



A novel strategy for synthesis of dichlorooctafluorocyclopentane and reaction mechanism investigation



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ABSTRACT

A novel method was used for preparing 1,1-dichlorooctafluorocyclopentane and 1,2-dichlorooctafluorocyclopentane through the reaction of 1,2-dichlorohexafluorocyclopentene, anhydrous hydrogen fluoride, and chlorine. A series of single- and multi-component catalysts were prepared by means of impregnation and coprecipitation, respectively. The catalyst containing Fe(III), Zr(IV), Co(II), Zn(II) and Cu (II) showed the highest catalytic activity among these catalysts. Moreover, the main reaction routes and catalytic mechanism were investigated through experiments and theoretical analysis. Given the environmental and economic benefits, this method has a great application potential in industrial production.

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1. Introduction

Organic molecules that contain fluorocyclocarbon backbone are recognized as potential replacements for ozone depleting substances (ODS) because of their zero ozone depletion potential and low global warming potential [1–3]. Octafluorocyclopentene, as a kind of fluorocyclocarbons, is widely used as an etching agent in optoelectronic devices. However, few methods can synthesize octafluorocyclopentene at low cost in industry besides dechlorination of 1,2-dichlorooctafluorocyclopentane [4–6]. 1,1,2,2,3,3,4-Heptafluorocyclopentane, which also contains a fluorocyclocarbon backbone, is used as an electronics cleaning solvent and an ideal replacement for HFC-225 and CFC-113 [7,8]. It can be easily produced through the Pd-catalyzed reaction of 1,1-dichlorooctafluorocyclopentane with hydrogen. Therefore, 1,1-dichlorooctafluorocyclopentane and 1,2-dichlorooctafluorocyclopentane are important raw materials for preparing ODS replacements.

1,2-Dichlorooctafluorocyclopentane can be produced by fluorination reaction of 1,2-dichlorohexafluorocyclopentene with vanadium pentachloride or cobalt trifluoride as catalyst in the liquid phase [9]. 1,1-Dichlorooctafluorocyclopentane may be synthesized through isomerization of 1,2-dichlorooctafluorocyclopentane or fluorination reaction of 1,2-dichlorohexafluorocyclopentene with antimony pentachloride and niobium pentachloride as catalysts [10]. However, these methods are not widely applied in industry

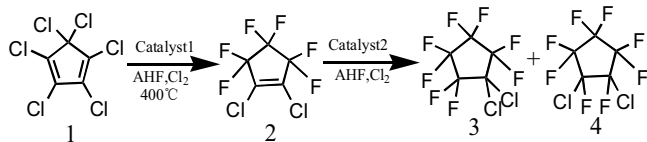
because catalysts are expensive and liquid solution is harmful to environment. Therefore, a low-cost and green synthetic method for preparing 1,1-dichlorooctafluorocyclopentane and 1,2-dichlorooctafluorocyclopentane should be investigated.

Vapor-phase catalytic fluorination is an environmentally friendly technology that is widely applied in industry to synthesize saturated HFCs [11,12]. Various catalysts, such as Cr₂O₃, CaF₂, AgF₂, AlF₃, MgF₂ and so on, are used in vapor-phase fluorination reactions. However, the vapor-phase fluorination reactions of five-membered cyclic olefins are more complex than those of straight-chain olefins. The formation of oligomers and/or coke in the reaction process gives higher requirement to catalysts. High valence metal fluorides have been applied to the fluorination reactions of halogen-containing olefins [6,13,14]. However, these high valence metal fluorides lead to serious environmental pollution [15]. Thereby, screening for a highly efficient and environment-friendly catalyst to fluorinate halogenated olefins is necessary.

In this study, dichlorooctafluorocyclopentane was synthesized using a vapor-phase method with 1,2-dichlorohexafluorocyclopentene, anhydrous hydrogen fluoride (AHF), and chlorine (Cl₂). A series of single- and multi-component catalysts were prepared through impregnation and coprecipitation, respectively. The optimal catalyst was obtained by comparing the efficiency, cost and environmental protection. The reaction mechanism for the synthesis of dichlorooctafluorocyclopentane was also investigated.

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Scheme 1. Synthetic route of dichlorooctafluorocyclopentane.

2. Results and discussion

2.1. Synthetic route of dichlorooctafluorocyclopentane

As shown in **Scheme 1**, 1,1-dichlorooctafluorocyclopentane (substance **3**) and 1,2-dichlorooctafluorocyclopentane (substance **4**) were prepared through the reaction of 1,2-dichlorooctafluorocyclopentene (substance **2**), AHF and Cl₂ in the presence of catalysts. The high-purity substance **2** from hexachlorocyclopentadiene was produced in our laboratory and the synthesis details are shown in the patent CA 103570490A [16].

2.2. Catalytic performance

Cl/F exchange reaction for the preparation of **3** and **4** from **2** is difficult because the molecule of **2** contains many fluorine atoms, which own strong electron-withdrawing ability. The double bond in molecule of **2** can also easily cause polymerization. Thus, further study on the catalysts for this fluorination reaction is required. Many metal fluorides or metal-based catalysts have been extensively used as catalysts for preparing HFCs and their advantages have been reported. Chromium can be converted to a chromium oxyfluoride, which shows high activity for the Cl/F exchange reaction [17]. Zinc is often used as a dopant, which can promote chromium dispersion, resulting in the formation of active centers for Cl/F exchange reaction and modification of HF absorption [18,19]. Magnesium and nickel can increase the surface area and catalytic activity by preventing crystallization of chromium oxide [20]. Copper is often used as an important catalyst in vapor-phase fluorination reaction [21,22]. Cobalt-zirconium-based catalyst possesses octahedral structure, which can promote catalytic activity [23]. Potassium fluoride is an important catalyst for the Michael addition of aromatic and aliphatic amines [24]. Calcium fluoride may act as a support to disperse potassium fluoride on its surface and enhance the nucleophilicity of potassium fluoride [25]. Stannum is usually used as an important dopant and affects the strength of surface acid sites [26].

These metals were initially prepared as single-component catalysts. The results of fluorination reaction of **2** with AHF and Cl₂ using these single-component catalysts are shown in **Table 1**. Ni(II)/C or Sn(IV)/C showed no catalytic activity. Sn(II)/C, K(I)/C, Ca(II)/C and Cr(III)/C exhibited low catalytic activity. Zr(IV)/C, Zn(II)/C,

Co(II)/C, Cu(II)/C and Fe(III)/C showed high catalytic activity and were considered as potential components in this reaction. Furthermore, by comparing the product selectivity in the presence of these single-component catalysts, we can know that catalyst efficacy was in the order of Zn(II) > Fe(III) > Cu(II) > Co(II) > Zr(IV). Commonly, multi-component catalysts exhibit better conversion and selectivity than single-component catalysts [27]. Therefore, we selected a combination of Zn(II) and Fe(III) as the basic components of the two-component catalysts.

The catalytic activity of two-component catalysts is shown in **Table 2**. The two-component catalysts showed higher catalytic activity than the single-component catalysts. These results possibly supported the above hypothesis. To further improve catalytic activity in this reaction, three-component catalysts were prepared based on the catalytic activity of two-component catalysts.

As shown in **Table 3**, the catalytic activity of the three-component catalysts was higher than that of the two-component catalysts. 1% Zn–0.2% Fe–0.2% Cu/C performed the highest catalytic activity in these three-component catalysts. Therefore, it was selected as the essential component for the four-component catalysts.

Similarly, the four-component catalysts, namely, 1% Zn–0.2% Fe–0.2% Cu–0.2% Co/C and 1% Zn–0.2% Fe–0.2% Cu–0.2% Zr/C, were prepared. These component catalysts exhibited better catalytic performance than the three-component catalysts (**Table 4**).

The catalyst having an additional component (1% Zn–0.2% Fe–0.2% Zr–0.2% Cu–0.2% Co/C) exhibited the ideal catalytic activity, yielding 30.2% conversion of **2**, 38.5% selectivity of **3** and 43.7% selectivity of **4** (**Table 5**). However, when the reaction proceeded at a higher temperature, the corresponding catalytic activity dropped quickly. This phenomenon may be attributed to the formation of coke caused by high temperature [25,28].

To improve the performance of 1% Zn–0.2% Fe–0.2% Zr–0.2% Cu–0.2% Co/C at high temperatures, we prepared Zn–Fe–Zr–Cu–Co (ZFZCC) catalyst by a coprecipitation method. ZFZCC catalyst exhibited higher yield, with 39.4% conversion rate, 40.1% selectivity of **3** and 49.5% selectivity of **4** (**Table 5**). Besides, ZFZCC catalytic activity at different temperatures was studied. The conversion of **2**, selectivity of **3** and selectivity of **4** for ZFZCC catalyst were obtained at 380 °C, 450 °C and 500 °C, respectively. The conversions of **2** were 35.1%, 42.4% and 43.4% at 380 °C, 450 °C and 500 °C, respectively. The selectivities of **3** were 38.6%, 36.3% and 39.7%, respectively, and the selectivities of **4** were 47.6%, 48.4% and 45.1%, respectively. More importantly, ZFZCC catalyst remained high catalytic activity when the reaction proceeded at 520 °C for 8 h.

2.3. Catalytic reaction routes

High temperature usually results in more by-products during the vapor-phase fluorination reaction, which is particularly serious

Table 1

Experimental results of catalytic performance for single-component catalysts.

Entry	Catalysts	Conversion of 2 (%)	Selectivity of 3 (%)	Selectivity of 4 (%)
1	1% Ni(II)/C	0.0	0.0	0.0
2	1% Sn(IV)/C	5.5	0.0	0.0
4	1% Sn(II)/C	2.3	3.3	4.9
5	1% K(I)/C	8.1	4.0	6.0
6	1% Ca(II)/C	2.5	3.0	3.1
7	1% Cr(III)/C	3.9	4.2	3.1
9	1% Zr(IV)/C	12.7	18.6	20.1
10	1% Zn(II)/C	24.4	35.6	32.2
11	1% Co(II)/C	9.4	26.8	36.1
12	1% Cu(II)/C	2.5	33.5	35.7
13	1% Fe(III)/C	5.9	28.4	42.9

Table 2

Experimental results of catalytic performance for two-component catalysts.

Entry	Catalysts	Conversion of 2 (%)	Selectivity of 3 (%)	Selectivity of 4 (%)
1	1% Zn–0.2% Fe/C	25.9	32.4	43.9
2	1% Zn–0.2% Cu/C	25.3	36.8	36.2
3	1% Zn–0.2% Co/C	24.7	31.8	37.1
4	1% Fe–0.2% Cu/C	19.5	32.7	38.7
5	1% Fe–0.2% Co/C	11.6	37.4	33.5

Table 3

Experimental results of catalytic performance for three-component catalysts.

Entry	Catalysts	Conversion of 2 (%)	Selectivity of 3 (%)	Selectivity of 4 (%)
1	1% Zn–0.2% Fe–0.2% Cu/C	27.8	37.4	39.9
2	1% Zn–0.2% Fe–0.2% Co/C	26.6	39.8	37.2
3	1% Zn–0.2% Cu–0.2% Co/C	26.5	38.8	37.1
4	1% Fe–0.2% Cu–0.2% Co/C	20.5	37.7	35.7

Table 4

Experimental results of catalytic performance for four-component catalysts.

Entry	Catalysts	Conversion of 2 (%)	Selectivity of 3 (%)	Selectivity of 4 (%)
1	1% Zn–0.2% Fe–0.2% Cu–0.2% Co/C	28.1	39.9	38.4
2	1% Zn–0.2% Fe–0.2% Cu–0.2% Zr/C	28.0	39.1	38.0

Table 5

Experimental results of catalytic performance for five-component catalysts prepared using different methods.

Method	Catalysts	Temp. (°C)	Conversion of 2 (%)	Selectivity of 3 (%)	Selectivity of 4 (%)
Impregnation	1% Zn–0.2% Fe–0.2% Zr–0.2% Cu–0.2% Co/C	400	30.2	38.5	43.7
Coprecipitation	ZFZCC catalyst	400	39.4	40.1	49.5

under the Lewis acid catalyzed conditions. When cyclo-olefins are used as raw materials, reactions, such as addition, elimination, polymerization and pyrolysis, may occur and generate a multitude of products [29]. Because determination of all possible reaction pathways for this process is difficult, the main reaction pathways for synthesis of **3** and **4** from **2** are discussed on the basis of the experimental results and theoretical analysis.

The vapor-phase reaction between **2**, AHF and Cl₂ were carried out at 400 °C for 8 h in the presence of ZFZCC catalyst. The products were identified by GC, GC–MS and FNMR. The results showed that there were 17.6% of substance **3**, 18.9% of substance **4**, 5% of 1-chloroheptafluorocyclopentene (substance **5**), 0.3% of 1-hydro-nonafluorocyclopentane (substance **6**), 1.7% of 1-chlorononafluorocyclopentane (substance **7**), 0.5% of octafluorocyclopentene (substance **8**) and 0.4% of heptafluorocyclopentane (substance **9**) in the products. The polymerization and pyrolysis products were not detected in this synthesis process. The vapor-phase fluorination process is often involved with Cl/F exchange, hydrohalogenation and dehydrohalogenation reaction. Thus, Cl₂ addition reaction, Cl/F exchange reaction, HF addition reaction and HCl addition reaction, may occur in the reaction pathways for synthesis of **3** and **4** from **2**.

To test the influence of HCl on the synthesis of **3** and **4**, a test was conducted by the reaction of **2**, HCl and Cl₂. Another test was also conducted by the reaction of **2** and HCl. Both tests failed to give 1,1,2-trichlorohexafluorocyclopentane. Thus, HCl addition reaction was difficult to occur in the synthesis of **3** and **4**. Available references also reported that HCl addition reaction was extremely difficult to take place except under drastic condition [30,31]. Given

the small amount of **6**, occurrence of HF addition reaction was also difficult.

To test the influence of Cl₂ on the synthesis of **3** and **4**, a test was conducted with **2** (6 g/h), AHF (9.871/h) and N₂ (0.551/h) in the presence of ZFZCC catalyst, that is, Cl₂ was replaced with an equal amount of N₂. In the absence of Cl₂, conversion of **2** was as low as 3.1% with 4.8% selectivity of **3** and 4.8% selectivity of **4**. These results showed that the presence of Cl₂ was crucial to the synthesis of **3** and **4**. In addition, the amount of **5** also decreased to 2.7%, which indicated that only a small amount of **2** reacted with AHF by Cl/F exchange reaction. It was because that the presence of excessive Cl₂ could maintain HF lability, which could improve catalytic activity. Thereby, Cl₂ addition reaction plays a significant role in producing **3** and **4**.

According to the above experimental results, Cl₂ addition reaction and Cl/F exchange reaction mainly occurred in this process. And Cl₂ addition reaction was more preferred than Cl/F exchange reaction for **2**. Fig. 1 shows the main reaction pathways for synthesis of **3** and **4**. Firstly, raw material **2** produced **5** and 1,1,2,2-tetrachlorohexafluorocyclopentane (substance **10**) by Cl/F exchange reaction and Cl₂ addition reaction, respectively. Then, **5** also produced **8** and 1,1,2-trichlorosevofluorocyclopentane (substance **11**) by Cl/F exchange reaction and Cl₂ addition reaction, respectively. Finally, **8** produced **4** by Cl₂ addition reaction and **10** and **11** generated **3** and **4** by Cl/F exchange reaction. In this process, **10** and **11** were not detected because they were intermediates and fluorinated to produce **3** and **4** immediately. Therefore, the main reaction routes that gave **3** and **4** were **2** → **10** → **3/4**, **2** → **5** → **11** → **3/4** and **2** → **5** → **8** → **4**. For the reaction route of **2** → **10** → **3/4**, Cl₂

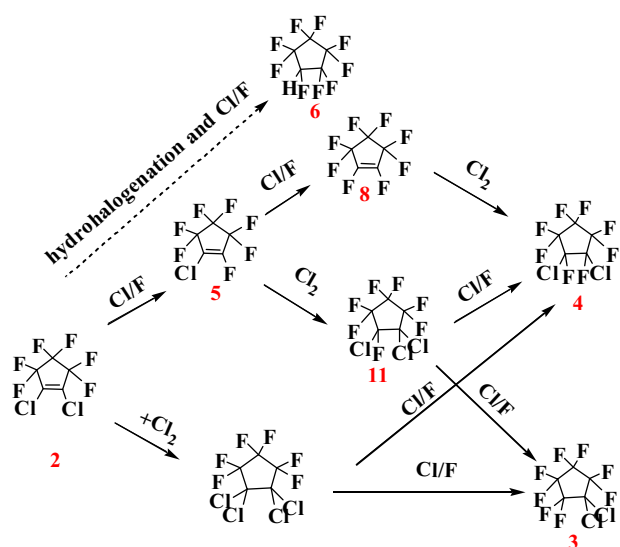


Fig. 1. Main reaction pathways for synthesis of 3 and 4 from 2.

addition reaction occurred firstly and Cl/F exchange reaction occurred as the second step. For the reaction routes of $2 \rightarrow 5 \rightarrow 11 \rightarrow 3/4$ and $2 \rightarrow 5 \rightarrow 8 \rightarrow 4$, Cl/F exchange reaction occurred firstly and Cl_2 addition reaction occurred as the second step. Because Cl_2 addition reaction was more preferred than Cl/F exchange reaction for the vapor-phase reaction between 2, AHF and Cl_2 , route

$2 \rightarrow 10 \rightarrow 3/4$ played a more important role than $2 \rightarrow 5 \rightarrow 11 \rightarrow 3/4$ and $2 \rightarrow 5 \rightarrow 8 \rightarrow 4$ in synthesis of 3 and 4.

2.4. Catalytic mechanism

To survey the catalytic mechanism for the fluorination reaction of substance 2, surface structure of ZFZCC catalyst was characterized by BET, SEM and XRD, respectively. As shown in Fig. 2a, the surface of precursor was smooth, and few pores were observed, which indicated that surface area was small. After precursor was treated with HF, surface area of ZFZCC catalyst increased from $20.7 \text{ m}^2/\text{g}$ to $109.4 \text{ m}^2/\text{g}$. The above results could be explained by irregularly shaped particles and amorphous crystalline phases that formed by the thermal decomposition of precursor and HF activation reaction. These irregularly shaped particles made ZFZCC catalyst exhibit the downy surface (Fig. 2b). When the reaction was carried out at 520°C for 108 h, the surface area of ZFZCC catalyst dropped from $109.4 \text{ m}^2/\text{g}$ to $60.8 \text{ m}^2/\text{g}$. This was because high reactant flux and temperature could result in the decrease of irregularly shaped particles and pores (Fig. 2c).

The XRD pattern of ZFZCC catalyst is shown in Fig. 3. The main crystalline phases of ZFZCC catalyst were FeF_3 , ZrF_4 , $\text{Co}(\text{ZrF}_6)$, ZnF_2 , CuZrF_6 and CuF_2 . Because all the d-orbitals of Zr^{4+} ion are unoccupied, Zr^{4+} ion lacks geometrical preference in the formation of stable compounds. In reality, Zr^{4+} usually exists in ZrF_6^{2-} form and the crystalline structure of ZrF_6^{2-} is octahedral [23,32]. And octahedral $\text{Co}(\text{ZrF}_6)$ and CuZrF_6 were observed in Fig. 3. FeF_3 often is applied in fluorination reaction due to its low cost and non-

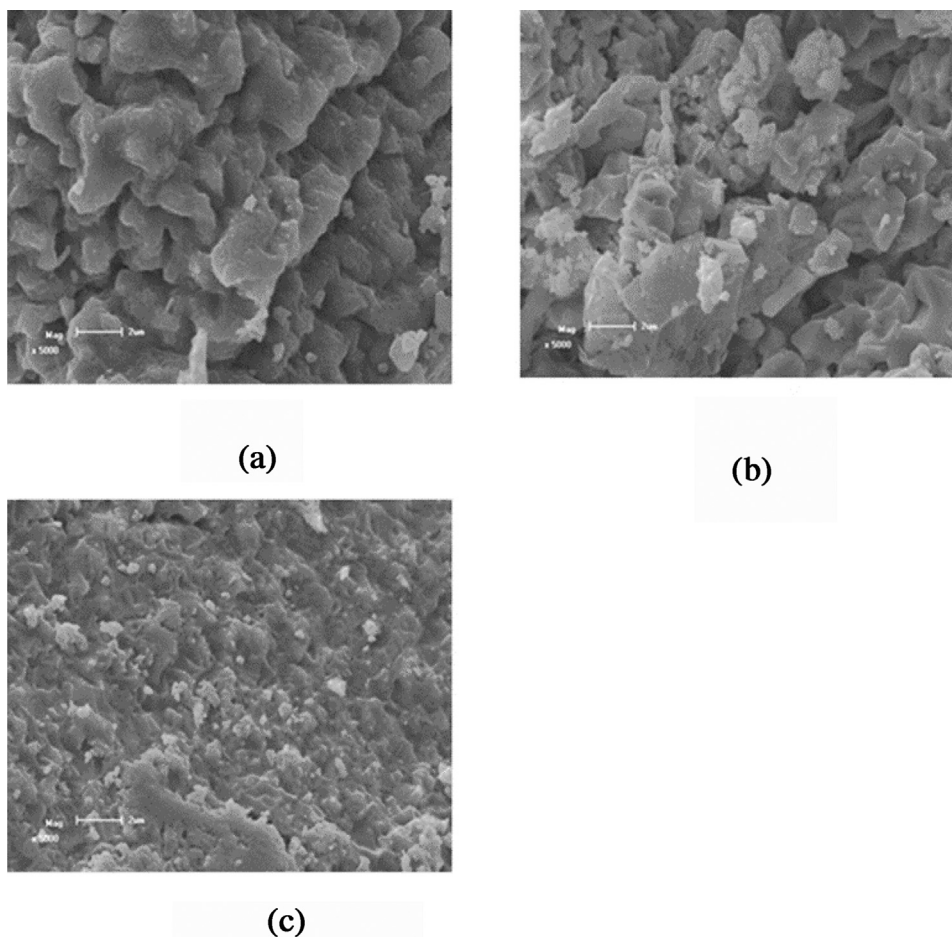


Fig. 2. (a) SEM image of precursor, surface area: $20.7 \text{ m}^2/\text{g}$; (b) SEM image of ZFZCC catalyst, surface area: $109.4 \text{ m}^2/\text{g}$; (c) SEM image of ZFZCC catalyst used for 108 h, surface area: $60.8 \text{ m}^2/\text{g}$.

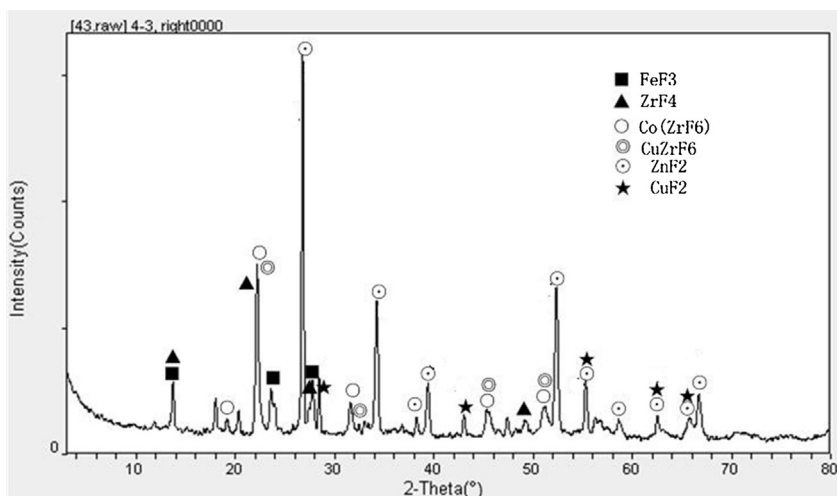


Fig. 3. XRD pattern of ZFCC catalyst.

toxicity. It is well known that the crystalline structure of FeF_3 is a rhombic structure. CuF_2 is also an important catalyst that is usually employed to produce fluorobenzene from benzene or chlorobenzene via vapor-phase reaction. In this process, the active sites were gradually covered by Cu metal and the catalytic activity

dropped [33]. Zinc compounds were chosen as dopants, which resulted in the formation of the active centers for Cl/F exchange reaction [18,34]. Moreover, in the presence of Zn dopant, the apparent activation energy decreased because of the perturbation of HF adsorption [22]. The typical structure of ZnF_2 is tetragonal.

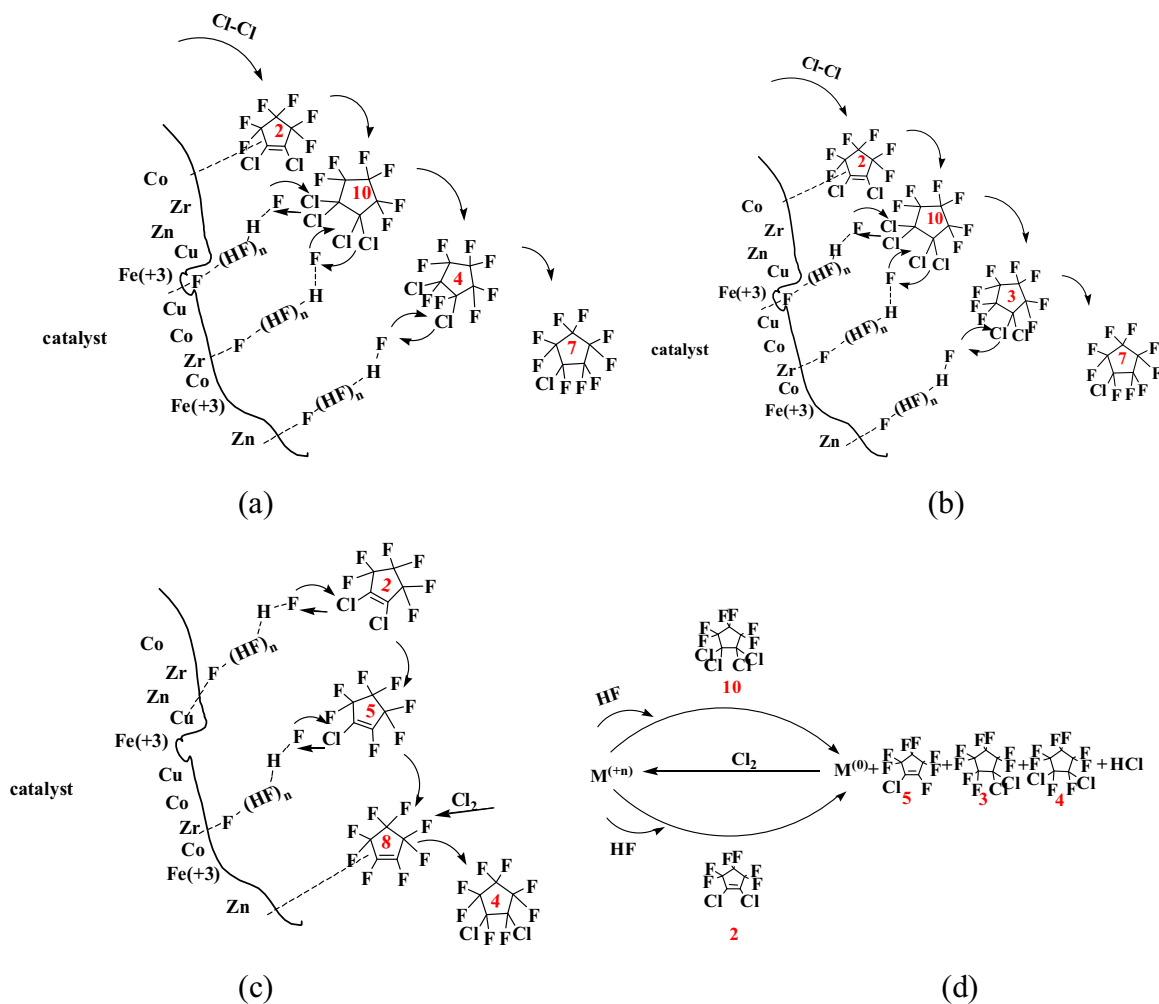


Fig. 4. Mechanism of producing 3,4 in the presence of ZFCC catalyst: (a) mechanism of route 2 → 10 → 4 → 7; (b) mechanism of route 2 → 10 → 3 → 7; (c) mechanism of route 2 → 5 → 8 → 4; (d) transition metal catalytic mechanism of ZFCC catalyst.

Because of the existence of “cavities” in the space lattice of solids and the strong field around the molecules of FeF_3 , ZrF_4 , $\text{Co}(\text{ZrF}_6)$ and CuZrF_6 , ZFZCC catalyst tended to adsorb Cl_2/HF molecule rapidly [35]. However, Cl_2/HF molecules must pack themselves into the space lattice cavities with enough compression in the reaction process.

AHF, as an important vapor-phase fluorinating agent, is speculated to be activated through an intermediary HF oligomer on chrome-based catalyst ($\text{CrF} \cdot (\text{HF}) \cdot \text{HX}$ ($\text{X} = \text{F}$ or Cl)), and the active catalytic atom is situated at the end of the oligomer [36]. This hypothesis was confirmed by Clark et al. [37], who reported that the end-fluorine of an oligomer was more labile. Therefore, the same type of oligomer may exist in this process even at high temperatures.

Steric effect is also an important factor in the fluorination reaction. From the stereochemical points of view, we can easily understand the reaction pathways. As for route $2 \rightarrow 10 \rightarrow 3/4$, when **2**, AHF and Cl_2 were exposed to the ZFZCC catalyst bed, Cl_2 addition reaction occurred first and then **3** and **4** were generated by Cl/F exchange reaction. Meanwhile, **7** was produced by fluorinating **3** and **4**. The explanation stated above is depicted in Fig. 4a and b. Because of steric effect, **3** and **4** should be obtained equivalently. However, the yield of **4** was generally higher than that of **3** which could be explained by route $2 \rightarrow 5 \rightarrow 8 \rightarrow 4$ (Fig. 4c). Fig. 4d illustrates transition metal catalytic mechanism. As the reaction proceeded, valence of the transition metal decreased, resulting in the loss of catalytic activity. Meanwhile, transition metal was oxidized by Cl_2 , the valence then increased, and the catalyst regained its catalytic activity.

3. Conclusion

1,1-Dichlorooctafluorocyclopentane and 1,2-dichlorooctafluorocyclopentane were prepared through the reaction of 1,2-dichlorohexafluorocyclopentene, AHF and Cl_2 . A series of single- and multi-component catalysts were then prepared and tested for synthesizing 1,1-dichlorooctafluorocyclopentane and 1,2-dichlorooctafluorocyclopentane. Multi-component catalyst containing Fe (III), Zr(IV), Co(II), Zn(II) and Cu(II) have high catalytic activity. Compared with other catalysts, the coprecipitated ZFZCC catalyst was more active. Moreover, the reaction routes for the synthesis of **3** and **4** from **2** in the presence of ZFZCC were discussed and the main routes were proposed. Catalytic mechanism was reported from the aspects of crystalline phase structure, BET surface area and sterical effect.

4. Experimental

4.1. Chemicals

Hexachlorocyclopentadiene (purity > 99.8%) was obtained from Jiangsu Anpon Electrochemical Co. Ltd. (Jiangsu, China). AHF (purity > 99.9%), nitrogen gas (purity > 99.9%) and chlorine gas (purity > 99.999%) were purchased from Beijing North Oxygen Specialty Gases Institute Co., Ltd. (Beijing, China). $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, SnCl_2 , FeCl_3 , KCl , CaCl_2 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, HNO_3 (conc. purity > 75.0%), 25% aqueous ammonia and coconut active charcoal were purchased from Xilong Chemical Co., Ltd., (Guangxi, China).

4.2. Instruments

Powder X-ray diffraction (XRD) was performed on a Rigaku D/MAX 2500 X-ray diffractometer.

Specific surface area was measured using nitrogen adsorption technique on a micromeritics ASAP 2020/Tristar 3000 instrument

and surface areas were determined by Brunauer-Emmett-Teller (BET) method.

^{19}F NMR spectra were recorded on a Bruker AV400 instrument at 376 MHz with CFCl_3 as an internal standard.

Gas chromatography–mass spectroscopy (GC–MS) was conducted using a Shimadzu-QP 2010 Ultra series system equipped with a jet separator for the 2010 GC. The capillary column was DB-5 with 0.25 mm i.d. and 30 m length (J&W Scientific Inc.).

Gas chromatography (GC) was used and its operation condition was as follows: capillary column, DB-5 with 0.25 mm i.d. and 30 m length (J&W Scientific Inc.); column temperature, 35 °C for 3 min and heated to 200 °C at a rate of 10 °C/min, then 200 °C for 3 min; injector temperature, 280 °C; detector temperature, 200 °C; split ratio, 80:1; and sample size, 0.1 μl .

Scanning electron microscope (SEM) images of the catalysts were obtained using a Shimadzu SS-550.

The apparatus for the vapor-phase fluorination reaction was composed of a pump for offering reactant (liquid phase), Cl_2 , AHF, N_2 mass flow controllers, and an electrically heated tubular Inconel reactor (14 mm in diameter and 300 mm in length) that was equipped with an inner Inconel tube for inserting type-K thermocouples with a 1-mm diameter. A thermocouple entered the reactor through a Monel-type fitting and extended into the catalyst bed to measure the temperature changes in different positions along the reactor.

4.3. Preparation of catalysts

4.3.1. Preparation of active charcoal

Active charcoal was typically pretreated as follows. A 1000 ml glass flask was initially charged with 50 g active charcoal, with a size of 20–40 mesh screens and $\sim 1000 \text{ m}^2/\text{g}$ surface area. Afterward, 300 ml HNO_3 (10%) was added gradually. Slurry was stirred with an electric stirrer at 300 r/min for 10 h. Subsequently, the slurry was filtered and washed several times with de-ionized water until pH was about 7. Finally, the slurry was dried at 100 °C for 12 h in a drying oven, and an active charcoal was obtained.

4.3.2. Catalysts prepared by an impregnation method

Pretreated active charcoal was impregnated into a FeCl_3 solution (about 3 wt.%) for 12 h, and the loading amount of FeCl_3 was about 1 wt.% on the active charcoal. Calcination was then conducted at 250 °C for 10 h (rate of N_2 : 150 ml/min) and 400 °C for 10 h (rate of N_2 : 200 ml/min). Afterward, 20 g catalyst was packed into the reactor and dried at 200 °C for 2 h under N_2 . The mixture of N_2 and AHF was passed through the reactor at 250 °C for 10 h (N_2 : AHF = 50: 100 ml/min); 250 °C for 10 h (N_2 : AHF = 0:150 ml/min); and 450 °C for 10 h (N_2 : AHF = 0: 150 ml/min). Finally, fluorinated catalyst 1% Fe(III)/C was prepared.

Similarly, catalyst 1% Ni(II)/C, 1% Sn(IV)/C, 1% Sn(II)/C, 1% K(I)/C, 1% Ca(II)/C, 1% Cr(III)/C, 1% Zr(IV)/C, 1% Zn(II)/C, 1% Co(II)/C, 1% Cu(II)/C, 1% Zn–0.2% Fe/C, 1% Zn–0.2% Cu/C, 1% Zn–0.2% Co/C, 1% Fe–0.2% Cu/C, 1% Fe–0.2% Co/C, 1% Zn–0.2% Fe–0.2% Cu/C, 1% Zn–0.2% Fe–0.2% Co/C, 1% Zn–0.2% Cu–0.2% Co/C, 1% Fe–0.2% Cu–0.2% Co/C, 1% Zn–0.2% Fe–0.2% Cu–0.2% Co/C, 1% Zn–0.2% Fe–0.2% Cu–0.2% Zr/C, and 1% Zn–0.2% Fe–0.2% Zr–0.2% Cu–0.2% Co/C were prepared.

4.3.3. Catalyst prepared by a coprecipitation method

ZFZCC was typically prepared as following process. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (32.15 g) and ZnCl_2 (41.61 g) were dissolved in 60 ml aqueous ammonia solution (25 wt%). The solution was then added dropwise to 300 g solution which contained 30 wt% FeCl_3 , 20 wt% $\text{Zr}(\text{NO}_3)_4$ and 10 wt% CuCl_2 under continuous stirring. The pH of the solution was about 8. The slurry of hydroxides was filtered, washed thoroughly with de-ionized water, dried, ground

and pelleted. The pellets were calcined at 400 °C under nitrogen to obtain the precursor.

Prior to use, the precursor was treated with AHF at 200 °C for 24 h (N₂: AHF=100: 20 ml/min); 250 °C for 24 h (N₂: AHF=50: 100 ml/min); 250 °C for 24 h (N₂: AHF=0:150 ml/min); and 450 °C for 24 h (N₂: AHF=0: 150 ml/min). Finally, the residual AHF was purged with nitrogen.

4.4. Synthesis processes

Substance **2** (6 g/h), AHF (9.87 l/h) and Cl₂ (0.55 l/h) were passed through the reactor with 10 cm³ of catalyst at 400 °C to prepare dichlorooctafluorocyclopentane. The products were collected in an ice bath and washed with a diluted KOH solution. Water was then removed using anhydrous sodium sulfate and molecular sieve (4 Å). The obtained products were analyzed by GC, GC–MS and ¹⁹F NMR.

Compound 2: 1,2-dichlorohexafluorocyclopentene, GC–MS, *m/z*: 244 (M⁺); 225 (M⁺-F); 209 (M⁺-Cl); 194 (M⁺-CF₂); 175 (M⁺-CF₃); 159 (M⁺-CF₂Cl); 155 (M⁺-FCl₂); 140 (M⁺-CF₃Cl); 125 (M⁺-CF₂Cl₂); 109 (M⁺-C₂F₄Cl); 90 (M⁺-C₂F₅Cl); 85 (M⁺-C₄F₄Cl); 69 (M⁺-C₄F₃Cl₂); 55 (M⁺-C₂F₅Cl₂); 31 (M⁺-C₄F₅Cl₂); 18 (M⁺-C₅F₅Cl₂). ¹⁹F NMR: δ (ppm), δ -113.75 (dt,4F); δ (ppm), -129.73 (ddt, 2F).

Compound 3: 1,1-dichlorooctafluorocyclopentane, GC–MS, *m/z*: 282 (M⁺), 263 (M⁺-F), 247 (M⁺-Cl), 228 (M⁺-ClF), 213 (M⁺-CF₃), 197 (M⁺-CF₂Cl), 178 (M⁺-CF₃Cl), 163 (M⁺-CF₃Cl₂) (base peaks), 147 (M⁺-C₂F₄Cl), 131 (M⁺-C₂F₄Cl₂), 100 (M⁺-C₃F₅Cl₂). ¹⁹F NMR: δ (ppm), -119.2 (s, 4F); δ (ppm), -122.5 (s,4F); (CCl₃F: 0 ppm).

Compound 4: 1,2-dichlorooctafluorocyclopentane, GC–MS, *m/z*: 282 (M⁺), 263 (M⁺-F), 247 (M⁺-Cl), 228 (M⁺-ClF), 213 (M⁺-CF₃) (base peaks), 197 (M⁺-CF₂Cl), 178 (M⁺-CF₃Cl), 163 (M⁺-CF₃Cl₂) (base peaks), 147 (M⁺-C₂F₄Cl), 131 (M⁺-C₂F₄Cl₂), 100 (M⁺-C₃F₅Cl₂). ¹⁹F NMR: δ (ppm), -139.0 (m,2F); δ (ppm), -126.7 (s, 1F), δ (ppm), -125.4 (s, 1F), -124.0 (m, 2F), -117.1 (m,2F); (CCl₃F: 0 ppm).

Compound 5: 1-chloroheptafluorocyclopentene, GC–MS, *m/z*: 228 (M⁺); 209 (M⁺-F); 193 (M⁺-Cl); 178 (M⁺-CF₂); 159 (M⁺-CF₃); 143 (M⁺-CF₂Cl); 124 (M⁺-CF₃Cl); 109 (M⁺-C₂F₅); 100 (M⁺-C₃F₃Cl); 93 (M⁺-C₂F₄Cl); 69 (M⁺-C₄F₄Cl); 62 (M⁺-C₃F₅Cl); 55 (M⁺-C₂F₆Cl); 31 (M⁺-C₄F₆Cl); 18 (M⁺-C₅F₆Cl). ¹⁹F NMR: δ (ppm), -113.52 (m,2F); δ (ppm), -118.41 (m,2F); δ (ppm), -129.19 (m,1F); δ (ppm), -129.50 (m,2F); (CCl₃F: 0 ppm).

Only GC–MS spectroscopic datas were obtained because the amount of other products was small. Their possible structures, which were determined using mass spectroscopic datas, are listed as follows.

Compound 6: nonafluorocyclopentane, GC–MS, *m/z*: 231 (M⁺); 213 (M⁺-F); 193 (M⁺-F₂); 163 (M⁺-F₃) (base peak); 143 (M⁺-F₄); 113 (M⁺-CF₅); 93 (M⁺-C₂F₆).

Compound 7: 1-chlorononafluorocyclopentane, GC–MS, *m/z*: 265 (M⁺); 247 (M⁺-F); 199 (M⁺-CF₃) (base peak); 149 (M⁺-C₂F₅); 109 (M⁺-CF₆Cl); 96 (M⁺-C₂F₆Cl).

Compound 8: octafluorocyclopentene, GC–MS, *m/z*: 212 (M⁺); 193 (M⁺-F); 185 (M⁺-Cl); 174 (M⁺-F₂); 162 (M⁺-CF₂); 155 (M⁺-F₃);

143 (M⁺-CF₃); 131 (M⁺-C₂F₃); 124 (M⁺-CF₄); 112 (M⁺-C₂F₄); 93 (M⁺-C₂F₅); 83 (M⁺-C₃F₅); 74 (M⁺-C₂F₆); 69 (M⁺-C₄F₅); 55 (M⁺-C₂F₇); 44 (M⁺-C₃F₇); 28 (M⁺-C₃F₈); 18 (M⁺-C₅F₇); 14 (M⁺-C₄F₈).

Compound 9: heptafluorocyclopentane, GC–MS, *m/z*: 196 (M⁺); 177 (M⁺-F); 157 (M⁺-HF₂); 131 (M⁺-C₂H₃F₂); 127 (M⁺-CF₃); 113 (M⁺-C₂H₂F₃); 100 (M⁺-C₃H₃F₃); 95 (M⁺-C₂HF₄); 82 (M⁺-C₃H₂F₄); 77 (M⁺-C₂F₅); 64 (M⁺-C₃HF₅); 51 (M⁺-C₄H₂F₅); 46 (M⁺-C₃F₆); 31 (M⁺-C₄H₃F₆); 27 (M⁺-C₃F₇); 18 (M⁺-C₅H₃F₆).

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