Catalytic decomposition of CFC-12 on solid acids SO_4^{2-}/M_xO_y (M = Zr, Ti, Sn, Fe, Al)

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The catalytic decomposition of dichlorodifluoromethane (CFC-12) in the presence of water vapor on a series of SO_4^{2-}-promoted solid acids was investigated. CFC-12 was decomposed completely on SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2, SO_4^{2-}/SnO_2, SO_4^{2-}/Fe_2O_3 and SO_4^{2-}/Al_2O_3 at 265℃, 270℃, 325℃, 350℃ and 325℃, respectively, and the selectivity to by-products was neglectable. Obvious deactivation was found on SO_4^{2-}/ZrO_2 and SO_4^{2-}/Al_2O_3 during several hours on stream, while the catalytic activity was maintained on SO_4^{2-}/TiO_2, SO_4^{2-}/SnO_2 and SO_4^{2-}/Fe_2O_3 for 240 h on stream.

Keywords   Environmental catalysis, freon decomposition, solid acids

Introduction

CFCs (chlorofluorocarbons, Freons) are a family of industrial compounds widely used as refrigerants, solvents, propellants, blowing agents, etc. However, in 1974, Molina and Rowland published a paper in Nature, pointing out that CFCs are killers of the ozone layer which protects life on earth against harmful ultraviolet radiation from the sun.[1] This conclusion has been continuously confirmed by thousands of studies. As a result, the Montreal Protocol, an international treaty to phase out and control CFCs, was signed by 163 countries including China and the 1995's Nobel Prize in chemistry said yes to Molina and Rowand.[2] Further investigations also indicated that CFCs are green-house gases which are warming up our earth. As earth warms up, disease threats will increase and iceberg will break away.[3]

In order to tackle these environmental problems,

many CFCs were banned without delay, however, there are still 2.25 million ton CFCs all over the world and numerous air-conditioning systems still use them. These CFCs are leaking out of existing equipment and will not be degraded in nature within 100 years because of their chemical inertness. Therefore, techniques that can eliminate CFCs either prior to or during their release to the environment are extremely desired.

The CFCs decomposition has attracted considerable public enthusiasm. A dozen of decomposition approaches such as incineration, cement kiln, high frequency induced plasma, super critical water, electrochemical decomposition, ultrasonic irradiation, reduction with sodium naphthalenide and catalytic decomposition have been developed.[4,5] Catalytic decomposition is very promising because of simple processes, requiring mild conditions and dioxins free. Many catalysts, such as γ-Al_2O_3, transition metal chloride promoted γ-Al_2O_3, SiO_2-Al_2O_3, TiO_2-SiO_2, TiO_2-ZrO_2, Pt/ZrO_2-TiO_2, fluorinated TiO_2, BPO_4, $AlPO_4$ and zeolites were found to be active in this reaction.[6-13] However, there are three difficult problems remaining to be tackled: (1) most of the catalysts decomposed CFCs at more than 400℃, which requires a lot of energy and would accelerate the deactivation rate; (2) measurable CFC-13 and even CO were reported to be the by-products; (3) obvious deactivation was often found during several hours on stream because HF produced in the reaction corroded the catalysts.

Although the CFCs decomposition mechanism has not been fully illuminated, it is interesting to note that all the efficient catalysts mentioned above are solid acids, while other materials such as CaO, SiO_2, car-

bon, ZnO, MgO and Fe_2O_3 showed rare activity for this reaction. This information may provide a useful clue to design efficient CFCs decomposition catalysts. The fundamental research of SO_4^{2-} or $S_2O_8^{2-}$-treated solid acids have been continuously pursued in our group for ten years.[14-18] In this paper, the application of SO_4^{2-}-promoted solid acids as efficient CFC-12 decomposition catalysts will be reported.

Experimental

$Zr(OH)_4$, $Ti(OH)_4$, $Sn(OH)_4$, $Fe(OH)_3$ and $Al(OH)_3$ were prepared by hydrolyzing $ZrOCl_2$, $TiCl_4$, $SnCl_4$, $Fe(NO_3)_3$ and $Al(NO_3)_3$ with ammonium hydroxide, washing, drying at 110℃ and powdering. Then they were immersed into 1 mol/L H_2SO_4 solution followed by filtering, drying at 110℃ and calcining at 500℃ for 3 h except that H_2SO_4-treated $Zr(OH)_4$ and $Al(OH)_3$ were both calcined at 650℃. These products are labeled as SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2, SO_4^{2-}/SnO_2, SO_4^{2-}/Fe_2O_3 and SO_4^{2-}/Al_2O_3, respectively. For comparison, ZrO_2, TiO_2, SnO_2, Fe_2O_3 and Al_2O_3 were obtained by calcining the hydroxides at the corresponding temperature.

The catalytic CFC-12 decomposition was carried out in a fixed-bed flow microreactor. CFC-12 (1, 000 ppm), water vapor (6,000 ppm) and balance air were mixed up and passed through 0.4 g of the catalyst with a space velocity (WHSV) of 6 $Lh^{-1} \cdot g\text{-}cat^{-1}$. Effluent gases were passing through KOH solution to eliminate HF, HCl and CO_2 produced during the reaction.

Before the KOH trap, gases were collected and identified. The main product was CO_2 and no by-product CO was detected for all the catalysts. However, another by-product was detected. GC-MS confirmed that it was CFC-13. After the KOH trap, unreacted CFC-12 and by-product CFC-13 were separated with a Apiezon grease L/SiO$_2$ (0.7 m) column at 70℃, then analyzed by a gas chromatography equipped with a flame ionization detector (FID). The conversion of CFC-12 and selectivity to CFC-13 were calculated as follows: [Conversion of CFC-12] = ([CFC-12]in-[CFC-12]out) / [CFC-12]in × 100%; [Selectivity to CFC-13] = [CFC-13] out/ ([CFC-12]in-[CFC-12]out) × 100%.

X-ray powder diffraction (XRD) measurements were performed on a Rigaku D/MAX-IIA instrument us-

ing CuK_α radiation with scan speed 16°/min and scan range 10—70°. Carbon deposit was analyzed by elementary analysis.

Results and discussion

Catalytic activity, selectivity and stability are three major indexes of catalysts for practical use. The catalytic properties of SO_4^{2-}-promoted solid acids for the CFC-12 decomposition will be discussed as follows.

Catalytic activity

Figs. 1 and 2 compare the CFC-12 conversion as a function of reaction temperature on pure and sulfated metal oxides. ZrO_2, TiO_2, SnO_2, Fe_2O_3 and Al_2O_3 decomposed CFC-12 completely at 380℃, 360℃, 500℃, 500℃ and 370 ℃, respectively. From the viewpoint of saving energy, decomposing CFC-12 at such high temperature was not economical. But when these oxides were modified by sulfate, drastic enhancement in activity was observed. SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2, SO_4^{2-}/SnO_2, SO_4^{2-}/Fe_2O_3 and SO_4^{2-}/Al_2O_3 decomposed CFC-12 completely at 265℃, 270℃, 325℃, 350℃ and 325℃, respectively. The 100% conversion temperatures of sulfated metal oxides were lower than those of their corresponding metal oxides for 45—175℃.
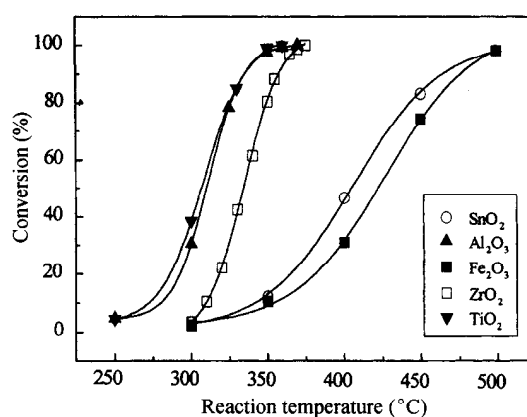

Fig. 1 Effect of reaction temperature on the conversion of CFC-12 over ZrO_2, TiO_2, SnO_2, Fe_2O_3 and Al_2O_3.

Although the CFCs decomposition mechanism has not been fully illuminated, it is generally accepted that acid catalysts play an important role in this reaction, and medium-strong and strong acid sites are more efficient for

the decomposition of CFCs because the rate-determining step for the CFCs decomposition is the rupture of C-Cl bond,[9,12,19] while the C-Cl bond energy is higher than 300 kJ/mol, then the great enhancement in CFC-12 decomposition activity can be accounted for by the great acidity and higher acid strength of SO_4^{2-}-promoted solid strong acids as compared with the corresponding metal oxides.
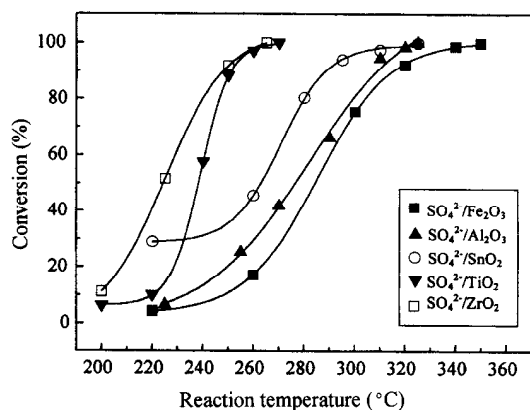

Fig. 2 Effect of reaction temperature on the conversion of CFC-12 on SO_4^{2-}/M_xO_y (M = Zr, Ti, Sn, Fe, Al).

Selectivity

The CFC-12 decomposition in the presence of water vapor is in accordance with the equation: CCl_2F_2 + $2H_2O \rightarrow CO_2$ + $2HCl$ + $2HF$, but CFC-13 and CO might be formed as by-products. Since CFC-13 and CO are both environmental pollutants, their formation is not preferred. In our results, no CO was found for all the catalysts and the selectivity to by-product CFC-13 on sulfated metal oxides was much lower than that on unmodified metal oxides when 100% conversion was achieved (Table 1).

Table 1 Selectivity to by-product CFC-13 over pure and SO_4^{2-}-promoted metal oxides

Catalysts	Selectivity to form CFC-13(%)				
	ZrO_2	TiO_2	SnO_2	Fe_2O_3	Al_2O_3
unmodified	1.89	4.88	5.25	4.81	3.79
SO_4^{2-}-modified	0	0.13	1.73	1.01	0.08

The CFC-13 formation mechanism on metal oxides can be generalized as follows:[6,8,10]

(1) $M\text{-}OH$ + $HF \rightarrow M\text{-}F$ + H_2O (M = Metal)

(2) $M\text{-}F$ + $CFC\text{-}12$ (CCl_2F_2) $\rightarrow$
$CFC\text{-}13$ ($CClF_3$) + $M\text{-}Cl$

(3) $M\text{-}Cl$ + $H_2O \rightarrow M\text{-}OH$ + HCl

That is to say, CFC-13 is formed only when metal oxides surface is fluorinated by HF produced during the reaction, while the fluorination of metal oxides stands for the partial replacement of surface OH groups by more electronegative fluorines.

Unmodified metal oxides are relatively easy to be fluorinated because all the surface OH groups are exposed to HF, but when metal oxides are treated by H_2SO_4, dehydration between $2H^+$ of H_2SO_4 and surface OH groups occurs[20] so that HF has less opportunity to bump and fluorinate the surface OH groups, then the selectivity to CFC-13 on sulfated metal oxides is much lower than that on pure metal oxides.

Stability

One of the most important targets of CFCs decomposition is to find out stable catalysts against HF produced during the reaction. It has been reported that many catalysts were efficient for the decomposition of CFCs, but the catalyst life was generally not reported or only examined for several hours, which is not sufficient.

In this study, the stability of all the SO_4^{2-}-promoted catalysts was tested and can be obviously classified into two groups based on their catalyst life. The CFC-12 conversion on sulfated metal oxides as a function of reaction time is shown in Fig. 3. It was found that the catalytic
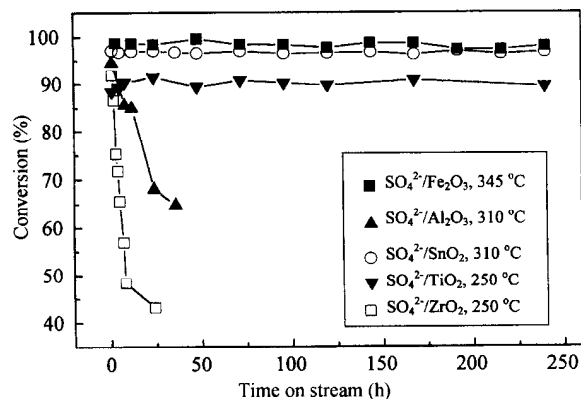

Fig. 3 CFC-12 conversion on SO_4^{2-}/M_xO_y (M = Zr, Ti, Sn, Fe, Al) at fixed different temperatures as a function of time on stream.

activity of SO_4^{2-}/ZrO_2 and SO_4^{2-}/Al_2O_3 decreased very quickly. On SO_4^{2-}/ZrO_2, the initial activity at 250°C decreased drastically from 91.9% to 48.4% during 8 h on stream, while the initial activity on SO_4^{2-}/Al_2O_3 at 310°C decreased from 94.5% to 64.7% during 36 h on stream. On the contrary, the CFC-12 conversion on SO_4^{2-}/TiO_2, SO_4^{2-}/SnO_2 and SO_4^{2-}/Fe_2O_3 all remained steady during 240 h on stream.

In order to illuminate the reasons why these catalysts showed different stability behavior, pure metal oxides were tested for 120 h. These results are shown in Table 2. The initial activity over Al_2O_3 at 365°C de-

creased from 97.5% to 68.0% during 24 h on stream. XRD peaks attributed to AlF_3 were detected. Similar phenomena were also reported for the decomposition of CFCs over γ-Al_2O_3, γ-Al_2O_3 and SiO_2-Al_2O_3 catalysts because Al_2O_3 are very easy to be corroded by HF produced during the reaction and transformed to relatively inactive AlF_3,[6,12] then it seems that using Al_2O_3 as CFC-12 decomposition supports is not practical. On the contrary, the CFC-12 conversion on TiO_2, SnO_2 and Fe_2O_3 all remained steady during 120 h on stream. These phenomena were in good agreement with the catalyst life of SO_4^{2-}/TiO_2, SO_4^{2-}/SnO_2, SO_4^{2-}/Fe_2O_3.

Table 2 CFC-12 conversion on pure M_xO_y (M = Zr, Ti, Sn, Fe, Al) at fixed different temperatures as a function of time on stream

Reaction time on stream (h)	CFC-12 conversion (%)				
	ZrO_2(375°C)	TiO_2(340°C)	SnO_2(475°C)	Fe_2O_3(475°C)	Al_2O_3(365°C)
1	98.8	98.4	98.8	99.0	97.5
3	99.2	98.8	98.2	99.2	78.7
5	99.8	98.4	98.3	99.1	73.0
8	100	98.8	99.0	99.2	68.2
24	98.9	98.6	100	97.3	68.0
48	100	98.1	100	97.5	–
72	100	98.7	100	98.1	–
96	100	97.7	100	98.9	–
120	100	97.7	100	97.8	–

Although TiO_2 and some metal oxides like that also tend to change into metal fluorides in the presence of HF from thermodynamic calculations, the role of water vapor can not be neglected. A contrast experiment was carried by Kramer and Greene:[8] the CFC-12 decomposition activity on pure TiO_2 decreased from 98% to 43% in 48 h without the supply of water vapor, while the conversion dropped only about 2% during 4 days on stream in the presence of water vapor. Li *et al*.[21] found the existence of water vapor suppressed the transformation of fluorides, progressed the formation of CO_2 and prolonged the catalyst life. Takita *et al*.[4] concluded that treating catalysts with both oxygen and water vapor promoted the removal of fluoride ions in sub-face layers of the catalysts, which is efficient for the recovery of the activity. That is, the reaction M-F + H_2O → M-OH + HF may occur to prevent the further accumulation of surface fluorine. It should be noted that once the surface fluorine is accumulated, the surface turns to be inactive metal fluo-

rides. Combining with our results, it can be concluded that TiO_2, SnO_2 and Fe_2O_3 are good supports in designing CFCs decomposition catalysts, although further modifications are required to improve catalytic activity of these metal oxides.

It's of interest to note that SO_4^{2-}/ZrO_2 showed high activity, but it was deactivated very quickly, while ZrO_2 showed good stability, so that the deactivation reason of SO_4^{2-}/ZrO_2 may be different from that of SO_4^{2-}/Al_2O_3. Carbon deposit of all the used SO_4^{2-}/M_xO_y (M = Zr, Ti, Sn, Fe, Al) catalysts was analyzed. No carbon deposit was detected on these used catalysts, indicating the deactivation of SO_4^{2-}/ZrO_2 can not be attributed to the deposition of carbon. The analysis of the effluent gas, which was absorbed in small amount of water, showed the presence of SO_4^{2-}. Thus, it may be concluded that sulfur escaped from SO_4^{2-}/ZrO_2 in the form of SO_3 during the reaction, then SO_4^{2-}/ZrO_2 was deactivated.

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