIL-100(Fe) _{423K}	1895	_	1794
MIL-100(Fe) _{503K}	1895	—	1816, 1796

adsorbed nitrosyls on coordinatively unsaturated sites (CUSs). The results are summarised in Table 2. NO adsorption experiments on the heterometallic MIL-100(Fe, Ni) activated at 150 °C, MIL-100(Fe, Ni)150 °C, reveal the appearance of two ν (NO) bands centred at 1895 and 1868 cm⁻¹. These bands are attributed to NO interacting with Fe³⁺ and Ni²⁺ CUSs, respectively.24,36 The intensity of these bands increases with the amount of NO introduced, this effect being more pronounced in the Fe³⁺ nitrosyl band (see the ESI[†]). When the sample is activated at higher temperature (MIL-100(Fe, Ni)230 °C), a new band centered at 1805 cm^{-1} appears, which is assigned to NO interacting with Fe²⁺ CUSs. These new Fe²⁺ sites will be generated by thermal reduction of Fe³⁺ under the activation conditions, as has been established in related trimeric-based MOF materials.37 Similar NO adsorption studies performed on the MIL-100(Fe) material activated at 150 °C (MIL-100(Fe) 150 °C) show that there is first a ν (NO) band at 1901 cm⁻¹ (Fig. 3). Its intensity increases rapidly with the amount of NO introduced while its wavenumber shifts to 1895 cm⁻¹ (Fig. S18[†]). Then, another very weak band is observed at 1793 cm^{-1} at the NO equilibrium pressure. As indicated above, these two bands are assigned to Fe³⁺ and Fe²⁺ nitrosyl species, respectively. The infrared spectra of MIL-100(Fe) activated at 230 °C (MIL-100(Fe)230 °C) and after NO adsorption display the expected very intense couple of bands around 1800 cm⁻¹, assigned to NO adsorption on Fe²⁺ CUSs, in agreement with the known formation of supplementary Fe^{II} metal sites upon higher activation temperatures.^{38,39} Notably, the ν (NO) band at 1868 cm⁻¹ has not been observed in MIL-100(Fe) as is expected for the pure iron based MOF.

This study not only corroborates the efficient incorporation of Ni²⁺ centers into the heterometallic MIL-100(Fe, Ni) structure based on the observation of free CUSs able to interact with NO, but also establishes their accessible Lewis acid character. Importantly, the characteristic partial reduction of Fe^{III} in MIL-100 is also evidenced in the heterometallic MIL-100(Fe, Ni) material upon activation at higher temperatures. Generation of Fe^{II} is likely to be due to the coexistence of both types of trimeric units, pure (Fe₃O) and mixed metal (Fe₂NiO) trimers, in the structure of MIL-100(Fe, Ni).

Catalytic activity

To determine the distinctive catalytic activity of the obtained heterometallic materials MIL-100(Fe, Ni) 1-3 with respect to that of their parent MIL-100(Fe) material, we tested them as solid catalysts in the acid-catalyzed Prins reaction.⁴⁰ In

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Fig. 4 (a) Time conversion plot of β -pinene, using as a catalyst either the mixed-metal MIL-100(Fe, Ni) **1**–**3** or homometallic MIL-100(Fe). (b) Hot filtration test and (c) reusability of mixed-metal MIL-100(Fe, Ni) **3** as a catalyst for the β -pinene conversion. Reaction conditions: catalyst (15 mg, 0.5 mol% total metal based), β -pinene (1 mmol) and paraformaldehyde (1 mmol) in MeCN at 80 °C. Legend (a): MIL-100(Fe, Ni) **1**(\bigcirc), **2**(\bigcirc) and **3**(\square); Legend (b): 1st use (\square), 2nd use (\bigcirc), 3rd use (\square), 4th use (\bigcirc) and 5th use (\blacktriangle). Inset: PXRD patterns of the fresh MIL-100(Fe, Ni) (black pattern) and after the 2nd and 5th reuse (red and blue patterns, respectively).

particular, the model reaction studied was the synthesis of nopol *via* Prins condensation of β -pinene and paraformaldehyde.³⁰

Prior to the catalytic reaction, the samples MIL-100(Fe, Ni) 1-3 and MIL-100(Fe) were thermally activated at 150 °C under vacuum overnight. In a typical procedure, the Prins condensation was carried out with the MIL-100(Fe, Ni) at 80 °C in MeCN, using 0.5 mol% (total metal based) of solid (Fig. S8⁺). It is worth mentioning that further increase in the amount of catalyst (up to 0.7 mol%) had no significant effect on the reaction rate. Fig. 4a shows the temporal evolution of β-pinene conversion to the corresponding nopol promoted by the mixed-metal MOF and the analogous MIL-100(Fe). After 10 h of reaction, all materials show a complete selectivity for the formation of nopol, and while the use of homometallic MIL-100(Fe) affords <20% conversion, the use of heterometallic samples as catalysts affords between 70 and 100% conversion. Indeed, only the MIL-100(Fe, Ni) 3 material resulted in a total conversion to nopol after 10 h. Therefore, the activity test clearly shows that the presence of Ni significantly increases the catalytic activity of MIL-100 as a Lewis acid, increasing the initial reaction rate with the percentage of Ni in the range under study. These catalytic data are in accordance with the increase of the Lewis acidity determined by CO titration upon incorporation of Ni²⁺. A plausible explanation for the observed improved catalytic behaviour may be associated with the distortion caused in the framework upon insertion of $\mathrm{Ni}^{\mathrm{II}}$ Lewis acid sites, as demonstrated by EXAFS experiments (see Fig. S10-S17†). It is believed that the formation of the mixed-metal trimers in the framework may facilitate access to the Fe^{III} Lewis acid sites, thus enhancing the catalytic activity of the catalyst.

The stability of the best MIL-100(Fe, Ni) 3 catalyst under the reaction conditions was established by recovering and reusing the material in five consecutive runs, observing that the initial reaction rate, final conversion and complete selectivity to nopol were maintained when the material was properly washed (uses 2, 4 and 5) (Fig. 4b). X-ray powder diffraction analysis of the fresh and the reused materials (Fig. 4b inset) confirmed the preservation of the crystallinity upon successive catalytic reactions, while analysis of the liquid phase after removal of the

solid catalyst established the absence of iron or nickel leaching from the solid to the liquid phase.

The heterogeneity of the catalytic procedure was ascertained by Sheldon's hot filtration test. Fig. 4 shows a comparison of the temporal profile of β-pinene conversion in the presence of MIL-100(Fe, Ni) 3 and upon hot filtration of the solid catalyst after 1 hour of reaction. Noticeably, the reaction did not proceed after removal of the catalyst, demonstrating that no catalytically active metal species are present in the filtrate and therefore establishing the heterogeneity of the MOF. A productivity test using a large excess of β -pinene (10 mmol) over a minimal amount of mixed-metal MIL-100(Fe, Ni) MOF (0.001 mmol Fe + Ni metal) was performed. Under these extreme conditions, full conversions were achieved at long reactions times (see Fig. S20⁺), reaching a turnover number of 1×10^4 . Importantly, a selectivity of 100% was maintained over the reaction. It should be pointed out that although the Prins reaction has been studied with other MOFs and zeolites, the selectivity of nopol has been found to decrease in the presence of adventitious Brønsted acidity that causes the undesirable isomerization and other side reactions of norbornadiene. Also, although a combination of Amberlyst 15 and montmorillonite has been reported as an efficient heterogeneous catalyst,41 the present mixed-metal MIL-100(Fe, Ni) is more versatile, still allowing for further optimization.

Conclusions

Heterometallic Fe^{III}/Ni^{II} MOFs of the MIL-100 type material with different metal ratios have been synthesized, exhibiting the thermal, chemical and structural stability of the parent MIL-100(Fe) MOF. The incorporation of Ni^{II} centers in the heterometallic MIL-100(Fe^{III}, Ni^{II}) structure was based on analytical data, EXAFS and *in situ* IR analysis, establishing both the homogeneous distribution throughout the network and their accessible Lewis acid character.

The mixed-metal MIL-100(Fe, Ni) MOF containing Ni and the parent MIL-100(Fe) material have been studied as heterogeneous catalysts in a model acid-catalyzed reaction, *i.e.*, the Prins reaction. It was observed that the initial reaction rate increases

gradually with the percentage of Ni^{II} incorporated in the material. An improvement of the catalytic activity of more than one order of magnitude has been determined in the case of the mixed-metal MIL-100(Fe, Ni) catalyst 3 (5% Ni). This catalytic behaviour, originating from the insertion of new Ni^{II} Lewis acid sites, is maintained over successive cycles and correlates with CO adsorption measurements. The improved catalytic activity may have its origin in the distortion originating upon inclusion of Ni^{II} ions in the framework, although local electronic modifications are also expected to play a role. A future in-depth study to gain a more exhaustive understanding of this catalytic improvement is envisioned.

It is proposed that the use of this simple and direct synthetic approach may be applicable in the preparation of other mixedmetal MOFs suitable as heterogeneous catalysts. Considering the wide use of MOFs as heterogeneous catalysts, the present results showing the enhancement of the catalytic activity in heterometallic MIL-100 open the way to prepare new generations of even more active materials by introducing appropriate amounts of two or more metals at the nodes.

Methods

Materials

Iron powder, 1,3,5-benzenetricarboxylic acid (95%) (trimesic acid), HNO₃ (65%) aqueous solution, paraformaldehyde, and β -pinene were purchased from Sigma-Aldrich. Solvents were used without further purification.

Synthesis of MIL-100(Fe) and mixed-metal MIL-100(Fe, Ni) MOFs (1-3)

The homometallic MIL-100(Fe) MOF was obtained by directly mixing 1.680 g of trimesic acid (8 mmol) and 0.670 g of Fe powder (12 mmol) in 90 mL of distilled H₂O, followed by the addition of a 65% HNO3 aqueous solution (0.424 mL, 6 mmol). The whole mixture was then heated to 85 °C for 24 hours. After cooling to room temperature, the solution was filtered and the obtained powder washed with water. The solid was then dispersed in 30 mL of EtOH and heated to 60 °C for 12 hours to remove excess of trimesic acid. After cooling to room temperature, the resulting compound was recovered by filtration and washed with water. For the mixed-metal MIL-100(Fe/Ni) MOFs 1-3 different molar M^{III}/M^{II} mixtures were used: 1 (11.88 and 0.12 mmol of Fe powder and Ni^{II} acetate, respectively); 2 (11.4 and 0.6 mmol); 3 (10.8 and 1.2 mmol). The amount of HNO3 aqueous solution added was adjusted in all cases to 0.5 mmol of Fe⁰. MIL-100 is formulated as Fe₃₋ $_x Ni_x O(C_6 H_3(CO_2)_3)_2 (OH)_x \cdot (H_2 O)_{3-x} \cdot (solvent).$

In situ IR spectroscopic analysis

For *in situ* IR analysis, samples were pressed into self-supported wafers (4–10 mg cm⁻²) and treated in a vacuum (10–6 mbar) at 150 °C or 230 °C for 12 h. NO-FTIR spectra were recorded by using a Nexus 8700 FTIR spectrophotometer, using an IR cell that allowed us to perform *in situ* treatments at a controlled temperature and was connected to a high vacuum system with

a gas-dosing facility. Transmission IR spectra were recorded in the 500–5600 cm⁻¹ range, at 4 cm⁻¹ resolution. After activation, the wafers were cooled to -125 °C under dynamic vacuum followed by NO dosing at an increasing pressure (0.4–6 mbar). IR spectra were collected after each dosage. All IR spectra that correspond to the NO adsorption measurement were normalized to the weight of the wafer.

Thermogravimetric analysis

The thermal stability was evaluated by thermogravimetric analysis (TGA). TG measurements were carried out with a Mettler Toledo TGA/DSC 1, STAR System apparatus under an O_2 flow of 50 mL min⁻¹, at a heating rate of 3 °C min⁻¹ to 500 °C.

Powder X-ray diffraction analysis

Polycrystalline samples of MIL-100(Fe, Ni) were lightly ground in an agate mortar and pestle and filled into 0.5 mm borosilicate capillaries prior to being mounted and aligned on an Empyrean PANalytical powder diffractometer using Cu K α radiation (λ = 1.54056 Å). For each sample, three repeated measurements were collected at room temperature ($2\theta = 2 - 20^\circ$) and merged into a single diffractogram.

Adsorption measurements

Adsorption/desorption isotherms for N_2 were measured at 77 K using a Tristar (Micromeritics). Samples were thoroughly dehydrated by heating at 150 °C for 5 h under vacuum. Adsorption/desorption isotherms for CO were measured at 303 K using a Quantachrome Autosorb automated gas sorption system (Quantachrome Instruments). Samples were dehydrated by heating at 150 °C for 12 h under vacuum.

EXAFS experiments

The Ni and Fe K edge XAS measurements were performed at the ROCK beamline at the SOLEIL synchrotron radiation facility.42 Pellets of the powdered samples diluted with boron nitride were prepared with sample masses optimized in order to achieve an edge jump of about 1 at the Fe K edge and \sim 0.1 to 0.2 at the Ni K edge. Data were collected at room temperature in transmission mode using a Si(111) channel cut monochromator and ionization chambers filled with nitrogen. Harmonic rejection was ensured using two mirrors with B4C stripes aligned to 2.8 mrad with respect to the incident beam. XAS analysis was carried out using Athena software.43 Energy calibration was done at the tabulated values using the first derivative maximum of iron (E_0) = 7112 eV) and nickel (E_0 = 8333 eV) metallic foils located between the second and third ionization chambers and recorded simultaneously with the samples. After linear pre-edge and atomic background removal, XANES spectra were normalized in the middle of the first EXAFS oscillation. Fe K edge and Ni K edge EXAFS spectra were k^3 -weighted before Fouriertransformation using a Kaiser-Bessel window in the 3.3-11 and 10 \AA^{-1} k range with dk = 2. Distances and Debye–Waller factors of the different contributions characterizing the local order of MIL-100(Fe) and mixed-metal MIL-100(Fe, Ni) MOFs

(2–3) were determined by least-squares refinements using the Artemis interface to IFeFFIT⁴² while the coordination numbers of those contributions were fixed at the values described in the MIL-100(Fe) crystallographic structure.⁴⁴

The amplitude reduction factors were obtained by fitting the EXAFS spectra of α -Fe₂O₃ and NiO and their values ($S_0^2 = 0.68$ (Fe K edge) and 1.23 (Ni K edge)) were kept fixed for the simulation of MIL-100(Fe) and mixed-metal MIL-100(Fe, Ni) MOFs (2–3) while the energy shift values which allow the match between theoretical and experimental *k*-scales were allowed to vary within the limits 7127.7 \pm 3.0 eV and 8345.6 \pm 3.4 eV. The reliability of the fits was assessed by the minimization of the EXAFS reliability factor $R_{\rm f}$ which measures the relative misfit with respect to the data and the reduced χ_{ν}^2 quality factor, two metrics defined by the IXS Standards and Criteria Committee.⁴⁵

Catalytic experiments

The required amount of catalyst (typically 10 mg, except for productivity tests) was added to a round-bottom flask (25 mL). Catalyst activation was performed at 150 $^{\circ}$ C under vacuum overnight. The reaction system was purged with molecular oxygen using a balloon, the substrate was introduced (20 mmol) and the system was sonicated for 5 min. Then, the reaction mixture was placed in a pre-heated bath at 80 $^{\circ}$ C and magnetically stirred.

The reusability of MIL-100(Fe, Ni) was evaluated under the general reaction conditions. At the end of the reaction the catalyst was filtered through a Nylon membrane filter of 0.2 mm. Then, the catalyst was washed by suspending the solid in methanol at 60 °C for 2 h. This washing procedure was repeated two more times. Finally, the catalyst was dried at 100 °C overnight and used in subsequent catalytic cycles. Product analysis was conducted as follows: previously filtered reaction aliquots (100 μ L) were diluted in a MeCN solution (500 μ L) containing a known amount of nitrobenzene as the external standard. Then, the reaction aliquots were analyzed by gas chromatography using a flame ionization detector. Quantification was carried out by using calibration curves of authentic samples.

Leaching measurements

After reaction completion, the reaction mixture was filtered while still hot. Then, the organic phase was processed to extract the metal ions by stirring in an aqueous nitric acid solution (HNO₃, 3 M) at 80 °C overnight. The metal content of the aqueous phase was analyzed by chemical analysis using an ICP-AES instrument.

Sheldon's hot filtration test

During this test, the catalyst was removed from the reaction by filtration while hot after 60 min of reaction, and the filtrate was monitored for continued activity.

Conflicts of interest

There are no conflicts to declare.

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