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Investigation into chromia-based catalyst and its application in preparing difluoromethane

Heng-dao Quan*, Masanori Tamura, Yasuhisa Matsukawa, Junji Mizukado, Takashi Abe, Akira Sekiya

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5-2, 1-1-1, Higashi, Tsukuba, Ibaraki 305-8565, Japan

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Abstract

The air-calcined chromia-based catalysts and nitrogen-calcined chromia-based catalysts are prepared and used for a vapor-phase catalytic fluorination reaction in preparing difluoromethane. It has been found that the air-calcined catalysts show much higher catalytic activity than that of nitrogen-calcined catalysts in the above mentioned reaction, which is attributed to the formation of a Cr species with high oxidation state on the air-calcined catalyst. Moreover, when the catalyst precursor is treated with anhydrous hydrogen fluoride at low temperature, the crystallized catalyst is easily formed and the catalytic reaction activity is decreased.

Keywords: Chromia-based catalyst; Vapor-phase fluorination; Difluoromethane

1. Introduction

Chromia-based catalysts have been some of the fundamental pillars for producing HFCs, since the vapor-phase catalytic fluorination technology began being used in industry [1–3]. HFCs, having a zero ozone depletion potential (ODP) in the stratosphere, a low global warming potential (GWP) and similar physical properties to chlorofluorocarbon (CFC), have been prime candidates for CFC alternatives [4,5]. In an attempt to reduce the cost of HFC production and to develop new alternatives, research has been focused on the development of a new and effective catalyst and the relationship between activity and catalytic structure [6,7]. Above all, to understand the effect of the Cr chemical state on catalytic activity is a key factor in the development of an effective catalyst. Kemnitz and co-workers [8] reported that chromium is formed in higher oxidation state (Cr^{4+} and Cr^{5+}) when oxygen treatment removes the coke deposits on catalyst. The fluorination activity of catalyst is highly enhanced by the presence of chromium in higher oxidation state. Chung et al. [9] also reported that a broad feature of the chromium species with different oxidation states exist when $CrF_3.4H_2O$ runs through air-calcination. The catalytic activity of the air-calcined catalyst of $CrF_3.4H_2O$ for the fluorination of CF_3CH_2Cl was 20 times higher than that of uncalcined $CrF_3.4H_2O$.

In this study, through the use of X-ray photoelectron spectroscopy (XPS), we found that a higher oxidation state of the species was formed when chromium hydroxide was calcined under atmospheric air. The highly oxidized species exhibits a higher catalytic activity than that of Cr(III) species used to prepare difluoromethane (HFC-32). Furthermore, when the catalyst precursor was treated with HF at low temperature, the crystallized catalyst was easily formed and the catalytic reaction activity was decreased.

2. Experimental

2.1. Instrument

The BET surface area and the distribution of catalyst pore diameter were determined by means of low temperature adsorption of nitrogen using a Micromeritics ASAP 2010 gas sorption meter. The sample was degassed under vacuum at 300 °C for 3 h before measurement.

* Corresponding author. Tel.: +81 298 4771; fax: +81 298 4771.
E-mail address: hengdao-quan@aist.go.jp (H.-d. Quan).

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^{1}H NMR and ^{19}F NMR of CH_2Cl_2, CH_2FCl and CH_2F_2 were recorded on a JNM-EX270 spectrometer (JEOL, 270 MH_Z) at 25 °C with Me_4Si and $CFCl_3$, respectively, as internal references in $CDCl_3$ solvent. Their patterns were compared with that of authentic samples.

X-ray diffraction (XRD) was used to determine the bulk crystalline phase of samples. The pattern of samples was recorded by a Mac Science MPX-18 diffractometer. X-ray diffraction was completed by using Cu Kα (0.1504 nm) radiation and the X-ray tube was operated at 40 KV and 150 mA.

XPS spectra of samples were taken by a PHI-ESCA 5800 electron spectrometer equipped with an aluminum anode (Al Kα = 1486.6 eV) operated at 100 W. No special treatments were applied to the samples in the UHV chamber. All binding energies were referenced to the C (1s) peak at 284.6 eV. The chemical state of components was identified by comparing measured XPS patterns of the catalyst with those found in the handbook of X-ray photoelectron spectroscopy [10].

The apparatus for the preparation and evaluation of catalyst consist of two mass flow controllers [one is for N_2 and the other for anhydrous hydrogen fluoride (AHF)] and an electrically heated tubular Inconel reactor (14 mm in diameter and 300 mm in length) equipped with an inside Inconel tube for inserting type-K thermocouples with a 1 mm diameter. A thermocouple enters the reactor through a type-Monel CAJON® fitting and penetrates to the whole of the catalyst bed to measure the temperature change at different positions along the reactor.

The product stream was scrubbed through a water bath at 60 °C to remove unreacted HF and avoid dichloromethane liquefied, then passed through a drier filled with Soda-lime, and finally analyzed by a shimadzu GC-14 A on-line gaschromatograph. The capillary column was a Pora plot Q with 0.32 mm i.d. and 25 m length from J&W Scientific Inc. The column was programmed as follows: initial temperature 80 °C for 15 min; increasing the temperature with the rate of 20 °C/min; final temperature 200 °C and hold for 5 min. Meanwhile, the instrumental parameters were set up like this: both the injection port and the TCD detector at temperature of 200 °C; The carrier gas is around 1 cc He/min. The products were determined by comparing their NMR patterns with those of authentic samples.

In order to calculate the conversion of CH_2Cl_2 and the selectivity of CH_2FCl and CH_2F_2, it is necessary to measure their GC relative response factor. Then, the vacuum line is used for the calculation of their absolute amount by measuring the pressure under a certain volume in the vacuum line. In this stage, the samples were regarded as ideal gas since fluorocarbons were found to approximate the gas law very closely at low pressure [11]. In the vacuum line, each 1 mmol sample was measured, and placed in a sample tube approximately 80 ml in volume. The above-mentioned mixture gas was carried to the GC by a carrier gas (He) under warm atmosphere and their relative GC areas were measured. Finally, to obtain the GC relative response factor, the following ratio was used: CH_2F_2:CH_2FCl:CH_2Cl_2 = 1:1.23:1.67. The data were used to calculate the conversion of CH_2Cl_2 and the selectivity of CH_2FCl and CH_2F_2 in vapor-phase catalytic fluorination.

2.2. Preparation of catalyst and fluorination procedure of dichloromethane

Twenty-eight percent aqueous ammonia was added dropwise to a solution of 4% $CrCl_3 \cdot H_2O$ in a water bath for 5 min under stirring. The flow rates of aqueous ammonia were being controlled until the pH of the reaction solution was around 7.0. The resulting slurry of hydroxides was filtered, considerably washed with deionized water, and dried at 120 °C overnight. The resulting solid was ground, mixed with 3% graphite and pelletized by a tableting machine. The pellets were calcinated at 400 °C for 4 h in air or N_2 atmosphere to form a catalyst precursor, and 10 ml of this catalyst precursor was charged into an Inconel reaction tube, treated with an HF steam diluted with N_2 (N_2:HF = 200:100) at atmospheric pressure for 1 h, then heated to 400 °C at a rate of 2 °C/min and kept at 400 °C for 4 h in a 100% HF steam without being diluted with N_2. In the end, the remaining AHF on the catalyst was removed by N_2. The prepared catalyst was then used in the fluorination procedure.

Dichloromethane was fed into the reactor via a vaporizer by a Masterflex (Cole-Parmer Instrument Co.) metering pump. Anhydrous hydrogen fluoride was drawn to the vapor phase in the vaporizer. The product stream from the reactor was scrubbed with warm H_2O at 60 °C, then passed through a drier (soda-lime) and then to the GC on-line.

3. Results and discussion

3.1. The investigation into chromia-based catalyst treated by N_2 or air

3.1.1. Fluorination of CH_2Cl_2 in the presence of chromia-based catalyst

Dichloromethane at a rate of 0.3 g/min and AHF at a rate of 300 ml/min were fed into the reactor, which was charged with 10 ml of catalyst to perform the fluorination. The results are shown in Table 1, which indicates that Cat. 1 (air-calcined) has an obviously higher catalytic activity than Cat. 2 (nitrogen-calcined) in the reaction used to prepare difluoromethane (HFC-32). To investigate the relationship between catalytic activity and catalyst structure, the catalysts were characterized by means of the BET nitrogen adsorption methods, XRD and XPS.

3.1.2. Characterization of catalyst by the BET nitrogen absorption method

The data for surface area and porous volume of air-calcined and nitrogen calcined catalysts are shown in Tables 2 and 3, respectively. The results show that the surface area (around 15 m^2/g) of the precursor of Cat. 1 is

Table 1
Fluorination of CH_2Cl_2 by HF in the presence of chromia-based catalyst calcined under air and nitrogen

Products	Reaction temperature (°C)					
	318		345		372	
	Cat. 1	Cat. 2	Cat. 1	Cat. 2	Cat. 1	Catalyst 2
CH_2F_2 (Sel.%)	85.7	78.1	83.6	77.0	82.0	79.2
CH_2ClF (Sel.%)	14.3	21.9	16.4	23.0	18.0	20.8
CH_2Cl_2 (conversion %)	86.9	74.2	85.7	76.6	83.7	83.7

Notes: Cat. 1: Cr_2O_3 calcined at 400 °C under air; Cat. 2: Cr_2O_3 calcined at 400 °C under N_2. Catalyst: 10 ml, HF: 300 ml/min, CH_2Cl_2: 80 ml/min, contact time: 1.6 S.

Table 2
Characterization of chromia-based catalyst calcined under nitrogen by BET

Calcination temperature (°C)	Surface area (m^2/g)	Porous volume vs. (cc/g)	Mean pore radius (Å)
120	20.4	0.02	16.6
350	196.7	0.10	10.6
400	194.6	0.10	10.8
500	253.3	0.17	13.5

Note: precursor of catalyst was calcinated under nitrogen.

Table 3
Characterization of chromia-based catalyst calcined under air by BET

Calcination temperature (°C)	Surface area (m^2/g)	Porous volume vs. (cc/g)	Mean pore radius (Å)
120	20.4	0.02	16.6
300	129.8	0.10	15.5
400	14.5	0.03	47.9
500	15.2	0.09	47.6
600	13.9	0.04	51.3

Note: precursor of catalyst was calcinated under air.

much smaller than that (around 200 m^2/g) of Cat. 2, but that the catalytic activity of Cat. 1 treated with HF is much higher than that of Cat. 2 in the reaction used to prepare HFC-32 (see Table 1). The above results are ascribed to the possibility that the oxygen in the air may be introduced to catalyst to form high oxidation state Cr species when the chromia-based catalyst was calcined at air. High oxidation state Cr is advantageous to the halogen-exchange than Cr(III) in the reaction used to prepare HFC-32.

3.1.3. Characterization of catalyst by X- photoelectron spectroscopy

X-ray photoelectron spectroscopy was applied to identify the chemical states of chromia on nitrogen-calcined catalyst and air-calcined catalyst. The O 1s spectra of the catalysts are shown in Fig. 1. In the air-calcined chromia sample, the O 1s spectrum of chromia shows a strong peak at 529.7 eV and a weak peak at about 531.5 eV. The weak peak is attributed to O 1s in chromia and the other strong peak is likely due to chromium species with higher oxidation states than Cr^{3+}, since Cr in CrO_2 and CrO_3 has a relatively small binding energy than Cr(III) [10]. This means a part of Cr(III) on the surface of the catalyst transferred to a high oxidation state during the calcination of chromia under air. In the nitrogen-calcined chromia sample, the single peak at 530.0 eV is assigned to O 1s in chromia.

The Cr2p spectra of catalyst samples are shown in Fig. 2. The Cr2p3/2 spectrum of air-calcined chromia shows two peaks. The prominent peak at 576.2 eV is ascribed to the Cr in Cr_2O_3. The other peak at 575.3 eV is likely attributed to a higher oxidation state Cr species [10]. In the

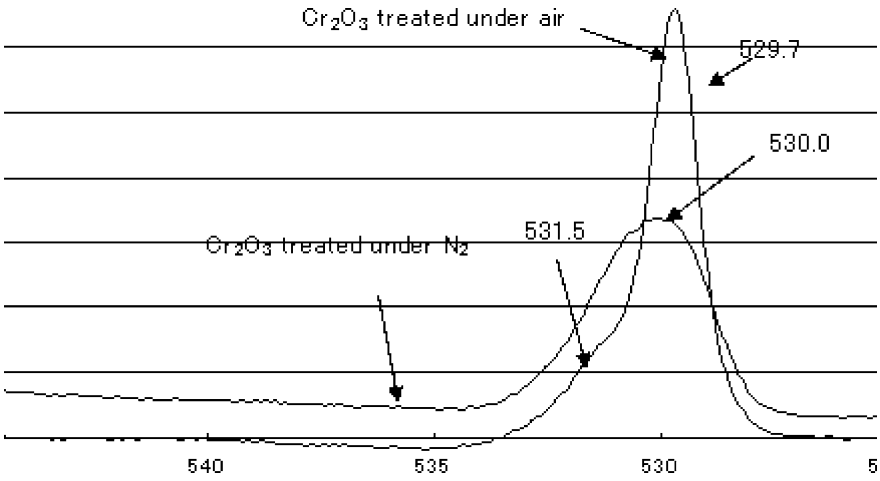

Fig. 1. XPS pattern of O in chromia-based catalyst.

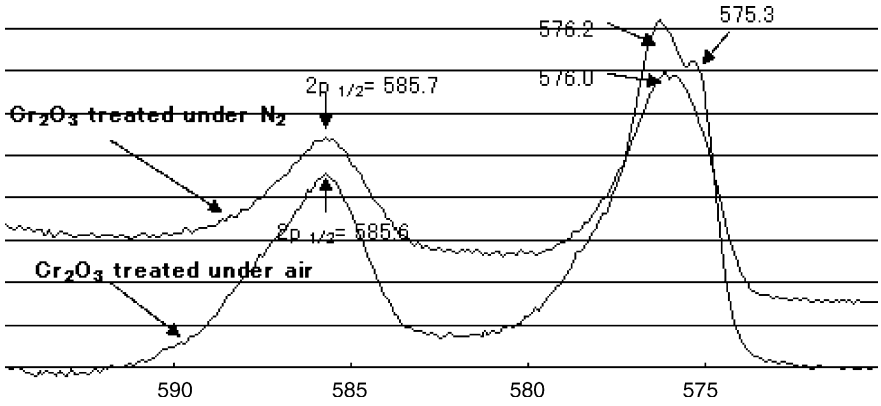

Fig. 2. XPS pattern of Cr in chromia-based catalyst.

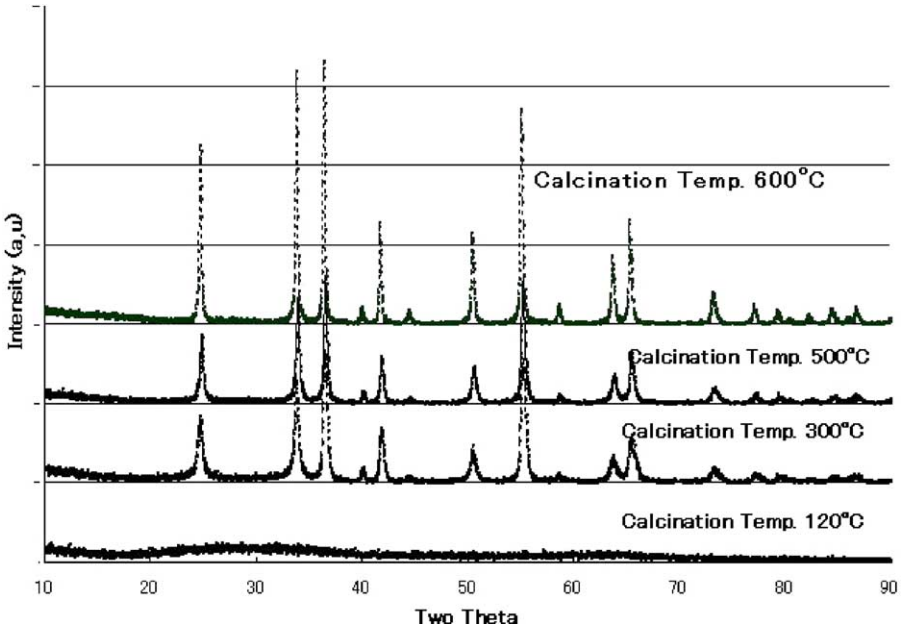

Fig. 3. XRD spectra of chromia-based catalyst calcined under air.

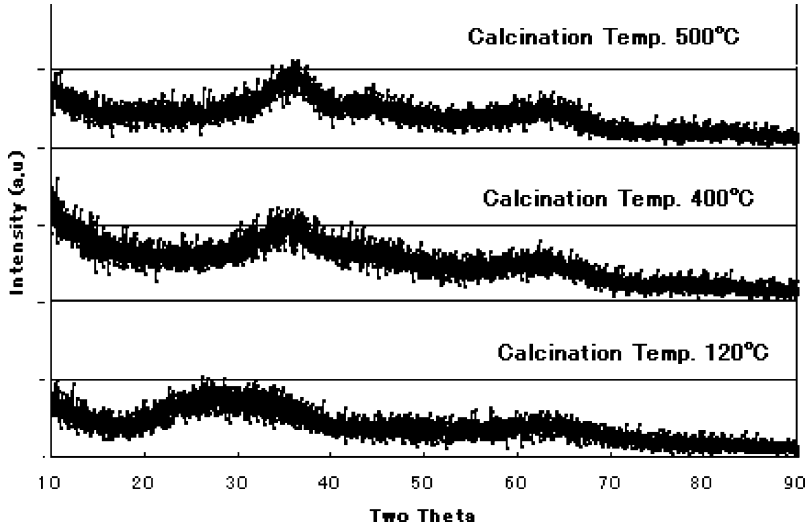

Fig. 4. XRD spectra of chromia-based catalyst calcined under nitrogen.

Table 4
Fluorination of CH_2Cl_2 by HF in the presence of chromia-based catalyst treated with HF at 40 °C

Reaction temperature (°C)	Products Sel. (%)		Concentration of CH_2Cl_2 (%)	Yield of products (%)	
	CH_2F_2	CH_2ClF		CH_2F_2	CH_2ClF
301	65.4	43.6	52.5	34.4	22.9
330	75.2	24.7	68.3	51.3	12.7
359	79.0	21.0	76.9	60.8	16.1

Notes: (1) Chromia-based catalyst was treated with HF at 40 °C, surface area: 6.4 m^2/g, (2) HF: 300 ml/min, CH_2Cl_2: 80 ml/min. Cat.: 10 ml, contact time: 1.6 S. No obvious reaction occurs when temperature is lower than 300 °C.

Table 5
Fluorination of CH_2Cl_2 by HF in the presence of chromia-based catalyst treated with HF at 140 °C

Reaction temperature (°C)	Products Sel. (%)		Concentration of CH_2Cl_2 (%)	Yield of products (%)	
	CH_2F_2	CH_2ClF		CH_2F_2	CH_2ClF
246	86.8	13.2	78.5	68.1	10.4
275	86.3	13.7	84.7	73.1	11.6
302	85.1	14.9	84.5	71.9	12.6
333	85.7	14.3	87.5	75.0	12.5
363	84.9	15.1	87.9	74.6	13.3

Notes: (1) Chromia-based catalyst was treated with HF at 140 °C, surface area: 35.2 m^2/g, (2) HF: 300 ml/min, CH_2Cl_2: 80 ml/min. Cat.: 10 ml, contact time: 1.6 S.

nitrogen-calcined chromia samples, the peak at 576.0 eV in Cr2p3/2 spectrum seems to be a single peak, which was assigned to Cr_2O_3.

Combining the results found in Figs. 1 and 2, we conclude that higher oxidation state Cr exists in the air-calacined chromia.

3.1.4. Characterization of catalyst by X-ray diffraction

The pattern of XRD of air-calcinated Cat. 1 indicates the catalyst remains amorphous when treated at 120 °C (see Fig. 3). A new crystalline phase appears on the surface of the catalyst when treatment temperature rises to 300 °C. The newly formed crystalline phase is similar to that of Cr_2O_3 when compared to the measured XRD pattern of catalyst using the JCPDS powder diffraction file data, but it might be a part of the higher oxidation state Cr species that exists in the catalyst, since the pattern of XRD does not show the typical crystalline phase of Cr_2O_3. On the other hand, the pattern of XRD for nitrogen-calcined Cat. 2 indicates that the catalyst almost remains amorphous (see Fig. 4), even though the calcination temperature is 500 °C. The evaluation of catalyst for preparing HFC-32 indicates that chromia-based catalysts calcined under air exhibit more robust catalytic activity than those calcined under nitrogen.

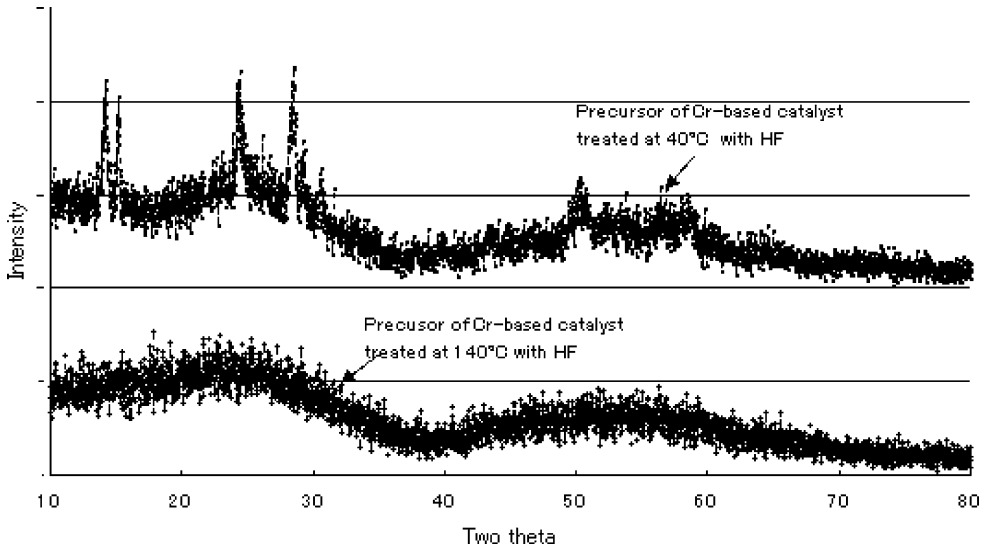

Fig. 5. XRD spectra of chromia-based catalyst treated with HF under different temperature.

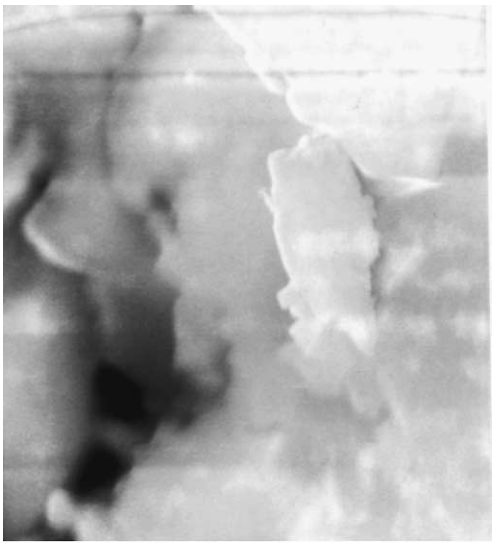

Fig. 6. SEM image of chromia-based catalyst treated with HF at 40 °C.

Fig. 7. SEM image of chromia-based catalyst treated with HF at 140 °C.

3.2. The catalytic performance of chromia-based catalyst treated with HF

3.2.1. Fluorination of CH_2Cl_2 in the presence of chromia-based catalyst

At room temperature, the chromia-based catalyst treated with HF exhibits a low surface area (6.4 m^2/g). However, the catalyst shows a relatively high surface area (35.2 m^2/g) when the precursor is treated with HF at 140 °C. The catalyst was used in the vapor-phase catalytic fluorination of dichloromethane and the results are shown in Tables 4 and 5. The results indicate that the catalyst prepared at high temperature exhibits higher catalytic activity.

3.2.2. Characterization of above catalysts

In order to understand the impact of treating temperature of precursor of catalyst with HF on activity and the catalyst structure, the two catalysts were characterized by BET, XRD and SEM.

The XRD pattern (Fig. 5) apparently shows that the catalyst treated at low temperature is crystallized and consequently exhibits a low surface area. The catalyst treated at high temperature maintains an amorphous crystalline phase.

Furthermore, the SEM pattern indicates the surface of the catalyst treated at low temperature (Fig. 6) is smooth, which may indicate that the most of the catalyst surface area was lost. The catalyst treated at high temperature still exhibits the downy surface like cotton and maintains a large surface area.

The above results could be explained as that the formed water in the process has an impact on the formation of catalyst crystalline phase. When chromia is treated with HF at room temperature, the formed water does not easily escape and thus makes chromia-based catalyst crystallized (Fig. 7).

4. Conclusion

Through the use of XRD and XPS, we have found that a high oxidation state of Cr species exists in the air-calcined chromium-based catalysts, which exhibit a high catalytic activity than nitrogen-calcined Cr(III) in the preparation of HFC-32 using vapor-phase catalytic fluorination. In addition, the lower initial reaction temperature for the treatment of chromia-based catalyst precursor with HF leads to easier crystallization of the chromia-based catalyst and a decrease in the reaction activity of the catalyst.

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