Catalytic hydrolysis of chlorofluorocarbon (CFC-12) over WO_3/ZrO_2

Weiming Hua, Feng Zhang, Zhen Ma, Yi Tang and Zi Gao *

Department of Chemistry, Fudan University, Shanghai 200433, PR China

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The catalytic decomposition of CFC-12 (CCl_2F_2) in the presence of water vapor was investigated over a series of solid acids WO_3/ZrO_2. Compared with tungstic acid, ammonium metatungstate is a better source of tungsten oxide for the preparation of WO_3/ZrO_2 catalysts. CFC-12 decomposition activities of WO_3/ZrO_2 catalysts are in good agreement with their acidities. Enhancing the acidities of catalysts is favorable to increase their CFC-12 decomposition activities. WO_3/ZrO_2 catalysts calcined at higher temperature exhibit good catalytic activity and stability for the hydrolysis of CFC-12, and show better structural stability during the reaction.

Keywords: freon decomposition, CFC-12, WO_3/ZrO_2, acid catalyst

1. Introduction

Due to their beneficial chemical properties and safety to humans, chlorofluorocarbons (CFCs) have been widely used as refrigerants, fire-extinguishing agents, foaming agents of foamed plastics and so on for more than 60 years. However, considerable evidence has indicated that CFCs diffused to the stratosphere are a major cause of ozone depletion [1,2]. Although there are several techniques to destroy CFCs, catalytic hydrolysis seems to be the most practical and energetically favorable approach because of the simple process and the availability of water, especially for treating small amounts of CFCs [3]. In addition, Karmakar et al. pointed out that the presence of water vapor in the feed stream could improve the catalytic stability of TiO_2 substantially for the decomposition of CFC-12 [4]. Li et al. also demonstrated that the coexistence of water vapor in the reaction system could suppress the transformation of oxides to fluorides, progress the formation of CO_2, and improve catalyst life for the HCFC-22 decomposition [5]. Owing to these advantages, the decomposition of CFCs in the presence of water vapor was investigated by several groups [6–14]. However, only a few catalysts having good stability for the hydrolysis of CFCs have been reported. The main problem in this research direction is catalysts durability during the reaction, because HF and HCl produced during the reaction may corrode the catalysts, thus cause catalysts deactivation.

In this work, decomposition of CFC-12 in the presence of water vapor over WO_3/ZrO_2 catalysts was reported for the first time. Effects of tungsten oxide source, calcination temperature and tungsten oxide content on the catalytic activity were investigated in detail. The activity was correlated with acidity of the catalysts, and catalysts life was also examined.

2. Experimental

Aqueous ammonia was added dropwise to a solution of $ZrOCl_2{\cdot}8H_2O$ till pH = 9–10. After washing the hydroxide and drying at 110 °C, it was impregnated with aqueous ammonium metatungstate followed by evaporating water, drying and calcining in static air at different temperature for 3 h. The obtained catalysts are designated as xWZ(t_c), where x stands for the content of WO_3 in g-WO_3/g-ZrO_2, and t_c stands for the calcination temperature in °C. For comparison, amorphous $Zr(OH)_4$ precipitate was kneaded with tungstic acid followed by calcination in static air at different temperature for 3 h. The prepared catalysts are labeled as xHWZ(t_c), where the meaning of x and t_c is the same as above.

X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX-IIA diffractometer using Cu Kα radiation with 40 kV and 40 mA, scan speed 16°/min and scan range 10–70°. The apparent dispersion thresholds of WO_3 on ZrO_2 were determined by XRD, using TiO_2 (anatase) as inner standard. The peak area for reflections 001, 020 and 200 of WO_3 and 101 of TiO_2 was measured. The peak intensity ratio I_{WO_3}/I_{TiO_2} (Y axis) was plotted versus amount of WO_3 added (X axis). An intercept on the X axis stands for apparent dispersion thresholds of catalysts. BET surface area, pore volume and pore size distribution of the catalysts were measured on a Micromeritics ASAP 2000 system under liquid N_2 temperature using N_2 as the adsorbate. NH_3-TPD were carried out in a flow system. The samples were pretreated at 500 °C under helium flow. NH_3 was adsorbed at 120 °C, and then the temperature was raised at a rate

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* To whom correspondence should be addressed.

Table 1
CFC-12 decomposition activity of WO_3/ZrO_2 catalysts prepared from different WO_3 sources.

Catalyst	Reaction temp. (°C)	Conversion (%) 0.5 h	1.0 h	1.5 h	2 h	4 h	6 h	8 h
0.15HWZ(500)	270	49.5	55.1	62.4	68.1	73.2	63.5	60.5
0.15WZ(500)	270	97.9	98.4	98.4	97.1	94.9	92.0	90.8
0.15HWZ(800)	300	83.5	85.0	84.8	85.5	85.0	85.4	85.0
0.15WZ(800)	300	94.5	95.5	95.8	96.2	96.5	96.3	96.4

of 10 °C/min from 120 to 550 °C. The amount of NH_3 desorbed was detected by gas chromatography.

The catalytic decomposition of CFC-12 in the presence of water vapor was carried out on a continuous-flow reaction apparatus at atmospheric pressure. CFC-12 (1000 ppm), water vapor (6000 ppm) and balance air were mixed up and passed through 0.4 g catalyst with space velocity (GHSV) of 10000 h^{-1}. The CFC-12 conversion on WO_3/ZrO_2 catalysts was measured 0.5–1 h after the reaction temperature was reached. The effluent gases were passing through KOH solution to neutralize HCl and HF generated during the reaction.

3. Results and discussion

3.1. Influence of tungsten oxide sources on catalytic activity

The CFC-12 hydrolysis proceeds according to the equation [4,15]

$$CCl_2F_2 + 2H_2O \rightarrow CO_2 + 2HCl + 2HF$$

However, by-products such as CO and CFC-13 are often generated during the reaction. The exhaust gas was collected and analyzed by GC-MS, and it has been demonstrated that $CClF_3$ (CFC-13) is the main by-product during the hydrolysis of CFC-12 on WO_3/ZrO_2 catalysts. When 100% conversion is achieved, the selectivity to CO_2 (defined as the ratio of moles of CO_2 produced to moles of CFC-12 decomposed) for all the WO_3/ZrO_2 catalysts employed in this paper is above 98%.

Table 1 gives CFC-12 decomposition activity of WO_3/ZrO_2 catalysts prepared from different WO_3 sources. At the same calcination temperature, WZ catalysts exhibit higher catalytic activity than HWZ catalysts, especially at lower calcination temperature (500 °C), indicating that ammonium metatungstate is a better source of tungsten oxide to prepare WO_3/ZrO_2 catalysts than tungstic acid. XRD patterns of the catalysts are depicted in figure 1. The WO_3 diffraction peaks are obviously observed in both HWZ catalysts calcined at 500 and 800 °C. However, the WO_3 diffraction peaks do not appear in the WZ(500) catalyst, but appear in WZ(800). The above XRD results show that WO_3 is better dispersed on the surface of zirconia for WZ catalysts than for HWZ. The number of acid sites measured by NH_3-TPD and BET surface area of the samples listed in table 2 show that WZ catalysts have higher surface area and more acid sites than the corresponding HWZ catalysts prepared under the same conditions. The surface area of the 0.15WZ(500) sample is ca. 50% higher than that of 0.15HWZ(500), while the acid sites of the former are 94% greater than those of the latter. In conclusion, when ammonium metatungstate is used as the source of WO_3 to prepare WO_3/ZrO_2 catalysts, WO_3 is better dispersed on the surface, which is beneficial to retain higher surface area of the samples after calcination at high temperature. In return, more acid sites are produced, which is the main reason why WZ catalysts are more active than HWZ catalysts for the decomposition of CFC-12, since acid sites

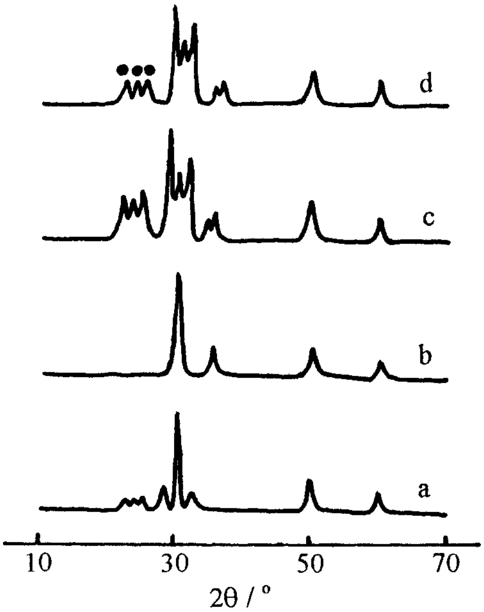

Figure 1. XRD patterns of the catalysts prepared from different WO_3 sources: (a) 0.15HWZ(500), (b) 0.15WZ(500), (c) 0.15HWZ(800) and (d) 0.15WZ(800); (●) crystalline WO_3.

Table 2
Surface area, acidity and CFC-12 decomposition activity of the catalysts.

Samples	Surface area (m^2/g)	Acid sites (mmol/g)	T_{90} (°C)
0.15HWZ(500)	56.7	0.33	–
0.15HWZ(800)	32.1	0.24	–
0.15WZ(500)	84.3	0.64	265
0.15WZ(600)	78.1	0.67	260
0.15WZ(700)	56.8	0.63	270
0.15WZ(800)	42.0	0.45	290
0.20WZ(600)	79.4	0.71	250
0.30WZ(600)	75.8	0.68	260
0.40WZ(600)	67.3	0.62	275

of the samples play an important role in the decomposition of CFCs [4,8,13,16]. Consequently, the following catalysts studied in this paper were all prepared from ammonium metatungstate.

3.2. Effects of calcination temperature and tungsten oxide content on catalytic activity

Figure 2 depicts the CFC-12 conversion on some typical WZ catalysts as a function of reaction temperature. Their activities increase with reaction temperature and show typical sigmoid curves. The temperatures at which 90% of the CFC-12 was converted (T_{90}) were read from the curves and used as a measure of the decomposition activities. The activity of 0.15WZ catalysts calcined at different temperatures for the CFC-12 decomposition is given in table 2 and figure 3. It can be seen that the catalytic activity of 0.15WZ catalysts increases with calcination temperature up to 600 °C and then decreases as the calcination temperature of the catalysts is further increased. The number of acid sites measured by NH_3-TPD of 0.15WZ catalysts calcined at different temperatures is also depicted in figure 3, and it is in good agreement with the activity of the catalysts. The maximum acid sites are observed for 0.15WZ(600) catalyst which exhibits the highest activity for the CFC-12 decomposition.

The influence of tungsten oxide content on the catalytic activity of WZ(600) samples for the decomposition of CFC-12 was also investigated and the results are shown in table 2 and figure 4. The activity increases with tungsten oxide content up to 0.20 g-WO_3/g-ZrO_2 and decreases as the content of tungsten oxide is further increased. As illustrated in figure 4, the number of acid sites on WZ(600) catalysts with different tungsten oxide contents correlates well with their catalytic activity. The highest activity is observed over 0.20WZ(600) which contains maximum acid sites.

Imamura et al. demonstrated that the decomposition of CFC-12 proceeded on the acid sites whose H_0 was more negative than -5.6 [16]. Takita et al. reported that the relatively weak acid sites were also active for the decomposition of CFC-12 [13]. Fu et al. suggested that the tremendous increase in activity for CFC-12 decomposition obtained by modifying TiO_2 with H_2SO_4 may be attributed to the superacidity of the sulfated catalyst [11]. Other authors also demonstrated that acid sites are the active centers for the CFCs decomposition [4,8]. However, relating the catalytic activity to surface acidity systematically has rarely been reported. Our results on the relationship between the CFC-12 decomposition activity of WZ catalysts and their acidities further demonstrate that acid sites of the catalysts play an important role in the decomposition of CFC-12. Increasing the acidity of the catalysts is favorable to the CFC-12 decomposition.

3.3. Stability of the catalysts

In order to select typical catalysts to investigate the catalyst stability in the CFC-12 hydrolysis, the apparent dispersion thresholds of catalysts prepared from ammonium metatungstate calcined at 600, 700 and 800 °C, respectively, were determined by XRD, using TiO_2 (anatase) as inner standard. The apparent dispersion thresholds of WZ(600, 700, 800) samples are 0.44, 0.34 and 0.11 g-WO_3/g-ZrO_2, respectively. The catalytic activities of selected catalysts with time on stream are listed in table 3. The CFC-12 decomposition activity of WZ(600) catalysts decreases gradually with time on stream, especially during the initial 20 h, no matter whether the tungsten oxide content is lower or higher than the apparent dispersion threshold, while that

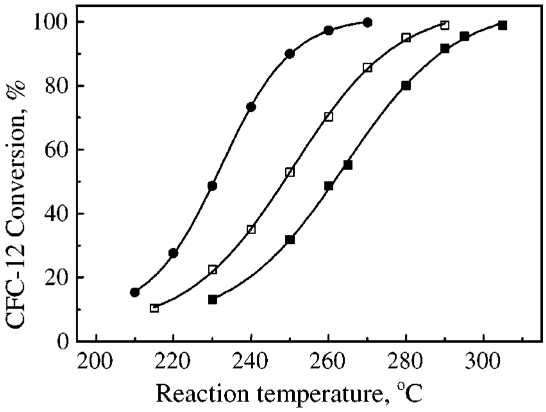

Figure 2. CFC-12 decomposition activity of some typical WZ catalysts: (■) 0.15WZ(800), (•) 0.20WZ(600) and (□) 0.40WZ(600).

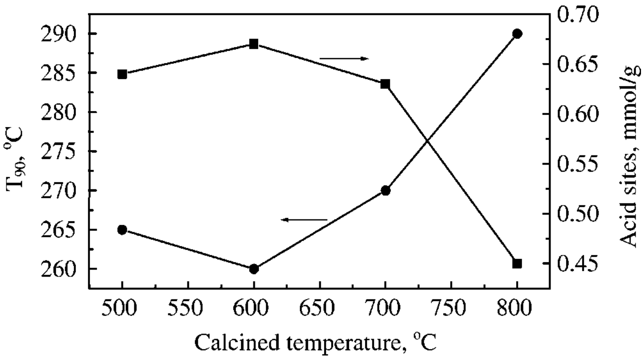

Figure 3. Relationship between CFC-12 decomposition activity of 0.15WZ catalysts calcined at different temperature and their acidities.

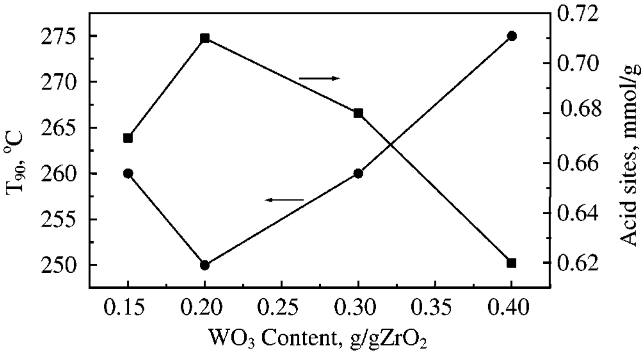

Figure 4. Relationship between CFC-12 decomposition activity of WZ(600) catalysts with different WO_3 content and their acidities.

Table 3
CFC-12 decomposition activities of selected catalysts with time on stream.

Catalyst	Reaction temp. (°C)	Conversion (%) 1 h	5 h	9 h	20 h	24 h	28 h	32 h
0.20WZ(600)	270	96.7	94.8	93.6	87.2	86.1	84.8	84.6
0.70WZ(600)	300	95.5	94.2	93.1	89.7	89.2	89.0	89.1
0.15WZ(700)	290	93.6	90.9	89.4	85.4	85.6	86.1	85.4
0.40WZ(700)	295	98.4	98.4	98.3	98.4	98.0	98.1	98.1
0.075WZ(800)	320	96.7	96.5	96.5	96.6	97.3	97.4	97.5
0.15WZ(800)	300	97.3	97.1	97.0	97.0	96.9	96.9	97.0

of WZ(800) catalysts keeps steadily during the reaction. As for WZ(700) catalysts, their activity is stable when the WO_3 content is above the apparent dispersion threshold, but unstable when the WO_3 content is below the apparent dispersion threshold.

The monolayer dispersion capacities of WZ(600, 700, 800) samples, calculated from the model on assuming that the WO_3 is dispersed as a close-packed monolayer on the ZrO_2 surface, are 0.22, 0.13 and 0.098 g-WO_3/g-ZrO_2, respectively. The apparent dispersion threshold of the WZ(800) sample detected by XRD approximately agrees with the calculated monolayer dispersion capacity of WO_3 on ZrO_2, while those of both WZ(600) and WZ(700) samples are much higher than the corresponding monolayer dispersion capacities of WO_3 on ZrO_2 calculated using the close-packed monolayer model, indicating that tungsten does not exist completely in the form of WO_3 on the surface of both WZ(600) and WZ(700) samples. It may exist partly in the form of polytungstate or the mixture of $H_2W_{12}O_{40}^{6-}$ and $W_6O_{19}^{2-}$ on the surface of catalysts, which was investigated by IR in our earlier results [17]. When the calcination temperature of WZ catalyst is higher (e.g., 800 °C), the tungsten on the catalyst surface exists in the form of WO_3, and the interaction between W and ZrO_2 may be stronger, thus the tungsten on the catalyst surface is not easy to lose, leading to the steady activity during the reaction. When the calcination temperature is lower (e.g., 600 °C), the interaction between W and ZrO_2 may be weaker, and the polytungstate or the mixture of $H_2W_{12}O_{40}^{6-}$ and $W_6O_{19}^{2-}$ partly existing on the surface of catalysts may be relatively easy to lose during the reaction, so the catalyst deactivates gradually, especially during the first 20 h.

To investigate the stability of WZ catalysts for longer term, the reaction has been run continuously for 120 h at 300 °C over 0.15WZ(800) and at 270 °C over 0.20WZ(600) which is most active for the CFC-12 hydrolysis among the catalysts tested, and the results are depicted in figure 5. It can be seen that the CFC-12 conversion on the 0.20WZ(600) catalyst decreases from 98.4 to 74.5% after 120 h on stream. While for the 0.15WZ(800) catalyst, its initial conversion of CFC-12 is 97.3%, and after on stream for 120 h it keeps steadily at ca. 97% without any observable trend of deactivation.

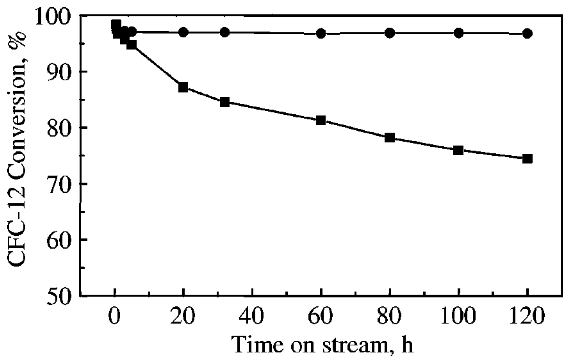

Figure 5. Long-term test of the catalysts: (●) 0.15WZ(800) and (■) 0.20WZ(600).

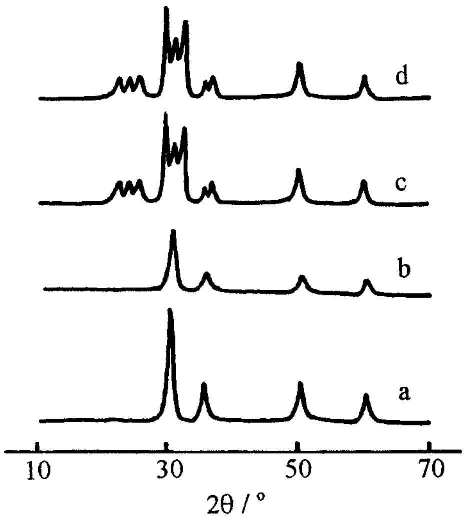

Figure 6. XRD patterns of the fresh and used catalysts: (a) fresh 0.20WZ(600), (b) used 0.20WZ(600), (c) fresh 0.15WZ(800) and (d) used 0.15WZ(800).

Table 4
Surface area and pore volume of the fresh and used catalysts.

Catalyst	S_{BET} (m^2/g) Fresh	Used	V (cm^3/g) Fresh	Used	D^a (nm) Fresh	Used
0.20WZ(600)	79.4	49.8	0.075	0.054	3.52	3.89
0.15WZ(800)	47.1	39.0	0.106	0.089	6.10	6.23

[a] Most probable pore diameter.

The physicochemical properties of the catalysts before and after the reaction for 120 h are compared. Figure 6 depicts XRD patterns of the fresh and used catalysts. An obvious drop in the peak intensities is observed for 0.20WZ(600) after the reaction, suggesting a partial destruction of the crystallite structure by the corrosion of the

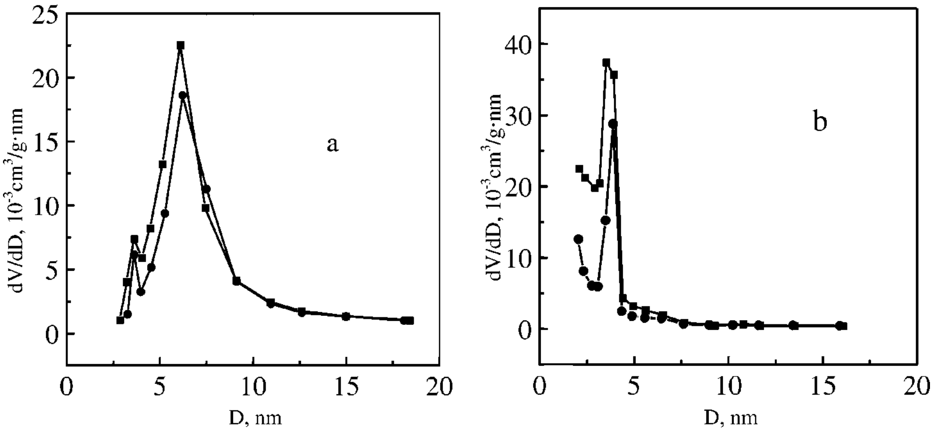

Figure 7. Pore size distribution of the fresh (■) and used (●) catalysts: (a) 0.15WZ(800) and (b) 0.20WZ(600).

reaction product HF. No appreciable drop in the peak intensities ($<5\%$) of the 0.15WZ(800) catalyst after 120 h of operation can be noticed, indicating that there is no loss in crystallinity for 0.15WZ(800) after the reaction. Table 4 compares the surface area and pore volume of the fresh and used catalysts. Compared with the fresh sample, the surface area and pore volume of the used 0.15WZ(800) catalyst decrease slightly, showing that the 0.15WZ(800) catalyst is stable with respect to the CFC-12 hydrolysis. However, the used 0.20WZ(600) catalyst has lost its ca. $1/3$ surface area and pore volume. In addition, as illustrated in figure 7, no significant changes in pore size distribution are observed for 0.15WZ(800) after the reaction, while for 0.20WZ(600) its most probable pore diameter increases by 11% after the long-term test. It is concluded that the 0.15WZ(800) catalyst which exhibits good catalytic stability shows much better structural stability during the CFC-12 hydrolysis than the 0.20WZ(600) catalyst which is most active for the reaction.

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