Catalytic Decomposition of CFC-12 over WO_3/TiO_2

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CFC-12 was decomposed completely on WO_3/TiO_2 in the presence of water vapor at 265 °C, and the selectivity to CO_2 was above 99.8%. The catalytic activity and selectivity remained steady during 120 h on stream. WO_3-modified Al_2O_3, SnO_2 and Fe_2O_3 showed less activity than WO_3/TiO_2 for the decomposition of CFC-12, but they were more active than the corresponding metal oxides, too.

The decomposition of chlorofluorocarbons (CFCs) has been a hot topic for several major reasons: (1) thousands of studies involving laboratory measurements, atmospheric observations and model calculations have continuously confirmed that CFCs are the killers of stratospheric ozone which protects life on earth against harmful ultraviolet radiation from the sun;[1] (2) CFCs are green-house gases which are warming up our earth; (3) the elimination of Cl-containing VOCs (volatile organic compounds) continues to attract considerable public concern and the CFCs decomposition catalysts might become candidates for the destruction of Cl-containing VOCs. Although there are several ways to eliminate CFCs, catalytic decomposition seems to be the most promising one because of simple process, requiring mild conditions and dioxin free, especially for treating small amount of CFCs. Investigations in this direction have been carried out by dozens of research groups, however, there is still some room for improving the catalytic activity, selectivity and stability. Recently, Takita *et al.*[2,3] reported that CFC-12 can be completely decomposed in the presence of water vapor over the $AlPO_4$-based catalysts at 350-450 °C and the catalysts have long life. In this paper, the application of WO_3/TiO_2 for CFC-12 decomposition in the presence of water vapor was investigated.

WO_3/TiO_2 catalyst with specific surface area 119.1 $m^2 \cdot g^{-1}$ was prepared by impregnating amorphous $Ti(OH)_4$ with aqueous ammonium metatungstate, evaporating water, drying at 110 °C, then calcining at 500 °C for 3 h. The content of WO_3 was 0.4 g/gTiO_2. The other WO_3/M_xO_y (M=Al, Sn, Fe) catalysts were also prepared by using $Al(OH)_3$, $Sn(OH)_4$ and $Fe(OH)_3$ as support precursors in a similar way. In comparison, WO_3/TiO_2-II catalyst was prepared by using TiO_2 (10.6 $m^2 \cdot g^{-1}$) directly as support and its WO_3 content was 0.05 g/gTiO_2. The specific surface area of WO_3/TiO_2-II was only 11.7 $m^2 \cdot g^{-1}$.

Table 1. The temperature of 50% and 95% CFC-12 conversion (T_{50} and T_{95}) on pure and WO_3-modified metal oxides

Catalysts	T_{50} / °C	T_{95} / °C
TiO_2	305	340
WO_3/TiO_2	225	255
Al_2O_3	315	350
WO_3/Al_2O_3	255	295
SnO_2	420	485
WO_3/SnO_2	270	315
Fe_2O_3	405	485
WO_3/Fe_2O_3	310	345

The catalytic decomposition of CFC-12 in the presence of water vapor was carried out using a conventional flow reaction apparatus. The reaction conditions were as follows: feed gas, CFC-12 1000 ppm, H_2O 6000 ppm, balance air; catalyst weight, 0.4 g; space velocity (WHSV), 6 l h^{-1} g-cat^{-1}. Effluent gases were passing through KOH solution to remove HCl, HF and CO_2 produced during the reaction.

The CFC-12 conversion over pure and WO_3-modified metal oxides as a function of reaction temperature were investigated. The temperatures of 50% and 95% conversion (T_{50} and T_{95}) were listed in Table 1 as measurements of the decomposition activity. It's obvious that metal oxides themselves showed poor decomposition activity, but when WO_3 was loaded on them, obvious enhancement in activity was observed. The T_{50} and T_{100} of WO_3-modified metal oxides decreased 55-170 °C as compared with the corresponding metal oxides. From the viewpoint of saving energy, this enhancement in activity is exhilarating. Since the catalytic activity of WO_3/TiO_2 was most pronounced, the decomposition of CFC-12 over WO_3/TiO_2 was researched in detail.

Figure 1 shows the CFC-12 conversion with regard to reaction temperature. It can be seen that WO_3 itself was almost inactive at temperatures below 300 °C, and even at 400 °C its activity was only 55.0%. 100% conversion of CFC-12 was achieved at 360 °C on TiO_2. However, when WO_3 was supported on TiO_2, an obvious enhancement in activity was observed. Moreover, the different modification methods led to different enhancement in activity. WO_3/TiO_2 prepared by using $Ti(OH)_4$ as support precursor decomposed CFC-12 completely at 265 °C, while WO_3/TiO_2-II prepared by using TiO_2 directly as support decomposed CFC-12 completely at 330 °C. Similar phenomenon was also observed for the skeletal isomerization and cracking of isopentane.[4]

The acid amounts of the catalysts were examined by NH_3-TPD. For WO_3/TiO_2, sole large desorption peak appeared at 260 °C and the desorption temperature even extended to 575 °C. The total acid amount of WO_3/TiO_2 was 0.78 mmol·g^{-1}, while the acid

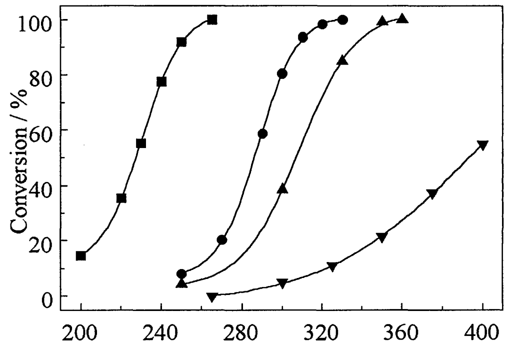

Figure 1. Effect of reaction temperature on the conversion of CFC-12 over (■)WO_3/TiO_2, (●)WO_3/TiO_2-II, (▲)TiO_2, (▼)WO_3.

amounts of WO_3, TiO_2 and WO_3/TiO_2-II were only 0.16, 0.31,and 0.36 mmol·g^{-1}, respectively. It is of interest to note that WO_3/Al_2O_3, WO_3/SnO_2 and WO_3/Fe_2O_3 are typical acid catalysts, too.[4,5] This may provide a clue to the reason why WO_3-modified metal oxides are efficient CFC-12 decomposition catalysts. That is to say, acid centers play an important role on the catalytic decomposition of CFC-12, which is also recognized by many researchers.[3,6-10]

The catalytic selectivity is one of the key factors for practical use. In our experiments, no CO was detected and the yield of by-product CFC-13 on WO_3/TiO_2 (0.18%) was much lower than that on unmodified TiO_2 (4.88%). CFC-13 is formed only when the TiO_2 surface is fluorinated,[8] while the fluorination means partial replacement of surface hydroxyls of TiO_2 by more electronegative fluorines.[9] Unmodified TiO_2 was relatively easy to be fluorinated by HF generated during the reaction because all the surface hydroxyls were exposed to HF, so that more CFC-13 was produced on TiO_2. As for WO_3/TiO_2, there was no Raman peak at 789 cm^{-1}, indicating the absence of crystalline WO_3, instead, the peak at 980 cm^{-1} which is assigned to the symmetrical W=O stretching model of the highly dispersed amorphous tungsten oxide species[11,12] was detected. The highly dispersed tungsten oxide species coordinated to the TiO_2 surface and gave TiO_2 less opportunity to meet with and be fluorinated by HF. Thus, very little CFC-13 was produced on WO_3/TiO_2.

The catalytic life is another important factor for practical use. Karmaker *et al.*[9] found that without the supply of water vapor, TiO_2 was irreversibly fluorinated and the CFC-12 conversion on TiO_2 dropped from 98% to 43% during 48 h on stream, but it's interesting to note that they also discovered the decomposition activity decreased only 5% during 4 days in the presence of water vapor. So it was supposed that TiO_2 could be a good CFC-12 decomposition support when water vapor exists, although further modifications are required to improve the activity. In our results, no deactivation was observed for CFC-12 decomposition over WO_3/TiO_2 during 120 h on stream at 265 °C and the selectivity to CFC-13 ranged between 0.15% and 0.19% (Figure 2).

The XRD patterns of WO_3/TiO_2 before and after the reaction for 120 h are both shown in Figure 3. As can be seen, all the peaks can be assigned to anatase TiO_2 and no crystalline WO_3 was detected, which is consistent with our LRS results. Those peaks intensity did not decrease after 120 h on stream. Furthermore, no diffraction peaks derived from TiF_4 was found for the used catalyst and no carbon deposit was detected by elementary analysis.The specific surface area of WO_3/TiO_2 decreased slightly from 119.1 m^2·g^{-1} to 103.2 m^2·g^{-1} after the stability test and no significant change in pore size distribution was observed, either. Perhaps it is amorphous tungsten oxide species which covered the TiO_2 surface that suppressed the fluorination thus deactivation. Similar protective effect was also reported for the γ-Al_2O_3 supported transition metal chloride catalysts.[10]

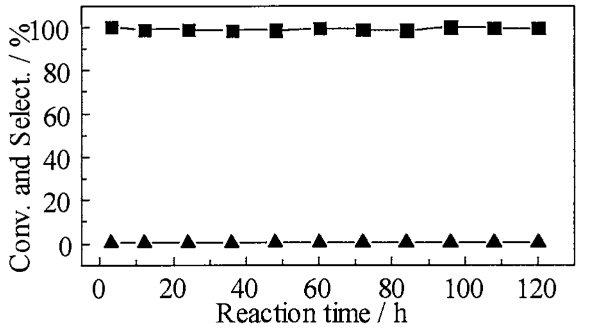

Figure 2. Decomposition of CFC-12 over WO_3/TiO_2 at 265 °C for 120 h. (■) CFC-12 conversion, (▲) selectivity to CFC-13.

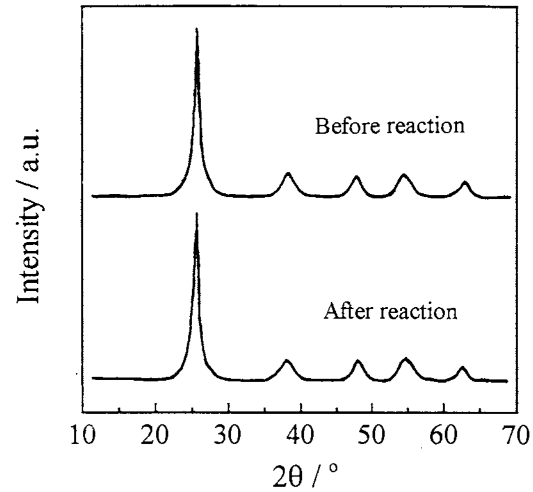

Figure 3. XRD patterns of the WO_3/TiO_2 catalyst before and after the CFC-12 decomposition for 120 h at 265 °C.

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