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Oxidative decomposition of dichlorodifluoromethane (CFC-12) in the presence of butane over Tungsten(VI) oxide catalysts supported on alumina–zirconia

Shizuka Tashiro[a,*], Hideo Nagata[1,a], Masahiro Kishida[a],
Koichi Mizuno[b], Katsuhiko Wakabayashi[a]

[a]Chemical Engineering Group, Department of Materials Process Engineering, Graduate School of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan
[b]Atmospheric Environmental Protection Department, National Institute for Resources and Environment, Onogawa, Tsukuba 305-8569, Japan

Abstract

The oxidative decomposition of dichlorodifluoromethane (CFC-12) in the presence of butane was investigated with tungsten(VI) oxide catalyst supported on alumina–zirconia. In this reaction, it is considered that CFC-12 might react with water formed by the combustion of butane at high temperatures above 773 K, and that most of CFC-12 might react directly with oxygen at low temperatures below 723 K. The CFC-12 conversion over the tungsten(VI) oxide catalyst decreased with the passage of time on stream at low temperatures below 673 K. This deactivation of the catalyst was attributed to the coke deposition on the acid sites of the catalyst as well as to the fluorination of the acid sites. The CFC-12 conversion at 4 h on stream became higher when the catalyst was loaded with platinum or palladium, but the butane conversion was not changed by loading. The amount of the coke deposited on platinum- or palladium-loaded tungsten(VI) oxide catalysts, which exhibited a high CFC-12 conversion at 4 h on stream, was very small. Accordingly, the depression of the catalyst deactivation might be caused by the combustion of the coke deposited on the acid sites due to the catalysis of platinum and palladium. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

A large amount of dichlorodifluoromethane (CFC-12) has widely been used as refrigerant, aerosol and foaming agent [1]. Thus, many researchers have investigated the decomposition method for CFC-12 (incineration method [2], chemical destruction method [3], plasma destruction method [4] and catalytic decomposition method [5–8]).

We have been investigating an original decomposition method, that is, a catalytic oxidative decomposition of CFCs in the presence of hydrocarbons [9–12]. In our previous studies, it was found that the tungsten(VI) oxide catalyst supported on the alumina–zirconia kept a high activity for the oxidative decom-

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*Corresponding author.

[1] Present address: Department of Chemical and Biological Engineering, Sasebo National College of Technology, Okishin-Machi, Sasebo, Nagasaki 875-1193, Japan.

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position of chloropentafluoroethane (CFC-115) in the presence of butane for a long time [12], and that the acidity of the catalyst played an important role [11].

In this study, the tungsten(VI) oxide catalyst supported on alumina–zirconia was investigated for the oxidative decomposition of CFC-12 in the presence of butane at comparatively low temperatures, and the metal-loading effects were also examined.

2. Experimental

2.1. Catalyst preparation

An alumina–zirconia with a molar ratio of zirconium to alumina of 0.3 was prepared by the following procedures [10,12]. Bohmite (AlO(OH)) and zirconyl nitrate were used as an alumina source and a zirconia source, respectively. A bohmite pellet (more than 48 mesh) was suspended in an aqueous solution containing zirconyl nitrate. An aqueous ammonium hydroxide solution was added to the suspension until the pH value became 8. The precipitate formed was washed with distilled water, and then was dried overnight at 373 K. The dried precipitate thus obtained was calcined in an air stream at 923 K for 3 h. Tungsten(VI) oxide catalysts supported on alumina–zirconia were prepared using an impregnation method. The content of tungsten(VI) oxide was 0.25 mmol/g-carrier. The tungsten(VI) oxide catalyst supported on alumina–zirconia was loaded with platinum-group metals using an impregnation method. Ruthenium(III) chloride, rhodium(III) chloride, palladium(II) chloride and hydrogen hexachloroplatinate(IV) were used as a platinum-group metal source. The content of platinum-group metals was 0.5 wt%.

2.2. Characterization

The acid strength of the catalyst was determined by the titration of Hammett's indicators. 2,4-Dinitrofluorobenzene ($pK_a=-14.52$), 2,4-dinitrotoluene ($pK_a=-13.75$), 2-nitrochlorobenzene ($pK_a=-13.16$), 3-nitrochlorobenzene ($pK_a=-12.70$), *m*-nitrotoluene ($pK_a=-11.99$) and *p*-nitrotoluene ($pK_a=-11.35$) were used as a Hammett's indicator. The acid amount of the catalyst was evaluated by the adsorption of ammonia using a Seiko Denshi thermal analyzer TG/DTA-22. The elemental analyses of the coke deposited on a catalyst were done using a Yanaco elemental analyzer MT-3 located at the Service Center of Elemental Analysis of Organic Compounds, Kyushu University.

2.3. Reaction procedure

The catalytic oxidative decomposition of CFC-12 in the presence of butane was carried out using a conventional flow reaction apparatus. The reaction conditions were as follows: feed gas, 1.0 ml/min CFC-12, 1.2 ml/min butane, 150 ml/min air; catalyst weight, 2.0 g; reaction temperature, 873 K; total pressure, 0.1 MPa. The products were identified using a Shimadzu gaschromatograph–mass spectrometer GCMS-QP5050A. The reactants and products were analyzed using two gas chromatographs (a TCD-type one and an FID-type one) simultaneously. The columns of MS-5A (for oxygen, nitrogen and carbon monoxide), Porapak-QS (for carbon dioxide) and PoraPLOT Q (for CFCs and hydrocarbons) were used.

3. Results and discussion

3.1. Effects of reaction temperature on CFC-12 and butane conversions

The oxidative decomposition of CFC-12 in the presence of butane was carried out with tungsten(VI) oxide catalyst supported on alumina–zirconia at temperatures from 573 to 873 K. Carbons of CFC-12 molecule were converted into carbon oxides (carbon dioxide and carbon monoxide) at temperatures above 673 K, and at low temperatures below 673 K, a small quantity of CFC-12 was converted into CFC-11 and CFC-13, which were disproportionation products from CFC-12. Hydrogen chloride and hydrogen fluoride were produced at temperatures above 773 K, and chlorine and fluorine molecules were produced only at low temperatures below 723 K. The temperature dependence of CFC-12 and butane conversions at 15 min on stream is shown in Fig. 1. The CFC-12 conversion was 100% at temperatures above 623 K, but it was about 50% at 573 K. The butane conversion was kept at 100% level only at temperatures above

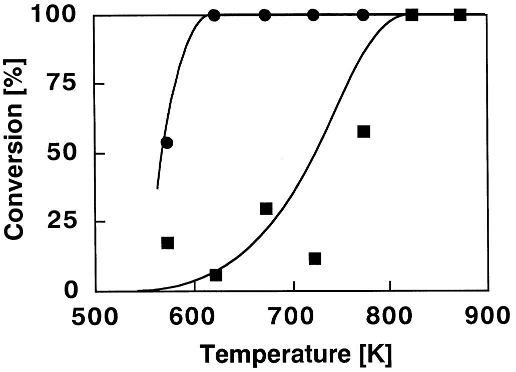

Fig. 1. Temperature dependence of CFC-12 and butane conversions at 15 min on stream. (●) CFC-12 conversion; (■) butane conversion. Feed gas, 1.0 ml/min CFC-12, 1.2 ml/min butane, 150 ml/min air; catalyst, tungsten(VI) oxide supported on alumina–zirconia; catalyst weight, 2.0 g.

823 K, and in the range below 823 K, the conversion decreased with a decrease in temperature.

In the oxidative decomposition of CFCs in the presence of hydrocarbons, CFC molecules reacted with water molecules formed by the combustion of hydrocarbon according to the following equations [11].

$$HC + O_2 \rightarrow CO_\chi + H_2O \quad (1)$$

$$CFC + H_2O \rightarrow CO_\chi + HCl + HF \quad (2)$$

According to Eqs. (1) and (2), the complete hydrolysis of CFC-12 needs butane conversion more than 40% under the reaction conditions in this work. The butane conversion was more than 40% at high temperatures above 773 K. Hydrogen chloride and hydrogen fluoride were produced, and chlorine and fluorine molecules were not detected. Accordingly, in conclusion, CFC-12 might react with water formed by the combustion of butane at high temperatures above 773 K (Eqs. (1) and (2)).

On the other hand, the butane conversion was less than 40% at low temperatures below 723 K, and halogens of CFC-12 were converted into halogen molecules with a small quantity of hydrogen halides (hydrogen chloride and hydrogen fluoride) at temperatures below 723 K. The oxidative decomposition of CFC-12 in the absence of butane was carried out over the tungsten(VI) oxide catalyst at low temperatures below 723 K. Carbons of CFC-12 molecule were converted into carbon oxides though a small quantity of CFC-12 was converted into CFC-11 and CFC-13, and chlorine and fluorine molecules were produced as a major product. The product distribution in the absence of butane was almost the same as in the presence of butane at low temperatures below 723 K. Accordingly, it is considered that most of CFC-12 might react directly with oxygen in the presence of butane at low temperatures below 723 K, as is shown by the following equation.

$$CFC + O_2 \rightarrow CO_\chi + Cl_2 + F_2 \quad (3)$$

3.2. *Effects of time on stream on CFC-12 conversion*

The CFC-12 conversion decreased with the passage of time on stream at temperatures below 723 K. The time dependence of CFC-12 conversions at 573, 623, 673 and 773 K is shown in Fig. 2. The CFC-12 conversion did not decrease with the passage of time on stream at 773 K. The CFC-12 conversions were kept at 100% level for early 2 h on stream at 673 K and for early 1 h on stream at 623 K, and then decreased with the passage of time on stream. The CFC-12 conversion at 573 K was low at 15 min on stream, and became almost zero after 2 h on stream. In general, the catalyst deactivation can be regarded as being attributed to a decrease in acidity due to the fluorination of the acid sites in the oxidative decomposition of

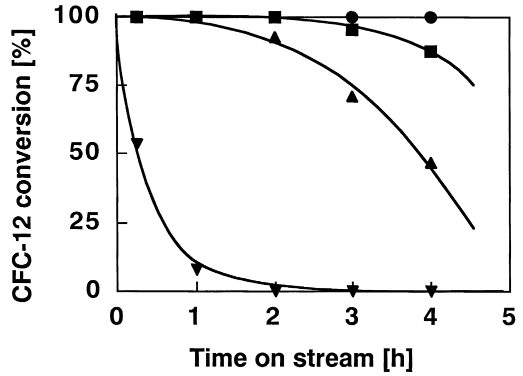

Fig. 2. Relationship between time on stream and CFC-12 conversion: (▼) at 573 K; (▲) at 623 K; (■) at 673 K; (●) at 773 K. Feed gas, 1.0 ml/min CFC-12, 1.2 ml/min butane, 150 ml/min air; catalyst, tungsten(VI) oxide supported on alumina–zirconia; catalyst weight, 2.0 g.

CFCs [13]. In this work, the color of the catalysts changed from white to black after 4 h on stream in the oxidative decomposition at 673, 623 and 573 K. Thus, the catalysts after subjected to the oxidative decomposition for 4 h on stream were calcined in air at 773 K for 3 h, and then they were subjected again to the oxidative decomposition of CFC-12 in the presence of butane. The activity of the calcined catalysts was restored up to more than 80% of the fresh catalyst. Accordingly, the catalyst deactivation was attributed to the coke deposition which was caused by the polymerization of butane on the acid sites, as well as to the fluorination of the acid sites.

3.3. *Effects of metal loading on butane conversion*

The tungsten(VI) oxide catalyst supported on alumina–zirconia was loaded with platinum-group metals to depress the catalyst deactivation due to the coke deposition by accelerating the combustion activity and to increase the CFC-12 conversion at low temperatures. The oxidative decomposition of CFC-12 was carried out over the tungsten(VI) oxide catalyst loaded with platinum-group metals in the presence of butane at 623 K. The butane conversions at 15 min and 4 h on stream are shown in Fig. 3. The conversions at 15 min on stream over the platinum- and palladium-loaded tungsten(VI) oxide catalyst were much higher than the other catalysts. However, the conversions over these two catalysts decreased with the passage of time on stream, and were almost the same as those over the other tungsten(VI) oxide catalysts at 4 h on stream. The high butane conversion might be attributed to the high activity of platinum and palladium for the hydrocarbon combustion [14–18], and the decrease in the butane conversion with time on stream might be attributed to the halogenation of platinum and palladium [19,20]. In conclusion, the combustion of butane was not necessarily promoted by loading the tungsten(VI) oxide catalyst with platinum-group metals.

3.4. *Effects of metal loading on the CFC-12 conversion*

The effects of metal loading on the CFC-12 conversion were also investigated at 623 K. Both the CFC-12 conversions at 15 min and at 4 h on stream over metal-loaded tungsten(VI) oxide catalysts are shown in Fig. 4. According to Eqs. (1) and (2), it is considered that the CFC-12 conversion increases with an increase in the butane conversion. However, the CFC-12 conversions were independent of the butane conversions over the metal- and non-loaded tungsten(VI) oxide catalysts, and were much higher than the butane conversions, as can be seen from Figs. 3 and 4. In addition, the product distribution in the presence of butane over metal-loaded tungsten(VI) oxide catalysts was almost the same as in the absence of butane over non-loaded tungsten(VI) oxide catalyst at 623 K, as mentioned above. Taking into considera-

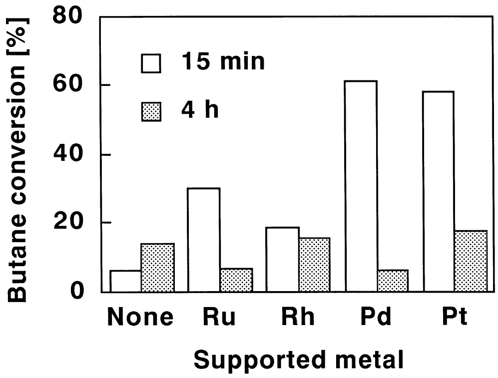

Fig. 3. Butane conversions at 15 min and 4 h on stream. Feed gas, 1.0 ml/min CFC-12, 1.2 ml/min butane, 150 ml/min air; reaction temperature, 623 K; catalyst, metal-loaded tungsten(VI) oxide supported on alumina–zirconia; catalyst weight, 2.0 g.

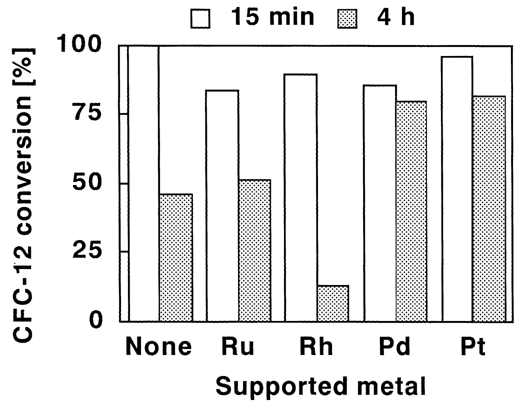

Fig. 4. CFC-12 conversions at 15 min and 4 h on stream. The reaction conditions are the same as in Fig. 3.

tion these findings, CFC-12 might react directly with oxygen over the metal-loaded tungsten(VI) oxide catalysts at low temperatures (Eq. (3)).

The CFC-12 conversions at 15 min on stream over the metal-loaded tungsten(VI) oxide catalysts were lower than that over the non-loaded tungsten(VI) oxide catalyst. It is known that the acidity of the catalyst plays an important role for the oxidative decomposition of CFCs in the presence of hydrocarbons [11]. Thus, the acid strength of the metal- and non-loaded tungsten(VI) oxide catalysts was determined by the titration of Hammett's indicators. As a result, it was found that the metal-loaded tungsten(VI) oxide catalysts had the same acid strength as the non-loaded tungsten(VI) oxide catalyst, and that these two kinds of catalysts had superacidity, $H_0 \leq -14.52$. The acid amounts of fresh metal- and non-loaded tungsten(VI) oxide catalysts were measured using the adsorption of ammonia. The results are shown in Fig. 5. The acid amounts of the fresh metal-loaded tungsten(VI) oxide catalysts were smaller than that of the fresh non-loaded tungsten(VI) oxide catalyst. Accordingly, the decrease in the CFC-12 conversion at 15 min on stream due to metal loading, as shown in Fig. 4, might be attributed to the decrease in the acid amount.

The CFC-12 conversion at 4 h on stream over metal- and non-loaded tungsten(VI) oxide catalysts increased in the following order:

rhodium < none ≈ ruthenium < palladium ≈ platinum.

A CFC-12 conversion as high as about 80% was obtained with platinum- and palladium-loaded tungsten(VI) oxide catalysts at 4 h on stream. Fig. 5 also shows the acid amount of metal- and non-loaded tungsten(VI) oxide catalysts after subjected to the oxidative decomposition of CFC-12 for 4 h. The order in the acid amounts was the same as that in the CFC-12 conversions at 4 h on stream. The catalyst deactivation at 623 K was attributed to the coke deposition on the acid sites due to the polymerization of butane as mentioned above. Thus, the amount of the coke deposited was measured with the metal- and non-loaded tungsten(VI) oxide catalysts. The results are shown in Fig. 6. The amount of the coke deposited was decreased by loading the tungsten(VI) oxide catalyst with platinum-group metals. Especially, the amount of the coke deposited on platinum- or palladium-loaded tungsten(VI) oxide catalyst, which exhibited a high CFC-12 conversion at 4 h on stream, was very small. Inui et al. [21] reported that iron incorporated into silicate framework exhibited a very high activity for the combustion of the coke deposited on ferrisilicate catalyst, but that iron did not exhibited a very high activity for the combustion of hydrocarbons [22]. This finding indicated that the catalytic combustion of the coke deposited occurred more easily than the catalytic combustion of hydrocarbons. Thus, it is considered that halogenated platinum and palladium might catalyze the combustion of the coke deposited on the acid sites, but that those might not catalyze the combustion of hydrocarbons (Fig. 3).

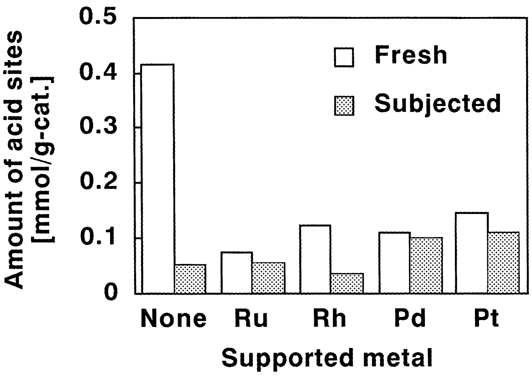

Fig. 5. Amount of acid sites of metal- and non-loaded tungsten(VI) oxide supported on alumina–zirconia (fresh and subjected for 4 h on stream).

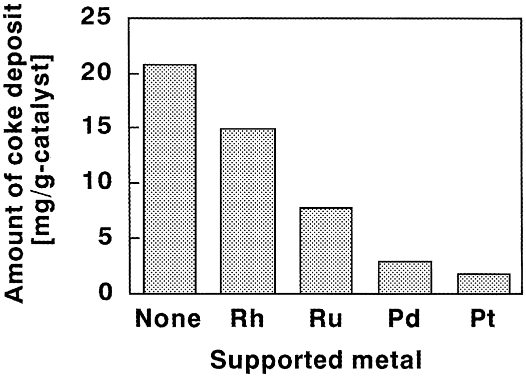

Fig. 6. Amount of coke deposited on metal- and non-loaded tungsten(VI) oxide supported on alumina–zirconia after oxidative decomposition of CFC-12 for 4 h.

Accordingly, it can be concluded that the decrease in the amount of the coke deposited on platinum- or palladium-loaded tungsten(VI) oxide catalyst might be attributed to the easy combustion of the coke deposited on the acid sites over halogenated platinum and palladium.

4. Conclusions

The catalytic oxidative decomposition of dichlorodifluoromethane (CFC-12) was carried out in the presence of butane over tungsten(VI) oxides supported on alumina–zirconia. The following conclusions were obtained:

1. CFC-12 reacted with water formed by the butane combustion at high temperatures above 773 K, and reacted directly with oxygen to a great extent at low temperatures below 723 K.
2. The deactivation of the catalyst was attributed to the coke deposited on the acid sites which was caused by the polymerization of butane, as well as to the fluorination of acid sites.
3. The catalysts loaded with platinum and palladium exhibited a higher CFC-12 conversion than the non-loaded catalyst because platinum and palladium might catalyze the combustion of the coke deposited on the acid sites.

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