



Nanostructured hybrid materials as precursors of mesoporous NiMo-based catalysts for the propane oxidative dehydrogenation



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ABSTRACT

Nanostructured hybrid materials made of guest ions and a self-assembled copolymer were used as precursors for the preparation of NiMo-based catalysts. The hybrids were calcined in air and the recovered materials were characterized and tested in propane oxidative dehydrogenation. A 6-fold improvement of the yield to propene is obtained as compared with classically prepared catalysts. The exothermic degradation profile of the copolymer is the key point of our approach as it allows to prepare a porous β -NiMoO₄, namely the phase particularly desired for its superior propene selectivity. More precisely, the polar backbone and the aliphatic side chains of the copolymer burn at different temperatures. The former ignites at moderate temperatures and initiates the early crystallization of β -NiMoO₄. Occurring at higher temperature, the decomposition of the aliphatic part then induces the formation of mesopores. A β -NiMoO₄ can thus be prepared at moderate temperatures whereas elevated calcination temperatures (>650 °C) are usually required. This peculiar behavior enables to prevent the texture of NiMoO₄ from sintering and to maintain at high levels its mesoporosity, specific area and thus catalytic activity. At the end, the use of our tailor designed copolymer template allows reaching the remarkably high propene yields obtained.

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1. Introduction

The development of new catalysts still remains a challenge in order to answer the growing demand for sustainable and environmentally-friendly chemical processes. Less waste of resources and higher efficiency are key indicators that should characterize the future chemical processes including those based on heterogeneous catalysis [1,2]. Therefore, the improvement of the physico-chemical properties responsible for better catalyst performances represents a widespread objective [3–5]. The synthesis method developed here is in line with this philosophy. We specifically target the oxidative dehydrogenation of propane to propene (ODHP). This reaction was chosen as it falls in with the efforts to valorise the light alkanes (C₂ – C₄) coming from natural gas [6,7]. Nickel molybdates, in particular, are here considered as they are known to activate propane [3]. Whereas non-porous α -NiMoO₄ are

generally synthesized, nanostructured and mesoporous β -NiMoO₄-based catalysts are especially targeted, and obtained thanks to a tailor designed hybridization strategy.

Two crystallographic phases of nickel molybdates are distinguished at atmospheric pressure: α -NiMoO₄ and β -NiMoO₄. Ni atoms occupy octahedrally-coordinated sites in both isomorphs, but as main structural difference, Mo atoms are located in octahedral or tetrahedral sites, respectively [8]. The α -phase is the most active in the ODHP reaction thanks to its high specific surface area, but is poorly selective to propene. At the opposite, β -NiMoO₄ is much more selective in the oxidation of several hydrocarbons [8,9]. However, it is metastable beyond 200 °C and its synthesis requires elevated calcination temperatures (>650 °C) [3,10]. The sintering occurring at such a high temperature diminishes the specific surface area and makes β -NiMoO₄ a poorly active material. To overcome this issue, numerous studies tried to stabilize β -NiMoO₄ without using harsh synthesis conditions. One effective strategy consists of the synthesis of supported NiMoO₄. Thanks to structural and chemical effects, the β -phase can thereby be stabilized on Al₂O₃ [11], SiO₂ [12–14], TiO₂ [15] or activated carbon [11]. The preparation of bulk co-precipitated NiMoO₄ having an excess of Ni (Ni/

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Mo > 1) is another widespread way. The nickel excess is indeed believed to form a solid solution within the β -NiMoO₄ network and thus to prevent the $\beta \rightarrow \alpha$ relaxation [11,16].

A third possibility rests on the use of organic additives like oxalic acid, citric acid or even agar-agar gel [13,16–19]. In such preparation protocols, the exothermic combustion of the organic fraction seems to facilitate a rapid crystallization of β -NiMoO₄. Up to now, this approach has given encouraging results in the ODHP reaction. However, the mechanisms and the parameters behind the corresponding synthesis approach remain badly understood and thus are not really controlled. The clarification of these aspects was envisaged in this work. Therefore, NiMo-based oxides were here prepared from nanostructured hybrid materials associating guest ions (Ni and Mo precursors) and a tailor designed self-assembled comb-like copolymer displaying different types of carbon species [20]. The copolymer plays the role of the organic compound.

In addition, an improvement of the NiMoO₄ textural properties is also desired so that the obtained bulk oxides develop a high specific surface area, maximizing the number of accessible sites, and thus the catalytic activity [21]. To simultaneously address this challenge, we also take advantage of the organization of our copolymer. During the calcination, the copolymer combustion is expected to liberate an organized volume corresponding to the creation of pores and should contribute to raise the NiMoO₄ specific surface area [22,23]. The calcined hybrids were characterized and tested in the ODHP reaction. Thermogravimetric analysis and scanning differential thermal analysis (TGA/SDTA) experiments were also carried out as the transformation of hybrids into mixed oxides is believed to be a decisive step. The properties and the catalytic performances of NiMoO₄ made via our hybridization approach were compared with those of a reference co-precipitated material. This comparison helped evidencing advantages and drawbacks linked to the use of our copolymer to prepare NiMo-based oxides being more efficient in catalysis.

2. Experimental

2.1. Synthesis of materials

The used comb-like copolymer (C12 matrix) results from the alternated copolymerisation of maleic acid with a diallylammonium salt substituted by a dodecyl side chain (Fig. 1). More details about the copolymer synthesis are available in Rullens et al. work [24]. A reference polymer (Homo-C12 matrix), made through the homopolymerisation of the diallylammonium salt, was also used in order to understand in more detail the combustion profile of the copolymer (Fig. 1). To synthesize hybrid materials, the C12 matrix was first dispersed in ethanol (99.9%, VWR). The suspension was then stirred overnight before the addition of distilled water and the adjustment of the pH (between 6.0 and 6.5) by using diluted NH₃ (5 mol L⁻¹, Sigma-Aldrich). Ni(NO₃)₂·6H₂O (>97%, Merck) and (NH₄)₆Mo₇O₂₄·4H₂O (>99%, Merck) were separately dissolved in distilled water and successively added to the copolymer solution. The copolymer was saturated in ions by adding 0.5 mol of nickel ions (Ni) and 0.5 mol of molybdenum ions (Mo) per 1 mol of copolymer repeating units. The addition of a larger ion amount is not recommended to prevent a substantial crystallisation of α -NiMoO₄ which is harmful for the propene selectivity of the final NiMo-based oxides [20,25]. The pH was kept constant during the whole ion addition by using diluted NH₃. The final solution was stirred for 2 h and freeze-dried in order to recover the hybrid material. A reference sample containing the copolymer only was also prepared via this protocol. The hybrids were then calcined for 4 h, in static air, in a muffle oven and at a temperature included between 300 and 550 °C. A reference catalyst (NiMo-Cop) was also

prepared via the co-precipitation method detailed by Del Rosso et al. and calcined for 4 h at 550 °C in air [8,9]. A 5 °C/min ramp was used to reach the desired temperature.

2.2. Characterization

X-ray diffraction (XRD) was performed on a Siemens D5000 diffractometer using the K α radiation of Cu (λ = 0.15418 nm). Diffractograms were recorded in the θ/θ mode between 5 and 75° at a rate of 1.2°/min. The crystalline phases were identified by using the ICDD-JCPDS database.

N₂ physisorption was performed at –196.15 °C on a Micromeritics TriStar 3000 instrument. Each sample (about 120 mg) was outgassed overnight at 150 °C in vacuum (7 Pa) before the measurement. The specific surface area was evaluated by the BET method between 0.05 and 0.30 P/P°. The pore features (size, shape and size distribution) were deduced from the desorption branch using the BJH method.

Scanning electron microscopy (SEM) was performed on a LEO 983 GEMINI microscope equipped with a field emission gun. The uncoated samples were exposed to an acceleration voltage of 1 kV.

Thermogravimetric analyses (TGA) and simultaneous differential thermal analyses (SDTA) were performed on a Mettler Toledo TGA/SDTA 851 apparatus. The samples (about 10 mg) were heated in a 30 mL/min air stream. Their degradation profile was recorded by heating the analysis cell from 30 to 600 °C with a 5 °C/min raising ramp. Furthermore, a two-step program was designed to mimic the calcination of the hybrid materials. Therefore, the analysis cell was heated with a 5 °C/min ramp until the desired temperature (between 300 and 550 °C) before maintaining it at this temperature for 4 h.

X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra spectrometer (Kratos Analytical) equipped with a monochromatized aluminum X-ray source powered at 10 mA and 15 kV. The following sequence of spectra was recorded: survey spectrum, C1s, O1s, N1s, Ni2p, Cl2p and C1s again. Molar fractions (%) were calculated by using peak areas normalized on the basis of acquisition parameters, the subtraction of a linear background, experimental sensitivity factors and transmission factors provided by the manufacturer. Element molar fractions were provided, excluding hydrogen which is not detected by XPS. Further experimental details on the XPS analyses are provided in the Supporting Information.

2.3. Catalytic tests

The NiMo-based materials (150 mg) were tested in a U-shaped quartz reactor, at 475 °C and in a 40 mL/min total flow (C₃H₈/O₂/N₂ = 10/12.5/77.5 vol %). The propane stability was checked in presence of O₂ and no conversion without catalyst was observed. The analysis of the reaction mixture was carried out on an on line Varian gas chromatograph. A Hayesep column coupled with a Molecular Sieve column and a thermal conductivity detector were used to separate and quantify O₂, N₂, CO, CO₂, C₂H₄, C₃H₈ and C₃H₆. The detection and the quantification of oxygenates were managed by means of an EC-Wax column coupled with a flame ionization detector. Traces of ethyl propionate, acrylic acid and acetic acid were sometimes detected but not quantified. Satisfactory carbon balances were calculated from the catalytic results. In this work, the catalytic performances are expressed in terms of propane conversion, product selectivity and propene yield. Correction coefficients were used to calculate the selectivity of the products of less than three carbon atoms (CO₂, CO, etc.). Finally, the product selectivities were normalized to get rid of the experimental variability.

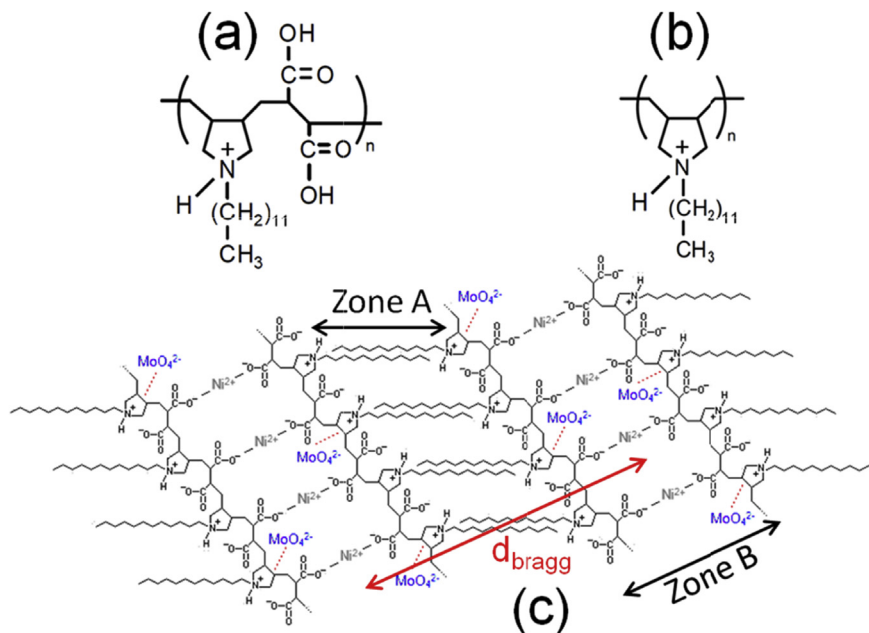


Fig. 1. Chemical structure of the C12 matrix repeating unit (a) and of the Homo-C12 matrix repeating unit (b), model envisaged for the supramolecular organization of the NiMo-C12 hybrid precursor (c, scheme redrawn from Farin et al. [20]). Hydrophobic (Zone A) and hydrophilic regions (Zone B) are distinguished.

3. Result

A self-assembled copolymer was used as a template agent for the preparation of NiMo-based materials. Its supramolecular organization results from hydrophobic interactions between its dodecyl side chains. It is evidenced by a low-angle peak of Bragg on its XRD pattern (Fig. 2). By using the Bragg law, the position of this peak is related to an interreticular distance (d_{Bragg}) repeated along the copolymer organization. For such a comb-like material, Rullens et al. envisaged a lamellar model based on the alternation of crystallized hydrophobic microdomains (Zone A) and amorphous hydrophilic microdomains (Zone B) (Fig. 1) [24,26]. Guest Ni and Mo ions were homogeneously dispersed along the copolymer thanks to the interactions they establish with the copolymer

charged moieties. These interactions promote the insertion of nickel ions inside the copolymer hydrophilic regions what induces an expansion of the copolymer organization [25,27]. The latter effect is suggested by the increase of the copolymer d_{Bragg} and the absence of XRD peaks related to inorganic NiMo-based crystalline phase on the diffractograms (Fig. 2). The scheme presented in Fig. 1 enables to conceptualize the organization of the hybrid precursor [20,25]. After their synthesis, the hybrid precursors were calcined in air.

In agreement with the literature, the XRD pattern of the NiMo-Cop sample displays α -NiMoO₄ as main crystalline phase [3,9]. One minor signal also reveals the presence of some β -crystals (Fig. 3A). At the opposite, the calcination of hybrids systematically induces the stabilization of a major β -phase even if α -NiMoO₄ is also detected. A β/α ratio was evaluated as a function of the calcination temperature (Fig. 3B). Precisely, for each sample, the area of the β -NiMoO₄ main peaks at $2\theta = 26.6$ and 27.2° was divided by the area of the α -NiMoO₄ main peak at $2\theta = 14.3^\circ$. For the β -phase, two peaks were considered as they were insufficiently resolved to evaluate their area separately. Increasing the calcination temperature progressively enhances the β/α ratio, indicating that higher temperatures favour the crystallization of the β -phase to the detriment of the α -phase.

According to the IUPAC nomenclature, the NiMo-Cop sample and the hybrids calcined at 300 and 350 °C display type II isotherms which reveal their non-porous nature (Fig. 4) [28,29]. However, the former is likely a finely divided powder as it possesses a not so small specific surface area (38 m²/g). The hybrid materials calcined at higher temperatures rather exhibit type IV isotherms finishing at high P/P° by an asymptotic increase of the N₂ uptake. The capillary condensation and decondensation of these isotherms reveal a H₃-type hysteresis loop at high relative pressures (0.46–0.98). These features are typical of mesoporous materials having plate-like particles that give rise to slit-shaped pores between them [28,30]. Increasing the calcination temperature beyond 400 °C progressively shifts the hysteresis to higher relative pressures and decreases the hysteresis area. This suggests the occurrence of sintering effects.

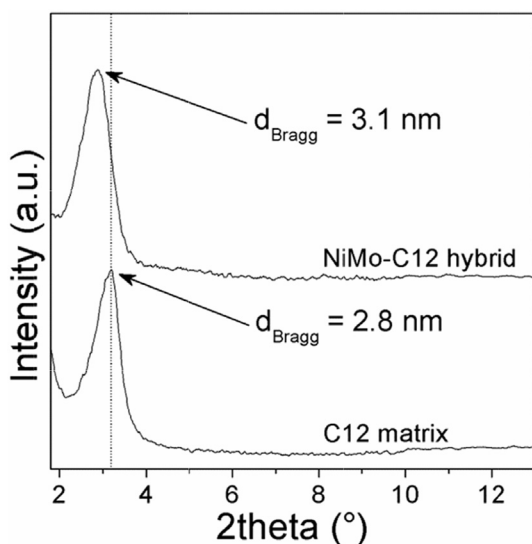


Fig. 2. Diffractograms of the C12 matrix and the NiMo-C12 hybrid. Exceptionally, they were recorded between 0.5–10° and 10–60° at a rate of 0.12 and 0.6°/min respectively.

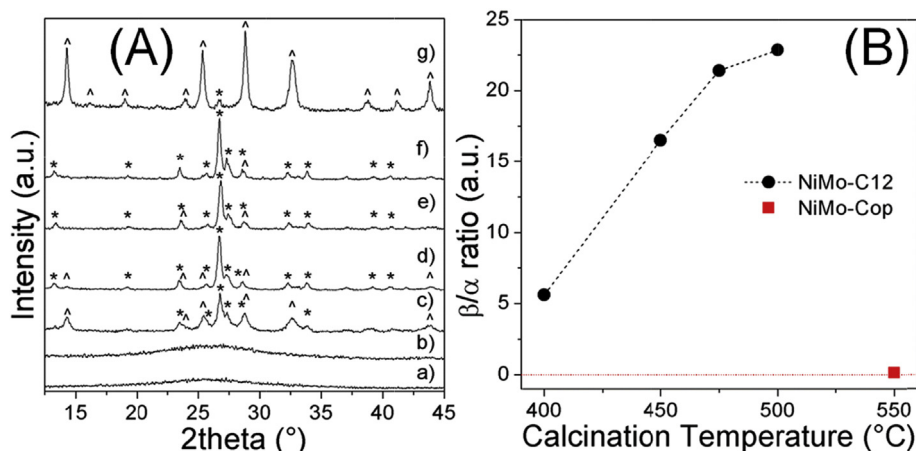


Fig. 3. (A) - X-ray diffractograms of the NiMo-C12 hybrid precursor calcined for 4 h at 300 °C (a), 350 °C (b), 400 °C (c), 450 °C (d), 475 °C (e) and 500 °C (f). The diffractogram of a co-precipitated material calcined for 4 h at 550 °C is also shown (g). α -NiMoO₄ (○) and β -NiMoO₄ (*) were both identified. (B) - Evolution of the β/α ratio of NiMoO₄ made from the NiMo-C12 hybrid as a function of the calcination temperature. The dotted red line represents the β/α ratio of a co-precipitated NiMoO₄. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

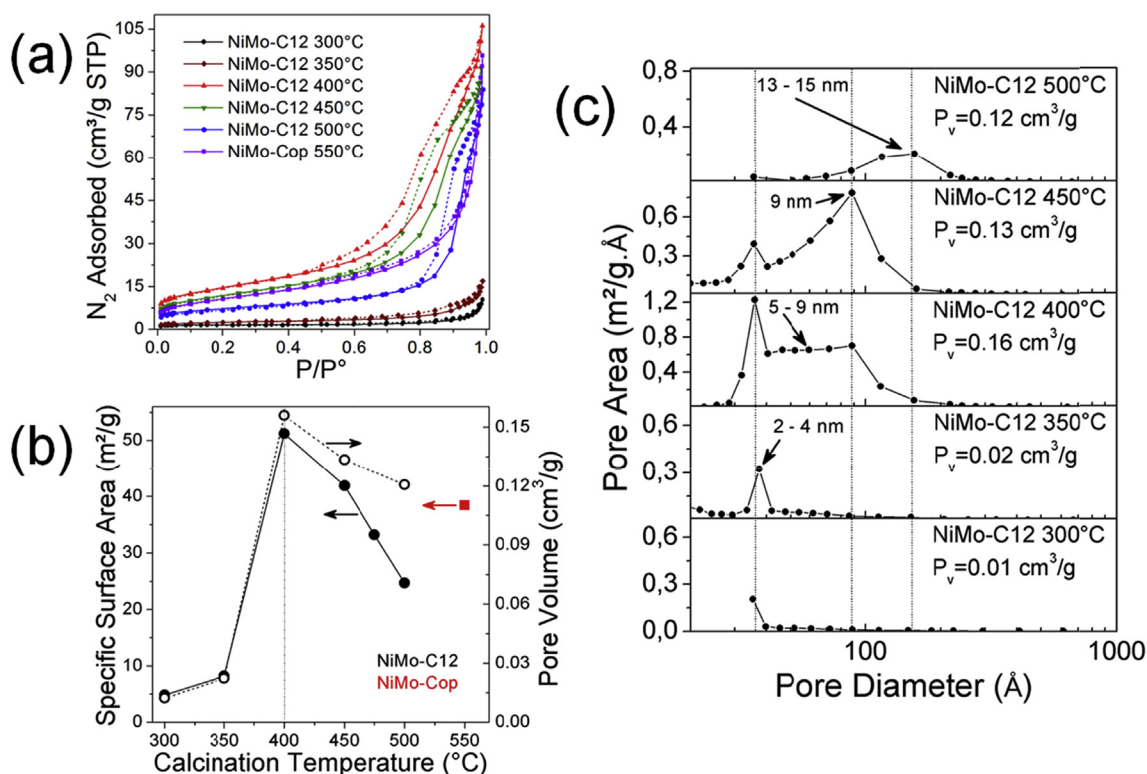


Fig. 4. Adsorption (solid line) and desorption (dotted line) N₂ physisorption isotherms of the NiMo-C12 precursor calcined at various temperatures. The isotherms of a co-precipitated material are also shown (a). Evolution of the specific surface area and the pore volume as a function the calcination temperature and the synthesis method (b). BJH pore distribution profile of the NiMo-C12 hybrid calcined at various temperatures (c).

The specific surface area of a NiMo-C12 hybrid calcined at 300 °C is low (Fig. 4). It progressively increases with the calcination temperature before reaching a maximum at 400 °C namely 51 m²/g. Beyond this maximum, a further increase of the temperature induces a specific surface area decrease. The pore volume and the specific surface area of calcined hybrids are maximized at the same temperature. The former also progressively increases with the calcination temperature before reaching a maximum. However, thermal treatments at more than 450 °C do not strongly affect the NiMoO₄ pore volume anymore. Besides, BJH pore size distribution

profiles reveal the existence of small mesopores (2–4 nm) when the NiMo-C12 precursor is calcined under soft conditions (350–400 °C) (Fig. 4). Increasing the calcination temperature leads to a progressive disappearance of these small mesopores in favor of larger mesopores.

The TGA derivative profile of the C12 matrix displays five signals around 45–60, 205–215, 240–260, 315–335 and 480–520 °C (Fig. 5). The first one (weight loss: 6.5%) is assigned to the desorption of the moisture trapped within the copolymer [31]. The second weight loss (weight loss: 21.0%) is attributed to the removal

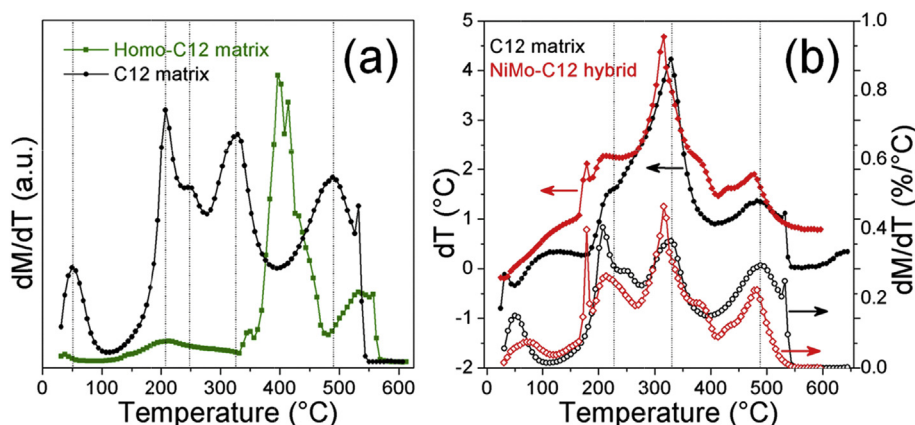


Fig. 5. TGA derivative profiles of the C12 and Homo-C12 matrices (a). TGA derivative (empty bullets) and SDTA (full bullets) profiles of the C12 matrix (black circles) and the NiMo-C12 hybrid (red diamonds) (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the strongly adsorbed residual water and to the decomposition of ammonia. The latter was used to buffer the pH of the solution in which the copolymer was dispersed [31]. The third peak (weight loss: 10.0%) is assigned to the degradation of the copolymer COO^- functions. This claim is strengthened by the absence of this signal on the TGA derivative profile of the Homo-C12 polymer which does not possess any carboxylic moieties. The fourth signal (weight loss: 30.5%) is attributed to the burning of the aliphatic part of the copolymer i.e. essentially the alkyl side chains. Indeed, organic components like surfactants, alkyl chains and so on, are known to burn around 300–400 °C in air [32–35]. Compared to the C12 matrix, the combustion of the Homo-C12 matrix aliphatic part is delayed by about 75 °C to higher temperatures (400 °C). The homopolymer thus appears more stable than the copolymer.

Finally, the fifth weight loss (weight loss: 32.0%) is attributed to the degradation of carbon residues formed during the copolymer burning [33,36]. However, the copolymer diallylamine cycles are known to be particularly stable and their degradation could then require high temperatures. Therefore, the signal observed around 480–520 °C could also reveal the diallylamine cycle combustion. The idea that a fraction of the C12 matrix cannot be degraded before 430 °C was confirmed by additional TGA experiments (Fig. 6). After a first temperature raise till 420 °C (5 °C/min), some hybrids underwent a second TGA analysis till 600 °C which also reveals an important weight loss around 480–520 °C. At this stage,

we speculate that this weight loss could be attributed to a fraction of each copolymer repeating unit namely a fragment of 9 methylene groups. This fragment could correspond to a diallylamine cycle that kept a part of its dodecyl side chain. The copolymer residue within calcined hybrids was also evaluated as a function of the calcination temperature (Fig. 6). It was deduced from TGA experiments that mimic the used 4 h calcination protocol. These experiments evidenced a complete degradation of the C12 matrix after calcination at 400 °C. This assumption is corroborated by XPS results. A similar carbon content is indeed observed in oxides prepared by both hybrid precursor and co-precipitation methods, while the latter is not based on the use of carbon matter. More information is available in the supporting information (Table S1).

Three exothermic signals can be distinguished on the C12 matrix SDTA profile namely at 200–230, 300–340 and 430–500 °C (Fig. 5). This is in line with the assignment of the corresponding TGA signals to different steps of the copolymer combustion. Besides, the endothermic SDTA signal observed below 110 °C is consistent with the removal of the water trapped within the matrix. The TGA derivative profile of the NiMo-C12 hybrid is similar to the one of the C12 matrix with the exception of one additional signal at 180 °C. This weight loss is partially attributed to a thermally induced oxidation-reduction reaction involving some copolymer COO^- functions and NO_3^- ions [4]. These nitrates come from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ used in the preparation of the hybrid materials. This

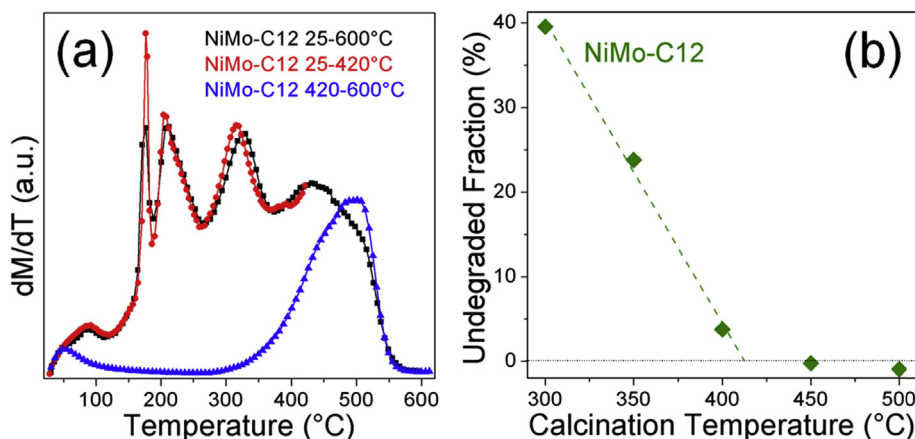


Fig. 6. TGA derivative profiles of the NiMo-C12 hybrid precursor (a), evolution of the undegraded fraction of the C12 matrix within the NiMo-C12 hybrid as a function of the calcination temperature.

process is known to be quite exothermic. At such temperatures, an endothermic decomposition of NO_3^- ions and NH_3 also occurs. It partially balances the exothermic process mentioned before [31]. This is why only a small signal is visible at 180 °C on the SDTA profile of the NiMo-C12 hybrid.

SEM pictures reveal the layered morphology of the NiMo-C12 hybrid at the macroscopic level (0.1–2 μm) (Fig. 7). This layered structuration likely comes from the original copolymer morphology and is somehow preserved after calcination (Fig. S1) [25]. SEM micrographs also show the finely divided nature of the co-precipitated NiMoO_4 which consists in the aggregation of nanometric hair-like particles tangled together.

Table 1 gathers the catalytic performances of NiMoO_4 made from co-precipitation and homogeneous hybrid materials. The NiMo-Cop sample presents a propane conversion of 12%. The calcined hybrids tend to be somewhat more active except the one calcined at 500 °C for 4 h. Besides, the NiMo-Cop sample rather deeply oxidizes propane into CO_x as its CO_2 (64.6%) and CO (20.1%) selectivities are both superior than its propene selectivity (14.4%). At the opposite, calcined hybrids preferentially produce propene to the detriment of CO_x . Calcination temperatures between 450 and 475 °C yield to most selective materials toward propene. Small quantities of ethene, acrolein, acetone, propanol and acetaldehyde were also detected but the sum of their selectivities never exceeds 5% (not shown). Compared to NiMo-Cop, calcined hybrids present a similar propane conversion but a better propene selectivity. Their propane yield is thus also superior.

4. Discussion

4.1. Improved propene selectivity thanks to the presence of beta phase

The calcination of hybrid precursors induces the crystallization of $\beta\text{-NiMoO}_4$ (Fig. 3). This result is interesting as this phase is normally metastable below 200 °C and makes NiMo-based oxides more selective in propene (Table 1) [9,37]. The preparation of bulk $\beta\text{-NiMoO}_4$ by using organic precursors has already been reported in the literature [16,17,19,35,38]. More particularly, first attempts to

use this copolymer precursor route with a similar C6 (hexyl) side chain on the diallylamine cycle [35], or more sophisticated formulations like diallyldimethylammonium cycles coupled with maleamic acids functionalized by N-methylpiperazine groups [38] resulted, after calcination at 600 °C, in mixtures of α - and β -phases of NiMoO_4 , and were successful in providing a pure β -phase only when Co was present, in the form of solid solutions $\text{Ni}_x\text{Co}_{1-x}\text{MoO}_4$. However, the reasons behind the stabilization of the β -phase at RT according to the various precursors and experimental conditions used still remain unclear. The exothermic degradation of carbonaceous matter seems to be the key point (Fig. 5). Our interpretation is that it promotes the crystallization of the β -phase at lower calcination temperatures than required when following a traditional preparation route as co-precipitation for instance. On the one hand, a rapid crystallization would lead to a difficulty to include all the nickel available within the precursor, making that a fraction of Ni can then stabilize the $\beta\text{-NiMoO}_4$ crystals by forming a solid solution with the mixed oxide network [3,16]. On the other hand, using moderate calcination temperatures (400–475 °C) enables to limit sintering and the ion mobility. The presence of defects linked to the rapid crystallization and the NiMoO_4 porosity (Fig. 4) also contributes to slow down the mobility of ions. As a result, the subsequent incorporation of the remaining nickel ions within crystals is partially hindered and thus prevents the $\beta \rightarrow \alpha$ relaxation at RT.

Increasing the β -phase purity is crucial to maximize the propene selectivity and appears sensitive to the calcination temperature (Fig. 3). According to the volcano curve presented in Fig. 8, a calcination temperature of at least 450 °C is necessary. In fact, such temperatures likely enhance the suddenness of the matrix combustion. This promotes the release of a punctual and dense amount of heat that favours the rapid crystallization of the β -phase to the detriment of the α -phase [39,40]. However, calcination temperatures >475 °C should not be used as they lead to structural modification of catalysts. For example, the sintering of isolated vanadium species into V_2O_5 crystals diminishes the propene selectivity of VO_x/SiO_2 materials in the ODHP reaction [41]. Here, higher calcination temperatures induce a further $\alpha\text{-NiMoO}_4$ crystallization and cause the formation of too reducible sites which promote the

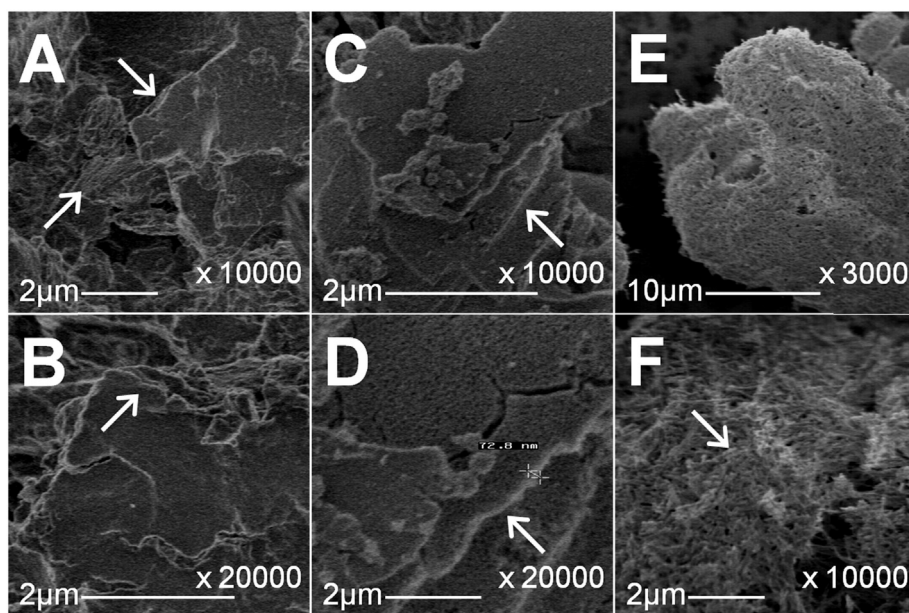


Fig. 7. SEM pictures of the NiMo-C12 hybrid (A, B), the NiMo-C12 hybrid calcined at 400 °C for 4 h (C, D) and a co-precipitated material calcined at 550 °C for 4 h (E, F). The arrows indicate layered structures or hair-like nanoparticles.

Table 1
Catalytic performance of catalysts made via co-precipitation and from hybrid precursors: propane conversion (C_{propane}), product selectivities (S_{product}) and propene yield (Y_{propene}). T calc refers to the temperature at which the catalysts were respectively calcined. The tests were all performed at 475 °C.

Catalyst	T calc (°C)	C_{propane} (%)	S_{propene} (%)	S_{CO_2} (%)	S_{CO} (%)	Y_{propene} (%)
NiMo-Cop	550	12.0	14.4	64.6	20.1	1.7
NiMo-C12	400	18.2	63.8	21.1	10.8	11.6
NiMo-C12	450	10.0	72.9	18.2	4.6	7.3
NiMo-C12	475	14.1	72.0	17.9	4.7	10.2
NiMo-C12	500	5.6	66.0	28.3	1.8	3.7

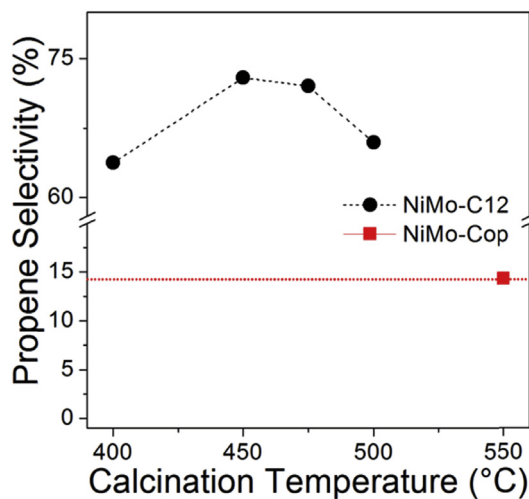


Fig. 8. Evolution of the propene selectivity as a function of the calcination temperature.

propene overoxidation. At the opposite, lower temperatures would rather induce an anarchical crystallization with punctual sites more efficient to selectively oxidize propane into propene.

4.2. An activity preserved by the creation of pores

As mentioned before, bulk oxides require a high specific surface area to maximize the number of their accessible sites and therefore their catalytic activity [21,42]. However, the preparation of β -NiMoO₄ often needs excessive calcination temperatures (>650 °C). This leads to poorly active materials due to sintering that diminishes their specific surface area. Such a constraint is here overcome by using our homemade copolymer. First the combustion of the copolymer induces the crystallization of the oxide at a lower temperature than usually required. Second, during the calcination, the burned copolymer hydrophobic regions liberate free volumes in the material corresponding to the formation of pores [23]. Insufficient calcination temperatures (300–350 °C) should be avoided because of the incomplete matrix degradation. The presence of carbon residues limits the creation of free volume what yields poorly porous oxides having a low specific surface area (Figs. 4 and 6). Calcination temperatures of at least 400 °C yield mesoporous oxides having a higher specific surface area ($\approx 51 \text{ m}^2/\text{g}$). The latter is even better with respect to what is usually obtained by co-precipitation namely a non-porous but finely divided oxide presenting a specific surface area between 30 and 45 m^2/g (Fig. 4) [3,9]. As a result, calcined hybrids display a similar or better propane conversion compared to co-precipitated α -NiMoO₄ (Table 1). Nevertheless, calcination temperatures of 500 °C and more have to be avoided as they lead to sintering effects and thus cancel the benefit provided by the use of our tailor designed preparation method of NiMo-based catalysts.

The nano-scale lamellar organization of the C12 matrix is believed to model and shape its macroscopic morphology toward agglomerated layered particles [22,43,44]. This plate-like morphology is still present (although perturbed) within calcined hybrids (Fig. 7). This suggests that Ni – Mo ions crystallize without losing the original copolymer morphology what gives rise to slit-shaped pores [28,30]. Consequently, using a copolymer matrix as a template strongly dictates the final morphology and the pore shape of bulk mixed oxides like NiMoO₄. Once again, excessive calcination temperatures should be avoided as they favour a decrease of the NiMoO₄ specific surface area (Fig. 4). They induce the sintering of small mesopores into larger ones.

4.3. Toward higher propene yields

Here, moderate calcination temperatures (between 400 and 475 °C) represent a compromise. They prevent sintering while maximizing the pore formation thanks to the complete matrix decomposition (Figs. 4 and 6). In parallel, the exothermicity of the copolymer combustion supplies the additional energy necessary to crystallize NiMoO₄. Indeed, no crystallization of a co-precipitated material is normally observed below 430–440 °C [3]. The most selective phase in propene can thus be prepared without sacrificing its specific surface area what maintains its activity level in the ODHP reaction remarkably high as well. Compared to NiMo-Cop, a higher propene selectivity coupled with a similar or better propane conversion makes calcined hybrids six times more productive in propene (Table 1). In fact, the hybrid method yields NiMoO₄ combining the activity level of the α -phase, together with the propene selectivity of the β -phase.

4.4. The copolymer matrix – a multifunctional template

The C12 matrix associates two types of carbon that burn at different temperatures: the polar backbone (which burns around 250 °C) and the aliphatic part including the diallylamine cycle (which burns around 500 °C). The predisposition of COO[−] functions to be degraded under soft conditions (around 230–250 °C) makes the copolymer sensitive to the temperature. *De facto*, the C12 matrix burns at lower temperatures than the Homo-C12 one (Fig. 6) [24]. Carboxylate functions can be seen as combustion activators that initiate the crystallization of NiMoO₄ at lower temperatures [39]. In this context, the copolymer diallylamine cycles are crucial. Their thermal stability offers the possibility to crystallize NiMoO₄ somewhat before or during but not after the complete copolymer removal. This is essential to synthesize stable, crystallized and porous bulk materials from a template precursor [21].

The temperature of the catalytic runs (475 °C) sometimes exceeds the one used to calcine hybrids. Such a practice is generally not recommended to prevent catalyst physico-chemical changes during a test. However, the stability over time (tests lasting 4 h where performed) of the NiMoO₄ activity suggests the absence of textural and structural modifications (Fig. S2). Furthermore, used NiMoO₄ does not display any drastic crystallinity change except a

further crystallization of some samples without change of the dominant β -phase (Fig. S3). The exothermic degradation of the matrix likely occurs by means of hot spots that strongly and locally increase the temperature in the close environment of Ni – Mo ions. These ions then crystallize thanks to temperatures which are locally superior to the one maintained in the calcination oven. NiMoO₄ resistant to sintering and stable at high temperatures (from 475 °C) are thus generated whatever the used calcination temperature.

In the end, the NiMoO₄ structural and textural properties tend to originate from the degradation of different parts of the copolymer repeating units. On the one hand, the COO[−] functions of the copolymer backbones seem to be behind the early crystallization of β -NiMoO₄. On the other hand, the aliphatic part including the alkyl side chains appears responsible for the creation of a mesoporous volume. Combining these chemical groups within one copolymer matrix ensures the formation of β -NiMoO₄ without sacrifice of its textural properties. To the best of our knowledge, a mesoporous and crystallized β -NiMoO₄ that displays a specific surface area of 51 m²/g has not yet been reported in the literature [3,9].

5. Conclusions

Nanostructured hybrid materials made of guest ions and a self-assembled copolymer were used as precursor to prepare bulk β -NiMoO₄. The latter is particularly desired for its superior propene selectivity but often requires excessive calcination temperatures (>650 °C) leading to poorly active oxides because of sintering that reduces their specific surface area. Such a drawback is here overcome by using our homemade copolymer matrix. The degradation profile of this matrix is the key point. In fact, each copolymer associates 2 different “types of carbon” that burn at different temperatures namely the polar backbone and the aliphatic part including the alkyl side chain. The former can be seen as a combustion activator that initiates the exothermic burning of the hybrids at low temperatures (230–250 °C). The released heat induces the rapid β -NiMoO₄ crystallization before the complete matrix removal. The subsequent decomposition of the matrix aliphatic part finally creates free volumes in the oxide corresponding to the creation of slit-shaped pores. The most selective phase in propene can thus be prepared at moderate temperatures. This enables the preservation of the NiMoO₄ texture from sintering what maintains its activity level in the ODHP reaction quite high as well. As a result, the calcined hybrids combine the activity level of the α -phase, together with the high propene selectivity of the β -phase. In the end, the use of the C12 matrix allows reaching propene yields (up to 11.6%) six times superior compared to what is obtained through coprecipitation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.micromeso.2017.01.025>

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