

Catalytic hydrolysis of CFC-12 over solid acid $\text{Ti}(\text{SO}_4)_2$

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Abstract: The catalytic hydrolysis of dichlorodifluoromethane (CFC-12) was investigated over solid acid $\text{Ti}(\text{SO}_4)_2$. The catalytic activity decreased with the calcination temperature. When space velocity was $6 \text{ l h}^{-1} \text{ g-cat}^{-1}$, the CFC-12 conversion at 310°C over $\text{Ti}(\text{SO}_4)_2$ calcined at 350°C remained about 98.5% during 360 h on stream, and the selectivity to by-products remained zero. The findings enlarged the scope of traditional catalyst systems for the CFCs decomposition.

Keywords: Chlorofluorocarbons, catalytic decomposition, solid acid $\text{Ti}(\text{SO}_4)_2$.

Due to increasing enthusiasm for environmental preservation, the synthesis of chlorofluorocarbons (CFCs) alternatives and the decomposition of existing CFCs have been two hot topics since the production and utilization of CFCs are banned by many countries. The former has been well carried out while the latter was rarely reported in China. Among a dozen of decomposition approaches, catalytic hydrolysis is very promising because of simple processes, requiring mild conditions, dioxins free and the availability of water¹. Investigations in this direction have been continuously pursued by dozens of groups overseas. Many catalysts, such as zeolites, single and mixed metal oxides are active for this reaction, however, there's still some room for improving the catalytic activity, selectivity and stability. Furthermore, the catalyst systems are remaining to be broadened. Recently, Takita *et al.*² reported that AlPO_4 decomposed CFC-12 completely at 450°C with long life. Their findings soared out of the traditional catalyst systems for the CFCs decomposition. Although the CFCs decomposition mechanism has not been fully illuminated, it is widely accepted that acid centers play an important role in this reaction. Arata³ once reported a novel solid acid $\text{Ti}(\text{SO}_4)_2$ which showed high activity for the cracking of cumene. In this paper, the catalytic decomposition of CFC-12 over $\text{Ti}(\text{SO}_4)_2$ with exceeding activity, selectivity and stability was reported.

Experimental

$\text{Ti}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$ was preheated in air at 350°C for 3 h to remove the crystal water and powdered below 100 mesh. Then the powder was calcined in air again at $350\text{--}650^\circ\text{C}$ for

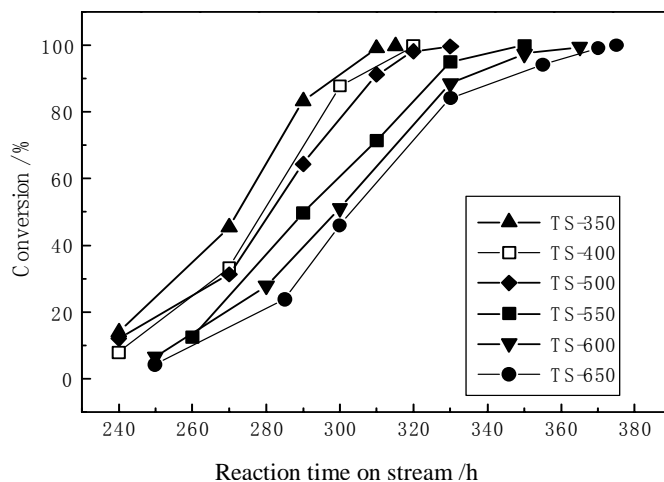
3 h. These products are labeled as TS-m, where m stands for the calcination temperature.

The catalytic hydrolysis ($\text{CCl}_2\text{F}_2 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{HCl} + 2\text{HF}$) 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 catalyst with flow rate varied between 20 and 160 ml/min. Effluent gases were passed through KOH solution to eliminate HF, HCl and CO_2 produced during the reaction. Unreacted CFC-12 and possible by-product CFC-13 were separated with a Apiezon grease L/ SiO_2 (0.7 m) column at 70°C , then analyzed by a gas chromatograph equipped with a flame ionization detector (FID). Possible by-product CO was converted to CH_4 with H_2 on ruthenium catalyst and detected by another FID. X-ray powder diffraction (XRD) measurements were performed on a Rigaku D/MAX-IIA instrument using Cu K α radiation with scan speed $16^\circ/\text{min}$ and scan range $10\text{--}70^\circ$.

Results and discussion

At first, the flow rate was fixed at 40 ml/min. The effect of calcination temperature on the CFC-12 decomposition activity was tested and depicted in **Figure 1**. From this figure, two pieces of information can be extracted: (1) the CFC-12 decomposition activity increased rapidly with the reaction temperature for all the catalysts; (2) the activity decreased with the calcination temperature obviously. TS-350 decomposed CFC-12 completely at 315°C , while TS-650 decomposed CFC-12 completely at 375°C . The optimum calcination temperature was 350°C .

Figure 1. Effect of calcination temperature on the CFC-12 conversion.



In order to illustrate the reason why the decomposition activity decreased with the calcination temperature, X-ray diffraction measurement of the catalysts was performed. All the XRD peaks of TS-350 can be assigned to $\text{Ti}(\text{SO}_4)_2$, however, characteristic

peaks of anatase TiO_2 appeared as the calcination temperature was raised to 500°C . The peak intensity of TiO_2 increased with the calcination temperature and the peak intensity of $\text{Ti}(\text{SO}_4)_2$ decreased concurrently. Finally, almost all the peaks of TS-650 can be assigned to anatase TiO_2 . From the XRD results, it can be concluded that the reaction $\text{Ti}(\text{SO}_4)_2 \rightarrow \text{TiO}_2 + 2\text{SO}_3$ occurred at elevated temperatures, which was also confirmed by TG³. The net result is that the acidic $\text{Ti}(\text{SO}_4)_2$ was decomposed to form relatively inactive TiO_2 , therefore the CFC-12 decomposition activity decreased with the calcination temperature.

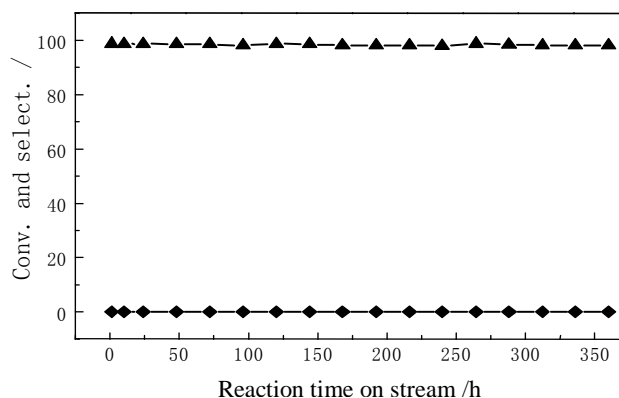
The effect of flow rate (space velocity) on the CFC-12 decomposition conversion of TS-350 was also investigated. The temperatures of 30%, 50% and 95% conversion (T_{30} , T_{50} and T_{95}) were listed in **Table 1** as measurements of the activity. The temperatures increased with the flow rate because of the cutdown in contact time. However, under all these reaction conditions, T_{95} was always achieved at no more than 350°C , which is meaningful.

Table 1. Effect of flow rate on the CFC-12 decomposition temperature over TS-350.

Flow rate (ml/min)	T_{30} ($^\circ\text{C}$)	T_{50} ($^\circ\text{C}$)	T_{95} ($^\circ\text{C}$)
20	255	265	295
40	260	270	305
80	295	305	335
160	300	315	350

The selectivity and catalyst life are two of the most important factors for practical use, hence the change in the selectivity to by-products and conversion of CFC-12 was studied at 310°C using the TS-350 catalyst. At this time, flow rate was 40 ml/min. The results are shown in **Figure 2**.

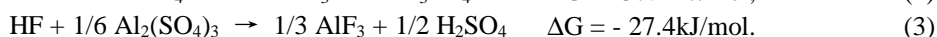
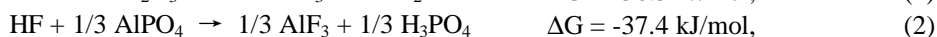
Figure 2. Effect of reaction time on CFC-12 conversion (\blacktriangle) and selectivity to by-products (\blacklozenge).



The initial conversion was 98.7% and the activity remained steady during 360 h on stream. The selectivity to by-products CFC-13 and CO all remained zero. The XRD patterns of the catalysts before and after the reaction for 360 h were recorded. The fresh

and used catalyst were both $\text{Ti}(\text{SO}_4)_2$. No essential change of the catalyst can be observed after 360 h on stream and no peaks such as the peaks of TiF_4 was observed, indicating no fluorination occurred.

As mentioned above, many catalysts were found to be active for the decomposition of CFCs, but obvious deactivation was often found. Take zeolites for example, the Al and Si atoms were removed easily from the framework by the reaction of HF and HCl produced during the reaction⁴. Some metal oxides, such as Al_2O_3 and SiO_2 are not stable in the CFCs decomposition because HF will react with them to form corresponding metal fluorides, especially at high temperature⁵. However, things are different for metal phosphates because the Gibbs free energy changes of the formation of metal fluorides from metal phosphates are much smaller than the corresponding metal oxides⁶, so that AlPO_4 has long life in this reaction². This explanation can be transferred to illuminate why metal sulfates are also supposed to be enduring against HF. For example:



Systematic investigations in this direction are being carried out. Preliminary results indicated that $\text{Zr}(\text{SO}_4)_2$ and SnSO_4 showed comparable high activity and good stability. $\text{Al}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3$, $\text{Ce}(\text{SO}_4)_2$ and NiSO_4 showed medium activity, while CaSO_4 and CuSO_4 were almost inactive even at 400°C . This may be ascribed to the different acid properties of these metal sulfates. In order to confirm our explanation, the activities of the samples toward isopropanol, an index reaction catalyzed by solid acid, were tested. The activities also showed the same tendency. Then it can be concluded that our findings also broadened the traditional catalyst systems for the decomposition of CFCs.

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