

Support information

Fe/hollow nano-MgF₂: a green and high-efficient alternative to classical Cr-based catalysts for gas-phase fluorination reaction

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Synthesis of catalysts. Commercially available $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used as the precursors without any further purification. The support, hollow nano- MgF_2 gel was prepared by a polyol mediated sol-gel process according to our recent method [1]. Brief procedure is as follows: (I) the required amounts of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and polyethylene glycol (PEG2000) ($M_w = 2000$, 99.9%) were dissolved in ethylene glycol (EG, 50 mL) at 60 °C (Mg concentration = 1.0 M, mass ratio of PEG2000/EG = 1:10) in a PTFE beaker. (II) The aqueous hydrofluoric acid (40 wt.%) was added to above solution in a calculated molar ratio of 1:4 for Mg/F under rigorous stirring for 6 h; then, a transparent and colorless sol was obtained. (III) The obtained sol was aged at 90 °C for 1 d, subsequently dried at 120 °C for 3 d to obtain the powder of dried gel.

The hollow nano- MgF_2 supported Fe samples were prepared by the incipient wetness impregnation method. The powder of dried gel was impregnated by an aqueous solution of the corresponding nitride of Fe, subsequent dried at 90 °C overnight, and finally calcined at 350 °C in air for 5 h. The content of iron salt in the solution was adjusted to give the calculated loading of 9.0 mol.% for Fe. The resulting powder was mixed with 2% graphite and shaped into cylindrical pellets (3 mm × 3 mm) as the catalyst. For comparison, the commercial nano- MgO (BET surface area: 220 m^2/g) was also purchased as the support from Zibo Reagent Co., ShanDong, China. The MgO supported Fe sample was prepared using the same procedure described above. In addition, the classic Cr_2O_3 catalyst was prepared by precipitating a solution of chromium chloride with aqueous ammonia according to our previous method [2].

To observe the potential transformation of aforementioned samples under the extremely corrosive conditions, all the pelletized samples (30 mL) were pre-treated in a nickel tubular reactor (2.5 cm × 70 cm) by a mixed gas of N_2 and HF ($\text{N}_2/\text{HF} = 4:1$) at 350 °C for 24 h. The pre-fluorinated sample were designated as F-Fe/ MgF_2 , F-Fe/ MgO and F- Cr_2O_3 , respectively, throughout the remainder of this paper.

Reaction procedure. Catalytic gas-phase fluorination reaction was performed in a continuous flow fixed bed reactor at atmospheric pressure over the pelletized catalyst (30 mL) after pre-treated by HF. The molar ratio of 1,1,1,3-tetrachloropropane (TCP) and HF was fixed at 1:10, and a contact time of 8 s with a reaction temperature of 260 °C was used for the catalytic test. Before reaction, the materials were preheated in a vaporizer at 250 °C. All tubings were thermostatted to avoid any condensation. After reaction the product gas was passed through a water bath to trap acid gases, then analyzed by a gas chromatograph (SICT GC-2000III) equipped with a flame ionization detector (FID) and a DB-5 capillary column (30 m × 0.25 mm). The relative composition of the products is based on peak areas and therefore do not represent the absolute yields because of difference in response factors.

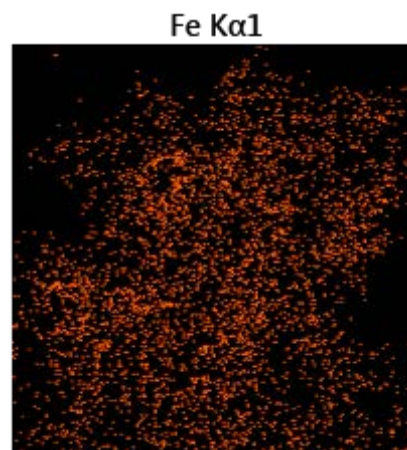
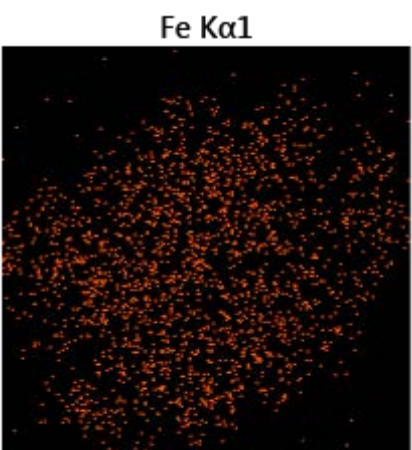
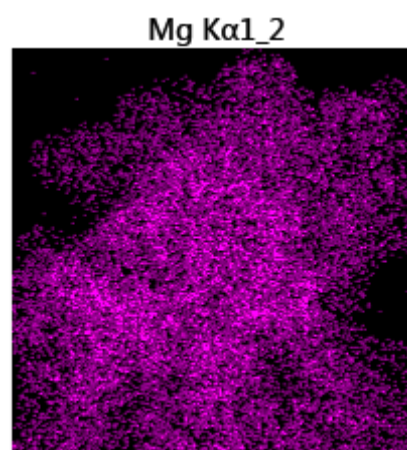
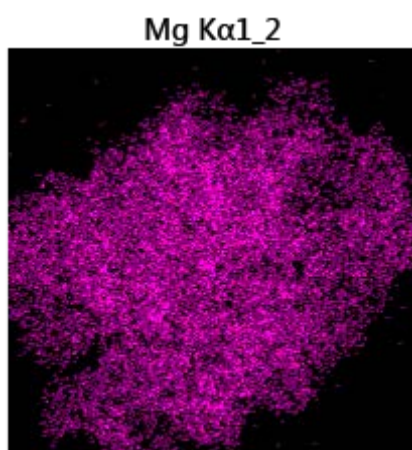
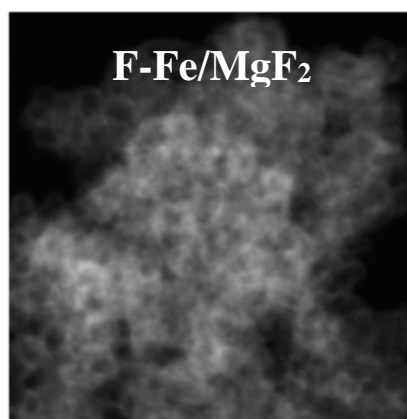
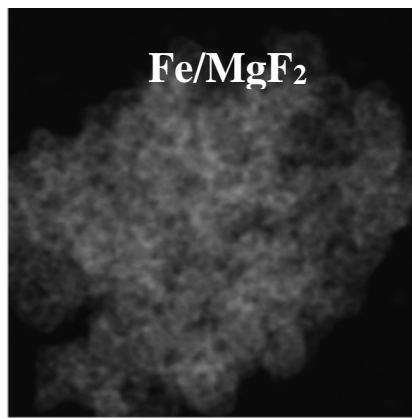
Characterization of catalysts. XRD patterns of the prepared samples were collected with an Empyrean, PANalytical X-ray diffractometer (Cu K α , $\lambda = 0.15418$ nm). The surface area of the sample was measured using nitrogen adsorption at 77 K and the Brunauer–Emmett–Teller (BET) method using a Micromeritics ASAP2020 system. All samples were degassed at 200 °C in vacuum for 8 h. Pore size distribution was determined by the Barret–Joyner–Halenda (BJH) method, applied to the desorption branch of the isotherm.

To determine the component in the sample, the elemental signals were detected by the Energy-Dispersive X-ray spectroscopy (EDS) (Oxford INCA Energy IE350) mapping method. The particle size and morphology of the samples were also observed using a transmission electron microscope (TEM) (FEI Tecnai G2 F20) operating on 200 kV.

The temperature-programmed desorption of ammonia (NH₃-TPD) measurement was carried on an AutoChem II 2920 instrument (Micromeritics, USA) for comparing the acidity of various samples. Prior to NH₃-TPD studies, a sample of 100 mg was first pretreated in pure He at 350 °C for 60 min, then cooled

to 110 °C and saturated at this temperature with anhydrous ammonia gas (10% in He) for 45 min. Weakly adsorbed NH₃ was eliminated by treatment under He at the same temperature for 60 min. The NH₃-TPD profile was recorded with a MS detector with a heating rate of 10 °C min⁻¹ from 110 to 580 °C in a He flow. After activation at 350 °C for 1 h, the Lewis and Brønsted acidity of the material was studied by an IR spectroscopy (PerkinElmer FT-IR Frontier), with adsorbed pyridine as a spectroscopic probe and a self-supported wafer of sample. Introduction of pyridine was performed at room temperature for 0.5 h and then evacuated under vacuum at 200 °C to remove physisorbed species.

Chemical environments on the surface of samples were analyzed using an X-ray photoelectron spectrometer (XPS) (Thermo Scientific K-Alpha) equipped with an Al monochromatic X-ray source (Al K_α = 1486.6 eV) under room temperature in high vacuum (about 1 × 10⁻⁹ Pa). The position of C1s BE at 284.8 eV was used as an internal standard for correcting any charge-induced peak shifts. Before the test, the pellet type samples were outgassed for about 2 h at 150 °C under a pressure of 1 × 10⁻⁶ Pa to minimize the surface contamination. Raman spectra were obtained on a Renishaw Raman System 2000 with exciting wavelength of 514 nm under ambient conditions.



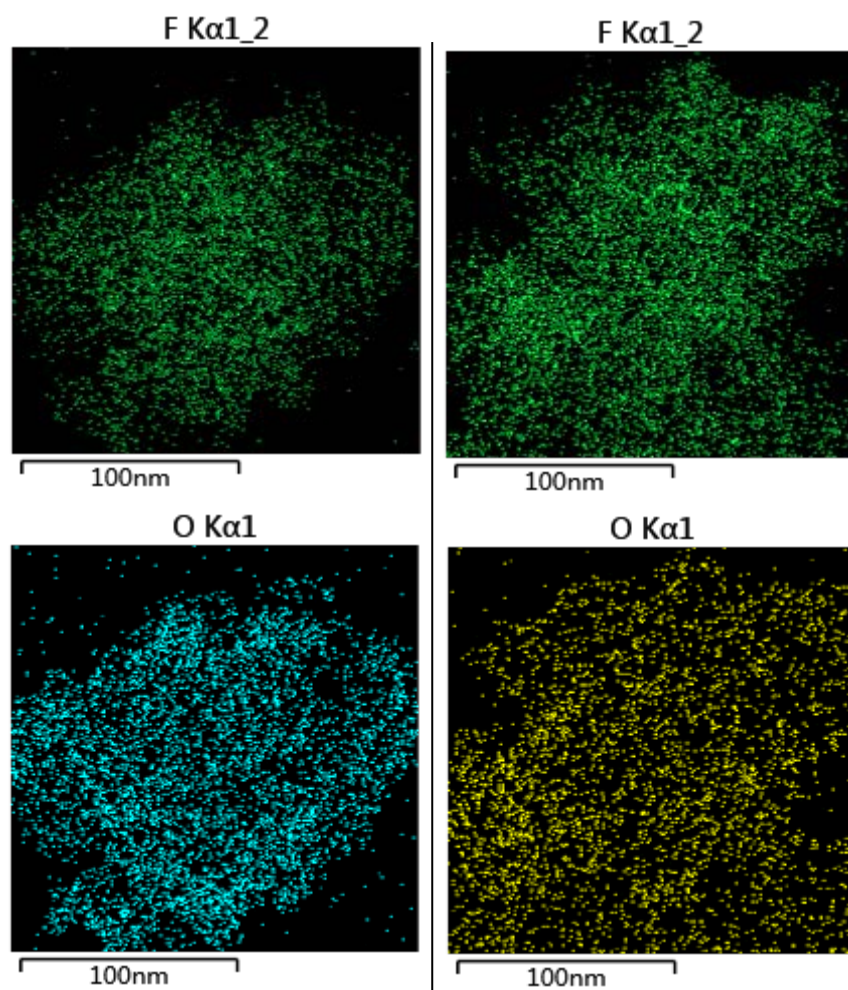


Figure S1 STEM EDS elemental mapping for Fe/hollow nano-MgF₂ before and after HF treatment.

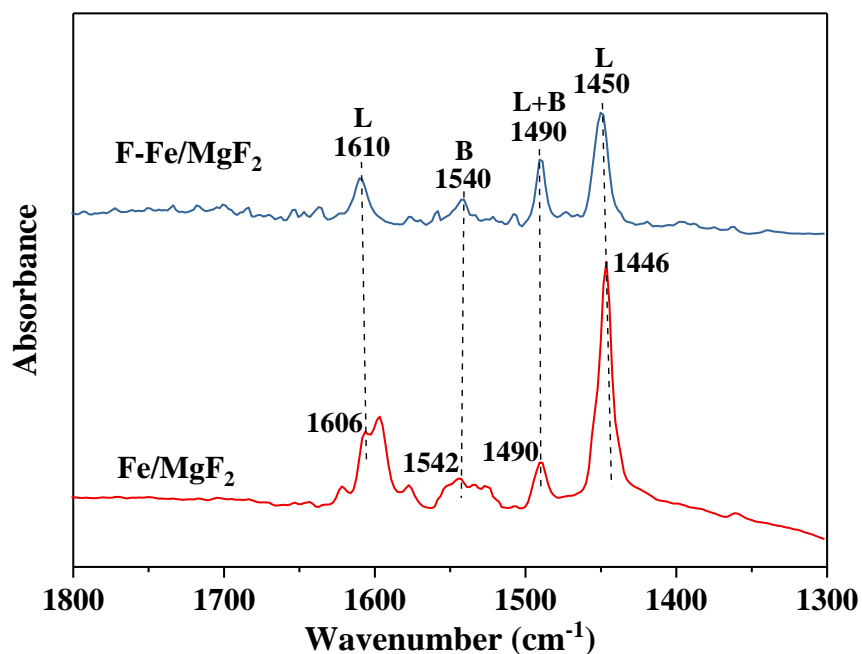


Figure S2 FT-IR spectra recorded after pyridine chemisorption of Fe/hollow nano-MgF₂ before and after HF treatment. Peaks at (B) are indicative for Brønsted acidity, and peaks at (L) for Lewis acidity.

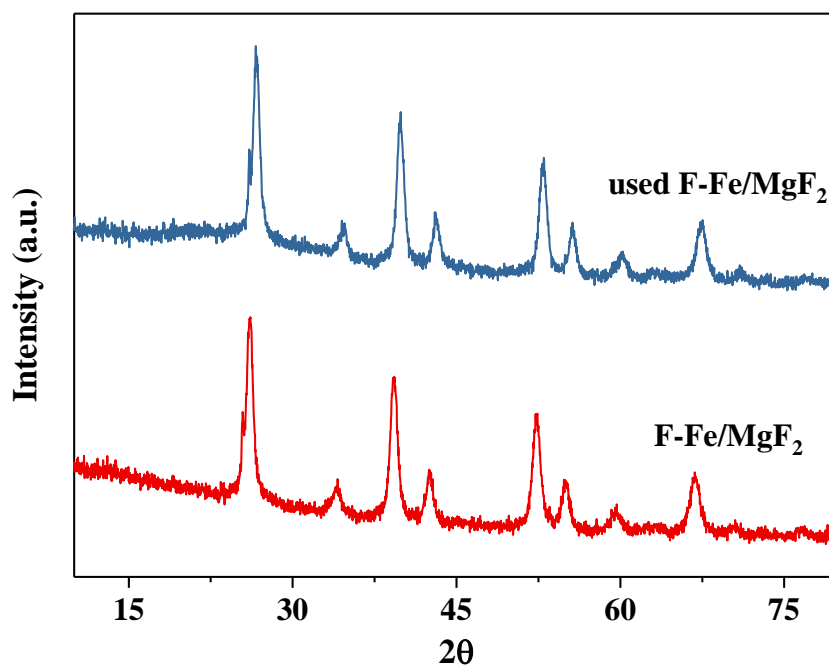


Figure S3 XRD patterns of Fe/hollow nano-MgF₂ catalysts before and after long-term reaction.

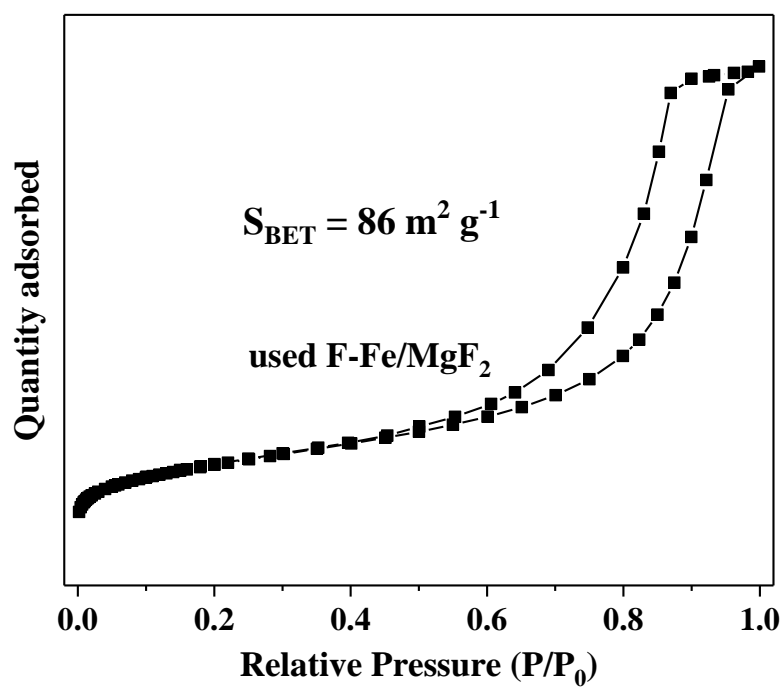


Figure S4 N₂ sorption isotherms of spent F-Fe/MgF₂.

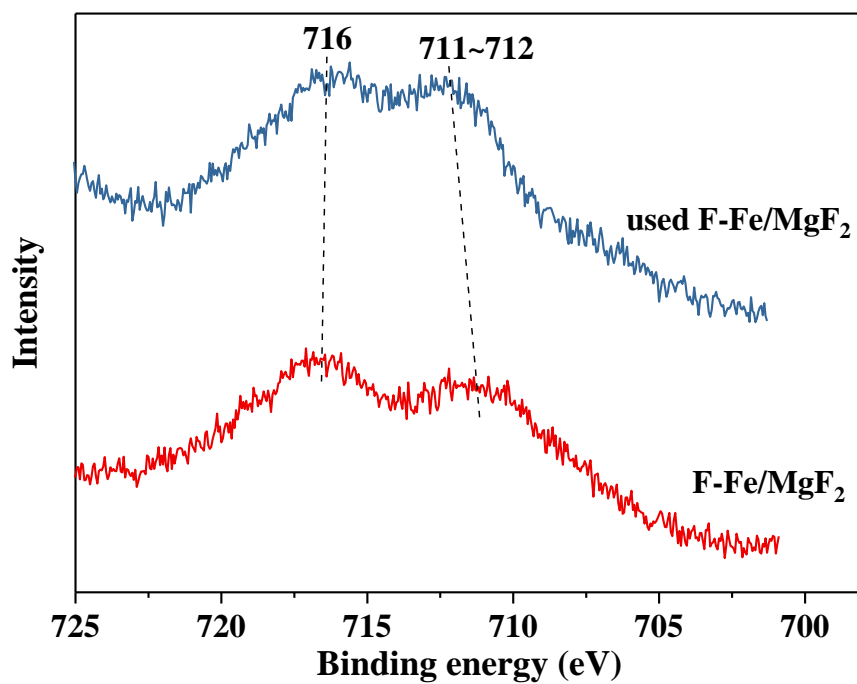


Figure S5 XPS Fe 2p_{3/2} spectra of spent F-Fe/MgF₂.

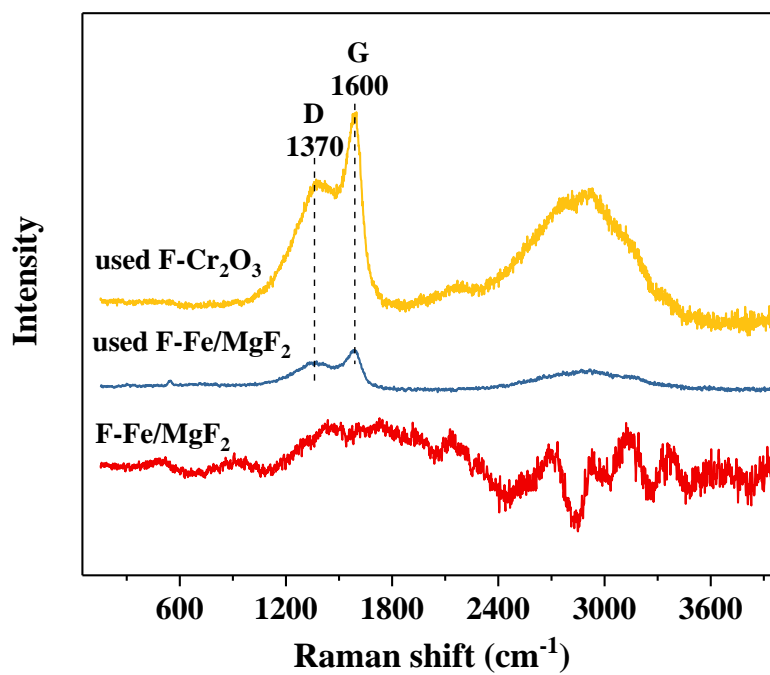


Figure S6 Raman spectra of spent F-Fe/MgF₂ and F-Cr₂O₃.

Table S1 elemental compositions of various samples detected by SEM-EDS.

Sample	C (wt.%)	O (wt.%)	F (wt.%)	Mg (wt.%)	Fe (wt.%)	Cr (wt.%)
Fe/MgF ₂	3.0	6.1	51.2	28.6	11.1	–
F-Fe/MgF ₂	2.0	2.9	57.0	25.3	12.8	–
spent F-Fe/MgF ₂	10.3	3.2	51.7	22.6	12.2	–
F-Cr ₂ O ₃	1.5	13.9	41.7	–	–	41.1
spent F-Cr ₂ O ₃	12.4	4.9	41	–	–	39.2

References

- [1] Z. H. Jia, W. Mao, Y. B. Bai, B. Wang, H. Ma, C. Li, J. Lu. Hollownano-MgF₂ supported catalysts: Highly active and stable in gas-phase dehydrofluorination of 1,1,1,3,3-pentafluoropropane. *Applied Catalysis B: Environmental* 238 (2018) 599–608.
- [2] W. Mao, L. G. Kou, B. Wang, Y. B. Bai, W. Wang, J. Lu. Catalytic gas-phase fluorination of 1,1,2,3-tetrachloropropene to 2-chloro-3,3,3-trifluoropropene over the fluorinated Cr₂O₃-based catalysts. *Applied Catalysis A: General* 491 (2015) 37–44.