

# Vinylidene Fluoride

Subjects: Others

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1,1-difluoroethylene (VDF) is one of the major fluoromonomers, which are the feedstock for the production of various resins, rubbers membrane and paints. The polymers derived from VDF (PVDF) or co-polymers with unique chemical resistance, stability at elevated temperatures, oxidation resistance, weatherability, piezoelectricity, dielectric and thermoelectricity, find wide applications in areas including petrochemical, electronic and electrical, and fluorocarbon coating. VDF is the second largest product among fluorocarbons with an annual production capacity of above 53,000 tons. The demand for VDF is increasing rapidly. At present, in industry, VDF is usually produced via the dehydrochlorination of 1,1-difluoro-1-chloroethane (HCFC-142b) at reaction temperatures above 650 °C

Keywords: barium chlorofluoride ; catalytic pyrolysis ; barium fluoride ; dehydrochlorination ; 1-chloro-1,1-difluoroethane ; vinylidene fluoride

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## 1. Introduction

1,1-difluoroethylene (VDF) is one of the major fluoromonomers, which are the feedstock for the production of various resins, rubbers membrane and paints <sup>[1]</sup>. The polymers derived from VDF (PVDF) or co-polymers with unique chemical resistance, stability at elevated temperatures, oxidation resistance, weatherability, piezoelectricity, dielectric and thermoelectricity, find wide applications in areas including petrochemical, electronic and electrical, and fluorocarbon coating <sup>[2]</sup>. VDF is the second largest product among fluorocarbons with an annual production capacity of above 53,000 tons. The demand for VDF is increasing rapidly. At present, in industry, VDF is usually produced via the dehydrochlorination of 1,1-difluoro-1-chloroethane (HCFC-142b) at reaction temperatures above 650 °C <sup>[3][4]</sup>. Dehydrochlorination is an efficient route for the preparation of 1, 1-dichloroethylene (VDC), vinyl chloride monomer (VCM), 2,3,3,3-tetrafluoropropene (HFO-1234yf), and ethylene oxychlorination <sup>[5][6][7][8]</sup>. As the dehydrochlorination of HCFC-142b is a highly endothermic reaction, very long reaction tubes are adopted to supply the reaction heat. Unfortunately, this also leads to the generation of carbon deposition during the reaction process at elevated temperatures. Consequently, the reactor needs to be cut off to remove the coke after a period of reaction, which significantly reduces the efficiency of continuous production. <sup>[1][2][3][4][5][6][7][8][9][10][11][12][13][14][15][16][17]</sup>

## 2. Specifics

We have reported that the dehydrochlorination of HCFC-142b is promoted by catalysts such as N-doped activated carbon <sup>[9]</sup>, N-containing mesoporous carbon <sup>[10]</sup>, and metal fluorides <sup>[3][4]</sup>. The presence of catalysts reduces the reaction temperature from 650 °C to lower than 350 °C, facilitating saving energy consumption and avoiding the formation of coke during reaction. Although N-doped activated carbon and mesoporous carbon materials exhibit a moderate conversion of HCFC-142b and high selectivity to VDF, they are difficult to recover following deactivation by coking. SrF<sub>2</sub> shows a high activity for the pyrolysis of HCFC-142b to VDF under moderate conditions. However, its selectivity and stability are rather low <sup>[4]</sup>. Although the preparation of SrF<sub>2</sub> microparticles with cubic structures improves the performance, the procedure is complicated and it is difficult to scale-up.

Due to the formation of highly corrosive byproducts, HCl and HF, during pyrolysis of HCFC-142b, there are very rare choices for the exploration of proper materials as the catalysts. Therefore, carbon materials and metal fluorides which are HF-corrosion-resistant are the potential catalysts. In addition to carbon materials, metal fluorides were also systematically investigated for the catalytic pyrolysis of HCFC-142b <sup>[11]</sup>. Among the various metal fluorides, barium fluoride shows relatively high activity in this reaction, with selectivity to VDF of 95% <sup>[11]</sup>. Other metal fluorides, such as MgF<sub>2</sub>, AlF<sub>3</sub> and fluorinated Cr<sub>2</sub>O<sub>3</sub> were found to be catalysts for dehydrofluorination reactions <sup>[12][13][14]</sup>. Similar to the chlorination of AlF<sub>3</sub> to aluminum chlorofluoride (ACF), BaF<sub>2</sub> also tends to be chlorinated to BaClF by Cl species under reaction conditions <sup>[15]</sup>. Consequently, a rapid decrease in the conversion of HCFC-142b and selectivity to VDF was observed. In a similar reaction system for dehydrofluorination, which was catalyzed by AlF<sub>3</sub>, strong Lewis acid promoted both

dehydrofluorination and coke deposition. As a result, a fast deactivation was seen. It was reported that the pre-deposition of carbon prior to reaction leads to the partial coverage of strong Lewis acid sites and improves the stability of catalysts [16]. As reported previously, BaF<sub>2</sub> converts to BaClF via reaction with HCl at reaction temperatures, resulting in the deactivation of the catalyst [11][17]. Clearly, the inhibition of chlorination of the BaF<sub>2</sub> catalyst by Cl species is one of the key challenges for the catalytic pyrolysis of HCFC-142b.

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