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## ARTICLE

## Supported High and Medium Entropy Nano Alloys from MOFs Catalyze Alkene Oxidation Reaction

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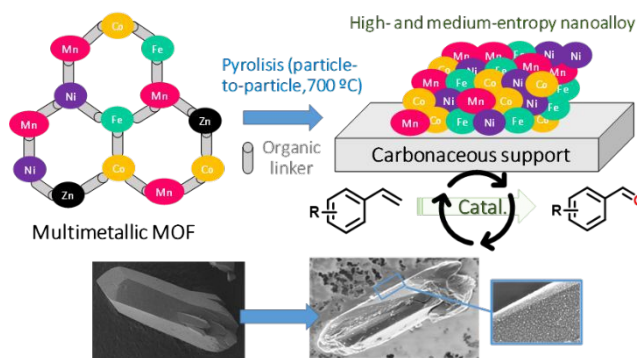
High- and medium-entropy alloys (HMEAs) are emerging as promising catalysts due to their different electronics and very good thermal stability. HMEAs have already exhibited remarkable catalytic performance in several electrocatalytic reactions involving small molecules, however, their use in thermal complex organic reactions is still in its infancy. Herein, we present a highly dense supported HMEA material (~50 wt% in metal) prepared by pyrolysis of a metal-organic framework (MOF), used as a template in virtue of its well-spaced single metal atoms, to obtain catalytic carbon-supported nano HMEAs in a particle-to-particle synthetic way. The solid material shows a remarkable catalytic activity for alkene oxidation reactions and can be recycled at least 10 times, however, a higher activity of the monometallic catalysts in terms of turnover number is found. These results constitute, to our knowledge, one of the first examples of catalytic HMEAs for organic synthesis.

## Introduction

Metals are of such social and historical significance that two eras are named for them, the Iron Age and the Bronze Age (as an alloy, bronze was the first truly engineered material).<sup>1</sup> Alloys began with one and rarely two principal elements, such as iron in steels or nickel in superalloys, with enhanced properties. However, despite the fact that humanity has been developed new alloys with metals since ancient times, it was about two decades ago when a new promising alloy design was proposed, involving mixing of multiple elements in an equimolar or near-equimolar composition.<sup>2–6</sup> These designed multicomponent alloys were termed as ‘high-entropy alloys’ (HEAs) by Yeh et al.,<sup>3</sup> which describes the high configurational entropy after the random mixing of metal elements. In the early days, HEAs were limitedly defined as alloys composed of five or more elemental components in equimolar ratios. Nowadays, medium-entropy alloys (MEAs) with 3–5 elements are also considered and, in both cases (HEAs and MEAs, i.e. HMEAs), the properties are significantly regulated by tuning the metallic component.<sup>7</sup> Unlike conventional metal alloys, which contain one and rarely two base metal elements, HMEAs comprise multiple principal elements, with the number of HMEA compositions extending considerably more than conventional alloys, and this metal combination not only regulates the electronic and geometric

structures to a large degree but also serves as a platform to construct catalysts with unexpected performance.<sup>8–16</sup>

The use of nanoparticles (NPs) is preferred respect to macroscopic metals in catalysis, since the high surface-to-volume of the former enables a higher interaction with external reactants. In view of this, a variety of strategies has been proposed to produce HMEA NPs, such as mechanical ball milling, plasma arc discharge, ultrasonication, deposition, fast moving bed pyrolysis and chemical methods involving carbothermal shock, hydrothermal, and solvothermal reactions.<sup>17–24</sup> However, these methods are often tedious and tend to produce a wide distribution of NP sizes. Here, we use a pre-formed, well-defined multimetallic metal-organic framework (MOF) as a template, a strategy rarely seen in the synthesis of catalytic HMEA NPs.



**Scheme 1.** Synthesis of the supported high- and medium-entropy alloy (HMEA) nanoparticles reported in this work, starting from a multimetallic metal-organic framework (MOF) and catalysing the oxidative breaking of styrenes to benzaldehydes, with microscopic images of the particle (MOF)-to-particle (HMEA) synthesis.

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Supplementary Information available: Supplemental experimental, Tables S1–S4 and Figures S1–S28. See DOI: 10.1039/x0xx00000x



MOFs are micro-structured solid materials that consist of organic linkers and metal centres, to form three-dimensional crystalline structures, as shown in Scheme 1.<sup>25,26</sup> The careful choice of these components enables a flexible structure design with well-defined pores sizes, surface area and functionalities. All of these properties make MOFs extremely advantageous not only in their use as a pure material or as a support for single atom or small clusters metal catalysts,<sup>27,28</sup> but also as a sacrificial precursor for other hybrid inorganic-organic nanostructures.<sup>29</sup> Particularly, the metal atoms in the crystal lattice and the organic linkers constitute a source of metal NPs and microporous carbon, respectively, when properly pyrolyzed.<sup>30-32</sup> In other words, MOFs drive to the manufacture of entropy-driven materials such as multi-metal oxides, metal carbides and sulphides, among others,<sup>33</sup> that cannot be synthesized following traditional approaches. Thanks to the previous construction of a MOF, the metal clusters coordinated by organic linkers effectively prohibit the agglomeration of the resultant metal NPs, providing a homogeneous distribution over the support after pyrolysis.<sup>34</sup>

MOFs were reported as a template for metal-supported carbonaceous materials in 2008<sup>35</sup> and, since that time, many variations of MOF material precursors and procedures have been developed. Just to mention a couple of examples, Co/C catalysts were synthesized by well controlled pyrolysis of ZIF-67 above 450 °C,<sup>36</sup> and other examples followed. Based on different characterizations methods, Co/C catalysts were confirmed to possess Co<sup>0</sup> entrapped in a carbon matrix, polished by a certain amount of pyridinic and graphitic N and a small portion of adsorbed oxygen, and these NPs were evaluated in the Fischer-Tropsch reaction. More recently, MOF based Cu-Pt bimetallic nanoparticles supported on nonporous carbon composite were prepared after using a slightly different approach.<sup>37</sup> The method involved carbonization of Cu-MOF-199 in N<sub>2</sub> atmosphere at 900 °C followed by partial galvanic replacement of Cu by Pt<sup>IV</sup> ions upon immersion in a hexachloroplatinic acid solution. The good performance of the alloy for the hydrogen evolution reaction (HER) was attributed to synergetic effect of the Cu-Pt metals uniform distribution of the Pt nanoparticles over the surface. The flexibility of the MOF structure allowed to introduce more than one metal into the lattice, in order to construct multi-metal MOFs to tune its properties,<sup>38</sup> and it is now accepted that the use of multi-metal MOFs as a template can lead to obtain alloy metal NPs with intrinsic characteristics. As compared to mono- or bi-metallic NPs, multimetallic NPs with controlled composition and size may exhibit distinct catalytic activity during reaction due to the metal-metal interactions on the alloy catalysts.<sup>39,40</sup> For example, bi- and trimetallic Co, Ni and Cu alloy nanoparticles have been prepared after the pyrolysis of the corresponding multimetallic MOF under inert atmosphere, to obtain highly dispersed and embedded metal NPs.<sup>41</sup> Despite of the many reported examples about use of MOF-driven alloy NPs, the synthesis of HMEAs from MOFs is still basically unknown since it requires to construct and pyrolyze MOFs of at least 5 different metal atoms, to create the basis for the supported HMEAs. In fact, MOFs are often limited to two to three metals,<sup>41-45</sup> and the simultaneous control over both the composition and the size of HMEA NPs remains a challenge, and the crucial interplay between the size, composition

and atomic structure of these new nanosystems has hardly been addressed from MOFs.<sup>46</sup>

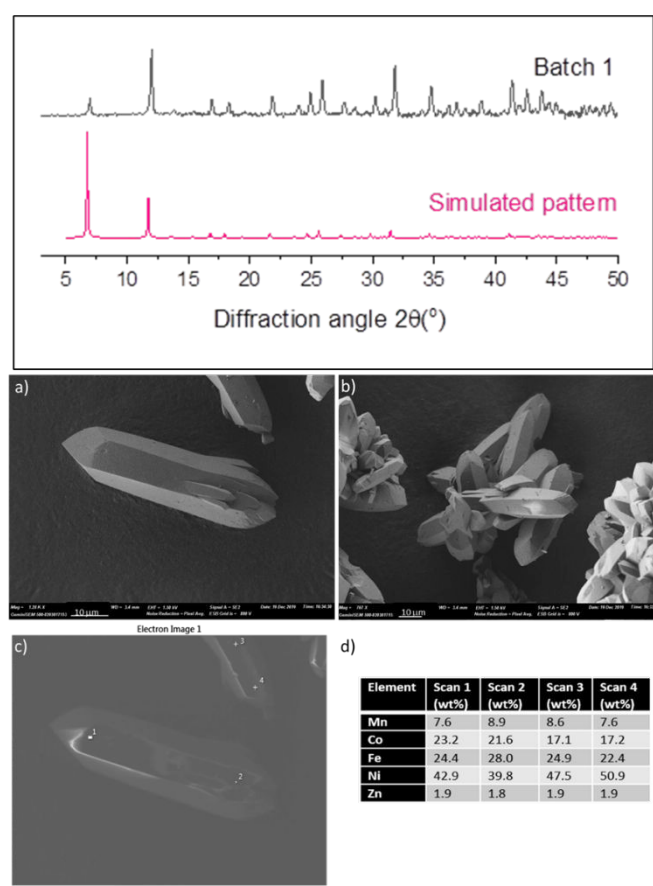
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Scheme 1 shows our approach reported here, that involves a simple particle-to-particle procedure to obtain a carbon matrix decorated with a high density of HMEA NPs (ca. 50 wt%), after pyrolysis of a multimetallic MOF, and its catalytic activity in alkene oxidation reactions. To our knowledge, this is the first time that HMEA based materials are applied as catalysts to oxidation reactions since, in general, HMEAs are applied to hydrogenation reactions.<sup>47-49</sup> Indeed, HMEAs are recognized as potential catalysts for a variety of reactions,<sup>17,50-54</sup> but their use in conventional thermal organic synthesis is still minor compared to electrochemical processes,<sup>55-58</sup> the former being relegated to mainly computational studies.<sup>59,60</sup>

## Results and discussion

### Synthesis and characterization of the HMEA precursor MOF 1 (Ni, Co, Fe, Mn, Zn)

In order to prepare a well-dispersed multimetallic MOF, we modified a described procedure for MOF-74,<sup>61</sup> using nitrate salts of Ni, Co, Zn and Mn, and Fe sulphate as metal sources (see experimental procedures in the Supplementary Material, SM, for more information).



**Fig. 1** Top: Diffraction patterns of the MOF 1 batch 1, compared with the simulated pattern. Bottom: a), b) Field emission scanning electron microscopy (FESEM) images of MOF 1 (Batch 1); c), d) representative energy-dispersive X-ray spectroscopy (EDS)



analysis of MOF 1 crystals in batch 1, at four different locations (scans 1–4). The peak observed at 8° is due to an impurity.

The election of a modified MOF–74 was based on its ability to accommodate up to ten different metals in the framework, with high metal content, and the presence of volatile Zn atoms in the material, which may help us to get unsaturated metal NPs with enhanced catalytic properties.<sup>62–64</sup> With this idea in mind, several batches of the penta–metallic MnCoFeNiZn MOF 1 were synthesized and characterized. Powder X–ray diffraction (PXRD) measurements were firstly carried out in order to confirm the robustness of the process, and Fig. 1 (top) shows the resulted patterns for one of the batches (see Fig. S1 for a three batches comparison), which matched the simulated MOF–74 powder PXRD. It is worth commenting here that the simulated pattern is performed for pure crystalline samples, thus only the peak position but not the intensity is expected to match (the intensity of the PXRD peaks can vary depending on the morphology of the sample, the crystallinity degree, the sample orientation and the grinding, among others). None or very little impurities present in the different spectra suggest good incorporation of the different metals inside the MOF 1 lattice. Anyway, it has to be said that the fact that no other signals are present does not necessarily means that other phases are not present, but that they might be amorphous.

The amount and percentage of each metal in the different batches was determined by inductively coupled plasma optical emission spectroscopy (ICP–OES, Table S1). Notice here that the wt%, at% and mol% values for the metals practically coincide since all metal atoms are neighbouring elements of the first transition row in the Periodic Table. It is true that the ICP–OES values for each metal differ somewhat from batch to batch (not more than 15%), however, considering the complexity of forming the multimetallic MOF and that the variation in initial metal content and proportions does not have a significant influence neither in the final HMEA structure or the catalytic behaviour (the metal content from nanoparticle to nanoparticle and the catalytic activity is quite similar, in average, see ahead), we can accept these variations within a reasonable limit.

The morphology and microstructure of the as–synthesized MOF 1 samples was investigated by field emission scanning electron microscopy (FESEM) images and energy–dispersive X–ray analysis (EDX), as shown in Fig. 1 (bottom). All crystals presented the same morphology with average crystal size around 50  $\mu\text{m}$  (Fig. 1a and 1b), and the metals content according to EDX was acceptably similar with the ICP–OES analysis for each batch, except for Zn, with showed lower values (Fig. 1c and 1d). This result may infer that Zn easily sublimates under the electron beam, independently of the location in the crystal.<sup>65,66</sup>

A thermogravimetry differential thermal analysis (TG/DTG) of MOF 1 shows two major weight–loss steps (Fig. S2). First weight loss takes place at 25–100 °C, which corresponds to the elimination of adsorbed and volatile water and guest solvent molecules, with a value around 24 wt%, also confirmed by differential scanning calorimetry (DSC). Then, small mass changes in the range 180–200 °C occur, which might indicate the presence of DMF guest molecules, due to insufficient methanol exchange time after synthesis. Finally, complete decomposition of the organic material in MOF 1 is observed at 330 °C, the remaining mass fitting the expected weight

of metals. These data allowed us to estimate the minimum temperature for the pyrolysis procedure. The surface area of the precursor MOF 1 is lower than expected for MOFs (294.1  $\text{m}^2 \text{g}^{-1}$ ). The low surface obtained for the MOF 1, compared to the typical ones obtained for these materials, it can be attributed to the soft reaction conditions for washing and drying (see reaction procedures in the ESI), that does not complete the removal of guest molecules obtaining a pore blockage and the presence of impurities. However, the area of HMEA–700 is 274  $\text{m}^2 \text{g}^{-1}$ , similar to the precursor, thus correct for the synthetic approach.

### Synthesis and characterization of the carbon–supported HMEA NPs (Ni, Co, Fe, Mn).

The temperature decomposition of MOF 1 serves as a starting point to study the formation of the HMEA NPs. Fig. 2 shows the PXRD of MOF 1 after pyrolysis, at 400 °C, 550 °C, 700 °C and 800 °C, during 4 h under a flow of  $\text{N}_2$  gas. Nearly complete decomposition of the pristine MOF 1 can be already seen at 400 °C, as assessed from the disappearance of the diffraction peaks in the corresponding PXRD analysis, this sample thereafter named HMEA–400 for the sake of clarity. When the pyrolysis temperature was increased to 550 °C, new but small diffractions at  $2\theta = 44^\circ$ ,  $51^\circ$  and  $75^\circ$  were observed. These diffraction peaks can be attributed to the (111), (200) and (220) lattice plane of metal alloy particles with face centred cubic (FCC) structure, very common phase for HEAs,<sup>10</sup> and their signals continuously intensified with increasing the temperature to 700 °C and 800 °C. Nevertheless, they remained broad, and the Scherrer equation gave values of <10–20 nm (9.7 nm, considering a shape factor = 0.9). Any peak at  $\sim 26^\circ$  was not observed, indicating that the organic linkers from MOFs turned into amorphous and not into any kind of crystalline carbon.

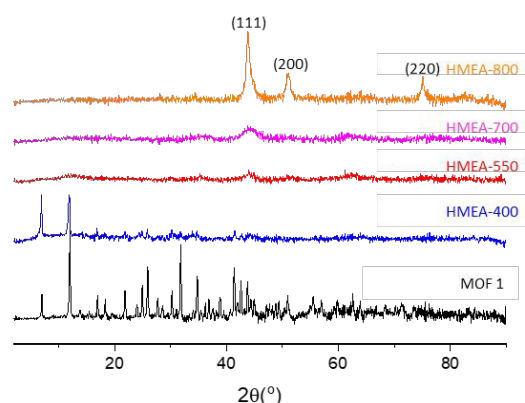
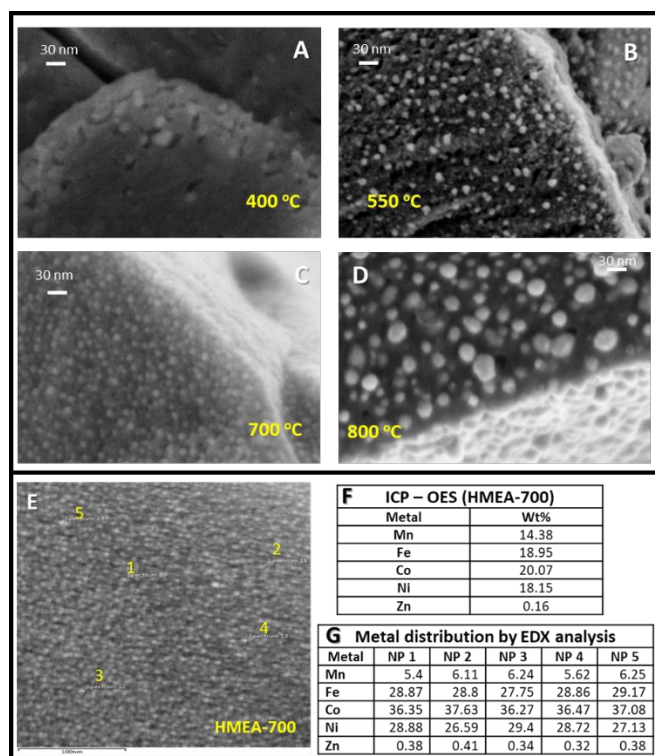


Fig. 2 Diffraction patterns (PXRD) of the MOF 1 sample pyrolyzed at increasing temperatures, compared to the as–prepared MOF 1 (bottom).

Subsequently, materials pyrolyzed at all tested temperatures, except at 800 °C, were followed by reduction under  $\text{H}_2$  (100 mL/min) at 400 °C for 4 h. We then examined all the reduced samples by FESEM to track morphological changes in the material, caused by the modification in pyrolysis temperature (Fig. 3). With pyrolysis at 400 °C (Fig. 3A), the material shows a



smooth surface with some alloy NPs appearing in an irregular manner, and with a wide particle size distribution centred around ~16 nm (Fig. S3). This result is in accordance with the TG/DTG and PXRD analysis, since the organic components of MOF **1** start to decompose at this temperature. The situation dramatically changed when the material was pyrolyzed at 550 °C, and the resulted sample HMEA-550 (Fig. 3B) shows more regular and abundant metal NPs (average size ~18 nm see Fig. S4), with formation of a nanoporous carbon structure having some cracks along the particle. Increasing further the pyrolysis temperature up to 700 °C enabled an optimum distribution of metal NPs (Fig. 3C) see also Fig. S5 and S6).



**Fig. 3** Field emission scanning electron microscopy (FESEM) images of the resulting materials after pyrolyzing MOF **1**: (A) at 400 °C (5 °C/min), (B) 550 °C (5 °C/min), (C) 700 °C (5 °C/min), and (D) 800 °C (10 °C/min) during 5 h. (E) HR-FESEM picture of HMEA-700 with ICP-OES analysis (F), and the metal distribution according to energy-dispersive X-ray (EDX) spectroscopy analysis of individual NPs (G) indicated in image E. Pyrolysis at all temperatures except at 800 °C were followed by reduction in H<sub>2</sub> (100 mL/min) at 400 °C for 4 h.

The sample HMEA-700 contains spherical NPs, equally dispersed and covering all the nanoporous carbon surface, with a very narrow particle size distribution centred around 11 nm (Fig. S5), a significantly smaller size than the materials pyrolyzed at 400 °C and 550 °C. At 800 °C (Fig. 3D), the material shows a defined structure but with bigger NPs (~30 nm) and a wider size distribution also (see also Fig. S6). For all the carbonized materials, the same morphology of parent MOF **1** can be observed, which indicates that the chemical transformation of MOF **1** occurs intraparticle during the pyrolysis process (see Fig. S7 with HMEA-550 as a representative example).<sup>67</sup> The conversion of the organic linkers into a carbon matrix should act as a reducing process for the metal cations, thus developing a

carbon-supported multi-metal hybrid nanomaterial after complete pyrolysis of the organic part. DOI: 10.1039/D5NR04879F

Fig. 3F–G shows the metal content in HMEA-700 according to ICP-OES analyses, and it can be seen that four of the metals (Mn, Co, Fe and Ni) are present in similar ratio (ca. 15–20 wt% each), while Zn has mainly disappeared. The examination of individual NPs was then accomplished by HR-STEM coupled with energy-dispersive X-ray (EDX) spectroscopy, and the results (see Fig. S8) also shows that most of the NPs in HMEA-700 exhibit a similar chemical composition: i.e., Fe<sub>29</sub>Ni<sub>45</sub>Co<sub>22</sub>Mn<sub>4</sub>, Fe<sub>31</sub>Ni<sub>38</sub>Co<sub>24</sub>Mn<sub>6</sub>, Fe<sub>27</sub>Ni<sub>43</sub>Co<sub>24</sub>Mn<sub>7</sub>, and Fe<sub>42</sub>Ni<sub>326</sub>Co<sub>29</sub>Mn<sub>3</sub>. However, a detailed speciation by TEM and STEM analysis shows that some NPs in the HMEA-700 sample are Ni-rich and others are Fe-rich (Fig. S8e). The Ni content in ICP-OES is lower compared to EDX since the latter somehow shows the composition near or at the surface of the sample and, as XPS measurements denote, Ni tends to be enriched on the surface of the NPs. The lack of Zn, also observed when analyzing the MOF **1** sample by FESEM (Fig. 1), can be explained by the sublimation of this metal, with much lower melting point (419.5 °C), compared to Fe (1538 °C), Ni (1455 °C), Co (1495 °C) and Mn (1246 °C). This low melting point might have provoked leaching Zn out of the material during the pyrolysis procedure and resulted in its deposition at the exhaust of the reactor, a phenomenon well-known in alloyed NPs synthesis to enhance the catalytic properties of the materials.<sup>64,68</sup>

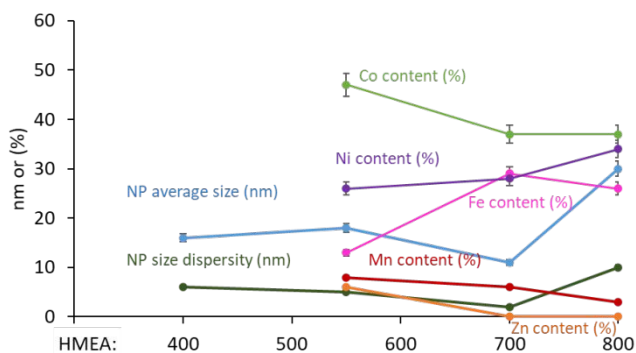
Another change in the chemical composition of the NPs respect to the MOF **1** ancestor is the lower amount of Mn in the NP but not in the overall metal content of the material, which cannot be explained by a potential sublimation. A closer look to the HMEA-700 sample by HR-TEM showed the presence of Mn-rich NPs (Fe<sub>1</sub>Co<sub>1</sub>Mn<sub>98</sub>) after measuring more individual NPs (Fig. S8a and S9f), which explains this decrease in Mn in the supported HMEA NPs. It is worthy commenting here that any Zn-rich NP could not be found. In order to confirm the formation of Mn-rich NPs in HMEA-700, carbon-supported Mn NPs were prepared by impregnation of active charcoal with Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and reduced under H<sub>2</sub> (100 mL/min) at 400 °C for 4 h (see experimental for details). The corresponding PXRD confirms the formation of Mn NPs in the HMEA-700 material after H<sub>2</sub> reduction (Fig. S10).

The HMEA-800 solid shows a similar composition for the NPs as in HMEA-700, i.e., Fe<sub>50</sub>Ni<sub>25</sub>Co<sub>22</sub>Mn<sub>3</sub>, Fe<sub>54</sub>Ni<sub>22</sub>Co<sub>21</sub>Mn<sub>3</sub>, Fe<sub>58</sub>Ni<sub>25</sub>Co<sub>15</sub>Mn<sub>2</sub>, and Fe<sub>56</sub>Ni<sub>27</sub>Co<sub>15</sub>Mn<sub>2</sub> (Fig. S11). A similar amount of Mn and the absence of Zn persist at 800 °C. Fast Fourier transform (FFT) patterns of selected HMEA NPs in HMEA-800 show a FCC structure for the alloyed NP, also recognizable in the corresponding PXRD (see also Fig. 2 and Fig. S11). This FCC structure is also visible in the NPs of the HMEA-700 materials before H<sub>2</sub> reduction (see Fig. 2), but not in the nascent NPs in HMEA-400 and HMEA-550, since it is not until 700 °C when true crystalline HMEA NPs in pure FCC phase are clearly formed.<sup>69</sup>



The comparison of individual NPs of the HMEA–550, HMEA–700 and HMEA–800 material was then performed (please notice that the HMEA–400 material still shows ill-defined NPs) and Fig. 4 shows that the amount of Zn and Mn is roughly the same for HMEA–550 in 12 different examined NPs (see also Fig. S12). Mn is the major metal component (>35 wt%) and the Zn amounts are significantly higher than in other NPs (>10 wt%), which indicates that Mn forms individual NPs and Zn sublimates already at 550 °C, concomitantly, and that these two effects could be chemically related since these early formed Mn-rich NPs contain significant amounts of Zn. On the contrary, the HMEA–700 (Fig. 3E and 3G) shows that the amount of each metal is similar in all the NPs examined, being lower than 7 wt% for both Mn and Zn. Indeed, only after Zn is not present, the solid material starts to be catalytically active (see ahead). All these results come from different MOF batches, that we consider statistically acceptable for the final application (catalysis), thus scientifically sounder than just one single “successful” batch.

All the above results strongly support that the HMEA NPs formed from MOF 1 are composed of similar amounts of Co, Fe and Ni (~20 wt%), with lower amounts of Mn (~5 wt%), remaining stabilized on amorphous carbon after hydrogenation and pyrolysis of MOF 1 at temperatures ~700 °C. In this way, densely distributed HMEA NPs (nearly 50 wt% in total metal content) with good size distribution ( $11 \pm 2$  nm average particle size) can be obtained. Based on the definition for HEAs and MEAs (Fig. S13 in the SI), we must consider the material here reported as a high- and medium-entropy alloy, since HMEAs refer to the alloys composed of three or more elemental components, with the concentration of each element being between 5 and 35 atomic percentage (at%).<sup>10–13</sup>



**Fig. 4** Comparison of the NP size, dispersity, and metal relative content for the different HMEA-supported materials obtained by energy-dispersive X-ray (EDX) spectroscopy. Error bars account for a 5% uncertainty.

#### In situ characterization during the MOF 1 pyrolysis.

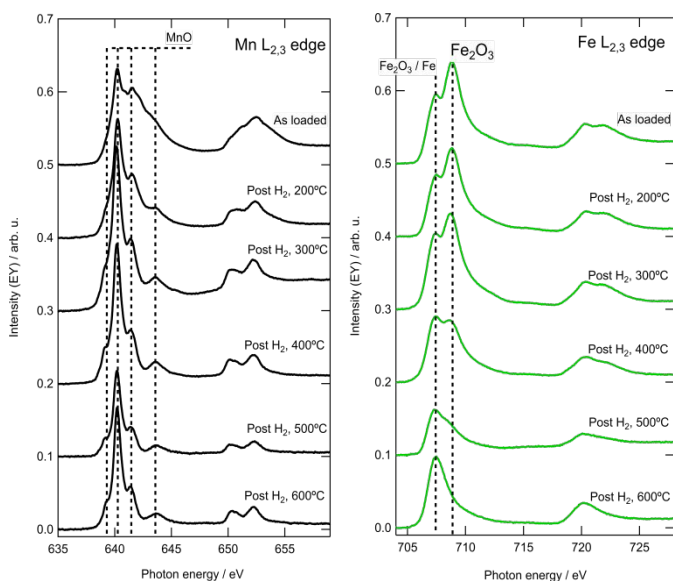
This study presents our first example of an HMEA synthesized via this method. We aim to understand its formation, metal distribution, and nature to improve its preparation and explore its catalytic applications. For this purpose, we employ in situ techniques. X-ray-based spectroscopies, such as XAS and XPS, are powerful tools for studying catalysts. XAS, including XANES,

provides information about elemental composition and oxidation states and is well-suited for in situ and operando studies. XPS, a surface-sensitive technique, reveals surface composition and chemical states but has limitations under high pressure due to photoelectron scattering. This challenge is addressed by ambient-pressure XPS (AP-XPS), which extends XPS capabilities to more realistic conditions using synchrotron radiation. AP-XPS enables detailed analysis of surface chemistry and active phases during reactions, often providing insights not accessible through ex situ methods.

The oxidation state of the individual elements in the different HMEA samples obtained after reduction in H<sub>2</sub> was studied using X-ray photoelectron spectroscopy (XPS). For this analysis, the HMEA samples were exposed to H<sub>2</sub> at different temperatures (100, 200, 300, and 400 °C) in the XPS prechamber, followed by vacuum evacuation of the gas, ensuring that any contact with air does not occur before the measurement. These analyses (Fig. S14) also provide a qualitative assessment of the relative amounts of each metal on the surface of the sample after reduction at different temperatures. High-resolution Co 2p XPS spectra of the fresh and reduced samples exhibit asymmetric peaks. This asymmetry can be attributed to the presence of two main contributions at approximately 784 and 779 eV, corresponding to oxidized Co<sup>2+</sup> and metallic Co<sup>0</sup> species, respectively. Due to the limited spectral resolution, quantitative deconvolution of these contributions is not reliable. However, a shift of the main band from 778.3 to 777.7 eV is observed with increasing reduction temperature, which is indicative of alloy formation with less electronegative elements such as Fe or Mn.<sup>70</sup> The Fe 2p high-resolution XPS spectrum of the fresh sample shows three peaks at 707.1, 710.9, and 715.5 eV, corresponding to Fe<sup>0</sup>, Fe<sup>2+</sup>, and Fe<sup>3+</sup> species, respectively. Upon reduction, the Fe<sup>3+</sup> contribution disappears, and Fe<sup>2+</sup> remains the dominant species up to 300 °C. After reduction at 400 °C, the spectrum can be deconvoluted into two peaks at 707.8 and 706.0 eV, indicating the formation of more reduced Fe species. Overall, increasing the reduction temperature leads to a higher fraction of metallic iron. For Ni, two main peaks are observed in the fresh sample and in samples reduced at 200, 300, and 400 °C, located at 855.8 and 856.1 eV, which are assigned to Ni<sup>0</sup> and Ni<sup>2+</sup> species, respectively. With increasing reduction temperature, these peaks shift toward lower binding energies, similar to the behaviour observed for Co, consistent with an alloy formation. In contrast, the sample reduced at 100 °C exhibits a single Ni peak at 854.7 eV, which does not follow the general trend observed for the other metals upon increasing reduction temperature. For Mn, the XPS results indicate that oxidized Mn species (~641 eV) remain stable at the surface across all reduction temperatures investigated. This suggests that Mn is not reduced under any of the applied H<sub>2</sub> treatment conditions. Overall, while Co and Ni are partially reduced to metallic and alloyed states at relatively low temperatures, Fe



remains predominantly oxidized until reduction at 400 °C, and Mn remains oxidized regardless of the reduction treatment.



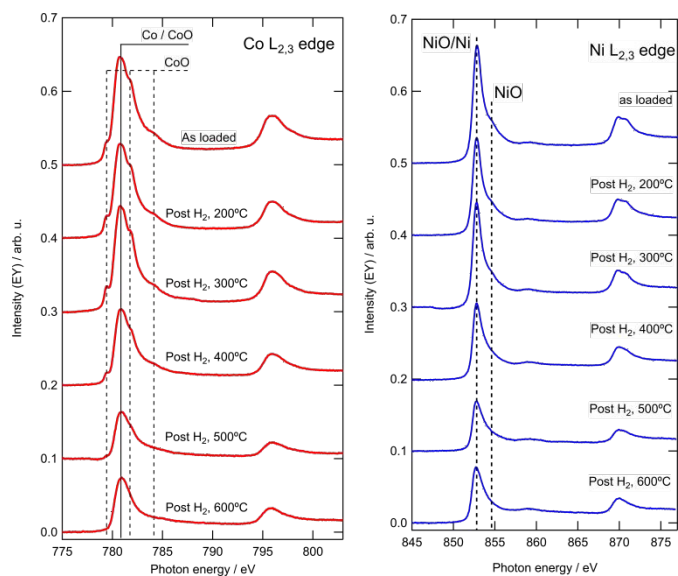
**Fig. 5** X-ray absorption spectroscopy (XAS) spectra of Mn  $L_{2,3}$  edges (left) and Fe  $L_{2,3}$  edges (right) recorded in high vacuum at 22–37 °C, as-loaded and after the progressive anneal steps. Spectra are collected via electron yield, normalised to the  $I_{\text{zero}}$  signal, background subtracted, and offset for clarity. Dashed lines indicate feature of the common oxides.

A deeper analysis was performed using near-ambient pressure (NAP) X-ray photoelectron spectroscopy and X-ray absorption spectroscopy (XAS) measurements (see SM for details in sample preparation, instrumentation and data collection). All the elements in the outer several nanometres of the HMEA nanoparticles of the as-loaded sample, which had been annealed to 800 °C in vacuum, were oxidised (Fig. 5 and 6). In agreement with the previous characterisation techniques, the Zn  $L_{2,3}$  edge was not observed (data not shown).

Fig. 5 shows that manganese is originally present as a mixture of oxides (top spectrum, Fig. 5a). Mild annealing to 200 °C in  $H_2$  is sufficient to drastically change the spectrum with the result resembling that of MnO. Further annealing does not lead to further changes and reduction beyond Mn(II). The spectrum obtained after annealing to 600 °C matched the earlier published spectra for MnO.<sup>71</sup> To quantify the intermediate spectra, the 600 °C spectrum was subtracted (after scaling), resulting in a spectrum that appears like  $Mn_3O_4$ . The  $Mn_3O_4$ /MnO ratio obtained was 3 (for the as-loaded sample) by measuring the relative edge jumps, describing an exponential drop, with hardly noticeable contribution from 500 °C onwards. The Fe  $L_{2,3}$  edges show that the initial spectrum is a combination of Fe and  $Fe_2O_3$  (Fig. 5, right). The spectrum only starts to give visibly changes after annealing to 400 °C. The final spectrum indicates fully reduced Fe. Focusing on the  $Fe_2O_3$ :Fe ratio, we can observe that  $Fe_2O_3$  reduction started already after the first anneal step, generally following a linear trend. The initial ratio

was 5:2, while the final spectrum did not show any contribution from  $Fe_2O_3$ .

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**Fig. 6** X-ray absorption spectroscopy (XAS) spectra of Co  $L_{2,3}$  edges (left) and Ni  $L_{2,3}$  edges (right) recorded in high vacuum at 22–35 °C, as-loaded and after the progressive anneal steps. Spectra are collected via electron yield, normalised to the  $I_{\text{zero}}$  signal, background subtracted, and offset for clarity. Dashed lines indicate feature of the common oxides.

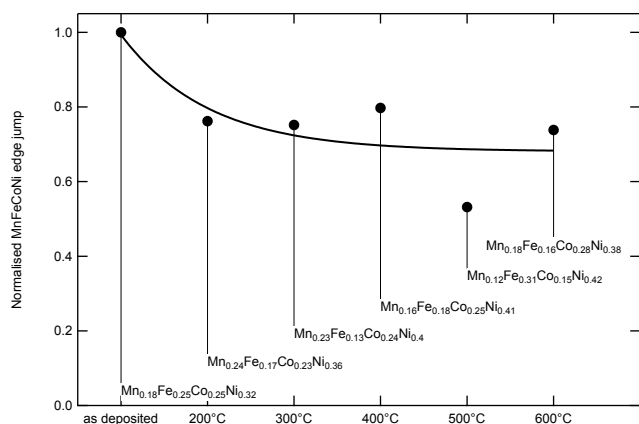
Fig. 6 shows that the same measurements were performed for the Co  $L_{2,3}$  and Ni  $L_{2,3}$  edges, in order to analyse their reduction behaviour. The results indicate that achieving a fully reduced Co signal requires annealing at temperatures up to 500 °C (left). In contrast, the NiO band gradually diminishes and completely disappears after annealing at 400 °C, suggesting that Ni is more easily reduced under these conditions compared to Co.

The XPS analysis of the HMEA-800 sample shows that, apart from a gradual intensity attenuation, the C K edge spectra (Fig. S15) of the powder as-loaded and after the anneal steps are quite similar and resemble previously reported spectra for graphite.

Near edge X-ray absorption fine structure (NEXAFS) spectra were then recorded (Fig. S16). The survey of the as-loaded HMEA-800 shows that most of the signal stems from carbon (C1s at  $248.9 \pm 0.2$  eV) and in much lesser extent from oxygen. Notice that the photoionisation cross section of O1s is roughly 3 times higher than C1s at a photon energy of 1200 eV, therefore, the C1s should be 3 times more intense. This C signal originates from the pyrolyzed organic linkers of the MOF, having become the support of the HMEA nanoparticles, while the latter could be located in the support as well as in oxidised HMEA nanoparticles. The O1s peak position of  $531.7 \pm 0.2$  eV and the FWHM of 4.8 eV suggest both cases. The spectra have clearly discernible features, (I) a strong peak assigned to the  $1s \rightarrow \pi^*$  transition at 285.3 eV and a peak with distinct shoulder (III & IV), which are typically assigned to  $1s \rightarrow \sigma^*$  transitions. In between, there are contributions of states associated with the oxygenates, such as oxidised carbon or adsorbed water (II). With increasing anneal temperature, these species disappear, consistent with



desorption/reduction. The intensity difference between below and above the absorption edge decreased with increasing anneal temperature, and this so-called edge jump is a quantitative measure for the amount of measured carbon.

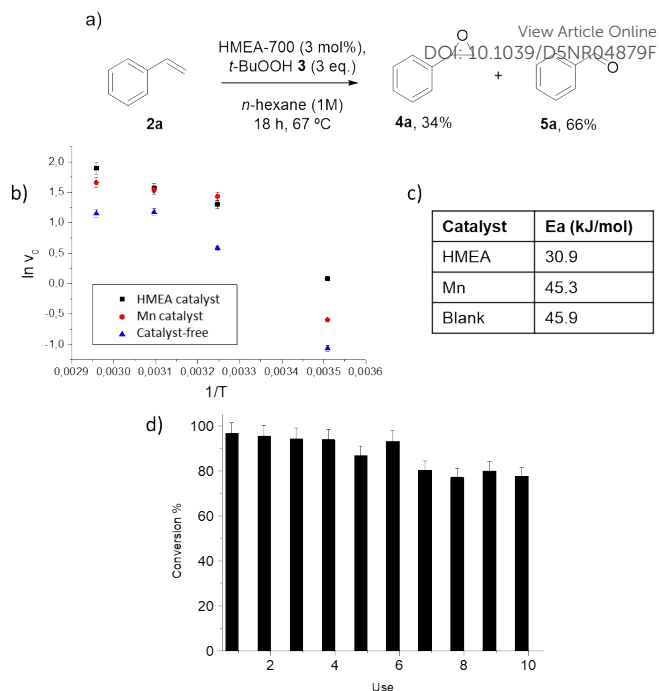


**Fig. 7** Total edge jump of the HMEA sample and normalised to the as-loaded sample. An exponential fit is plotted to guide the eye. Molecule formulae give the average particle composition in the near surface region for all data points.

The total edge jump, i.e., the summed edge jumps of the four metals, showed a modest intensity decrease of around 30% with increasing the annealing temperature. The NEXAFS spectra measured via electron yield are surface sensitive, probing the region within a few nanometres of the surface (see Fig. S16). So, the reduction in total edge jump originates from a reduction of the total surface area of the HMEA particles. Because the as-loaded sample had already been annealed in vacuum to 800 °C, higher than probed in the *in situ* NEXAFS measurements, the surface area reduction can be linked to the H<sub>2</sub> atmosphere. In this way, an estimated average composition in the near surface region for the HMEA particles can be calculated, and the results shown in Fig. 7 indicate that the NP is enriched in Ni, as it was also observed by *ex situ* XPS analysis after the reduction processes (see Fig. S14). Overall, one can say that the composition of the HMEA-NP surface is a truly equimolar mixture of Mn, Fe, CO and Ni, somewhat enriched in the latter.

#### HMEA-700 as a heterogeneous catalyst for the alkene oxidation reaction.

The small size and narrow distribution of the alloyed NPs in the HMEA-700 material, with a rather considerable surface/volume ratio, together with the high surface area obtained (274.5 m<sup>2</sup> g<sup>-1</sup>), prompted us to test this material as a catalyst for an organic reaction. We studied the oxidation of styrene **2a** with an excess of *t*-BuOOH **3** (3 equivalents), as shown in Fig. 8. This oxidation reaction requires the concomitant activation of the alkene and the peroxide on metal atoms.<sup>72–74</sup> Gratifyingly, complete conversion of **2a** to styrene epoxide **4a** and benzaldehyde **5a** was observed when using a 3 mol% of HMEA NPs, with a selectivity **4a:5a** of 1:2.



**Fig. 8** (a) Reaction scheme and first results for the oxidation of styrene **2a** with *t*-BuOOH **3** (3 equivalents) catalysed by HMEA-700 (3 mol%) in *n*-hexane as a solvent. (b) Arrhenius curves for the calculation of the activation energy for the HMEA catalyst, the Mn catalyst and a blank reaction. (c) Activation energies. (d) Reuses of HMEA-700 solid catalyst. The selectivity epoxide/aldehyde keeps similar to the first use (see also Table S2). Error bars account for 5% uncertainty.

The presence of Mn-rich NPs on the material arises the question of which types of NPs are actually responsible for the catalytic activity observed in HMEA-700 NPs for the styrene oxidation reaction (the FeCoNiMn NPs or the Mn NPs). In order to determine this, a batch of Mn NPs were synthesized by the impregnation methods (see Fig. S10 for characterization) and tested for the reaction. Fig. 8b and 8c show the calculated activation energy for the reaction (see also Fig. S17 for complete kinetics at different temperatures between 20 and 65 °C), and the Mn catalyst did not give any significant variation compared to the blank, while the HMEA solid present a considerably lower activation energy (30.9 kJ/mol) respect to the blank experiment (45.9 kJ/mol). Even at the highest temperature used, the initial rate of the HMEA-700 is superior to Mn and blank tests strongly supporting that the FeCoNiMn NPs are actually the active species for the oxidation of styrene. Moreover, we also tested the stability of them by hot filtration test, observing a minor activity from any leached species (Fig. S18). Any auto-oxidation process triggered by the catalyst in combination with the O<sub>2</sub> in the air can be excluded since the reaction operates similarly to the blank experiment when the catalyst is removed. Besides, the oxidation of benzyl alcohol in the presence of HMEA-700 (0.8 mol%) under neat O<sub>2</sub> (3 atm) only gave an 8 % conversion and a 5 % yield of benzaldehyde **5a** after 78 h, discarding any O<sub>2</sub>-triggered, free-radical autooxidation process (Fig. S19). Additionally, the oxidative cleavage of styrene **2a** in the presence of BHT as free-radical scavenger was performed with yields around 90% with only 0.8 mol% of HMEA-700 (Fig. S20),

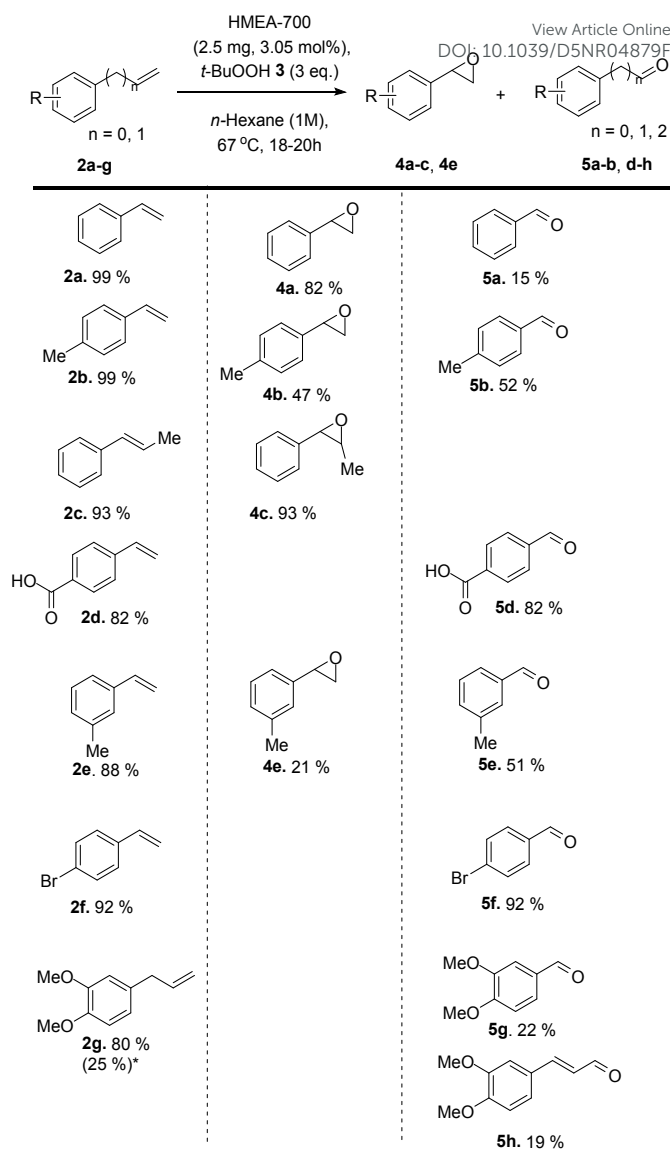


corroborating that the reaction does not follow a free-radical pathway. In accordance, the reaction under N<sub>2</sub> atmosphere gave the same result than under air.

In accordance with the robustness of the HMEA-700 and the lack of leaching during reaction, Fig. 8d shows that the catalyst can be reused up to 10 times conserving most of the catalytic activity (with 78 % conversion in the 10<sup>th</sup> use, see Table S2 for the selectivity results). It is true that a loss of 21% is significant, however, this is after 10 cycles, thus a loss of 2.1% per reuse in average occurs, which might be considered acceptable for a complex supported metal catalyst under oxidizing reaction conditions. Indeed, the final conversion obtained after 10 times is still more than twice the conversion obtained without catalyst (40 %). Please notice that reuse experiments at intermediate conversion will be near of the blank (40% conversion), thus the results might be confused with the blank and not be representative of the catalytic activity loss.

The catalytic results obtained for styrene **2a** was compared with previous results for the synthesis of the epoxide **4a** in the literature, under similar reaction conditions (Table S3).<sup>75</sup> It can be seen that the 82% yield of **4a** obtained is among the best results reported,<sup>76–78</sup> with the additional advantage that our catalyst here is easily recovered and reused. These results must be remarked in the context of modern sustainable synthesis with supported metal nanoparticles.<sup>79,80</sup>

At this point, the scope of the oxidation reaction catalysed by the HMEA-700 solid was studied. It must be remarked here that the scope study was performed with 2.5 wt% of the solid catalyst, which account for ≈3 mol% of metals. Fig. 9 shows that a variety of styrene and allylbenzene derivatives **2a–g**, including terminal and internal alkenes, can undergo the oxidative cleavage reaction catalysed by HMEA-700, with moderate to high yields. In some cases, the selectivity of the reaction was very good, and the internal styrene **2c** gives the epoxide as the only product (**4c**), while Br and methoxy groups in the para position of the ring direct selectively to the aldehyde products (**5f** and **5g**). The turnover number (TON) of the metal catalyst approaches 30 in some cases (the TON is calculated as moles of **4a** produced/moles metal atoms). Other styrene derivatives proved being reactive, but a complex mixture of oxidative breaking products was obtained under the catalytic reaction conditions (Fig. S21). Moreover, an alkyl alkene such as 7-tetradecene was also tested under these reaction conditions, obtaining a mixture of oxidative breaking compounds in the presence of the HMEA catalyst (Fig. S22). H<sub>2</sub>O<sub>2</sub> was tested as an oxidation agent and it was found unreactive either with HMEA-700 catalyst or not (Figure S23).

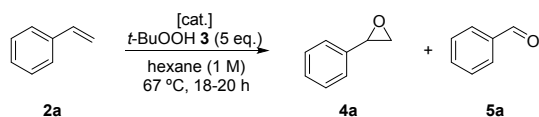


**Fig. 9** Scope of the HMEA-700 catalysed oxidative cleavage of alkenes. Conversion (**2**) and yields (**4,5**) calculated by GC, using *n*-dodecane as internal standard. Conditions: 1 mmol alkene **2**, 3 eq of *t*-BuOOH **3**, 1 mL hexane, 2.5 mg HMEA-700 (3.05 mol%), 67 °C, 18–20 h. \*Unidentified oxidative products.

### Comparison of the HMEA-700 catalyst with the individually supported monometallic catalysts.

To demonstrate the potential synergic effect of FeCoNiMn NPs of HMEA-700 in the catalytic oxidative cleavage, monometallic carbon-supported catalysts with Mn, Co, Ni, Fe and even Zn were prepared by impregnation methods (see Fig. S10, S24–27 for characterization) and tested as catalysts. Table 1 shows that, for the oxidative cleavage of styrene **2** with a metal loading of HMEA-700= 3.05 mol% and with large excess of *t*-BuOOH **3** (5 equiv.), the monometallic-carbon materials of Fe, Ni and Zn showed yields under 63%; while Mn, Co and HMEA-700 materials exhibited a better performance with yields over 96%.

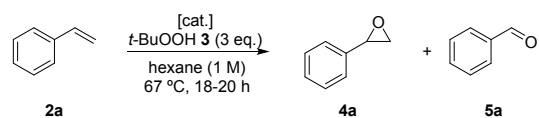




**Table 1** Comparative of oxidative cleavage catalysed by HMEA-700 and monometallic carbon-supported metal NPs with 5 equivalents of *t*-BuOOH. Conversion (**2a**) and yields (**4a,5a**) calculated by GC, using *n*-dodecane as internal standard. Conditions: 1 mmol styrene **2a**, 5 equiv. of *t*-BuOOH **3**, 1 mL hexane. Turnover number (TON) considers all metal atoms in the NPs.

Entry	Catalyst	Mn	Metal load (mol %)				Conv.	Yield (%)		TON
			Co	Fe	Ni	Zn		4a	5a	
1	HMEA-700	0.6	0.8	0.8	0.8	-	>99	80	20	33
2	Mn (C)	0.6	-	-	-	-	96	86	10	147
3	Co (C)	-	0.8	-	-	-	>99	85	15	124
4	Fe (C)	-	-	0.8	-	-	63	58	5	78
5	Ni (C)	-	-	-	0.75	-	49	45	4	65
6	Zn (C)	-	-	-	-	0.4	52	48	4	130

These results indicate that the monometallic catalysts, by separate, perform better than the HMEA-700 catalyst, particularly if TONs are considered (supposing all metal atoms in the NPs). However, taking in account that the HMEA-700 catalyst requires much less solid than the combination of individual supported metals to be added into reaction, this has obvious physical advantages for HMEA-700 (with 97% yield) respect to the physical combination of all individual metals, but not to the Co and Mn materials (88% and 72% yield, respectively), as shown in Table 2. The same result was obtained with 1.5 equivalents of *t*-BuOOH **3** (Figure S28).



**Table 2** Comparative of oxidative cleavage catalysed by HMEA-700, Mn(C), Co(C) and the physical mixture of all individual metals with 3 equivalents of *t*-BuOOH. Conversion (**2a**) and yield (**4a,5a**) calculated by GC, using *n*-dodecane as internal standard. Conditions: 1 mmol styrene **2a**, 3 equiv. of *t*-BuOOH **3**, 1 mL hexane. Zn is not shown since there is not any. Turnover number (TON) considers all metal atoms in the NPs.

Entry	Catalyst	Metal load (mol %)				Conv. (%)	Yield (%)		TON
		Mn	Co	Fe	Ni		4a	5a	
1	HMEA-700	0.65	0.8	0.8	0.8	97	82	15	31
2	Mn (C)	0.65	-	-	-	72	65	7	111
3	Co (C)	-	0.8	-	-	88	74	14	100
4	Mn+Co+Fe+Ni (C)	0.65	0.8	0.8	0.8	97	80	17	31

## Experimental

**Synthesis of MOF 1.** The synthesis of MOF **1** was performed after modifying a previously reported procedure.<sup>61</sup> Briefly, 1 mmol of each metal salt: Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Fe(SO<sub>4</sub>) or FeCl<sub>2</sub>, and 2.5 mmol of the organic linker 2,5-dihydroxyterephthalic acid (H<sub>4</sub>DOT) were dissolved in 60 mL of DMF/EtOH/water (in a 15:1:1 v:v ratio, respectively)

and heated to 120 °C for 20–24 h in an autoclave. The resulting crystals were washed 3 times with 50 mL of fresh DMF solvent, and soaked in MeOH for solvent exchange (3 exchanges over a 3-day period). The resulted material was then activated under vacuum (100–200 mTorr) overnight at 80 °C, to remove all the solvent.

**Synthesis of the supported HMEA-NPs.** A portion of MOF **1** was transferred to the quartz tube reactor and connected to a vertical calcination oven equipped with a N<sub>2</sub> inlet. The gas flow was set up at 100 mL/min for each experiment. The temperature and heating ramp was adjusted separately, and the same sample of material was pyrolyzed at different temperatures 400 °C (5 °C/min), 550 °C (5 °C/min), 700 °C (5 °C/min) and 800 °C (10 °C/min) for 5 h. Pyrolysis at all temperature except 800 °C were followed by reduction with H<sub>2</sub> (100 mL/min) at 400 °C for 4 h. After each pyrolysis, a small portion of the material was separated and saved for further characterization, in order to follow the morphological changes.

**Synthesis of Metal-C-NPs.** A round bottom flask containing the one of the selected nitrate salts: Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O or Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.8 mmol) and methanol (50 mL) is placed in an ultrasonic bath for 5 minutes. Active carbon (1g) is added, and the suspension is sonicated for 2 h at rt. Then, methanol was removed on a rotary evaporator, adjusting the bath temperature at 40 °C. The solid was transferred to a crystallizing dish and dried at 100 °C for 12 h. Then, the reaction mixture was cooled down to room temperature and grounded to a powder. The powder was placed in a quartz glass tube reactor and connected to vertical reduction oven. The reactor was flushed with N<sub>2</sub> for 10 min and then reduced with H<sub>2</sub> (100 mL/min) at 400 °C for 4 h (heating ramp 5 °C/min). As-prepared carbon-supported catalytic materials were characterized by ICP-OES and powder X-ray diffraction.

**General procedure for the oxidative cleavage of styrene derivatives catalysed by HMEA-700 NPs.** Typically, a styrene derivative **2** (1 mmol), hexane (1 mL, 1M) and HMEA-700 (2.5 mg) are placed in a reactor flask containing a stirring bar. Then, *tert*-butyl hydroperoxide **3** solution (5.0–6.0 M in *n*-decane, 3 mmol) is added, and the reaction is stirred in a pre-heated oil bath or a steel block at 67 °C (or the desired temperature for the calculation of the activation energy) for 18 h. Distilled water is added to quench the reaction, and the mixture is extracted with diethyl ether and filtrated if necessary. The products are analysed by GC, GC-MS and <sup>1</sup>H NMR in order to determine the structure. The GC conversion is calculated by the loss of starting material compared to an internal standard (*n*-dodecane) at time = 0 s, and also when finishing the reaction. The yields of each product are calculated by GC, considering the response factors calculated for, for instance, styrene, styrene oxide and benzaldehyde (Fig. S28).

## Conclusions



Well-defined high and medium entropy alloy NPs were successfully obtained by pyrolysis of a multi-metallic MOF at 700 °C under inert atmosphere (N<sub>2</sub>). The examination on the morphological changes during the pyrolysis treatment at different temperatures (400 °C, 550 °C, 700 °C and 800 °C) showed that the particle size and distribution can be controlled by adjusting the experimental conditions. The composition of the NPs strongly resembles the pristine MOF's crystals composition, also preserving the original shape. A temperature of 700 °C was optimal, with uniformly dispersed alloy NPs of narrow size distribution (~10 nm), combining 4 transition metals (Fe, Ni, Co, Mn) in one alloy NP. These structural characteristics reflect on its catalytic performance,<sup>83,84</sup> and the solid material catalyses the oxidative cleavage of alkenes in good yields and is reusable for 10 times. Despite the monometallic counterparts can also efficiently catalyse the reaction, with higher TONs than the HMEA, the results here indicate that stable HMEA nanoalloyed particles supported on a carbonaceous material can be prepared from MOFs in a particle-to-particle fashion and be used as efficient and recyclable catalysts in a relatively complex organic reaction,<sup>85,86</sup> with future potential application in other relatively complex organic reactions and also in the field of electrocatalysis.

### Author contributions

A. N., A. L.-T. and A. S.-M. synthesized and characterized the materials. J. O.-M. and M. A. v. S. designed and performed the in-situ characterization of the materials. A. L.-T. conducted the catalytic and kinetic experiments. A. S.-M. conducted the catalytic experiments with monometallic materials. A. L.-P. conceived the idea and supervised the project. All authors contributed to the discussion, participated in the writing of the original draft, and revised the manuscript.

### Conflicts of interest

There are no conflicts to declare.

### Data availability

A document with the supplemental experiment procedures, Tables S1-S4, and Figures S1-S28 can be found as Supplementary Material. The new HMEAs materials are available under reasonable request. The data that support the plots within this paper, and other finding of this study, are available from the corresponding authors upon reasonable request.

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### Data availability

A document with the supplemental experiment procedures, Tables S1-S4, and Figures S1–S28 can be found as Supplementary Material. The new HMEAs materials are available under reasonable request. The data that support the plots within this paper, and other findings of this study, are available from the corresponding authors upon reasonable request.

