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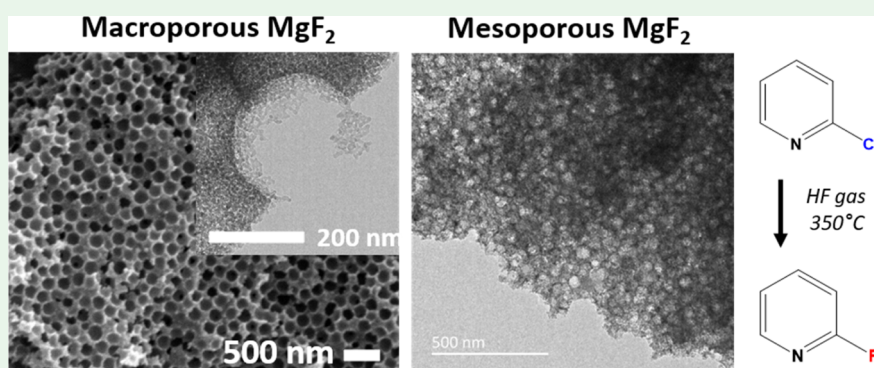
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ABSTRACT: The successful preparation of organized porous inorganic fluorides (OPIFs) with a high specific surface area is demonstrated for MgF₂. For the first time, macroporous MgF₂ OPIFs with a surface area of above 200 m² g⁻¹ and mesoporous MgF₂ powder were prepared through the assembly of preformed MgF₂ nanoparticles and homemade polymer templates with a tunable size. These OPIF materials have been fully examined at different synthesis stages by means of powder X-ray diffraction, N₂ sorption, scanning electron microscopy, and transmission electron microscopy analyses and ¹⁹F and ¹H solid-state nuclear magnetic resonance. The relation between the nature, the size, and the amount of polymer template on the porous structure was deeply investigated. The MgF₂ OPIFs present a higher thermal stability under air and F₂ calcination than MgF₂ NPs as the structuration of the OPIF composite considerably slows down the crystallite growth during thermal treatment under air. OPIF materials were evaluated for the first time as heterogeneous catalysts for the fluorination of 2-chloropyridine under HF gas as a fluorinating agent at 350 °C. This study evidences catalytic sites with two Lewis acidity strengths (medium and low).

KEYWORDS: magnesium fluoride, organized porous inorganic fluorides (OPIFs), polymer template, nanoparticles, heterogeneous catalyst, HF gas fluorination, 2-chloropyridine

1. INTRODUCTION

Owing to their outstanding characteristics such as a high specific surface area, tunable pore size and shape, various structures, and multiple compositions, three-dimensional (3D) porous inorganic materials have been used in various applications such as catalysis, adsorption sensors, lithium-ion batteries, drug delivery, and nanodevices.^{1–3} Since the discovery of organized mesoporous silica in the early 1990s,⁴ 3D porous inorganic materials have been extensively studied for metal oxides, metal sulfides, and carbons, and their synthesis relies on template-assisted methodologies including (i) the soft-templating method, (ii) the hard-templating method, and (iii) the colloid crystal templating (CCT) method^{3,5} (Scheme S1). Briefly, the soft-templating method using surfactants or block copolymers as the template is mainly

used for the preparation of mesoporous silica and mesoporous metal oxides.^{3,5,6} This method is based on evaporation-induced self-assembly of the organic template with the inorganic precursors to form an ordered organic–inorganic composite. Template removal by calcination results in the mesoporous inorganic material. In the second template-assisted approach, known as hard-templating or nanocasting, ordered mesoporous

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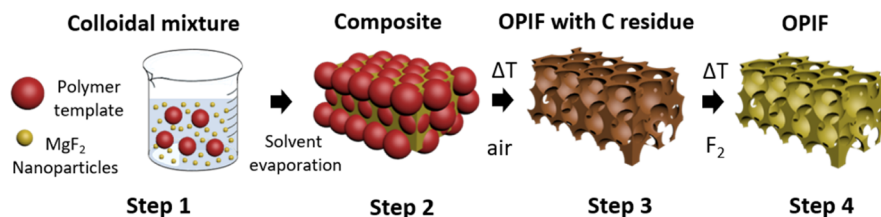


Figure 1. Schematic representation of the different steps of the MgF_2 OPIF synthesis.

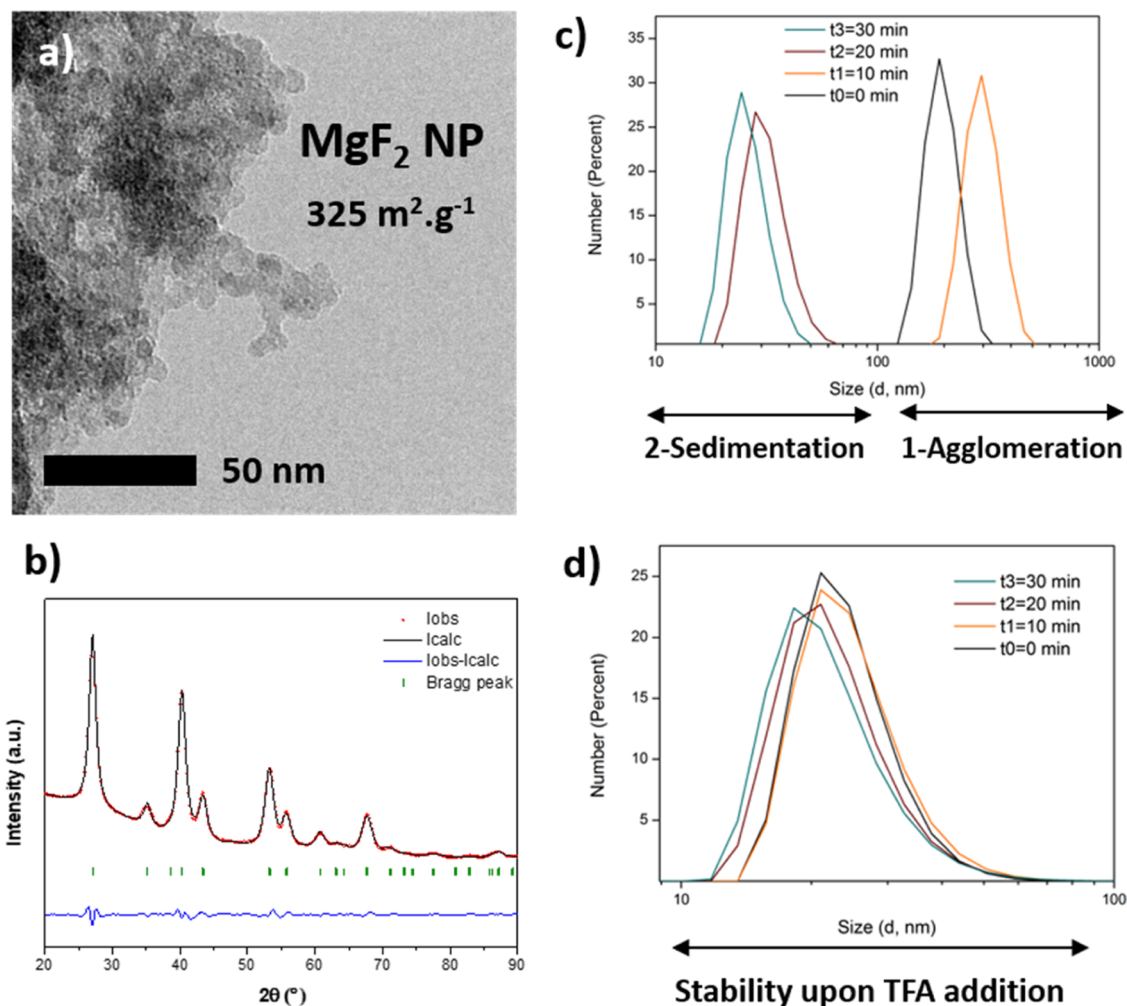


Figure 2. (a) TEM image of MgF_2 NPs. (b) Le Bail refinement of MgF_2 NPs. Vertical markers give the Bragg peak positions of the tetragonal space group $P4_2/mnm$ (no. 136). DLS of MgF_2 NPs dispersed in water with time (c) without TFA and (d) with TFA as the stabilizing agent.

silica (SBA-15 or MCM-41) or alumina is used as a mold by introducing metallic precursors into the pore channels.^{7–10} The rigid template is chemically removed to obtain ordered nano-objects. The last approach, CCT strategy,^{3,5} often mixed in the literature with the hard-templating approach, is frequently used to create 3D macroporous replica, also called the inverse opal structures. CCT is based on the formation of a colloid crystal of close-packed and uniformly sized spheres (polymers or silica) with the interstitial spaces filled with the inorganic precursors or preformed nanoparticles (NPs). Despite the remarkable properties of fluorinated materials and their well-established large application domains in heterogeneous catalysis,^{11–14} energy production and storage,¹⁵ microelectronics, and photonics,¹⁶ these well-controlled synthetic strategies described above are sparsely applied for

the elaboration of 3D porous fluorinated materials. Indeed, the soft-templating method was only reported for the synthesis of mesoporous MgF_2 thin films using polyvinyl acetate¹⁷ or amphiphilic block copolymers as the structure-directing agent to introduce controlled mesoporosity.¹⁸ The synthesis of $(\text{Ca},\text{Sr},\text{Ba})\text{F}_2$,⁸ $\text{NaYF}_4:\text{Eu}$, Tb ,¹⁰ and LaF_3 nanowires by the hard-templating method using different porous molds (SBA-15 and Al_2O_3) was reported in the 2000s. Finally, the most applied templating route for the synthesis of porous fluorides is the CCT method using poly(methyl methacrylate) (PMMA) or polystyrene (PS) spheres. Indeed, in the last decade, the preparations of macroporous doped- NaYF_4 ,^{19–21} MgF_2 , CaF_2 , AlF_3 ,²² and lanthanide oxyfluorides²³ were reported. Such sparse literature on organized porous inorganic fluorides (OPIFs) confirms unequivocally that these materials represent

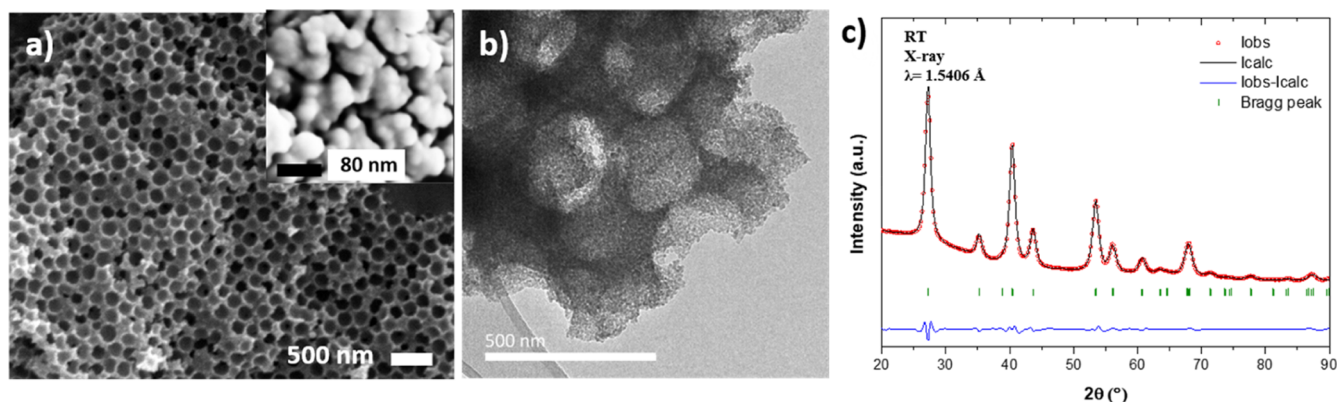


Figure 3. (a) SEM and (b) TEM images of macroporous MgF_2 OPIF-200. (c) Le Bail refinements of OPIF-200 after calcination under air at 375 °C and under F_2 . Vertical markers give the Bragg peak positions of the tetragonal space group $P4_2/mnm$ (no. 136).

a new class of porous materials to be explored. This lack of study on the elaboration of 3D porous fluorides could be explained by the poor stability of fluorides at high temperature and the difficult preparation of fluoride NPs smaller than 10 nm,^{14,24,25} which could be used as building blocks for porous material preparation.

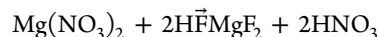
In this paper, we report on the successful and unprecedented preparation of tunable pore-sized OPIFs as exemplified for MgF_2 . For the first time, macroporous MgF_2 with a surface area of above 200 m² g⁻¹ and mesoporous MgF_2 powder were prepared and carefully characterized. Almost not applied on fluorides, the synthetic route is based on the assembly of two building blocks: the polymer template and preformed MgF_2 NP, which is depicted in Figure 1. After subsequent calcinations of the OPIF composite material under air and F_2 , carbon-free and slightly hydroxylated MgF_2 OPIFs are obtained. We present the pioneering application of these OPIF materials as heterogeneous catalysts for the gas-phase fluorination of the 2-chloropyridine under HF as the fluorinating agent. Indeed, MgF_2 NPs have attracted strong interest as catalysts for a variety of organic reactions^{26–32} such as dehydrochlorination and dehydrofluorination reactions,²⁷ the acylation of 2-methylfuran by acetic anhydride,²⁹ or the fluorination of chlorinated reactants^{11,12} and a catalyst support for gas-phase reaction such as dehydrofluorination reaction³³ or the fluorination of 1,1,1,3-tetrachloropropane with HF to 3,3,3-trifluoropropene,¹³ for example.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of MgF_2 OPIFs. As shown in Figure 1, our synthetic methodology to target OPIF MgF_2 porous materials comprises four steps: (i) syntheses of the two building blocks (fluoride NPs and polymer template) and their dispersion as a homogenous aqueous colloidal mixture, (ii) fluoride NP/polymer template assembly process via solvent evaporation to obtain the OPIF composite, (iii) calcination including concomitant polymer removal and inorganic fluorinated network densification, and (iv) final thermal treatment under F_2 to remove the carbon residue.

2.1.1. Step 1: Preparation of the Two Buildings Blocks (MgF_2 NPs and the Polymer Templates) and Their Colloidal Dispersion. In the first step, MgF_2 NPs were synthesized via a microwave-assisted solvothermal route using aqueous HF (40%) as the fluorinating agent, methanol as the solvent, and

magnesium nitrate as the metal precursor at 90 °C for 30 min according to the reaction¹¹



The profile refinement of the powder X-ray diffraction (PXRD) pattern confirms the rutile-type crystal structure of MgF_2 NPs (space group $P4_2/mnm$) with cell parameters $a = 4.6544(6)$ Å and $c = 3.0476(3)$ Å (JCPDS 01-072-1150, Figure 2). A diameter of about 7 nm was determined from PXRD refinement (D_{XRD}) and transmission electron microscopy (TEM) analysis (Figure 2, D_{TEM}). PMMA and PS were chosen as the template due to their facile thermal decomposition at temperature lower than 400 °C (Figure S1). To access to homogeneously sized polymer spheres with a tunable diameter, three different polymerization processes were used: surfactant-free emulsion polymerization and conventional emulsion polymerization to obtain macrosized polymer templates^{25,34–36} and microemulsion polymerization for the polymer templates with a diameter of under 100 nm.³⁵ Home-synthesized polymer template latexes present the advantage of low polydispersity (PDI) in size and a controlled surface through the absence (surfactant-free emulsion polymerization) or the presence (conventional emulsion polymerization) of a surfactant (SDS, sodium dodecyl sulfate). Furthermore, the choice of the initiator in comparison with commercial latex (ammonium persulfate (NH_4)₂S₂O₈ vs potassium persulfate K₂S₂O₈) allows the decomposition without a K₂SO₄ residue. Electronic microscopy analyses show the obtention of spheres with diameters of ≈200 nm (PMMA), ≈85 nm (PMMA–SDS), and ≈45 nm (PS–SDS) (Figure S2). These aqueous latexes are stable as evidenced by a negligible change in polymer bead size after 1 month, as confirmed by dynamic light scattering (DLS, see Figure S3).

The dispersion of the NP and polymer template as a homogenous aqueous colloidal mixture aims to ensure uniform templating with evenly distributed pores through the OPIF material. The MgF_2 NP was dispersed in water, and the stability of the NP sol was investigated by DLS (Figure 2). Hydrodynamic diameters (D_h) of pristine NPs are about 200 nm. They increase and reach about 300 nm after 10 min, suggesting the formation of aggregates (Figure 2c). After 20 min, aggregate sedimentation occurs, and only smaller agglomerates (with the diameter ranging from 20 to 30 nm) remain in suspension. Upon the addition of trifluoroacetic acid (TFA) as the stabilizing agent, D_h values are significantly

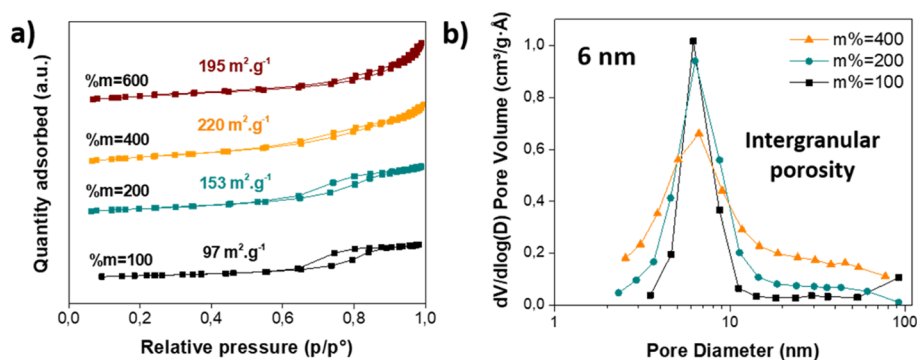


Figure 4. (a) N₂ adsorption–desorption isotherms of OPIF-200 with different % *m*. (b) Corresponding BJH pore size distributions.

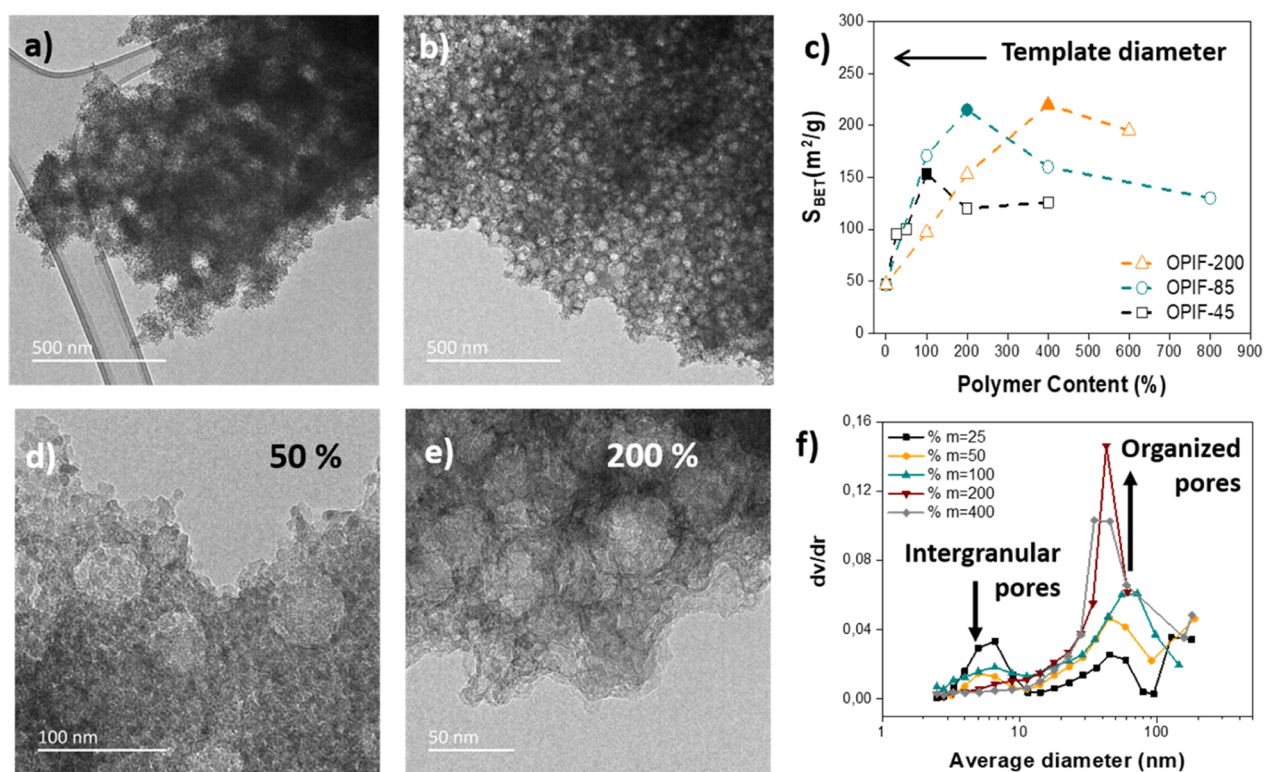


Figure 5. TEM images of (a) OPIF-85 and (b) OPIF-45 and (c) S_{BET} of MgF₂ OPIF materials synthesized using three polymer templates (OPIF-200 in orange, OPIF-85 in blue, and OPIF-45 in black) with varied polymer contents (% *m*). Solid points correspond to OPIF materials with the highest S_{BET} . TEM images of OPIF-45 with (d) % *m* = 50 with porosity coming from the organized pores and intergranular pores and (e) % *m* = 200 with porosity coming solely from organized pores. (f) BJH pore size distribution from the adsorption branch of the N₂ sorption isotherm.

reduced to 25 nm and remain unchanged for at least 30 min. This supports the ability of TFA to prevent NP agglomeration (Figure 2d). This phenomenon can be explained by the increase in positive zeta potential (ζ) of the MgF₂ NP (ζ = 40 mV)³⁷ with the pH decrease induced by TFA. Indeed, the NP stability in solution is ensured by higher repulsive particle interactions due to the enhanced surface charge, preventing from agglomeration.³⁸

2.1.2. Preparation of MgF₂ OPIFs with Tunable Pore Sizes.

The polymer template dispersed in water was added to this TFA-treated MgF₂ NP sol. Centrifugation and solvent evaporation were performed to assemble the NP with the polymer template and to obtain an OPIF composite, as depicted in Figure 1, step 2. The resulting composite material was calcined under air at 375 °C to remove the template and to obtain porous OPIF materials (step 3). The macroporous MgF₂ OPIF was successfully prepared [scanning electron

microscopy (SEM) and TEM, Figure 3] using a PMMA template with a diameter of \approx 200 nm (OPIF-200). The OPIF-200 is homogeneously templated with a pore diameter of around 200 nm corresponding to the PMMA diameter. TEM/SEM images evidenced the macroporosity and mesoporosity emerging from the voids between the NPs of the OPIF walls.

The PXRD diagram shows that the MgF₂ crystal structure is preserved after thermal treatment under air, and TEM analysis reveals that the walls are composed of MgF₂ NPs with $D_{\text{TEM}} \approx$ 9 nm, consistent with the crystallite size obtained from PXRD Le Bail refinements ($D_{\text{XRD}} = 7$ nm, Table S2). It is important to note that the structuration of the OPIF composite (NP + template) considerably slows down the crystallite growth during thermal treatment under air. Indeed, the calcination under air at 350 °C of pristine MgF₂ NPs leads to MgF₂ NPs (NP-ref-OPIF in the following) with a diameter of \approx 18 nm, inducing a large decrease in the specific surface area from 320

Table 1. Specific Surface Areas (S_{BET}), NP Diameter (NP D), V_{total} , and V_{int} of OPIF Samples before and after F_2 Thermal Treatment

	before F_2				after F_2				after HF	
	S_{BET} (m^2/g^{-1})	$^a\text{NP D}$ (nm)	$^bV_{\text{total}}$ (cm^3/g)	V_{inter} (cm^3/g)	S_{BET} (m^2/g^{-1})	$^a\text{NP D}$ (nm)	$^bV_{\text{total}}$ (cm^3/g)	V_{inter} (cm^3/g)	S_{BET} (m^2/g^{-1})	$^a\text{NP D}$ (nm)
NP-ref-OPIF	45(5)	16	0.19	0.06	45(5)	17	0.19	0.07	45(5)	20
OPIF-200	155(5)	10	0.37	0.29	140(5)	10	0.35	0.25	60(5)	15
OPIF-85	215(5)	9	0.76	0.41	130(5)	10	0.54	0.34	65(5)	15
OPIF-45	155(5)	9	0.46	0.12	75(5)	11	0.49	0.05	60(5)	15

^aNP D determined by TEM/XRD. ^bTotal cumulative pore volumes (V_{tot}) were calculated at $p/p^0 = 0.99$.

189 to $45 \text{ m}^2 \text{ g}^{-1}$ (Figure S4). After nanostructuring of the NP
190 into OPIFs, the specific surface area (S_{BET}) only decreases
191 from 320 to $220 \text{ m}^2 \text{ g}^{-1}$ for OPIF-200-200%, for example.
192 As the final porous morphology and S_{BET} depend on the
193 template content, different polymer to particle mass ratios (m
194 $\% = m_{\text{polymer}}/m_{\text{NP}} = 100, 200, 400$, and 600) were tested.
195 Increasing m improves the homogeneity of pore distribution
196 (Figure S5). The S_{BET} reaches a maximum of $220 \text{ m}^2 \text{ g}^{-1}$ for m
197 $\% = 400$ but slightly decreases to $195 \text{ m}^2 \text{ g}^{-1}$ for m $\% = 600$.
198 To gain more insights into the porous structure, N_2
199 adsorption-desorption isotherms were recorded (Figure 4a).
200 According to the IUPAC classification,³⁹ MgF_2 OPIFs have
201 type IV isotherms for $\% m = 100, 200$, and 400 with a
202 hysteresis loop at relative pressure p/p^0 between 0.6 and 0.9
203 which correspond to the mesoporous material. This meso-
204 porosity is associated with the intergranular pores between the
205 MgF_2 NPs forming the walls, as confirmed by TEM and SEM
206 analysis (Figure 3). The Barrett-Joyner-Halenda (BJH)
207 model applied for type IV profiles on the desorption branch
208 implies a monomodal pore size distribution centered at 6 nm
209 (Figure 4b). The OPIF with $\% m = 600$ shows a type II curve,
210 characteristic of nonporous or macroporous materials. The
211 absence of type IV is probably related to the loss of the
212 intergranular porosity combined with the partial collapse of the
213 structure due to the thinness of the walls leading to a decrease
214 in the surface area. We conclude that the porosity in OPIF
215 materials comes both from the 3D porous structure and the
216 interspaces between NPs. In the rest of the manuscript, the
217 porosity from the main pores and from the interspaces will be
218 named organized porosity and intergranular porosity, respec-
219 tively.
220 OPIF materials were also prepared using templates with
221 smaller diameters. As already mentioned, two polymer
222 templates were synthesized by conventional emulsion polymer-
223 ization using SDS as the surfactant: PMMA with a diameter of
224 85 nm (PMMA-SDS) and PS with a diameter of 45 nm (PS-
225 SDS). Various polymer to particle mass ratios ($\% m$) led to
226 highly organized porous MgF_2 OPIFs (respectively, named
227 OPIF-85 and OPIF-45 in the following, Figure Sa,b). The S_{BET}
228 evolution of OPIF-85 and OPIF-45 with the $\% m$ is shown in
229 Figure 5c and compared with that of OPIF-200. The decrease
230 in the template size shifts the optimum polymer content (blue
231 circle) to 200% ($S_{\text{BET}} = 215 \text{ m}^2 \text{ g}^{-1}$) for OPIF-85 and to 100%
232 for OPIF-45 ($S_{\text{BET}} = 155 \text{ m}^2 \text{ g}^{-1}$).
233 Both OPIF-85 and OPIF-45 show type IV nitrogen sorption
234 isotherms for different $\% m$ (Figure S6). The pore size and its
235 evolution as a function of polymer content were carefully
236 studied by the BJH method. In the case of OPIF-85, only the
237 intergranular porosity could be observed ($d \approx 6\text{--}11 \text{ nm}$) as
238 the diameter of organized pores is out of range ($>50 \text{ nm}$) for
239 this analysis (Figure S7). For OPIF-45, the organized porosity

(pore diameter $\approx 45 \text{ nm}$) is confirmed, as shown in Figure 7a. 240
It is interesting to note that by increasing $\% m$, a transition 241
from bimodal (organized pores + intergranular pores) to 242
monomodal (organized pores) pore distribution is observed. 243
This difference of the porous structure is confirmed by TEM. 244
Indeed, the presence of the intergranular mesoporosity is 245
observed between the NPs with low polymer content (50% , 246
Figure 5d), while individual NPs are no longer observable in 247
 200% (Figure 5e). This observation coupled with the abrupt 248
reduction of S_{BET} beyond 100% in OPIF-45 suggests that the 249
structural change is not only linked to the variation of polymer 250
content but also depends on the presence of intergranular 251
porosity. 252
The intergranular volumes (V_{int}) were calculated by 253
subtracting cumulative pore volumes of pores with a width 254
of $>10 \text{ nm}$ (V_{or}) from the total cumulative pore volumes (V_{int} 255
 $= V_{\text{total}} - V_{\text{or}}$). Figure S8 shows V_{int} and V_{or} as a function of 256
 m , demonstrating a maximum-minimum relation with the 257
polymer content. Indeed, the obtention of high S_{BET} is a 258
compromise between organized and intergranular pores where 259
the highest S_{BET} for each template size occurs when $V_{\text{int}} + V_{\text{or}}$ 260
(i.e., V_{total}) is maximized. To validate the beneficial effect of 261
intergranular pores on the S_{BET} , OPIF-45 with $m = 100\%$ was 262
prepared by the removal of the polymer template with 263
tetrahydrofuran (THF) (Figure S9). When the PS is removed 264
chemically, the volume of the intergranular porosity ($V_{\text{int-thermal}}$ 265
 $= 0.12 \text{ cm}^3 \text{ g}^{-1}$; $V_{\text{int-THF}} = 0.25 \text{ cm}^3 \text{ g}^{-1}$) and the S_{BET} increased 266
($S_{\text{BET-thermal}} = 155$ to $S_{\text{BET-thermal}} = 180 \text{ m}^2 \text{ g}^{-1}$). These results 267
evidence the densification of the NP network during removal 268
of the template by thermal treatment, therefore confirming that 269
the S_{BET} strongly relies on both intergranular porosity and 270
organized porosity. 271
2.1.3. Calcination under F_2 for Carbon Residue Removal. 272
OPIF samples with different pore sizes and with the highest 273
surface areas were selected for a subsequent thermal treatment 274
under F_2 gas to remove the carbon residue ($\text{C} + 2\text{F}_2 \rightarrow \text{CF}_4$) 275
and eventual hydroxyl groups ($2\text{OH}^- + \text{F}_2 \rightarrow \text{O}_2 + 2\text{HF}$). 276
Indeed, the residual carbon could affect the porous structure 277
and the S_{BET} and block the active sites for the transformation 278
of 2-chloropyridine. The selected OPIFs were OPIF-85: 200% 279
and OPIF-45: 100% . For OPIF-200, 200% was selected as it 280
allows the preparation of MgF_2 OPIFs with high S_{BET} and 281
lower carbon content (Figure S10). After thermal treatment 282
under F_2 , the color changed from brown to white and this 283
carbon removal was confirmed by Fourier transform infrared 284
(FTIR) spectroscopy analysis (Figures S11 and S12). Before 285
 F_2 treatment, all FTIR spectra exhibit bands at 1405 cm^{-1} 286
assigned to stretching vibrations of the CO_3^{2-} groups.²³ The 287
bands at 1150 cm^{-1} are associated with the C-F groups.²³ 288
Two bands are also observed at 3393 and 1598 cm^{-1} 289
corresponding to $-\text{OH}$ of hydroxyl groups or adsorbed 290

291 water molecules on the OPIF surface. After F_2 thermal
 292 treatments, the removal of the CO_3^{2-} , C-F, and -OH groups
 293 is evidenced by the disappearance of the related bands. TEM
 294 investigations showed the stability of the porous structure
 295 under F_2 despite a decrease in the specific surface area (Figure
 296 S13 and Table 1). The S_{BET} of the macroporous OPIF (OPIF-
 297 200 and OPIF-85) remains above $130\text{ m}^2\text{ g}^{-1}$ ($D_{XRD} = 10\text{ nm}$)
 298 even after the harsh thermal treatment under F_2 . In
 299 comparison, NP-ref-OPIF shows the largest particle size (16
 300 nm) and a three times smaller specific surface area after F_2
 301 treatment, emphasizing the importance of 3D structuration on
 302 the thermal stability by introducing organized and intergr-
 303 nular pores. This stability could be explained by the presence
 304 of pores which could prevent particle mobility and therefore
 305 NP sintering.

306 **2.2. Modification of the Physicochemical Properties**
 307 **of OPIF Samples after HF Treatment.** 2.2.1. *Character-*
 308 *ization by PXRD, N_2 Sorption, TEM, and ^{19}F and 1H Solid-*
 309 *State MAS NMR.* Prior to catalytic transformation of 2-
 310 chloropyridine under a HF atmosphere, the catalysts were
 311 activated *in situ* by HF for 1 h at 350°C (activation step). This
 312 step corresponds to the stabilization of the materials under a
 313 HF atmosphere and allows us to characterize the properties
 314 (amount and strength) of the active sites involved in the Cl/F
 315 exchanges. The influence of this treatment on the structural
 316 properties of OPIF samples was first investigated by PXRD, N_2
 317 sorption, and TEM. Despite the severe condition, the rutile
 318 phase of MgF_2 is preserved under HF (Figure S14).
 319 Unfortunately, this step induces an adverse effect as the S_{BET}
 320 decrease to $\approx 60\text{ m}^2\text{ g}^{-1}$ related to a particle size increase to 15
 321 nm (Table 1, TEM in Figure S15) which is close to NP-ref-
 322 OPIF (S_{BET} of $45\text{ m}^2\text{ g}^{-1}$ and particle size of 20 nm).

323 Further structural information was obtained from ^{19}F and
 324 1H solid-state MAS NMR studies of samples OPIF-45 before
 325 and after the HF activation step, OPIF-85, OPIF-200, and NP-
 326 ref-OPIF after HF treatment. The nuclear magnetic resonance
 327 (NMR) spectra are reported in Figure 6 and compared with
 328 the pristine MgF_2 NP (without the calcination step) that we
 329 recently studied,¹¹ that is, MgF_2 NP prepared from the nitrate
 330 precursor, after HF activation. For the rutile-type crystal
 331 structure of MgF_2 involving a single F crystallographic site,⁴⁰ a
 332 single ^{19}F NMR line is expected and observed [at δ_{iso}
 333 (isotropic chemical shift) = -197.3 ppm] on its spectrum.⁴¹
 334 In contrast, all ^{19}F spectra presented in Figure 6 exhibit one
 335 main asymmetrical line with a maximum at a similar value (δ_{iso}
 336 $\approx -197.7\text{ ppm}$) and a shoulder toward higher δ_{iso} values (three
 337 resonances with close δ_{iso} values are necessary to reconstruct
 338 the spectra correctly). In addition, a second contribution
 339 appears distinctly at about -183 ppm and even (except for
 340 MgF_2 NPs prepared from the nitrate precursor, after HF
 341 activation) a third contribution appears at about -178 ppm
 342 (Figure 6, fits and results of these fits are given in Figure S16
 343 and Table S3). Moreover, compared with the ^{19}F NMR line of
 344 a microcrystalline sample (line width of 795 Hz),¹¹ these lines
 345 are broader (line widths from 853 Hz for MgF_2 NPs prepared
 346 from the nitrate precursor, after HF activation, to 1032 Hz for
 347 OPIF-45 before HF activation) (Figure S17). This broadening
 348 mirrors chemical shift distributions due to disorder around
 349 fluorine atoms in relation with the slightly higher specific
 350 surface area (from 45 to $75\text{ m}^2\text{ g}^{-1}$) and partial hydroxylation,
 351 the latter resulting additionally in the shoulders and
 352 contributions at high ^{19}F δ_{iso} values. The increase in the ^{19}F
 353 δ_{iso} value with the hydroxide content, that is, the number of

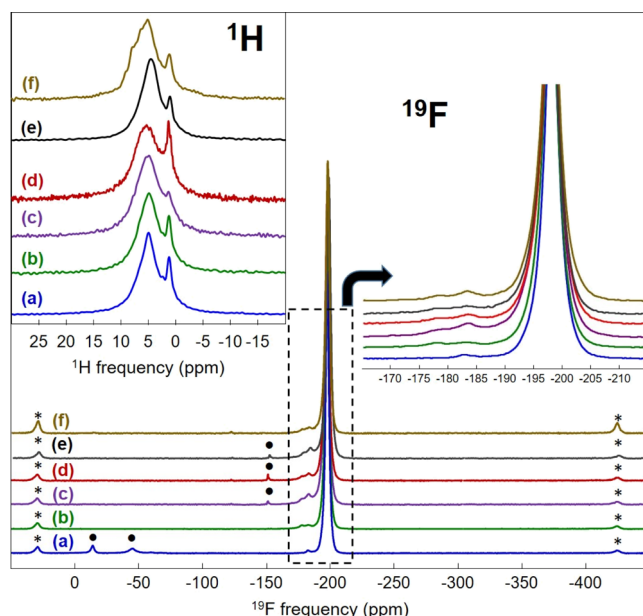


Figure 6. 1H solid-state MAS NMR spectra (inset) and ^{19}F solid-state MAS (64 kHz) NMR spectra of (a) MgF_2 NPs prepared from the nitrate precursor, after HF activation, (b) NP-ref-OPIF, OPIF-45 before (c) and after (d) HF activation, OPIF-85 (e), and OPIF-200 (f), after HF activation. The isotropic lines of the ^{19}F spectra are expanded in the inset on the right. The star symbols indicate the spinning sidebands. The dot symbols (a–e) indicate fluoride impurities of (a) MgF_2 NPs prepared from the nitrate precursor, after HF activation (60 kHz), (b) NP-ref-OPIF, OPIF-45 (64 kHz), (c) before (60 kHz) and (d) after (64 kHz) HF activation, OPIF-85 (e), and OPIF-200 (f), after HF activation.

hydroxyl groups in the environment of the fluoride ion in
 hydroxyfluorides, is a well-known phenomenon which has been
 observed in magnesium hydroxyfluorides (up to 40 ppm).⁴²
 Nevertheless, due to the very large number of different
 environments of fluoride ions in partially hydroxylated
 magnesium fluorides, $MgF_{2-x}(OH)_x$, the assignment of the
 additional lines seems to be unrealistic. Indeed, due to the
 presence of eleven anions as the next nearest neighbors at four
 different distances (ranging from 2.58 to 3.35 \AA , Table S4⁴⁰),
 there are several inequivalent $FMg_3F_{11-y}(OH)_y^{6-}$ environ-
 ments for each of the ten $0 < y < 11$ values. In any case, the
 proportion of fluoride ions in the fluoride (FMg_3F_{11})
 environment can be estimated within the range 86 – 68 with,
 in decreasing order, the samples after HF activation: MgF_2
 NPs prepared from the nitrate precursor (86%), NP-ref-OPIF
 (78%), OPIF-200 (74%), OPIF-45 (71%), and OPIF-85
 (68%) and then OPIF-45 before HF activation (Table S3 and
 Figure S16). Assuming a random distribution of OH^- and F^-
 ions at anionic sites (Table S5), only rates of OH groups
 ranging from ≈ 1.5 to 3.5% ($0.03 \leq x \leq 0.07$) satisfy such
 proportions of the FMg_3F_{11} environment. Even if they are
 slightly superior to that of NP-ref-OPIF and to that of MgF_2
 NPs prepared by microwave-assisted solvothermal synthesis
 and activated under HF¹¹ (including MgF_2 NPs prepared from
 the nitrate precursor), the rates of OH groups in the OPIF
 samples, before and after HF activation, remain low.

The 1H solid-state MAS NMR spectra of all MgF_2 samples
 (Figure 6, fits and results of these fits in Figure S18 and Table
 S6) present one main broad contribution (ranging from 0 to
 10 ppm) with δ_{iso} values at the maximum ranging from 4.5 to 5

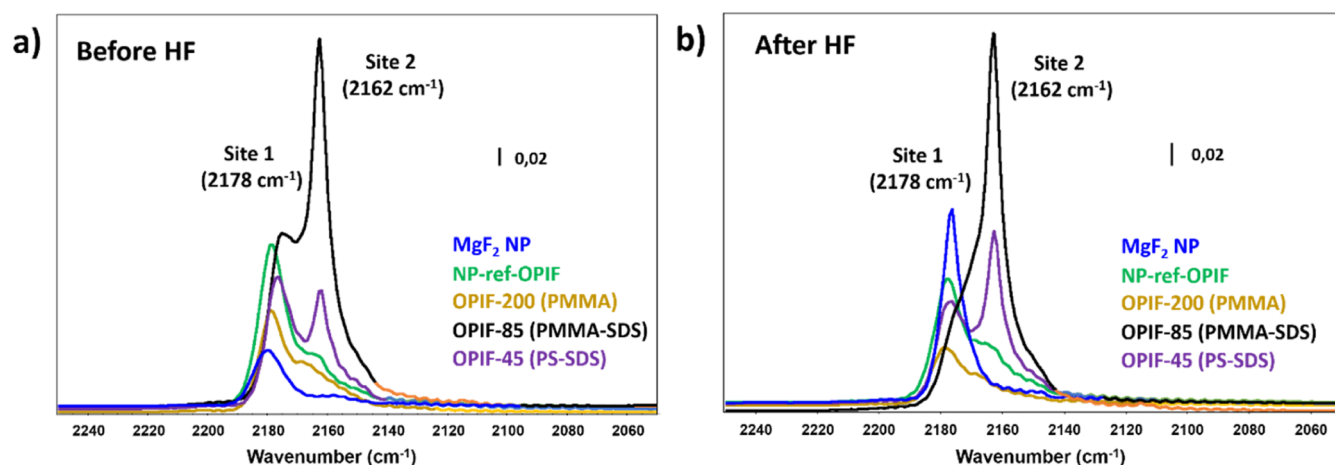


Figure 7. CO adsorption followed by IR over OPIF catalysts (a) before and (b) after HF treatment.

384 ppm, assigned to surface-adsorbed H₂O molecules and/or OH
385 groups where hydrogen atoms are involved in H-bonds and a
386 smaller contribution with δ_{iso} values at the maximum ranging
387 from 1.1 to 1.2 ppm, assigned to Mg₃-OH environments
388 where hydrogen atoms are not involved in H-bonds.⁴³
389 However, the main contribution of the spectra of the OPIF-
390 45 samples before and after HF activation is broader, whereas
391 those of OPIF-85 and OPIF-200 after HF activation are
392 narrower. Moreover, the latter two have an additional
393 contribution at higher δ_{iso} values (≈ 6 or ≈ 8 ppm). These
394 differences which reflect different chemical shift distributions
395 are difficult to interpret since these samples have similar
396 specific surfaces. At last, the spectra of the OPIF-45 samples
397 differ from each other by the larger relative intensity of the
398 contribution assigned to Mg₃-OH environments after
399 activation (13.4 vs 10.0%; Table S6) but above all by a
400 smaller intensity of the NMR spectrum (evidenced by the
401 lower signal-to-noise ratios although recorded with the same
402 number of transients). This can be explained by a decrease in
403 the amount of adsorbed H₂O molecules, related to the
404 decrease in the specific surface area of the NPs (75 vs 60 m²
405 g⁻¹; Table 1).

406 **2.2.2. Characterization of the Actives Sites by CO**
407 **Adsorption Followed by IR.** The properties (quantity and
408 strength of Lewis acid sites) of the catalytic sites were
409 characterized by adsorption of CO as the probe molecule
410 followed by IR spectroscopy before and after the activation
411 step by HF (Figure 7). CO is a suitable probe molecule for the
412 characterization of Lewis acidity as the (CO) vibration
413 frequency is very sensitive to the local cationic environment
414 of the coordinatively unsaturated magnesium centers.

415 All samples show the presence of coordinatively unsaturated
416 magnesium centers where CO can be adsorbed. For the MgF₂
417 NP prepared from the nitrate precursor,¹¹ NP-ref-OPIF, and
418 OPIF-200, a CO adsorption band was mainly observed at 2178
419 cm⁻¹ (site 1). Interestingly, OPIF-85 and OPIF-45 clearly
420 present two CO adsorption bands centered at 2178 cm⁻¹ (site
421 1) and 2162 cm⁻¹ (site 2) with different intensities before and
422 after HF activation. These bands are attributed to two different
423 magnesium environments corresponding to two types of low
424 (site 2) to intermediate (site 1) strength of CO adsorption
425 sites. According to Wuttke et al.,⁴⁴ the presence of these bands
426 at 2178 and 2162 cm⁻¹ corresponds to tetracoordinated
427 (Mg_{4c}²⁺) and pentacoordinated (Mg_{5c}²⁺) magnesium atoms

located in the edge and in-plane of a crystal of MgF₂,
respectively. After HF treatment (Figure 7b), the intensity of
the higher strength Lewis acid site (site 1) decreased in favor
of the weaker sites (site 2) (Table 2). This evolution

Table 2. FTIR CO Characterization of Various MgF₂ Samples^a

	before HF			after HF		
	Q_{sites_T}	Q_{sites_1}	Q_{sites_2}	Q_{sites_T}	Q_{sites_1}	Q_{sites_2}
MgF ₂ NPs prepared from the nitrate precursor ¹¹	79	79	0	90	90	0
NPs-ref-OPIF	201	114	87	123	52	71
OPIF-200	203	81	122	117	117	N.A.
OPIF-85	525	183	342	328	76	252
OPIF-45	318	133	185	226	81	145

^aQuantification of sites ($\mu\text{mol g}^{-1}$), Q_{sites_T} : total quantity of sites; Q_{sites_1} : quantity at 2178 cm⁻¹; and Q_{sites_2} at 2162 cm⁻¹ (N.A., nonapplicable). Estimated relative uncertainty: 10%.

corresponds to a change in the coordination degree of
magnesium atoms from 4 to 5 and to a favored adsorption
of CO on sites located in-plane of a crystal of MgF₂. The
presence of site 2 in a larger amount could be explained by the
higher amount of SDS surfactant used during the conventional
emulsion polymerization synthesis for the synthesis of
PMMA-SDS (85 nm) and PS-SDS (45 nm). Indeed,
localized Na and S were evidenced by energy-dispersive X-
ray (EDX)-TEM analysis (Figure S18). Regarding the
quantification of these sites by the integration of the
corresponding bands, an increase in the total number of active
sites from 79 to 201 $\mu\text{mol g}^{-1}$ is observed between MgF₂ NPs
prepared from the nitrate precursor and NPs-ref-OPIF; this
might be influenced by the addition of TFA for the preparation
of NPs-ref-OPIF. This statement will be further investigated.
Regarding the OPIF materials, a significant gain in the number
of total sites to 525 $\mu\text{mol g}^{-1}$ is achieved for OPIF-85
corresponding to the OPIF with the highest total cumulative
pore volumes (V_{tot}) (Table 1). After HF activation, a decrease
in the total number of sites is observed for all samples. The
amount of site 2 remains higher than that of site 1 except for
OPIF-200 (PMMA). The same tendency is observed for the
number of sites per surface area (Table 3).

Table 3. Concentration Sites $\mu\text{mol m}^{-2}$ ($C_{\text{sites}_T} = C_{\text{sites}_1} + C_{\text{sites}_2}$; Site 1 at 2178 cm^{-1} and Site 2 at 2162 cm^{-1}) before and after Activation by HF (N.A., nonapplicable)

	before HF			after HF		
	C_{sites_T}	C_{sites_1}	C_{sites_2}	C_{sites_T}	C_{sites_1}	C_{sites_2}
MgF ₂ NPs prepared from the nitrate precursor ¹¹	0.5	0.5	0	2.8	2.8	0
NPs-ref-OPIF	6.7	3.8	2.9	2.4	1.0	1.4
OPIF-200	1.5	0.6	0.9	1.9	1.9	N.A.
OPIF-85	5.2	1.8	3.4	5.2	1.2	4.0
OPIF-45	5.7	2.4	3.3	4.0	1.4	2.6

2.3. Catalytic Performances for the Transformation of 2-Chloropyridine. MgF₂ OPIFs were tested for the first time as catalysts for the transformation of 2-chloropyridine measured at 350 °C in the presence of HF gas. All OPIF materials present a good ability with a 100% selectivity toward 2-fluoropyridine (2FPy) (Table 4). Unfortunately, the catalytic

Table 4. Activity per Gram and per Surface Area for the Transformation of 2-Chloropyridine ($T = 350\text{ °C}$, $t = 4\text{ h}$), and HF/N₂/2-ClPy Molar Ratio = 6.4/1.7/1.0) and Estimated Relative Uncertainty: 5%

	activity		TOF
	$\text{mmol h}^{-1} \text{g}^{-1}$	$\text{mmol h}^{-1} \text{m}^{-2}$	
MgF ₂ NPs prepared from the nitrate precursor ¹¹	31	0.63	340
NP-ref-OPIF	24	0.47	195
OPIF-200	27	0.43	230
OPIF-85	25	0.40	76
OPIF-45	25	0.40	102

activity of OPIF materials and their reference (MgF₂-ref-OPIF) is similar ($\approx 25\text{ mmol h}^{-1} \text{g}^{-1}$), and this value is slightly lower than the catalytic activity obtained with MgF₂ from the nitrate precursor¹¹ ($31\text{ mmol h}^{-1} \text{g}^{-1}$). This result could be explained by the different amounts and strengths of the catalytic sites, given that all materials have the same specific surface area ($\approx 60\text{ m}^2 \text{g}^{-1}$). Indeed, for this reaction, the catalytic sites require a medium Lewis acid strength (CO adsorption band at 2176 cm^{-1} , site 1), confirming that MgF₂ NPs prepared from the nitrate precursor with a higher amount of site 1 corresponds to the highest activity per site (turnover frequency, TOF).¹² Therefore, even if site 2 may have a contribution to the catalytic activity, it seems to be lower. Further experiments are required to explain the origin of site 2 having a weak Lewis acidity together with the influence of Na and S traces on the catalytic properties. Despite the lower performance of MgF₂ OPIFs, a graduation of Lewis acidity strength could be valuable for other reactions as the catalytic activity depends on both the number and properties of active sites.

3. CONCLUSIONS

MgF₂ OPIFs ($S_{\text{BET}} > 150\text{ m}^2 \text{g}^{-1}$) with tunable pore sizes (200, 85, and 45 nm) were synthesized, and highly organized mesoporous MgF₂ powder was obtained for the first time. The synthetic route is based on the assembly of two building blocks, homemade polymer templates and preformed MgF₂ NPs. After subsequent calcinations of the OPIF composite

material under air and F₂, carbon-free MgF₂ OPIFs with a significant specific surface area were prepared. These OPIF materials were characterized at each synthesis step by PXRD, N₂ sorption, SEM and TEM analyses, and ¹⁹F and ¹H solid-state NMR. This work shows that OPIF structures strongly rely on both the intergranular pore volume and template size. The MgF₂ OPIF with an organized pore size of 85 nm and an intergranular pore size of 9 nm exhibits the highest specific surface area ($215\text{ m}^2 \text{g}^{-1}$). Interestingly, the nanostructuring into OPIFs leads to a better stability of the surface area during thermal treatment under air or F₂ in comparison with MgF₂ NPs. As the first application, MgF₂ OPIFs were tested for the catalytic transformation of 2-chloropyridine under severe conditions (HF gas atmosphere, 350 °C). The OPIF activity, slightly lower than that of MgF₂ NPs, was related to the lower Lewis acidity strength of the part of active sites. The presence of these two kinds of sites represents a real originality which could be explored for other catalytic reactions requiring various active sites. In future work, as we successfully demonstrated that the nature and the size of the template could be tuned to prepare MgF₂ OPIF materials with different pore sizes, it will give access to the preparation of OPIF materials with pore diameters under 40 nm to exert a strong influence on the catalytic behaviors.

4. EXPERIMENTAL SECTION

4.1. Synthesis of the Polymer Templates. **4.1.1. Materials.** All reagents were purchased from Sigma-Aldrich and used as received unless otherwise noted. Methyl methacrylate (MMA, $\geq 99\%$), ammonium persulfate (APS, 98%), styrene (S, $\geq 99\%$), aluminum oxide (activated, neutral, Brockmann I), SDS (99%, Acros Organics), acetone ($\geq 99.8\%$, VWR), and 1-pentanol ($\geq 99\%$, Alfa Aesar) were used. MMA and S were passed through a column of aluminum oxide prior to polymerization. Ultrapure water was obtained from a PureLab ELGA system and had a resistivity of $18.2\text{ M}\Omega \text{ cm}^{-1}$ at 25 °C.

4.1.2. Polymer Template Syntheses and Characterizations. The free-emulsion polymerization of MMA was typically started by charging 0.2 g of APS as the initiator, 20 mL of acetone, and 60 mL of ultrapure water into a three-neck flask (reaction medium) that was connected to a reflux condenser and an ice bath. While the mixture was homogenized using a magnetic stirrer, nitrogen gas was purged to the reaction medium to remove free oxygen. After 30 min, 1 mL of MMA was added to the mixture, the temperature was increased to 70 °C, and the reaction continued for 4 h under nitrogen flow. Finally, the reaction medium was cooled down to room temperature, and the white polymer latex was used without purification. The D_h and PDI values of the resulting polymer template were measured by DLS: (D_h)_{DLS} = 206 nm and PDI = 0.02. The PMMA beads were further characterized by SEM. A SEM image is shown in Figure S3a. This polymer template is named PMMA-200 nm.

For the conventional emulsion polymerization of MMA, 1.65 g of SDS was initially added to the reaction medium, and the previous method was followed. The polymer template dispersed in water was used without further purification. (D_h)_{DLS} = 85 nm and PDI = 0.09. A SEM image of PMMA beads is shown in Figure S3b. This PMMA template is named PMMA-85 nm.

Microemulsion polymerization of styrene (S) was started by charging 33 mg of APS, 1.65 g of SDS, 1 mL of 1-pentanol, and 42 mL of ultrapure water in a three-neck flask connected to a reflux condenser and an ice bath. After 30 min of mixing under nitrogen flow, 7 mL of styrene was added to the mixture and temperature was increased to 70 °C. While nitrogen gas was purged to the flask, the reaction continued for 3 h. Synthesis was terminated by cooling down the flask to room temperature, and the polymer template was used without purification. (D_h)_{DLS} = 44 nm and PDI = 0.05. A SEM image of PS beads is shown in Figure S3c. This PS template is named PS-45 nm.

4.2. Synthesis of MgF_2 NPs. Magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%) and TFA ($\text{CF}_3\text{CO}_2\text{H}$) were purchased from Alfa Aesar. Hydrofluoric acid (HF, 40%) and methanol (CH_3OH , 99.8%) were purchased from Sigma-Aldrich. All reagents were of analytical grade and used as received without further purification. In a typical synthesis, 2.56 g of magnesium nitrate hexahydrate was dissolved in 2 mL of methanol in a Teflon reactor under stirring. Afterward, 0.88 mL of HF and 8 mL of methanol were added to the mixture and microwave heating was applied at 90 °C for 30 min. The resulting gel was washed with ethanol to remove any unreacted reagents and methanol and subsequently used for preparation of OPIF materials.

4.3. Synthesis of OPIF Materials. In general, 0.75 g of MgF_2 NP gel was sonicated in 20 mL of water to obtain a clear sol and 300 μL of TFA was added dropwise to the dispersion (2.75 mg mL^{-1} MgF_2 NP and maximum concentration tested, 5 mg mL^{-1}). While stirring, a given amount of polymer template latex (PMMA-200 nm, PMMA-85 nm, and PS-45 nm as described in the previous section) was gradually added to the medium (Table S1). After stirring for 24 h, the resulting mixture was centrifuged at 800 rpm for 1 h, dried at 110 °C, and calcined at 375 °C for 2 h (heating rate 2 °C min^{-1}) under an air atmosphere to remove the template and densify the MgF_2 network. As a reference, MgF_2 NPs (NP-ref-OPIF) were prepared according to the technique described above without the addition of polymer latex, and they were used for catalyst tests.

Soxhlet extraction was utilized to chemically remove the polymer template (PS-SDS). A porous thimble loaded with the dried sample was placed inside the main chamber of the Soxhlet extractor. The extraction cycle was repeated for 24 h by refluxing the 70% (v/v) solution of THF through the thimble using a condenser with cold water entering at the bottom and exiting above. The extraction was terminated by cooling down the flask to room temperature. The sample was washed with distilled water and dried at 60 °C.

4.4. F_2 Treatment. The calcination of OPIF compounds under F_2 gas to remove the carbon residue was carried out in a specific equipment dedicated to molecular fluorine, automatically controlled in order to guarantee constant experimental conditions. The OPIF compound was spread evenly in a passivated nickel boat that was introduced in a nickel reactor surrounded by a classic horizontal split furnace. The samples were then dehydrated at 140 °C under dynamic primary vacuum followed by filling of the reactor with nitrogen. The temperature was set to $T = 100$ °C for OPIF-200 and $T = 400$ °C for OPIF-85 and OPIF-45, and a mixture of 10% F_2 in nitrogen (Air Liquide) was flowed through the reactor under dynamic conditions for 2 h before being flushed by nitrogen.

4.5. HF Activation and Catalytic Measurements. As described previously,^{12,45} the activation by HF and the catalytic activity of the various MgF_2 materials for the transformation of 2-chloropyridine were carried out in a fixed-bed reactor. The different MgF_2 samples were diluted with 6 cm^3 of Lonza graphite (size grains between 125 and 200 μm). The catalyst was activated *in situ* by HF under nitrogen (HF/ N_2 molar ratio: 1/4) for 1 h at 350 °C (activation step). Then, 2-chloropyridine was introduced into the reactor using a syringe pump. The partial pressures of the various components were 0.806 bar for HF, 0.075 bar for 2-chloropyridine, and 0.132 bar for nitrogen (HF/(2ClPy/ N_2): 10.8/1/1.7). The organic gas products were trapped into 1,2-dichloroethane. HF and HCl were quenched in an aqueous solution of potassium hydroxide at the outlet of the reactor. The organic components were analyzed with a Scion 456 gas-phase chromatograph (Bruker) equipped with a DB5 capillary column (inside diameter: 0.2 mm, thickness of the film: 1 μm , and length: 30 m). The oven temperature was increased from 100 to 200 °C at a rate of 5 °C min^{-1} .

The catalyst performances were compared at isoconversion of 2-chloropyridine lower than 25% in order to be in a differential regime. In all cases, only 2FPy was observed as the reaction product and HCl as the byproduct. Thus, the selectivity toward 2FPy was equal to 100% and the conversion of 2-chloropyridine corresponded to the 2FPy yield. In these experiments, the molar balance was always higher

than 90%. No thermal decomposition of 2-chloropyridine was observed.

The catalytic activity A ($\text{mmol h}^{-1} \text{g}^{-1}$) was defined as the conversion of 2-chloropyridine multiplied by the flow of 2-chloropyridine (mol h^{-1}) and divided by the mass of the catalyst. The intrinsic catalytic activity A_i ($\text{mmol h}^{-1} \text{m}^{-2}$) was calculated by taking into account the specific surface area of the catalyst after the activation step by HF. The TOF (h^{-1}) was calculated from the catalytic activity (A : $\text{mmol h}^{-1} \text{g}^{-1}$) divided by the number of active sites defined as coordinatively unsaturated metallic sites (Q : $\mu\text{mol g}^{-1}$) measured by CO adsorption followed by IR. Gaseous HF (cylinder of 800 g) was provided by Air Liquide, and 2-chloropyridine was provided by Sigma-Aldrich.

4.6. Technical Characterizations.
4.6.1. Dynamic Light Scattering. The measure of D_h of polymer templates and MgF_2 NPs was conducted on a Nanosizer ZS Malvern device with a wavelength of 633 nm (Ne-He laser) at an angle of 173°. Each measure was repeated five times at 25 ± 1 °C with a delay of 60 s between the tests.

4.6.2. X-ray Diffraction. PXRD patterns of the MgF_2 NPs were recorded with a PANalytical θ/θ Bragg-Brentano Empyrean diffractometer (Cu $K\alpha_{1+2}$ radiations) equipped with a PIXcel1D detector. Data were collected in the $[15-110^\circ]$ 2θ angle range for a total acquisition time of 3 h with 0.499° steps. The NIST Standard Reference Material LaB_6 (NIST SRM 660b) was used to take into account the instrumental broadening. The PXRD pattern of LaB_6 was recorded with the conditions (step and counting time) used for the analysis of MgF_2 samples. PXRD patterns were fitted using the Le Bail method⁴⁶ implemented in the Fullprof program.⁴⁷ The line broadening due to the nanometric size of the sample was calculated using the Thompson-Cox-Hastings pseudo-Voigt function⁴⁸ that includes size and strain-broadening terms for both Lorentzian and Gaussian components. The two parameters (Y and F) of the Lorentzian component of this function were refined to calculate the apparent crystallite size $\langle L \rangle$ calculated by Fullprof using Langford's method.⁴⁹ The diameter D_{XRD} of the spherical particles is related to $\langle L \rangle$ using the following formula $D_{\text{XRD}} = 4/3 \times \langle L \rangle$.

4.6.3. Scanning Electron Microscopy. SEM images were obtained either using a JEOL microscope (JSM 6510 LV) at 20 kV or a Zeiss SUPRA 55-VP microscope at an acceleration voltage of 5 kV. All samples were coated by gold or gold/palladium (70/30) before analysis. The mean pore diameters were deduced by statistical evaluation of about 100 particles using ImageJ software.⁵⁰

4.6.4. Transmission Electron Microscopy. TEM studies were performed on a JEOL JEM 2100 HR electron microscope operating at 200 kV. The samples for transmission electron microscopy investigation were prepared by ultrasonically dispersing the raw powders in ethanol, depositing a drop of the resulting suspension onto a holey carbon-coated copper grid, and finally drying the grid in air. Mean diameters of the NPs (D_{TEM}) or pores were deduced by statistical evaluation of about 100 particles using ImageJ software.⁵¹

4.6.5. ^1H and ^{19}F and Solid-State MAS NMR. ^1H and ^{19}F solid-state MAS NMR experiments were performed on a Bruker Avance III spectrometer operating at 7.0 T (^1H and ^{19}F Larmor frequencies of 300.1 and 282.4 MHz, respectively), using a 1.3 mm CP-MAS probe head. The ^1H and ^{19}F MAS spectra were recorded using a Hahn echo sequence with an interpulse delay equal to one rotor period. The 90° pulse lengths were set to 2.4 and 1.25 μs ; the recycle delays were set to 120 and 900 s; and 24 to 64 and 32 to 48 transients were accumulated for ^1H and ^{19}F , respectively. ^1H and ^{19}F spectra refer to TMS and CFCl_3 , respectively, and they were fitted using DMFit software.⁵²

4.6.6. N_2 Sorption. The OPIF specific surface areas were measured at 77 K using a TriStar II 3020 (Micromeritics). The powders were degassed under vacuum at 100 °C for 12 h prior to measurement. The S_{BET} was calculated using the Brunauer-Emmett-Teller (BET) method. The porosity was evaluated from desorption branches of the N_2 isotherms using the BJH model. The total pore volumes were estimated from the adsorbed amount at the relative pressure $p/p^0 = 0.99$.

691 4.6.7. *FTIR Spectroscopy*. FTIR spectra of OPIFs after F₂
692 treatment were collected in air at room temperature with a Bruker
693 Alpha FT-IR spectrometer equipped with the Platinum QuickSnap
694 ATR sampling module. The spectral resolution is 4 cm⁻¹ in the 400–
695 4000 cm⁻¹ range.

696 As described previously,¹¹ CO adsorption was followed by FTIR
697 on a Thermo Nicolet NEXUS 5700 spectrometer with a resolution of
698 2 cm⁻¹, and 64 scans per spectrum were collected. Samples were
699 pressed into thin pellets (10–60 mg) with a diameter of 16 mm and
700 pretreated *in situ* during one night under nitrogen at 300 °C. After
701 that, the cell was cooled down with liquid nitrogen to 100 K. A
702 background spectrum was collected which was then subtracted from
703 the following spectra obtained after CO adsorption. Then, successive
704 doses of CO were introduced quantitatively, and an infrared spectrum
705 was recorded after each adsorption until saturation. The final
706 spectrum was recorded with 1 Torr of CO at equilibrium pressure
707 (saturation). All spectra were normalized to an equivalent sample
708 mass (25 mg). The quantification of the amount of Lewis acid sites Q_L
709 (μmol g⁻¹) was carried out by the integration of the total area of the
710 IR bands at saturation between 2100 and 2200 cm⁻¹ using the molar
711 absorption coefficient ε determined for MgF₂ and equal to 1.53 μmol
712 cm⁻¹.⁴⁵

713 ■ ASSOCIATED CONTENT

714 ■ Supporting Information

715 The Supporting Information is available free of charge at
716 <https://pubs.acs.org/doi/10.1021/acsanm.1c01768>.

717 XRD patterns and results of Le Bail refinements of MgF₂
718 NPs and OPIF materials, analysis of polymer templates
719 (PMMA and PS) by TGA, MEB/TEM and DLS, DLS
720 of MgF₂ NPs dispersed in water, MEB of OPIF-200 with
721 different *m* % ratios, N₂ adsorption–desorption
722 isotherms and BJH of OPIF-85 and OPIF-45 with
723 different template contents, TEM and N₂ analysis of
724 OPIFs obtained by chemical removal of the polymer
725 template, pictures and FTIR of the OPIF catalyst before
726 and after F₂ thermal treatment, TEM images of OPIF-
727 200 after F₂ and HF treatment, ¹⁹F and ¹H MAS NMR
728 spectra of the different OPIF materials, and TEM–EDX
729 of OPIF-45 (PS-SDS) after HF activation (PDF)

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