



Preparation of N-doped ordered mesoporous carbon and catalytic performance for the pyrolysis of 1-chloro-1,1-difluoroethane to vinylidene fluoride



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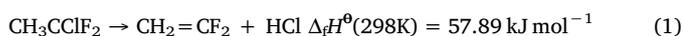
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ABSTRACT

N-doped ordered mesoporous carbons (NOMC) were prepared with mixed solution of urea and sucrose as carbon source and nitrogen source. SBA-15 was adopted as the hard template. The effect of urea to sucrose molar ratio on NOMC was investigated. NOMC samples were characterized by techniques such as BET, TEM, XPS and TG. The catalytic performances of NOMC catalysts were evaluated for the pyrolysis of 1-chloro-1,1-difluoroethane (HCFC-142b, CH₃CClF₂) to vinylidene fluoride (VDF, CH₂=CF₂). The catalytic reactions were carried out at 400 °C and space velocity of 600 h⁻¹ (based on HCFC-142b). The results indicate that NOMC exhibits a stable activity at 400 °C with high HCFC-142b conversion and selectivity to VDF. The textural parameters of NOMC play a major role in VDF selectivity and N species over the carbon surface are responsible for NOMC catalytic performance. Compared with the temperatures of industrial manufacture of VDF at 650–700 °C, the NOMC catalysts provide a promising pathway to produce VDF at much lower temperatures (below 400 °C).

1. Introduction

Vinylidene fluoride (VDF) is one of most important fluorinated alkenes [1–3], which is applied in many fields, such as the feedstock for the production of polyvinyl fluoride (PVDF) [4,5], copolymerizing with hexafluoropropylene and vinylidene chloride, and as an additive in fluorine-containing resins and fluorine-containing rubbers. Thermal dehydrochlorination of HCFC-142b (1-chloro-1,1-difluoroethane, CH₃CClF₂) is the main route to manufacture VDF. Thermal dehydrochlorination of 1-chloro-1,1-difluoroethane is performed industrially at the temperatures of 550–700 °C with the reaction expressed in equation (1) [6,7], which provides an HCFC-142b conversion of about 80–100% and selectivity to VDF about 85–95%. However, the production suffers from the coking deposition in the tubular reactors and has to be shut down for decoking process with certain intervals.



In addition, the thermal dehydrochlorination is not an eco-friendly route because of the energy consuming for decomposing HCFC-142b. Therefore, catalyst is highly desired and is an effective and environment friendly way to solve these problems. In the presence of a catalyst, the reaction temperature is expected to be reduced significantly. Furthermore, resistance of coking deposition is improved dramatically

due to the relatively low reaction temperatures. Aiming at catalytic pyrolysis of HCFC-142b to VDF, various catalysts such as metal chlorides, metal fluorides, metal oxides, activated carbon (AC), and metal salts impregnated on activated carbon have been attempted with minor success [8–11]. Mueller et al. used NiCl₂ as the catalyst for HCFC-142b dehydrochlorination, achieving 80% conversion of HCFC-142b and 100% selectivity of VDF [8]. R. Geetha et al. reported that BaCl₂/AC catalyst suppresses side reaction greatly on the HCFC-142b dehydrochlorination. Unfortunately, the stability of catalyst is not satisfactory [10]. Wang et al. suggested three metal chlorides (FeCl₃, CuCl₂, NiCl₂) impregnated on activated carbon as catalysts, achieving 10%–90% conversion of HCFC-142b and 60%–90% selectivity to VDF at 400–630 °C [11].

It is well known that nitrogen-doped carbon materials have been extensively studied and applied for the oxygen reduction reactions (ORR) [12–15] and CO oxidation reaction [16–19]. The nitrogen dopants in carbon materials enhances the polarity, alkalinity, oxidability, conductivity and surface hydrophilicity [20–22]. More recently, nitrogen-doped carbon materials were considered as non-metallic catalysts for acetylene hydrochlorination [23–26] with satisfactory performance. In addition, N-doped carbon materials also function as a kind of dehydrochlorination catalysts. For example, vinyl chloride monomer (VCM) was manufactured by the thermal pyrolysis of 1,2-

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dichloroethane (1,2-DCE). The introduction of carbon-based catalysts decreased the reaction temperatures and improved the yield of VCM. In our previous work [27], we found that the N-doped carbon materials (NAC) are efficient catalysts in dehydrochlorination of HCFC-142b. Especially, NAC-2 with proper N doping, it exhibits superior catalytic activity with the HCFC-142b conversion of 55% and selectivity to VDF of 96% at only 350 °C. Similarly, NOMC finds its important application in many fields [28–31] such as the adsorption separation, energy storage materials, catalyst carrier, drug delivery. Its ordered pore structure, high specific surface area, larger pore volume and rich mesoscopic structure facilitate the achievement of stable catalytic activity.

Vinu et al. reported the preparation of two-dimensional (2D) hexagonal structured NOMC materials with polymerization of ethylenediamine (EDA) and carbon tetrachloride (CTC) as precursors, and SBA-15 as the template [32]. N Liu et al. fabricated the NOMC with diaminobenzene (DAB) as both the carbon and nitrogen precursors, and ammonium peroxydisulfate (APDS) as the oxidant [33]. Herein, we synthesized NOMC materials with high specific surface area and nitrogen doping content with SBA-15 as the hard template and mixed solution of urea and sucrose as the nitrogen and carbon precursors.

2. Experimental

2.1. Reagents and materials

Urea (≥ 99.5) and HF solution (40 wt%) were purchased from Aladdin Industrial Corporation (Shanghai, China). HCFC-142b (99.8%) from Juhua Group Corporation (Quzhou, China), was adopted as feed gas without further purification. Sucrose, sodium hydroxide ($\geq 99.9\%$) and ethanol ($\geq 99.5\%$) were obtained from Sinopharm Chemical Reagent Co. LTD in China.

Similar with the method reported by Zhao et al. [34], SBA-15 silica were synthesized with Pluronic P123 triblock copolymer (EO₂₀-PO₇₀-EO₂₀) as the template. A 20.0 g sample of Pluronic P123 was dissolved in 650 mL water and 100 mL HCl solution (37 wt%). Then, 32 mL of Tetramethyloxysilane (TMOS) was added drop wisely and the resulting mixture was stirred for 20 h at 40 °C and then kept at 100 °C for 24 h without stirring. Following washing for several times with ethanol and deionized water, the mixture was dried at 110 °C for 12 h and calcined in a muffle furnace at 550 °C for 10 h in air with a temperature ramp of 5 °C/min.

2.2. Catalyst preparation

In a typical process, 2.64 g urea and 3.75 g sucrose were dissolved in 13 mL water. Then 3 g SBA-15 was introduced to the solution. The samples obtained were labeled as NOMC-4, where 4 represents the ratio of urea to sucrose. The compositions of other samples were listed in Table 1. The synthesis process is illustrated in Fig. 1. The samples were recovered after the removal of the silica framework in 40 wt% HF solutions. Catalysts precursors were treated by filtration, washed for several times with ethanol and deionized water, dried at 100 °C for 12 h. Finally, samples were pre-carbonized at 160 °C for 6 h and calcined in a tubular furnace at 850 °C for 3 h with a heating rate of 10 °C/min in N₂ atmosphere with a flow rate of 50 mL/min.

Table 1

Fabrication conditions of OMC and NOMCs.

Samples	Urea/g	Sucrose/g	H ₂ O/ml	SBA-15/g	Urea/Sucrose (mol ratios)
OMC	0	3.75	13	3.0	0
NOMC-4	2.64	3.75	13	3.0	4
NOMC-8	5.28	3.75	13	3.0	8
NOMC-16	10.56	3.75	13	3.0	16
NOMC-24	15.84	3.75	13	3.0	24

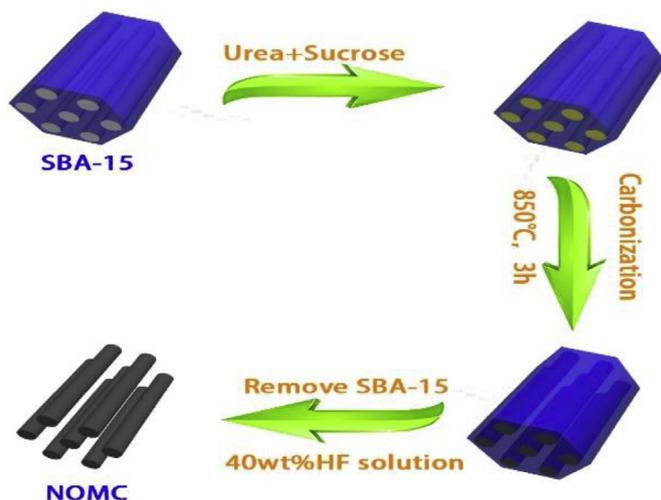


Fig. 1. Illustration of the synthesis process of the NOMCs.

2.3. Catalyst activity evaluation

The performances of catalysts were evaluated by a fixed-bed reactor (nickel tube with i. d. of 22 mm). The system was first purged with nitrogen to remove water vapor and air before each evaluation experiment at reaction temperatures. Then the gas phase of HCFC-142b with the GHSV of 600 h⁻¹, mixed with equivalent flow of nitrogen, passed through the reactor. The effluent gas from the reactor passed into a scrubber containing about 1 M NaOH solution (450 mL) to remove the acid gas of HCl and trace amounts of HF, followed by the composition analysis with an FULI GC-9790 gas chromatograph equipped with a thermal conductivity detector (TCD).

2.4. Catalyst characterization

For the morphology investigation, SEM (scanning electron microscope) was carried out on a FESEM, Hitachi S-4700 at an accelerating voltage of 15 kV equipped with an X-ray energy spectrometer (EDS). TEM was adopted to further explore the microstructure of catalysts over Joel 2100 F Transmission Electron Microscope at an acceleration voltage of 200 kV. The BET surface area and total pore volume of catalysts were measured by N₂ adsorption-desorption at -196 °C with Quantachrome Autosorb Automated Gas Sorption System from USA. The catalyst samples were degassed at 200 °C for 6 h under vacuum before measurements. The X-ray photoelectron spectroscopy (XPS) measurements of the catalysts were performed by Thermo ESCALAB 250XI, equipped with monochromatised Al K α X-ray as the excitation source (24.2 W), with an analyzer pass energy of 187.85 eV for survey scans and 46.95 eV for detailed elemental scans. The XPS spectra were analyzed by the XPS peak software with Gaussian functions after subtraction of a Shirley background. To subtract the surface charging effect, binding energies were referenced to C1s binding energy of carbon, taken to be 284.6 eV. Thermogravimetric analysis (TGA) was performed on a TA TGA Q500 instrument. The samples were heated in platinum crucibles up to 800 °C from room temperature with a heating rate of 10 °C per min in 30 mL/min air flow.

3. Results and discussion

3.1. Structure and textural properties of NOMC samples

3.1.1. SEM and TEM characterizations of NOMC samples

The morphology and structure of the obtained OMC and NOMCs samples were investigated by SEM technique. Fig. 2 shows the different magnification SEM images of the OMC and NOMC-24. Other samples

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