

Catalytic Decomposition of Dichlorodifluoromethane (CFC-12) Over Solid Super Acid MoO₃/ZrO₂

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Catalytic decomposition of dichlorodifluoromethane (CFC-12) in presence of water vapour and oxygen was studied over a series of solid super acids that have different ZrO₂ content using a fixed-bed reactor. CO₂ and CClF₃ were the main-products and no CO was detected as by-product. The decomposition activity depended on the calcination temperature and the ZrO₂ content. Calcined at 450 °C and 20-40 % ZrO₂ content were the best catalyst preparation conditions. Adopting low concentration of oxygen and CFC-12 and high concentration of water vapour is preferable to the achievement of high conversion of CFC-12 and selectivity for CO₂. The catalytic activity of MoO₃/ZrO₂ remained steady for 100 h on stream.

Key Words: Dichlorodifluoromethane, Catalytic decomposition, Solid super acid, MoO₃/ZrO₂.

INTRODUCTION

Chlorofluorocarbons (CFCs) have been used for 40 years because of their beneficial chemical properties. However, chloro-radicals derived from CFCs by UV irradiation can decompose ozone into oxygen in the stratosphere¹. Used CFCs must be decomposed without being liberated into the atmosphere in order to protect the global environment. So it is significant to decompose CFCs and recycle the residual fluorides.

Many methods for the decomposition of CFCs have been proposed including incineration, induced plasma², cement kiln, supercritical water³, chemical reagents, *e.g.*, sodium naphthalenide⁴, irradiation by UV, γ -rays or ultrasonic waves⁵⁻⁷ and catalysts⁸⁻¹¹. Among these methods, decomposition using incineration, the cement kiln methods and catalysts are considered to be the most useful as far as large-scale treatment is concerned. However, the incineration method has the disadvantage of forming dioxin as a by-product¹². The cement kiln method is not always useful because the cement produced tends to corrode any reinforcing steel due to its high

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concentration of chlorine. The catalytic method is thought to be the most suitable process for CFCs decomposition, because it can be achieved under mild reaction conditions. In other words, it can be said to be an economical and benign decomposition method. So far, there has been a concerted effort to explore the catalysts effectiveness in CFCs decomposition¹³⁻¹⁸.

In order to decompose CFC and recycle the residual fluorides, we have studied a number of catalysts that are effective for CFCs decomposition in the presence of water vapour in order to develop industrial usable practical catalysts. In this paper, a new catalyst, solid super acid $\text{MoO}_3/\text{ZrO}_2$, was investigated to decompose CFC-12.

EXPERIMENTAL

Catalyst preparation: $\text{Zr}(\text{OH})_4$ was obtained by hydrolyzing of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (AR grade) with ammonium hydroxide (AR grade). The precipitate was washed with distilled water and dried at 100 °C for 24 h. The hydroxide was then impregnated with aqueous ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ (AR grade) followed by evaporating water, drying at 100 °C and calcining in air at variance temperatures for 3 h. These catalysts were labeled as MoZr_{a-b} , where "a" means the ZrO_2 content (g/g) in catalyst, "b" stands for the calcining temperature.

Experimental procedure: The catalytic reactions were carried out under atmosphere pressure using a continuous flow reaction system with a fixed-bed reactor. The mixture of CFC-12 (CCl_2F_2), nitrogen and oxygen was fed into a 15 mm diameter tubular flow reactor made of stainless steel. Water was supplied into an evaporator using a micro-liquid-feeder. The gas effluent from the reactor was washed with distilled water to remove HCl and HF formed.

Analysis of the reaction products was carried out using a Shimadzu GC-8ATP gas chromatograph (thermal conductivity detector) with a Parapak Q column (4 mm × 30 m) and a column containing 5 Å molecular sieves (4 mm × 30 m), HP5890 GC with HP5970 mass spectrometer. Analysis of the products by GC was carried out after reaching the required reaction temperature for 1 h.

The X-ray diffraction patterns (XRD) were measured by a Rigaku RINI-2500HF system. The specific surface areas of the fresh and used catalysts was determined by the Brunauer Emmett Teller (BET) method (N adsorption) using a Carlo Erba SORPTY-1750 analyzer.

RESULTS AND DISCUSSION

Effect of the catalyst composition on the decomposition activity: The optimum composition of the $\text{MoO}_3/\text{ZrO}_2$ system was examined in relation to pure MoO_3 from commerce $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and calcined ZrO_2 . The feed gas composition was 1 mol % CCl_2F_2 , 40 mol % H_2O (g), 10.0 mol % O_2 , mol % N_2 49. Total flow rate was 12 cm^3/min and catalyst was 1 g. Calcining temperature was 450 °C and reaction temperature was 250 °C.

The results are shown in Table-1. It is clear that pure MoO₃ and ZrO₂ were less active than mixtures for the decomposition of CFC-12, with MoO₃ almost inactive (5 %). Although these catalysts showed significantly high selectivity to CO₂, more than 80 %, conversion of CFC-12 was rather low. The catalysts composed of pairs of MoO₃ and ZrO₂ showed high activity. Especially high conversion was observed over MoO₃/ZrO₂ that had 20-40 % ZrO₂.

TABLE-1
DECOMPOSITION OF CFC-12 OVER VARIOUS COMPOSITION CATALYSTS

ZrO ₂ content (gZrO ₂ /g cat)	Conv. (%)	SSA (m ² /g)	Selectivity (%)			Yield (%)	
			CO ₂	CClF ₃	CCl ₃ F	CO ₂	CClF ₃
0 ^a	5.6	6.1	86.2	11.1	–	4.8	0.6
20 ^b	95.7	118.2	65.4	27.6	1.3	62.6	26.4
40 ^b	93.8	100.7	65.3	27.1	1.1	61.3	25.4
60 ^b	84.2	90.5	67.9	32.1	–	57.2	27.0
80 ^b	76.5	79.6	73.0	27.0	–	55.8	20.7
100 ^c	53.3	15.4	80.0	20.0	–	42.6	10.7

a: Decomposition of (NH₄)₆Mo₇O₂₄·4H₂O (commercial), b: Preparation, c: Calcined Zr(OH)₄; SSA = Specific surface area.

In addition to the main decomposition products CO₂ and CClF₃, a small amount of CCl₃F, CO and other unidentified gases were formed. Takita *et al.*¹³ reported that the rate of CClF₃ consumption is smaller than that of CCl₂F₂ over ZrO₂/Cr₂O₃. The order in hydrolysis of chlorocarbons and chlorofluorocarbons is reported to be CCl₄ > CCl₃F > CCl₂F₂ > CClF₃¹⁴. Selectivity for CClF₃ was higher than that for CCl₃F, which suggests that CClF₃ is formed by a pathway other than disproportionation. Since the decomposition of CCl₂F₂ generates F⁻ ions on the catalyst surface, the reaction between F⁻ ions and CClF₂⁻ or CCl₂F₂ species on the catalyst surface would be responsible for the formation of CClF₃¹⁵.

With an increase of the specific surface area an increase in the conversion of CCl₂F₂ could be achieved. The amount of active acidic sites in the catalyst is increased with growing surface area.

Effect of calcination temperature on the decomposition activity: In order to estimate the optimum calcination temperature, the CFC-12 decomposition activity was studied over MoZr series catalysts calcined at various temperatures (Fig. 1). All data were obtained after reaching the required reaction temperature for 1 h. The calcination temperature of the catalyst affected the catalytic activity. The CFC-12 conversion over MoZr 0.2 series catalysts rose slightly and then decreased significantly with the calcination temperature. For example, the 95 % conversion temperature (T₉₅) of MoZr 0.2-450.0 was 250 °C, while the T₉₅ of MoZr 0.2-400.0 and MoZr 0.2-500.0 demanded 300 °C. The T₉₅ of MoZr 0.2-350.0, MoZr 0.2-550.0 and MoZr 0.2-600.0 were not achieved under these experimental conditions. In general, too high or low calcination temperatures are not preferable. It can be suggested that the different calcination temperatures may affect the number of acid sites for reaction. As far as the MoZr 0.2 series catalysts were concerned, the optimum calcination temperature was 450 °C.

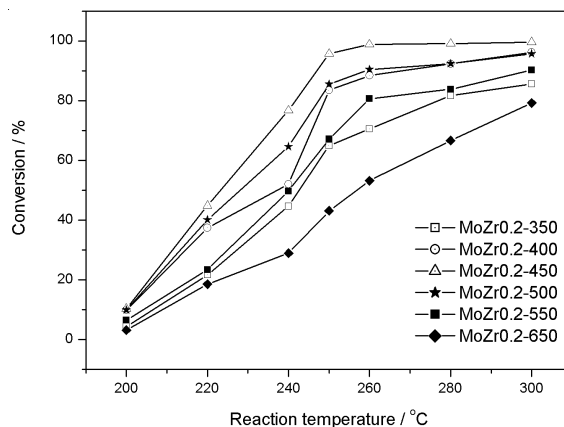


Fig. 1. Effect of calcination temperature on the CFC-12 conversion over MoZr 0.2 series catalysts

The specific surface area of MoZr 0.2 series catalysts that were fired at different temperatures were measured when they are fresh and used 100 h (Fig. 2). MoZr 0.2 series catalysts calcined at 350, 400, 500, 550 and 600 °C, gave a specific surface area of 83.4, 107.5, 118.2, 97.8, 76.4 and 64.4 m²/g, respectively. After use, their specific surface area were decreased to 80.3, 92.4, 99.6, 78.3, 62.7 and 55.9 m²/g, respectively. As previously reported¹⁹, there are some obvious differences in the crystalline structures of MoO₃/ZrO₂ depending on their production history. After firing, ZrO₂ is in cubic form (ZrO₂(t)) and MoO₃ reacts with ZrO₂(t) and turns into bulk Zr(MoO₄)₂ at 500 °C. MoO₃-O-Zr surface species could be detected by IR band at 1000-500 cm⁻¹. It may not be concluded that specific surface area always determined the decomposition activity. However, at the same catalyst composition, the different calcination temperatures influence the local structure and properties of catalysts dramatically.

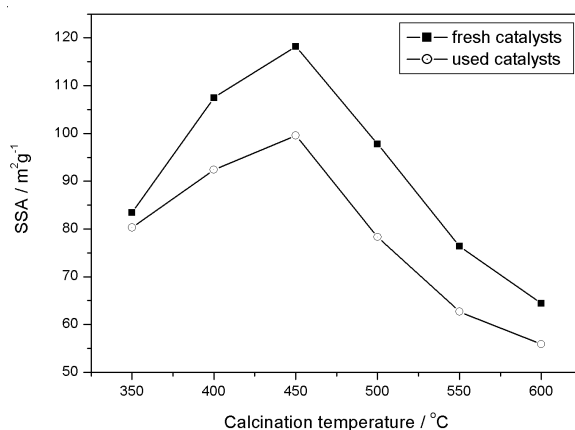


Fig. 2. Effect of calcination temperature on the MoZr 0.2 series catalysts' specific surface area

Effect of the composition of the feed gas on the decomposition reaction: As shown in Table-1, a small amount of CClF_3 was formed during the decomposition of CFC-12 over MoZr series catalysts at high conversion levels. In order to decrease the formation of by-products, the effect of the concentration of oxygen, water vapour and CFC-12 on the decomposition were studied and the results are shown in Figs. 3-5.

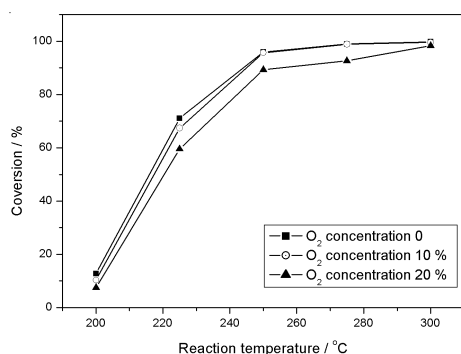


Fig. 3. Effect of O_2 concentration on the CFC-12 decomposition

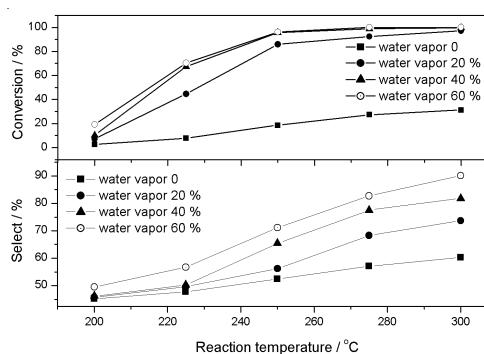


Fig. 4. Effect of water vapour concentration on the CFC-12 decomposition

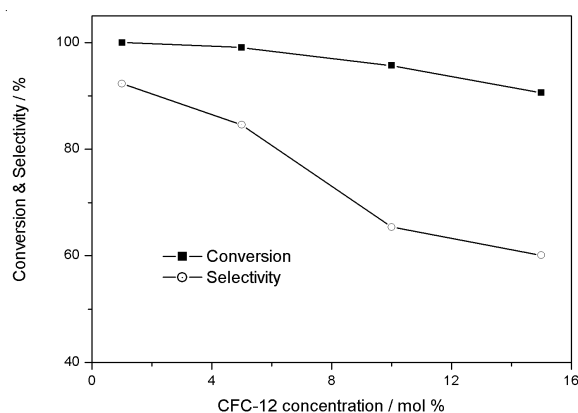


Fig. 5. Effect of CFC-12 concentration on the CFC-12 decomposition

As can be seen from Fig. 3, the conversion was slightly reduced with the increased concentration of oxygen and the selectivity for CO_2 was almost the same as in the presence of oxygen. As far as the effect of reaction temperature on the conversion of CFC-12 and selectivity for CO_2 at the same oxygen concentration was concerned, a high reaction temperature produced high conversion and selectivity for CO_2 . Therefore, it can be said that the presence of oxygen has no obvious effect on the decomposition rate, but there is a need to control oxygen at low concentration.

On the contrary, the concentration of water vapour significantly affected the reaction (Fig. 4). Without water vapour the conversion reached only 30-50 % at

250-300 °C and almost equivalent amounts of CO₂ and CFCI₃ were produced. The introduction of water vapour brought drastic changes in both conversion and selectivity. It is obvious that the higher the concentration of water vapour, the higher was the conversion at lower reaction temperatures. The CO₂ selectivity was also increased in the presence of water vapour, which exceeded 85 % at both 40 and 60 mol %. These results suggest that the major reaction of decomposition is a hydrolysis of CFC-12.

The concentration of CFC-12 also significantly affected the reaction, especially in the selectivity (Fig. 5). The conversion of CFC-12 was 90 % when the feed gas contained about 1.5 mol % CFC-12 and increased steadily with decreasing concentration of CFC-12. The CO₂ selectivity was 60 % when the feed gas contained about 1.5 mol % CFC-12. However, selectivity increased steadily with decreasing concentration of CFC-12 and approach 92 % at around 0.1 mol % CFC-12. The C-containing by-product was CClF₃ which was studied over the whole temperature range. As discussed above the decomposition of CFC-12 is accompanied by the formation of F⁻ and Cl⁻ ions on the catalyst surface. The concentration of halogen atoms on the catalyst surface should be very small under the reaction conditions, because the concentration of water vapour adopted in this study was very high. Therefore, hydrolysis is predominant. It can be concluded, that the complete decomposition of CFC-12 can be achieved over MoZr 0.2-450.0 catalysts, provided that the CFC-12 concentration in the feed gas is kept below 0.1 mol %.

Catalysts life: The catalyst life is one of the most important factors, especially from the viewpoint of practical usage. The results of the long-term experiment are shown in Fig. 6. The experiment conditions are: feed gas composition is 1 g CFC-12, 40 g H₂O, 10 g O₂, balance N₂; the total flow rate is 12 cm³ min⁻¹; catalyst quantity is 1 g and reaction temperature is 250 °C. The catalytic reaction was carried out over MoZr 0.2-450.0 for 100 h. The temperature used in the reaction was 250 °C because the CFC-12 conversion did not reach 100 %, thus to better clarify the changes in the activity.

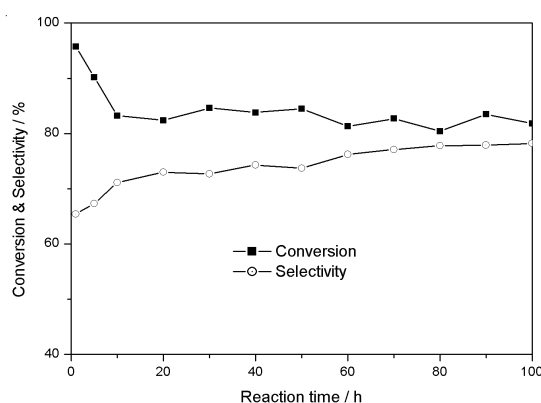


Fig. 6. Effect of reaction time on the catalytic activity and the selectivity

As can be seen from Fig. 6, the conversion decreased by 10 % for the initial 10 h, but the conversion takes a steady value for the following 90 h. Although the changes in specific surface area during the reaction could not be measured, the specific surface area of the MoZr 0.2-450.0 catalyst decreased from 118.2-83.7 m²/g after 100 h. Therefore the decrease in the CFC-12 conversion for the initial 10 h may be due to the decrease in the specific surface area of the catalyst. The CO₂ selectivity remained at about 75 % during 100 h and the only other product was CClF₃. The CO₂ selectivity increases with the decrease in the CFC-12 conversion in the reaction, an outcome with needs further investigation for clarification.

The structure of the catalyst has studied by means of XRD patterns and the results are shown as previously reported¹⁹. The catalyst before reaction is amorphous Zr(MoO₄)₂. The XRD pattern of the catalyst after reaction for 100 h consisted of small peaks due to ZrO₂ and a very small diffraction peak derived from fluoride had appeared. Furthermore, no carbon deposit was detected by elementary analysis. The specific surface area, pore volume and the most probable pore diameter of MoZr 0.2-450.0 listed in Table-2. There are minor changes after the long-term test and no significant change in pore size distribution was observed either.

TABLE-2
SPECIFIC SURFACE AREA, PORE VOLUME AND THE MOST PROBABLE PORE
DIAMETER OF MoZr 0.2-450.0 BEFORE AND AFTER 100 h USAGE

Catalyst		SSA/m ² g ⁻¹	V/cm ³ g ⁻¹	D/nm
MoZr 0.2-450.0	Fresh	118.2	0.102	3.45
	used	83.7	0.084	3.41

In addition, the role of water vapour in this reaction cannot be neglected. Some studies found that the existence of water vapour suppresses the transformation of fluorides, promotes the formation of CO₂ and prolongs the catalyst life. Takita *et al.*¹²⁻¹⁶ concluded that treating catalysts with both oxygen and water vapour promotes the removal of fluoride ions in subsurface layers of the catalysts, which is effective for the recovery of the activity. Once surface fluorine is accumulated, the surface turns into inactive metal fluorides.

Conclusion

The MoZr series catalysts were prepared, which can decompose CFC-12 at above 250 °C in the presence of both oxygen and water vapour. The optimum composition of the catalyst is between 20-40 % ZrO₂. The optimum composition of the feed gas was determined to below concentration of oxygen, low concentration of CFC-12 and high concentration of water vapour in order to achieve a complete decomposition of CFC-12.

In the presence of both oxygen and water vapour, CFC-12 can be decomposed to CO₂ by hydrolysis at 250-300 °C with MoZr 0.2-450.0 catalyst. And catalytic activity decreases slightly at the beginning of reaction and then reaches a steady

state 75 % as been shown in a long time experiment of 100 h. Hence, MoZr 0.2-450.0 may be a potent catalyst for the selective decomposition of CFC-12.

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