

Synthesis of a porous chromium fluoride catalyst with a large surface area

Heng-dao Quan*, Hui-e Yang, Masanori Tamura, Akira Sekiya

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

Received 2 November 2004; revised 21 January 2005; accepted 24 January 2005

Abstract

A novel approach to the preparation of a porous chromium fluoride catalyst with a large surface area is reported. The pores were generated by introduction of a siliceous material into the precursor of the catalyst and then removal of the material by reaction with anhydrous hydrogen fluoride. During the reaction, the formation and escape of a volatile gas (SiF_4) from the precursor enlarged the surface area of the chromium fluoride. This process provided for the first time a porous chromium fluoride with a surface area of $187 \text{ m}^2/\text{g}$ and a pore volume of $0.58 \text{ cm}^3/\text{g}$. Furthermore, the porous chromium fluoride exhibited excellent chemical stability in the presence of HCl, HF, and F_2 . It was catalytically active for halogen exchange in a fixed-bed fluorination reaction, and it exhibited excellent catalytic performance in mitigating the coke formation on the surface of the catalyst during vapor-phase catalytic fluorination.

© 2005 Elsevier Inc. All rights reserved.

Keywords: Vapor-phase catalytic fluorination; Porous chromium fluoride; Porous metal fluorides; Organo-fluorine compounds; Difluoromethane (HFC-32); Anhydrous hydrogen fluoride (AHF)

1. Introduction

Porous materials are widely used in catalysis, molecular separation technologies, selective reaction, optics, and solar cell materials [1–5]. Porous materials are usually prepared by calcination of metal salts or hydrous oxides [6], aerogel and sol-gel processes [7,8], and micellar systems [9,10]. Because most porous materials are composed of silicates and metal oxides, they are unstable; the porous structure collapses in the presence of corrosive media, such as HCl, HF, and F_2 . Porous metal fluorides are inert, but existing metal fluorides have only a small surface area [11–14]. High-surface-area metal fluorides have been exploited for their high activity and long catalyst life. Stacy et al. have reported a novel method for converting zeolites to high-surface-area AlF_3 by means of plasma-assisted fluorination with nitrogen trifluoride. Kemnitz et al. developed a nonaqueous synthetic

route to X-ray amorphous metal fluorides with surface areas of approximately $206 \text{ m}^2/\text{g}$ by means of the reaction of an organic intermediate with HF [15,16].

Chromium-based catalysts are important for the production of several compounds [17]. Fluorinated chromia has been a foundational pillar of vapor-phase catalytic fluorination reactions, and its preparation has been investigated extensively [18–20]. Because of the higher activity of high-surface-area catalysts, lower reaction temperatures can be used, which minimizes side reactions and increases selectivity for the desired product [21].

Here we report a facile preparation of a porous chromium fluoride (PCrF) catalyst with a large surface area. The pores were generated by the introduction of a siliceous material into the precursor of the catalyst and then removal of the material by reaction with anhydrous hydrogen fluoride (AHF). During removal of the siliceous material, the escape of a volatile gas (SiF_4) from the precursor enlarged the surface area of the PCrF [22]. The resulting amorphous PCrF had a $187.0 \text{ m}^2/\text{g}$ surface area and $0.58 \text{ cm}^3/\text{g}$ pore volume. In addition, the new PCrF exhibited excellent thermal stability below $500 \text{ }^\circ\text{C}$; chemical stability in the presence of HCl,

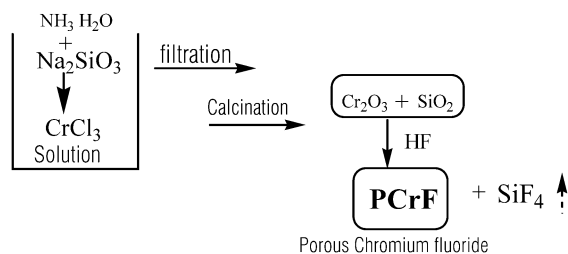
* Corresponding author. Fax: +81-298-4771.

E-mail address: Hengdao-quan@aist.go.jp (H.-d. Quan).

HF, and F₂; and high catalytic performance in mitigating the coke formation on the surface of the catalyst.

2. Experimental

The Brunauer–Emmett–Teller (BET) surface areas, pore volumes, and Barrett–Joyner–Halenda (BJH) adsorption pore distributions were determined for the samples by means of low-temperature adsorption of nitrogen with a Micromeritics ASAP 2010 instrument. The bulk crystalline phase of the samples was determined by X-ray diffraction (XRD) with a Mac Science, MPX-18 diffractometer. Differential scanning calorimetry and thermogravimetry patterns of the samples were recorded, respectively, on Rigaku Thermoplus DSC-8230 and Thermoplus 8120 instruments. Scanning electron microscopy and energy-dispersive X-ray (EDX) analysis of samples were performed on a Hitachi S4800 field-emission scanning electron microscope (SEM). Representative transmission electron micrographs of samples were recorded with a JEOL JEM 2010 transmission electron microscope (TEM) operated at 200 kV. The typical process for preparing PCrF and its precursor is as follows:



Na₂SiO₃ (9 g) was dissolved in 14 ml of 28% aqueous ammonia solution, and the solution was added dropwise to 240 g of a rapidly stirred 30% CrCl₃ solution. The pH of the solution was approximately 7.5. The resulting slurry of hydroxides was filtered, washed thoroughly with de-ionized water, dried, ground, and pelleted. The pellets were calcined at 400 °C under nitrogen and then treated with anhydrous hydrogen fluoride (AHF) at 350 °C for 100 h. Finally, the residual AHF in the PCrF was purged with nitrogen. For the preparation of difluoromethane (HFC-32), dichloromethane (0.3 g/min) and vapor-phase AHF (300 ml/min) were fed into a reactor charged with 10 ml of the prepared PCrF catalyst. The product stream from the reactor was scrubbed with H₂O at 60 °C and then passed first through a dryer packed with CaCl₂ and then through a gas chromatograph (Shimadzu GC-14 A on-line) with a Poraplot Q capillary column (i.d. 0.32 mm; length 25 m; J & W Scientific Inc.). The column temperature program was as follows: 80 °C for 15 min; 20 °C/min to 200 °C; hold for 5 min. Both the injection port and the thermal conductivity detector were maintained at 200 °C, and the carrier gas was He introduced at a rate of 10 ml/min. To determine the conversion of CH₂Cl₂ and the yields of CH₂FCl and CH₂F₂, their GC relative response factors (CH₂F₂/CH₂FCl/CH₂Cl₂ = 1:1.23:1.67) were used in the calculations [23].

3. Results and discussion

The results of BET analysis (Table 1) indicate that the addition of Si increased the surface area and pore volume of the PCrF and its precursor. When the percentage weight of Si relative to Cr was approximately 3%, the surface area and the pore volume of precursor were 470.0 m²/g and 0.79 cm³/g, respectively. After fluorination of the siliceous precursor by HF at 350 °C for 100 h, the surface area and pore volume of PCrF were 187.0 m²/g and 0.58 cm³/g, respectively. The surface area of the chromium fluoride prepared by means of this novel approach was twice that of chromium fluoride prepared by the conventional method. This increase is ascribed to the fact that the formed SiF₄ escaped from the precursor, thus enlarging the surface area during the reaction of the siliceous precursor and HF. SiF₄ is reported to be formed by the reaction of SiO₂ and gaseous HF at high temperature in a fluidized bed reactor [22]. The surface area of PCrF decreased to 149.4 m²/g when the Si weight percentage was increased to 5%.

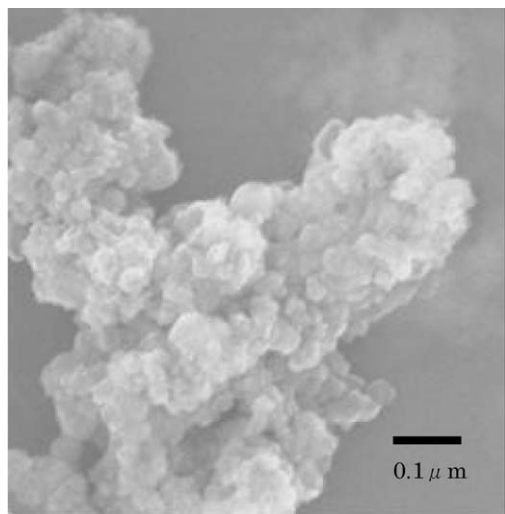
The pore-diameter distribution was calculated from the adsorption isotherm branch of the nitrogen isotherms by the BJH method. The results of the analysis indicate that the pore size distributions of PCrF and its precursor were wide, ranging from 20 to 300 Å. The wide pore size distribution might be attributable to the fact that control of the co-precipitating process was difficult because the chromic hydroxide was produced rapidly in the presence of ammonia solution. The particle size of the formed chromic hydroxide varied drastically. When the calcined chromic hydroxide was treated with HF, the SiO₂ in the precursor was removed, leaving a wide pore size distribution.

Furthermore, the SEM/EDX integrated analysis indicated that several kinds of particles coexisted in the siliceous precursor, some containing 6.1 wt% Si and some containing 3.5 wt% Si. EDX analysis confirmed that the siliceous precipitate of chromic hydroxide was not a uniform mixture, and this nonuniformity led to the different size pores in the PCrF. The SEM images (Figs. 1a and 1b) show clearly that the amorphous PCrF and its precursor were piled up in irregularly shaped particles and were composed of pores with different diameters. The pore size distribution was not uniform,

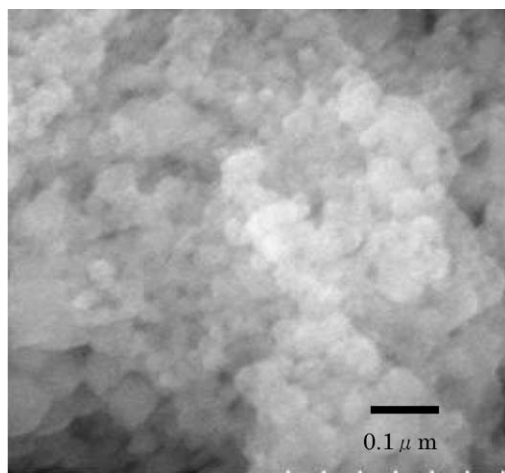
Table 1
Characterization of PCrF and its precursor by the BET method

Sample	Si ^a (wt%)	Surface area (m ² /g)	V _p (cm ³ /g)	Mean pore radius (Å)
CrSi-0	0	298.9	0.48	32.3
F–CrSi-0		90.2	0.30	66.9
CrSi-1	1	399.2	0.62	31.0
F–CrSi-1		184.3	0.47	51.2
CrSi-3	3	470.0	0.79	33.9
F–CrSi-3		187.0	0.58	55.8
CrSi-5	5	354.7	0.40	60.9
F–CrSi-5		149.4	0.45	60.3

^a These values are the wt% of Si to Cr in the precursor of PCrF; F–: CrSi fluorinated with HF.



(a)



(b)

Fig. 1. (a) Representative scanning electron micrograph of the siliceous precursor with a $470.0 \text{ m}^2/\text{g}$ surface area. (b) Representative scanning electron micrograph of PCrF with a $187.0 \text{ m}^2/\text{g}$ surface area.

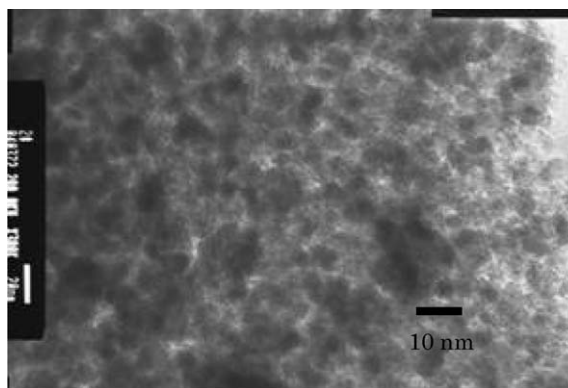


Fig. 2. TEM image of PCrF.

which is consistent with the BET results obtained by the BJH method. The surface of the PCrF appeared to be downy, which is ascribed to the fact that the addition of silicon in chromia obviously enlarged the surface area of PCrF when the siliceous precursor reacted with AHF. EDX/SEM analysis indicates that the PCrF consisted mainly of Cr and F, a certain amount of O, and trace amount of Si when the precursor was treated with AHF at 350°C for 100 h. The presence of oxygen promotes the activity of the catalyst [24]. Fig. 2 shows TEM images of the PCrF. The TEM image can be seen in domains of about 10 nm, which indicates that the PCrF was composed of differently sized pores with irregular shapes. Again, the image is consistent with the pore size distribution results obtained by BET analysis.

DSC and TG analyses showed that the thermal stability of the PCrF was much better than that of conventionally prepared chromium fluoride. The PCrF showed no obvious decomposition until 600°C , whereas the traditional chromium fluoride began to decompose at 570°C . The loss of TG wt% of PCrF was much less than that of traditional chromium fluoride in the range from 50 to 500°C . We speculate that the thermal stability of the catalyst was improved by the pres-

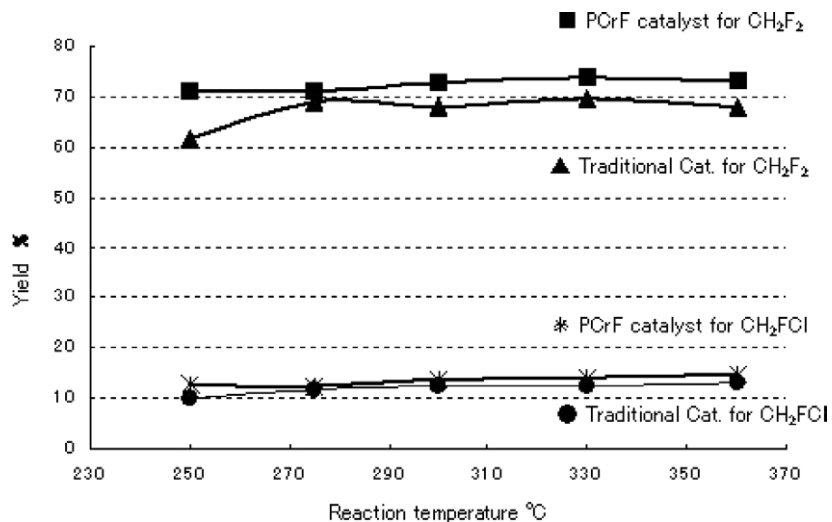


Fig. 3. Comparison of PCrF and traditional chromium fluoride in the reaction of dichloromethane: catalyst, 10 ml; HF, 300 ml/min; CH_2Cl_2 , 80 ml/min; GHSV, 2280 h^{-1} ; contact time, 1.6 s.

ence of residual trace amounts of Si. XRD results indicate that PCrF and its siliceous precursor heated at 120 or 400 °C under nitrogen were X-ray amorphous. As reported in the literature [25], amorphous chromium fluoride is advantageous for F/Cl exchange in vapor-phase catalytic fluorination.

In the preparation of difluoromethane (HFC-32), our PCrF catalyst exhibited higher activity than conventional chromium fluoride (Fig. 3). We ascribe these results to the fact that the larger surface area of PCrF was advantageous for F/Cl exchange in the vapor-phase catalytic fluorination. Coke formation on the catalyst surface during the preparation of HFC-32 is responsible for deactivation of the catalyst in vapor-phase catalytic fluorination. We found that after 100 h of reaction, the PCrF prepared from the siliceous precursor exhibited less coke formation than did chromium fluoride prepared from chromia when both types of chromium fluoride were used as process catalysts in the preparation of HFC-32. As indicated by EDX analysis, the carbon amount on the surface of used catalysts increased to approximately 3 wt% in PCrF and 12 wt% in conventional chromium fluoride. The decrease in coke formation may be attributable to the decreased Lewis acid strength of the Cr-based catalyst caused by trace amounts of Si in the catalyst. In fact, weak Lewis acid strength is advantageous for decreasing coke formation, which prolongs the lifespan of the catalyst. When the PCrF was used for 350 h in a fluorination reaction of dichloromethane, the efficiency of the catalyst decreased to 85% of the original value. The components (wt%) on the catalyst surface determined by EDX analysis were as follows: Fresh catalyst: C 4.2, O 6.2, F 58.4, Si 0.8, Cr 30.4, F/O 9.4, F/Cr 1.9; Used catalyst after 350 h: C 25.0, O 3.0, F 54.9, Si 0.2, Cr 16.9, F/O 18.4, F/Cr 3.3. The results indicate that the decrease in the amount of oxygen on the catalyst surface is another factor in catalyst deactivation.

Acknowledgments

We thank Dr. Zhi-heng Wu and Dr. Bo Yang for their assistance in obtaining SEM images of samples, and Dr.

Ming-deng Wei for his help in measuring X-ray diffraction patterns.

References

- [1] Y.F. Lu, R. Gangguli, C.A. Drewien, M.T. Anderson, C.J. Brinker, W.L. Gong, Y.X. Guo, H. Soyez, B. Dunn, M.H. Huang, J.I. Zink, *Nature* 389 (1997) 364.
- [2] U. Ueno, H. Horiuchi, M. Tomita, O. Niwa, *Anal. Chem.* 74 (2002) 5257.
- [3] H.D. Quan, M. Tamura, J. Murata, R.X. Gao, A. Sekiya, *J. Fluorine Chem.* 106 (2000) 121.
- [4] H.S. Zhou, I. Honma, *Adv. Mater.* 11 (1999) 683.
- [5] Do Trong On, *Langmuir* 15 (1999) 8561.
- [6] F. Schüth, K.S.W. Sing, J. Weitkamp, *Handbook of Porous Solids*, vol. 1, Wiley-VCH, Weinheim, 2002, p. 4.
- [7] H. Bozorgzadeh, E. Kemnitz, M. Nickkho-Amiry, T. Skapin, J.M. Winfield, *J. Fluorine Chem.* 110 (2001) 181.
- [8] P. Chanho, G.L. Haller, *Micropor. Mesopor. Mater.* 48 (2001) 165.
- [9] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.I. Schlenker, *J. Am. Chem. Soc.* 114 (1992) 10834.
- [10] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.
- [11] H.D. Quan, M. Tamura, J. Murata, R.X. Gao, A. Sekiya, *J. Fluorine Chem.* 99 (1999) 167.
- [12] H.D. Quan, M. Tamura, R.X. Gao, A. Sekiya, *Tetrahedron* 57 (2001) 4111.
- [13] M. Wojciechowska, B. Czajka, M. Pietrowski, M. Zieliński, *Catal. Lett.* 66 (2000) 147.
- [14] H.D. Quan, M. Tamura, J. Murata, R.X. Gao, A. Sekiya, *J. Fluorine Chem.* 116 (2002) 65.
- [15] J.L. Delattre, P.J. Chupas, C.P. Grey, A.M. Stacy, *J. Am. Chem. Soc.* 123 (2001) 5364.
- [16] E. Kemnitz, U. Groß, S. Rüdiger, C.S. Shekar, *Angew. Chem.* 42 (2003) 4251.
- [17] C. Pak, G.L. Haller, *Micropor. Mesopor. Mater.* 48 (2001) 165170.
- [18] D.R. Coulson, P.W.J.G. Wijnens, J.J. Lerou, L.E. Manzer, *J. Catal.* 140 (1993) 103.
- [19] Swamer, F.W.U.S. Patent 3,258,500 (1966), to El du Pont Company.
- [20] T. Skapin, E. Kemnitz, *J. Non-Crystall. Sol.* 225 (1998) 163.
- [21] L.E. Manger, M.J. Nappa, *Appl. Catal. A: Gen.* 221 (2001) 267.
- [22] *Gmelin Handbook*, Si suppl. B, vol. 7, 1992, p. 117.
- [23] H.D. Quan, M. Tamura, Y. Matsukawa, J. Mizukado, T. Abe, A. Sekiya, *J. Mol. Catal. A: Chem.* 219 (2004) 79.
- [24] S.B. Brunet, D. Martin, *J. Catal.* 171 (1997) 284.
- [25] S. Akashi, I. Yoshio, K. Satoshi, EP 0514932 (1992), to Daikin Ind. Ltd.