Metal–Organic Framework-Derived Strategy for Improving Catalytic Performance of a Chromia-Based Catalyst in the Chlorine/Fluorine Exchange Reactions for Unsatuated Fluorocarbons

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ABSTRACT: Hydrofluoroolefins (HFOs) and cyclic hydrofluorocarbons (c-HFCs) have been the most favored alternatives of the ozone depletion substances; however, because of the poor performance of the present chlorine/fluorine (Cl/F) exchange catalysts, the development and production of HFOs and c-HFCs are hindered. Here, we first report a novel and facile route to fabricate high-performance Cl/F exchange catalysts via a metal–organic framework (MOF) carbonization method. The MOF-derived catalyst not only has high selectivity but also can significantly lower the reaction temperature. Moreover, benefiting from the stable structure and coke-inhibiting ability, the MOF-derived catalyst has a long service life compared with the traditional precipitation method. Furthermore, the nanoscopic MOF-derived catalyst can greatly reduce the Cr dosage, which would help to minimize the risk of Cr contamination.

1. INTRODUCTION

Since the Montreal Protocol (1987) was signed by many nations of the world, chlorofluorocarbons (CFCs) have been phased out because of their ozone depletion potential (ODP), and varieties of CFC alternatives have been developed in the past decades. As one of the alternatives to CFCs, the hydrofluorocarbons (HFCs) have zero ODP but high global warming potential (GWP). Accordingly, they were also placed in the basket of controlled greenhouse gases in the Kyoto Protocol (1997) and phased down in the Kigali amendment to the Montreal Protocol (2016). In recent years, as the most promising CFC alternatives, hydrofluoroolefins (HFOs) and cyclic hydrofluorocarbons (c-HFCs) have attracted tremendous research attention because of their zero ODP and low GWP (their unsaturated structures could lead them to fast degradability in atmospheric environment).

However, there are still several challenges for the synthesis of HFOs and c-HFCs via the chlorine/fluorine (Cl/F) exchange catalytic reaction, which was the most important method in the production of HFOs and c-HFCs. First, because of the unsaturated structures of the cyclic structure and/or double bond, addition reactions may take place in the process of fluorination and further induce the formation of oligomers and/or cokes on the surface of catalysts and thus, reduce the service life of catalysts. Second, for many polychlorinated reactants (Cl ≥ 4), deep fluorination always needs high reaction temperatures; however, the high reaction temperatures not only further result in oligomers and/or cokes but also aggravate equipment corrosion, which are not favored in industrial production. Third, heavy-metal pollution is another drawback of utilization of Cr-based catalysts in great amounts because the mostly used Cl/F exchange catalyst is a chromia-based catalyst and Cr element is one of the environmental pollutants.

To solve the above-mentioned problems for the synthesis of HFOs and c-HFCs, a high-performance catalyst with high selectivity, low reaction temperature, and low amount of chromium usage must be developed. Nanotechnology is one of the most effective ways to improve the performance of catalysts. Kemnitz reported a fluoroolytic sol–gel synthesis method which could provide nanoscaled metal fluorides (e.g., AlF3, BaF2, and MgF2) with about 200–400 m2/g surface areas and, compared with the traditional precipitation method, the nanoscopic catalysts exhibited distinctly higher reactivity. However, there are no fluorinated chromia catalysts reported with such a method.

In recent years, metal–organic frameworks (MOFs) have gained significant attention as catalysts because of their ultrahigh surface area, crystalline nature, structural diversity, and tailorability. More interestingly, MOFs can also be used as precursors or templates to derive various metal oxide/carbon nanocomposites by applying thermal treatments. Compared with conventional nanomaterials, MOF-derived nanoma-
The carbonization mechanism and process for MIL-101(Cr) under N2 atmosphere is shown schematically in Figure 1. Thermogravimetric analysis–mass spectroscopy (TGA–MS) study was carried out to evaluate the carbonization mechanism and process for MIL-101(Cr) (Figure S2). For the first mass-loss stage (below ca. 100 °C), the adsorbed solvent (H2O) was evaporated and for the second mass-loss stage (below ca. 550 °C), the framework was decomposed and pyrolysis gaseous products (such as H2, CO2, and C2H4) were released. Variable temperature in situ XRD experiments of MIL-101(Cr) also confirmed the TGA–MS observations and further indicated that the phase of the formed chromium oxide converted from an amorphous structure to crystalline structure with increasing carbonization temperature from 700 to 900 °C (Figure S3). Thus, to systematically study MIL-101(Cr)-derived chromia-based catalysts, MIL-101(Cr) was carbonized at 700, 800, and 900 °C, and the corresponding samples were denoted as Cr-700, Cr-800, and Cr-900, respectively.

SEM observations show that the carbonized samples retained the octahedral cubic morphology of the pristine MIL-101(Cr), and TEM analysis reveals that the particles of all carbonized samples were composed of carbon microparticles and chromia nanoparticles (Figure S4). Furthermore, with the temperature increasing, the sizes of chromia nanoparticles increased from ~10 nm for Cr-700 to ~40 nm for Cr-900. In addition, high-resolution TEM (HRTEM) clearly indicated that the morphology of chromia nanoparticles for Cr-800 and Cr-900 were crystalline, and this is consistent with the XRD analysis results.

X-ray photoelectron spectroscopy (XPS) was applied to identify the chemical states of chromium. From Figure S5, one can see that the Cr 2p3/2 core level spectrum of Cr-700, Cr-800, and Cr-900 all show a single peak at ~576.5 eV which is attributed to the Cr2O3 phase, indicating that all carbonized samples were dominated by chromium oxide and no Cr0 was present. It is interesting to note that, unlike Zn-based MOFs46 Co-based MOFs47,48 and Fe-based MOFs49 Cr ions in the MIL-101(Cr) precursor will not be reduced to Cr metal in the process of carbonization. This is important for the MOF-derived method to prepare the Cl/F exchange catalyst because only the chromium oxide can be converted to the active constituent by pre-fluorination. Raman spectra for all samples are shown in Figure S6; all spectra exhibited D and G bands at 1350 and 1590 cm−1, respectively. As is well known, the intensity ratio of the G-band and D-band (Ig/Id) illustrates the crystallization degree of graphitic carbon.50–52 The values of all carbonized samples were around 1.04, which indicates that the obtained carbon materials were amorphous carbon, and this is in coincidence with the XRD pattern.

The carbonized materials of Cr-700, Cr-800, and Cr-900 were pre-fluorinated by HF to prepare Cl/F exchange catalysts and the corresponding pre-fluorinated samples were denoted as F-Cr-700, F-Cr-800, and F-Cr-900, respectively. The XRD patterns of pre-fluorinated samples are shown in Figure S7. As can be seen, F-Cr-800 and F-Cr-900 all showed strong diffraction peaks of CrF3, which are consistent with their precursors. Whereas compared with the amorphous structure of Cr-700, F-Cr-700 exhibits very weak diffraction peaks of CrF3, which may be resulted from the severe exothermic fluorination. Most of all, the diffraction peaks of CrF3 are not observed for all pre-fluorinated samples, which indicates that the resultants of the pre-fluorination are amorphous.

From TEM images (as shown in Figure 2), one can see that the structures of the pre-fluorinated samples have no obvious changes compared with their corresponding precursors, which indicates that the textural structure of the carbonized MIL-101(Cr) is very stable and it will not collapse even after pre-fluorination with AHF. This result was also confirmed by the N2 adsorption isotherms (Figures S8–S13 and Table S1): the isotherms and pore-size distributions before and after pre-fluorination were consistent. The HRTEM images of F-Cr-700, F-Cr-800, and F-Cr-900 (Figure 2b,e,h) showed lattice fringes with interplanar spacings of ca. 0.36 nm and ca. 0.25 nm, corresponding to the (012) plane and (110) plane of the Cr2O3 phase, respectively. This further confirms the results of XRD analysis. Furthermore, energy-dispersive X-ray spectrometry (EDX) maps (Figure 2c,f,i) clearly showed that the elemental distributions of Cr, O, and F were consistent, which indicates that the chromia nanoparticles had been effectively pre-fluorinated. From the element contents analysis by EDXS (as shown in Table S2), it is found that the fluorine content decreases with increasing carbonization temperature, indicating that the sample carbonized at high temperature (e.g., 900 °C) is difficult to be fluorinated compared to those carbonized at low temperature (e.g., 700 °C), which may be due to the more stable...
structure of the crystalline Cr₂O₃ than the amorphous ones and the low specific surface area of the large Cr₂O₃ particles.

It was reported that the CrOₓFᵧ component on the surface of the Cr-based catalyst plays a key role in the F/Cl exchange reactions.⁵³⁻⁵⁶ Thus, the component analysis of CrOₓFᵧ is very important to understand the activity of the Cr-based catalyst. The formation of CrOₓFᵧ on the surface of the pre-fluorinated samples can be determined by XPS analysis. From Figure 3, one can see that the Cr 2p₃/₂ peaks for all pre-fluorinated samples can be deconvoluted with three components by a curve fitting procedure. For F-Cr-700, F-Cr-800, and F-Cr-900, except the chromia species (binding energy around at 576.5 eV), there were two new peaks belonging to CrOₓFᵧ (binding energy larger than 577.0 eV).¹⁵,⁵⁷ Generally, the binding energy of CrOₓFᵧ is determined by its F % content, and the higher the F % content, the higher the binding energy. Thus, the pre-fluorinated samples of F-Cr-700, F-Cr-800, and F-Cr-900 all have two kinds of CrOₓFᵧ with different F ratios. Furthermore, with the carbonization temperature raising, the binding energies of CrOₓFᵧ were boosted, indicating that CrOₓFᵧ obtained from the higher-temperature-carbonized samples will contain higher F ratio. When F ratio reaches the maximum value, CrF₃ is formed (the binding energy at ~580.4 eV).¹²,⁴₄,⁴₅ It should be noted that although F ratio in CrOₓFᵧ increased with the carbonization temperature raising, the F content of the whole catalysts decreased (as shown in Table S3), which may be caused by the lower specific surface area for the higher-temperature-carbonized samples.

NH₃-TPD experiment was conducted to study the acid strength of the catalyst surface. As can be seen from Figure 4, F-Cr-700 has a large desorption peak above 300 °C and two small desorption peaks below 300 °C, F-Cr-800 has a middle desorption peak above 300 °C, and F-Cr-900 has a very small desorption peak above 400 °C, which indicates that, with increasing calcination temperature, the weak acid disappeared and the amount of total acid sites also decreased (the calculated surface acid densities based on the desorption peak area are shown in Table S4). The vanishing of the weak acid may be resulted from the high F ratios in CrOₓFᵧ for the high-temperature-carbonized samples as revealed from XPS results. Moreover, TEM images and BET analysis clearly show that the size of the Cr₂O₃ particle grows larger and the specific surface area of the catalysts become lower with the carbonization temperature raising, and this will reduce the active sites because the active component (CrOₓFᵧ) can only form on the surface of the catalysts. As a result, the amount of total acid sites decreased.
for the high-temperature-carbonized samples. Furthermore, NH<sub>3</sub>-TPD of the catalyst (F-Cr<sub>2</sub>O<sub>3</sub>) prepared by the coprecipitation method shows that the main desorption peak is between 100 and 300 °C (as seen in Figure S14), which demonstrates that most of the acid sites of F-Cr<sub>2</sub>O<sub>3</sub> are weak acids. Thus, compared with the acidity of F-Cr<sub>2</sub>O<sub>3</sub>, the acidity strengths of the MOF-derived catalysts are stronger.

To evaluate the catalytic performance of the prepared catalysts, the Cl/F exchange reaction of HCBD and AHF over F-Cr-700 and F-Cr-800 (Scheme 1) was studied. In fact, the fluorination of HCBD has been researched using chromia-based catalysts prepared with the coprecipitation method in our previous work. The desired product is 1,2-dichlorotetrafluorocyclobutene (DTB), which is a cyclic fluorocarbon and has wide applications. However, there were two main drawbacks for that reaction with respect to industrial applications. First, the reaction temperature (390 °C) was too high, which would increase energy consumption and aggravate equipment corrosion. The other, because of the high reaction temperature, the byproducts were increased.

Figure 5a shows the catalytic activities of F-Cr-700, F-Cr-800, and F-Cr<sub>2</sub>O<sub>3</sub> (prepared by the coprecipitation method) at different reaction temperatures with AHF/HCBD ratio of 7:1 and contact time of 12 s. One can see that for all MOF-derived catalysts, the conversions of HCBD increased with the reaction temperature raising, but the selectivity of DTB decreased. This is because some of the reaction intermediates in the fluorination of HCBD are prone to undergo addition reaction and/or cracking reaction at high temperatures. For example, there are a large amount of addition products (i.e., CF<sub>3</sub>CCl=CCl(CF<sub>3</sub>) and decomposition products (i.e., CF<sub>3</sub>CCl=CCl<sub>2</sub>) formed in the fluorination of HCBD over F-Cr<sub>700</sub> at 390 °C (as shown in Figure S16), whereas the main products generated at 230 °C are the fluorinated compounds (C<sub>2</sub>F<sub>2</sub>Cl<sub>2</sub>, C<sub>3</sub>F<sub>4</sub>Cl<sub>2</sub>, C<sub>4</sub>F<sub>6</sub>Cl<sub>2</sub>, and C<sub>4</sub>F<sub>8</sub>Cl<sub>4</sub>) and there are almost no addition products or decomposition products, as shown in Figure S17. Moreover, as revealed in our previous work, the reaction temperature is high at 390 °C for the catalysts prepared by the coprecipitation method to get the best catalytic performance (73% conversion of HCBD and 38% selectivity of DTB). However, for MOF-derived catalysts prepared in this work, a comparative performance (88.9% conversion of HCBD and 20.5% selectivity of DTB) can be achieved at a low reaction temperature of 230 °C. Furthermore, the catalytic performances of MOF-derived catalysts are far better than that of F-Cr<sub>2</sub>O<sub>3</sub> for the same reaction condition at 230 °C (product analysis of F-Cr<sub>2</sub>O<sub>3</sub> was shown in Figure S18). Also, from the product distributions (Figure 5b), it can be seen that the main products for MOF-derived catalysts are deep fluorinated compounds (C<sub>4</sub>F<sub>4</sub>Cl<sub>2</sub> and C<sub>4</sub>F<sub>3</sub>Cl<sub>3</sub>), whereas for F-Cr<sub>2</sub>O<sub>3</sub> the main products are mild fluorinated compounds (C<sub>4</sub>F<sub>2</sub>Cl<sub>4</sub> and C<sub>4</sub>F<sub>1</sub>Cl<sub>5</sub>), which indicates the high fluorination ability of the MOF-derived catalysts.

The reasons for the improved performance of the MOF-derived catalysts may include the following aspects: first, the stronger acidity. Generally, stronger acidity can effectively enhance the catalytic activity, as the chlorine/fluorine exchange reaction is a Lewis acid-catalyzed reaction. The stronger acidity may be resulted from the high F ratios in the active component (CrO<sub>4</sub>F<sub>y</sub>) as revealed by XPS analysis. Second is the nanostructure and high surface area. Benefiting from the structure of Cr-MOF, the nanoscaled catalysts with a high specific surface area can be obtained by the calcination method. As is known to all, the nanostructure and high surface area for the catalyst will help to expose more active sites and further improve the catalytic activity. Third is the crystalline structure. As usual, the catalysts prepared by the coprecipitation method are almost amorphous. However, Kemnitz had pointed out that the crystalline catalysts exhibit under-coordinated sites and should act as solid Lewis acids, but because of the usually very low surface areas of these crystalline catalysts, just a very limited number of these surface sites are available in catalytic reactions. The MOF-derived catalysts, especially for F-Cr-800, possess both the crystalline structure and high specific surface area (433.9 m<sup>2</sup> g<sup>-1</sup>) and achieve an excellent catalytic performance.

The stability of the MOF-derived catalyst for the fluorination of HCBD at 230 °C was also evaluated. From Figure 6, one can see that the conversion and the selectivity were quite stable with time on stream for F-Cr-700 compared with F-Cr<sub>2</sub>O<sub>3</sub>, indicating the high stability of F-Cr-700. It has been reported that the structure collapse of the chromia-based catalyst during the fluorination with HF was one of the major causes of deactivation. However, the chromia-based catalysts prepared in this work were loaded on the porous carbon matrix and carbon is inert to HF, thus the structure of MOF-derived catalyst can keep stable during the fluorination. Furthermore, XPS

**Scheme 1. Reaction Products for the Fluorination of HCBD with HF**

![Scheme 1](https://example.com/scheme1.png)

**Figure 5.** (a) Catalytic activity of F-Cr-700 (square), F-Cr-800 (star), and F-Cr<sub>2</sub>O<sub>3</sub> (triangle) at different reaction temperatures (AHF/HCBD = 7:1, contact time = 12 s). (b) Product distributions of F-Cr-700, F-Cr-800, and F-Cr<sub>2</sub>O<sub>3</sub> at 230 °C.
surface element analysis showed that there was no obvious increase of carbon content on the catalyst surface at different reaction time, which indicates that the MOF-derived catalyst can effectively reduce the formation of coke (Table S5 and Figure S20). It should be noted that although the Cr2O3 nanoparticles respectively. As can be seen that the catalytic e indicates that MOF-derived catalysts can improve the utilization of MOF-derived catalysts were confined in the carbon, the relatively high surface and pore structure of carbon facilitate the exposure of the Cr2O3 nanoparticles. In other words, the MOF-derived method will not cover the catalytic sites by the formed carbon.

In addition, benefiting from the nanosized chromia particles, the activity of F-Cr-700 is about 7.8 times that of F-Cr2O3 for a certain amount of Cr (the calculation method was shown in the Supporting Information Part I), which can significantly reduce the Cr dosage and minimize the risk of Cr contamination. Furthermore, the turnover frequency (TOF) of F-Cr-700, F-Cr-800, and F-Cr2O3 were also obtained (the calculation method was shown in the Supporting Information Part I), and the corresponding values were 0.92, 1.94, and 0.50 min⁻¹, respectively. As can be seen that the catalytic efficiencies of MOF-derived catalysts are far more higher than those of the catalysts prepared by the coprecipitation method, which also indicates that MOF-derived catalysts can improve the utilization efficiency of Cr and it will help to reduce the risk of Cr contamination.

3. CONCLUSIONS

A series of chromia-based catalysts was prepared by the MOF-derived method and their catalytic performances were studied through the fluorination of HCBD. Compared with the conventional coprecipitation method, the MOF-derived method showed a huge advantage in fabricating Cl/F exchange catalysts, which is summarized as follows:

1. Nanoscaled chromia-based catalysts with high specific surface area were obtained, and the acidity of the catalyst can be adjusted through the carbonization temperature.

2. A lower reaction temperature was achieved for the fluorination of HCBD and the conversion and selectivity were quite high.

3. The catalyst exhibited a long service life due to its high stable structure and ability to suppress carbon deposition.

4. MOF-derived catalyst has a lower amount of chromium usage and higher utilization efficiency of chromium, and this will help to minimize the risk of Cr contamination.

In a word, the present study shows that employing MOFs as the template can provide a novel method to improve the catalytic performance of Cl/F exchange catalysts, especially for the synthesis of unsaturated fluorocarbons.

4. EXPERIMENTAL SECTION

4.1. Materials. All reagents were commercially available and used as received without further purification. HCBD (98%) was obtained from Letai Chemical Industry Co., Ltd. (Tianjin, China). Anhydrous HF (AHF) (>99.9%) and nitrogen gas (>99.9%) were purchased from Beijing North Oxygen Specialty Gases Institute Co., Ltd. (Beijing, China). Hydrofluoric acid (40%) and NH4H2O (30%) were obtained from Beijing Chemical Co., Ltd. (Beijing, China). Analytical-grade Cr(NO3)3·9H2O (>99%), 1,4-benzenedicarboxylic acid (H2BDC) (>99%), and furfuryl alcohol (98%) were purchased from J&K Scientific Ltd.

4.2. Catalyst Preparation and Activation. MIL-101(Cr) was synthesized and carbonized according to the previous reports after a minor modification. Typically, the mixture of Cr(NO3)3·9H2O (2 g, 5 mmol), terephthalic acid (0.83 g, 5 mmol), hydrofluoric acid (5 mmol), and H2O (30 mL) was placed in a 50 mL Teflon autoclave and then heated at 220 °C for 8 h. After natural cooling, the mixture was collected by centrifugation. The resulting powder was ultrasonically washed with H2O, DMF, and ethanol. A light-green powder of MIL-101(Cr) was obtained by drying in a vacuum oven (80 °C) for 8 h. Then, MIL-101(Cr) (1.5 g) was vacuum dried at 200 °C for 12 h and then mixed with furfuryl alcohol (10 mL) while stirring for 24 h to ensure complete saturation. After filtration, the furfuryl alcohol/MIL-101(Cr) mixture was washed with absolute ethanol to remove furfuryl alcohol adsorbed on the surface. The furfuryl alcohol/MIL-101(Cr) mixture was transferred into a ceramic boat which was placed in a quartz tube fixed in a tube furnace. The mixture was initially heated at 150 °C for 24 h to carry out the polymerization of furfuryl alcohol inside the pores of MIL-101(Cr) template, and then carbonization was carried out at 700, 800, and 900 °C for 5 h under N2 gas atmosphere to obtain the corresponding carbonized samples: Cr-700, Cr-800, and Cr-900, respectively, which were the precursors of the catalysts (note: the heating rates for all samples are 5 °C min⁻¹).

Before reaction, pre-fluorination was carried out to activate the precursors. A 1.0 g sample of the carbonized sample (Cr-700, Cr-800 or Cr-900) was packed into the reactor. A mixture of N2,
samples were calculated by the BET method and mA) in the 2
QMS403C under N2 atmosphere with the ramping rate of 10
local density functional theory method.
and the average pore diameters were determined by the non-
vacuum at 300
°
sorption system at
decreased to 10 mL/min and the AHF
was pretreated at 400
°
minute. A 50 mg portion of the catalyst
monitored by an online chemisorption analyzer (Quantach-
TPD, which was conducted in a quartz U-shaped reactor and
rate of 30 mL/min. Finally, the pre-fluorination catalysts were
formed and were denoted as F-Cr-700, F-Cr-800, and F-Cr-900,
respectively.

The detailed process for Cr2O3 catalysts prepared by the
traditional coprecipitation method was as follows: Cr(NO3)3,
9H2O was dissolved in the distilled water and then NH4·H2O
(30%) was added to the above solution under stirring until the
pH value of the suspension reached 8.0. After continuous
stirring for 2 h, the precipitated solid was filtered and washed
with distilled water several times. The solid was dried at 120
°
onight and calcined at 400
°
get the final catalyst. The pre-fluorination of the coprecipitated Cr2O3 was carried out by
the same procedures as above, and the fluorinated Cr2O3 was
denoted as F-Cr2O3.

4.3. Characterization of Catalysts. The adsorption–desorption isotherm of nitrogen was measured by Micromeritics ASAP 2460 or MicrotracBEL BELSORP-max automated gas
 sorption system at −196
°
the sample was degassed under vacuum at 300
°
4 h. The specific surface areas of all samples were calculated by the BET method and t-plot method, and the average pore diameters were determined by the non-
local density functional theory method.
Simultaneous thermogravimetry analysis and mass spectroscopy
(TG–MS) was used to determine the combustion process of MIL-101(Cr) on a NETZSCH STA449F3-
QMS403C under N2 atmosphere with the ramping rate of 10
°
minute. In situ XRD was obtained by use of a high-temperature Anton
PAAR HTK 16N chamber (Pt strip) installed in a PANalytical Empyrean diffractometer using Cu Kα radiation (40 kV and 100
mA) in the 2θ range from 5 to 80
°
with a scan rate of 5° min−1
under N2 atmosphere.
The XRD patterns of the samples were recorded on a Rigaku
D/max-2500 power diffractometer using Cu Kα radiation (40
kV and 100 mA) in the 2θ range from 5 to 80
°
with a scan rate of 5° min−1
. Raman microscopy was performed on a WITec CRM200 using 514 nm laser.
SEM analyses were performed (JEOL, Model JSM-7500F) at
an acceleration voltage of 10 kV.
TEM images were acquired on a FEI Tecnai G2 F20 operating
at 200 kV. Diffraction patterns were recorded on a Gatan
UltraScan1000XP CCD camera. TEM samples were prepared by drop-casting 100 µL of the sample suspension (ground sample powder dispersed in ethanol) on carbon grids.
XPS measurements were acquired on a Kratos Axis Ultra
DLD multitechnique X-ray photoelectron spectrometer (UK)
equipped with a monochromatic Al Ka X-ray source (hv = 1486.6 eV). All XP spectra were recorded using an aperture slot measuring 300 μm × 700 μm. Survey and high-resolution spectra with pass energies (within ±0.2 eV) were determined with respect to the position of the adventitious C 1s peak at 284.6 eV.
The surface acidity of the catalysts was measured by NH3-
TPD, which was conducted in a quartz U-shaped reactor and monitored by an online chemisorption analyzer (Quantachrome, Model Chem Bet 3000). A 50 mg portion of the catalyst was pretreated at 400
°C for 1 h in a helium flow (30 mL/min),
then cooled to 100
°C, and finally saturated with 5% NH3/He. The sample was subsequently purged with helium for 30 min to eliminate all physically absorbed ammonia, followed by heating the sample up to 600
°C with a ramp of 10
°C/minute. The desorbed NH3 was monitored continuously via a TCD detector.

4.4. Catalytic Fluorination and Analytical Procedures. All catalytic fluorination reactions were carried out with a gas-
phase catalytic apparatus. The gas-phase catalytic apparatus was composed of a pump for transferring HCBD (liquid phase), mass flow controllers to control HF and N2, and an electrically heated tubular Inconel reactor (6 mm in diameter and 300 mm in length) equipped with an inner Inconel tube for the insertion of type-K thermocouples with a diameter of 1 mm. Carbon fiber was used to hold the catalyst powders in the reactor. The thermocouple enters the reactor through a Monel-type fitting and extends into the catalyst bed to measure the temperature changes in different positions along the reactor. Typically, a 1.0 g
sample of the catalyst was packed into the reactor, and a mixture of HCBD (6 mg/min) and AHF (4 mL/min) was passed through the reactor at 230–390
°C. Subsequently, the products were collected below −80
°C and then the products were washed with KOH solution and H2O successively. The final products were analyzed by GC–MS. The desired product, DTB, was obtained by distillation, and its molecular structure was confirmed by 19F NMR spectra.
Gas chromatography-mass spectroscopy (GC–MS) was carried out on a Shimadzu-QP 2010 Ultra series system that was equipped with a jet separator for the 2010 GC. The capillary column model was DB-WAX (inner diameter 0.25 mm, length 30 m, and film 0.5 μm) or DB-VRX (inner diameter 0.25 mm, length 30 m, and film 1.4 μm) Agilent Technologies, Inc. The column temperature was set at 35
°C for 3 min and then heated to 200
°C at a rate of 10
°C/minute and held at that temperature for 2 min. The injector and detector temperatures were set at 280
°C and 210
°C, respectively. The split ratio was 80:1, and the sample size was 0.1 μL.
Fluoride-ion nuclear magnetic resonance (19F NMR) spectra were recorded on a Bruker AV400 instrument at 400 MHz using CDCl3 as a solvent.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01128.

Specific activity and TOF calculation method; SEM image, XRD pattern, in situ XRD patterns, and TGA-MS curve for MIL-101(Cr); SEM image, TEM image, and Raman spectra for all carbonized samples; XRD patterns for the MOF-derived catalysts; N2 adsorption isotherms and pore diameters for the carbonized samples and the corresponding fluorinated samples; NH3 TPD profiles for F-Cr2O3; GC–MS spectrum for F-Cr-700 catalyst at 230 and 390
°C and F-Cr2O3 catalyst at 230
°C; EDX and XPS analysis of element for MOF-derived catalysts; and surface acid densities for all catalysts and XPS surface element of F-Cr-700 at different reaction time (PDF)

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Funds for the Central Universities (no. 3122018C026).
The authors gratefully acknowledge the Fundamental Research

ACKNOWLEDGMENTS

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge the Fundamental Research Funds for the Central Universities (no. 3122018C026).

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