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# Reaction between carbon dioxide and elementary fluorine

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#### Abstract

Reactions between carbon dioxide and fluorine were examined at temperatures of 303-523 K under various pressure and mixture ratios of both gases. Reactions were carried out similarly under the existence of NaF, CsF and EuF<sub>3</sub>.

After the reaction, fluorine was removed and the reaction products were analyzed using FT-IR, GC/FT-IR and GC/MS. The major products were  $CF_3OF$ ,  $COF_2$ ,  $CF_4$  and  $CF_2(OF)_2$ .

The best yield of  $COF_2$  was 11.1% under the reaction condition of  $CO_2/F_2 = 76$  kPa/76 kPa with temperature of 498 K for 72 h in a direct reaction. The formation rate of  $COF_2$  in the direct reaction was estimated as 0.232 dm<sup>3</sup> mol<sup>-1</sup> h<sup>-1</sup> under the reaction conditions of  $CO_2/F_2 = 76$  kPa/76 kPa, at 498 K. In the presence of CsF, it was estimated as 1.88 dm<sup>3</sup> mol<sup>-1</sup> h<sup>-1</sup> at  $CO_2/F_2 = 76$  kPa/76 kPa at 498 K.

The activation energy of the  $COF_2$  formation in the direct reaction was estimated as 45.7 kJ mol<sup>-1</sup> at  $CO_2/F_2 = 76$  kPa/76 kPa at 498 K. In addition, 24.2 and 38.9 kJ mol<sup>-1</sup> were evaluated at  $CO_2/F_2 = 76$  kPa/76 kPa at 498 K, respectively, in the presence of CsF and EuF<sub>3</sub>. © 2006 Elsevier B.V. All rights reserved.

Keywords: Carbon dioxide; Fluorine gas; Carbonyl fluoride; Reaction mechanism; Catalyst

## 1. Introduction

The reaction between CO<sub>2</sub> and  $F_2$  to form COF<sub>2</sub> takes place spontaneously even at room temperature because the Gibbs free energy change of the reaction is calculated as -220 kJ mol<sup>-1</sup>[1].

 $\mathrm{CO}_2 + \mathrm{F}_2 \, \rightarrow \, \mathrm{COF}_2 + (1/2)\mathrm{O}_2 + (-\Delta G)\, 220\, \mathrm{kJ}\,\mathrm{mol}^{-1}$ 

Some reports have addressed preparation of  $COF_2$  [2,3] and  $CF_3OF$  [2] from CO and  $F_2$ ; few reports have examined the reaction between  $CO_2$  and  $F_2$ . Only three reports have described formation not of  $COF_2$ , but of  $CF_2(OF)_2$ , using CsF as a catalyst [4–6]. To confirm the conversion of  $CO_2$  into  $COF_2$ , the reaction between  $CO_2$  and  $F_2$  has been tried at various temperatures from 303 to 523 K under various pressure and mixing ratios of both gases. This reaction was carried out similarly in the presence of NaF, CsF and EuF<sub>3</sub>. Catalytic abilities of these metal fluorides to form  $COF_2$  were examined. In addition, the reaction mechanism and reaction rate are discussed in this paper.

## 2. Results and discussion

#### 2.1. Reaction product

Fig. 1 shows FT-IR spectra of the reaction products of the direct reaction of  $CO_2$  and  $F_2$  have many peaks. The absorption peaks corresponded to O–F, C–F and CF=O bonds that appeared, respectively, at 800–1000, 1200–1300, and around 1930 cm<sup>-1</sup>. The absorption peaks at 2360 and 3700 cm<sup>-1</sup> indicate the presence of residual CO<sub>2</sub>. Some fluorocarbon compounds, including CF<sub>3</sub>OF, were inferred to have been produced.

Gram-Schmide spectra of the reaction product measured using GC/FT-IR are shown in Fig. 2. They confirmed that three products existed, with retention times of 18.95–18.96, 19.04–19.06 and 19.23–19.27 min.

The IR spectra of the products separated by GC/FT-IR are shown in Fig. 3. IR spectra of the product sampled at the retention times of 18.95-18.96, 19.04-19.06 and 19.23-19.27 min are also shown in Fig. 3(a)-(c). Fig. 3(a) shows that the product with retention time of 18.95-18.96 min had a characteristic absorption peak at  $1282 \text{ cm}^{-1}$  corresponding to a C–F bond. Similarly, the product with retention time of 19.04-19.06 min had characteristic absorption peaks at  $1929 \text{ cm}^{-1}$  (C–F),  $1256 \text{ cm}^{-1}$  (C–F) and  $977 \text{ cm}^{-1}$  (C–F), as shown in

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Fig. 1. FT-IR spectrum of the product in the direct reaction.  $CO_2:F_2 = 76$  k-Pa:76 kPa, reaction temperature 498 K, and reaction time 5 h.

Fig. 3(b), and the product with the retention time of 19.23– 19.27 min had characteristic absorption peaks at 2331 cm<sup>-1</sup> (CO<sub>2</sub>), 2361 cm<sup>-1</sup> (CO<sub>2</sub>) and 3700 cm<sup>-1</sup> (CO<sub>2</sub>), as shown in Fig. 3(c). Matching with HR Nicolet Vapor Phase Library (Thermo Nicolet Japan Inc.) revealed that the respective products were CF<sub>4</sub> [7], COF<sub>2</sub> [8] and CO<sub>2</sub>.

Fig. 4 shows the total ion chromatogram of the gaseous reaction product and GC/MS spectra in the direct reaction. Three peaks existed at the retention times of 9.02, 9.15 and 9.45 min. The numbers in the figure indicate the m/z values. Fig. 4(b) shows the mass chromatogram of m/z = 69, 47, 66 and 44. Ions with m/z = 69, 47, 66 and 44 corresponded, respectively, to  $CF_3^+$ ,  $COF^+$ ,  $COF_2^+$  and  $CO_2^+$  [9]. Fig. 4(c) and (d) were mass spectra of the products sampled at 9.02 and 9.15 min, where the peaks attributable to  $N_2$  and  $O_2$  were subtracted as a background. However, as shown in Fig. 4(c), one ion indicated m/z = 32 because the oxygen in air mixed with the sample injection could not be subtracted sufficiently. The ion with m/z = 69, corresponding to  $CF_3^+$  was detected at the retention time of 9.02 min; ions with m/z = 47 and 66 corresponding to COF<sup>+</sup> and COF<sub>2</sub><sup>+</sup> were detected at the retention time of 9.15 min. Comparing the spectra to the data in NIST Library, the MS spectra at 9.02 and 9.15 min correctly corresponded, respectively, to  $CF_4$  [7],  $COF_2$  [8]. In addition,



Fig. 2. Gram-Schmide spectra of the product measured using GC/FT-IR.  $CO_2$ :F<sub>2</sub> = 50.7 kPa:101.3 kPa, reaction temperature 498 K, and reaction time 50 h.



Fig. 3. GC/FT-IR spectra of the products at retention times of 18.95-18.96 min (a), 19.04-19.06 min (b) and 19.23-19.27 min (c).  $CO_2:F_2 = 50.7$  k-Pa:101.3 kPa, reaction temperature 498 K, and reaction time 50 h.

the result of positive CI–MS also suggested that  $CF_4$  [7] and  $COF_2$  [8] were produced.

It is noteworthy that the ions with m/z = 85 and 54 corresponding, respectively, to CF<sub>3</sub>O<sup>+</sup> and OF<sub>2</sub><sup>+</sup> were not observed by GC/MS analysis. However, CF<sub>3</sub>OF was confirmed by FT-IR spectra, as shown in Fig. 1. The characteristic absorption peak corresponding to OF<sub>2</sub> was also observed at 860 cm<sup>-1</sup>. Moreover, CF<sub>3</sub>OF and OF<sub>2</sub> were not observed by GC/FT-IR and GC/MS [10] because these products had adsorbed on the column strongly and reacted with the column. Some fluorocompounds, such as CH<sub>3</sub>SiF<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>SiF<sub>2</sub> and fluorobenzene, were detected during measurements.

Results show that  $CF_3OF$ ,  $COF_2$  and  $CF_4$  were the major products of the direct reaction between  $CO_2$  and  $F_2$  around 473 K. It is noteworthy that the reaction between  $CO_2$  and  $F_2$ proceeded very slowly at room temperature. Confirmation of the  $CF_3OOCF_3$  formation was not possible in the direct reaction. The generated  $OF_2$  at the reaction, along with  $F_2$ , was eliminated by vaporization at 77 K. Little  $OF_2$  remained in the product.

## 2.2. In the presence of metal fluorides

Reaction between  $CO_2$  and  $F_2$  in the presence of metal fluoride was carried out under various conditions. In the presence of NaF and EuF<sub>3</sub>, the results of this reaction were similar to that of the direct reaction. However, the FT-IR



Fig. 4. GC/EI–MS spectra of the products. (a) Total ion chromatogram, (b) mass chromatogram at m/z = 69, 66, 47 and 44, (c) mass spectra at the retention time of 9.02 min, and (d) at the retention time of 9.15 min. CO<sub>2</sub>:F<sub>2</sub> = 50.7 kPa:101.3 kPa, reaction temperature 498 K, reaction time 40 h, and GC oven temperature 223 K.

spectrum of the reaction in the presence of CsF differed from that in the absence of metal fluoride and the presence of  $EuF_3$  and NaF.

The FT-IR spectra of the reaction product in the presence of 3 g (2  $\times$  10<sup>-2</sup> mol) CsF are shown in Fig. 5. The shape of the absorption profile changed between 1100 and  $1300 \text{ cm}^{-1}$ . Absorption peaks at 1167 and 1202  $\text{cm}^{-1}$  newly appeared and the absorption peak at  $1285 \text{ cm}^{-1}$  shifted to  $1289 \text{ cm}^{-1}$ . Fig. 5(b) shows that the reaction product was clearly different at each reaction temperature. In the case reacted at 303 K, the product displayed strong absorption peaks at 1267, 1248, 1202, 1186 cm<sup>-1</sup>, etc. The strong peak at 1202 cm<sup>-1</sup> became weak at temperatures over 373 K. The amount of the product having this strong peak decreased with increasing temperature. It disappeared completely at 473 K. On the other hand, the strong peak of  $1167 \text{ cm}^{-1}$  appeared clearly at 498 K. Strong absorption peaks at 1267, 1248, 1202, 1186 cm<sup>-1</sup>, etc. were attributed to CF<sub>2</sub>(OF)<sub>2</sub> [11]. At high temperatures over 373 K, the amount of CF<sub>3</sub>OF in the products increased at an increasing rate [12]. Moreover, the peak at 1167 cm<sup>-1</sup> appeared at 498 K and was identified as that of CF<sub>3</sub>OOCF<sub>3</sub> [13,14].

In the presence of 260 mg  $(1.65 \times 10^{-3} \text{ mol})$  CsF at various temperatures, CF<sub>3</sub>OF and OF<sub>2</sub> formed and CF<sub>2</sub>(OF)<sub>2</sub> did not form, even at 303 K. The result was similar to that of the direct reaction when the amount of CsF was small.

Fig. 6 shows the mass chromatogram and MS spectra of the gaseous reaction product between  $CO_2$  and  $F_2$  in the presence of CsF. Fig. 6(a) shows that there were three peaks detected at the retention time of 9.04, 9.17, and 9.39 min. Peaks with m/z = 69 corresponding to  $CF_3^+$  appeared in the MS spectra (Fig. 6(b) and (d)) at the retention time of 9.04 and 9.39 min. Ions with m/z = 47 and 66, corresponding, respectively, to  $COF^+$  and  $COF_2^+$ , were observed at the retention time of 9.17 min. Especially, as shown in Fig. 6(d), the product had peaks with m/z = 151 and 170 corresponding to  $C_2F_5O_2^+$  and  $C_2F_6O_2^+$ . Comparing the spectra to the data in the NIST Library, the products at 9.04, 9.17 and 9.39 min corresponded, respectively, to  $CF_4$ ,  $COF_2$  and  $CF_3OOCF_3$ .

Fig. 7 shows the reaction temperature dependence of the mass chromatogram of the reaction products in the presence of CsF. Two peaks at 8.96 and 8.99 min were detected in the profile, corresponding, respectively, to m/z = 47 and 66. The



Fig. 5. FT-IR spectra of products in the presence of CsF at various temperatures.  $CO_2$ :  $F_2 = 76$  kPa:76 kPa and reaction time 50 h. Sampling amount 2 kPa (a) and 0.4 kPa (b).

peak at 8.99 min disappeared at temperatures greater than 423 K. The MS spectrum for the product at 8.96 min was determined as  $COF_2$ . The two peaks in Fig. 7(a) proved that  $COF_2$  was produced in two different pathways.

The GC/MS oven temperature was reduced to 224 K from 242 K to separate the two peaks. Fig. 8(a) shows a mass chromatogram of m/z = 47, 66 and 69. The two peaks in Fig. 7(a) were separated and two peaks with the fragment ion of m/z = 47 and 66 were apparent at the respective retention times of 9.16 and 9.23 min; the MS spectra of the two peaks also agreed with COF<sub>2</sub>, as shown in Fig. 8(b)-2 and (b)-3. The intensity ratio of the two peaks was about 1:3. This peak intensity at the retention time of 9.23 min tended to decrease during storage of the sample. The peak disappeared completely

after 18 days storage. It is inferred that  $CF_2(OF)_2$  decomposed in the glass container to form SiF<sub>4</sub>. It seems that one of two pathways of COF<sub>2</sub> formation must occur through the process of the decomposition of  $CF_2(OF)_2$  [11] in the GC column; the other pathway requires  $COF_2$  to be produced in the reaction between  $CO_2$  and  $F_2$ . The product that had m/z = 69 at the retention time of ca. 9.37 min was also  $CF_3OOCF_3$ . The amount of  $CF_3OOCF_3$  that was produced at 303 K was less than that at 498 K. Apparently, the formation of  $CF_3OOCF_3$  of more than 498 K occurred under the low fluorine content condition. It was unrelated with the decomposition of  $CF_2(OF)_2$  at 303 K. Formation of  $CF_4$  did not proceed compared to the direct reaction.

The electronic states of metal fluorides before and after the reaction were analyzed using XPS. The color of  $EuF_3$  and NaF changed from white to light yellow, whereas XPS profiles of the F 1s electron of  $EuF_3$  and NaF did not change through the reaction. The color of CsF changed from white to pink in parts that contacted the nickel container. The color of CsF did not change in the parts that did not contact with the container. After a few days, the pink sample turned to yellow-green.

Fig. 9 shows XPS spectra [15] of the F 1s electron in CsF before (a) and after (b) used as the catalyst. The peak at 683.9 eV appeared in the case of CsF before use. The peak at 685.6 eV is visible in Fig. 9(a). This peak must correspond to the F 1s electron of the organic compound adsorbed in CsF. This peak disappeared at 685.6 eV after 20 min of Ar ion etching, as shown in Fig. 9(a)-2. Therefore, it seems that the peak at 685.6 eV corresponded to some impurities on the surface of CsF. In Fig. 9(b), the peak at 687.1 eV appeared, no peak was detected at 684 eV before etching. The peak at 684.3 eV appeared after Ar ion etching, indicating that there must be two types of fluoride. The CsF surface was covered by some organic compound.

## 2.3. Yields

Quantitative analysis using the calibration line in Fig. 15 was carried out and the yield was calculated as a rate to CO<sub>2</sub>. The yield of the whole gaseous reaction product after eliminating F<sub>2</sub> is shown in Table 1. In the direct reaction, yields of COF<sub>2</sub>, CF<sub>3</sub>OF, CF<sub>4</sub> and CF<sub>3</sub>OOCF<sub>3</sub> increased with increasing reaction temperature and increasing reaction time, as shown in Fig. 10. The reaction rate under the condition of  $CO_2/F_2 = 76$  kPa/76 kPa was smaller than that of  $CO_2/F_2 = 50.7$  kPa/101.3 kPa. However, the yield of COF<sub>2</sub> of the reaction at  $CO_2/F_2 = 76$  kPa/76 kPa was larger than that at  $CO_2/F_2 = 50.7$  kPa/101.3 kPa.

In the presence of CsF (3 g), the yields of COF<sub>2</sub>, CF<sub>3</sub>OF, CF<sub>4</sub>, CF<sub>3</sub>OOCF<sub>3</sub> and CF<sub>2</sub>(OF)<sub>2</sub> were measured under the conditions of CO<sub>2</sub>/F<sub>2</sub> = 76 kPa/76 kPa, with 50 h reaction time. The yields, which are shown in Fig. 11, did not increase monotonously with increasing reaction temperature. The yield of CF<sub>2</sub>(OF)<sub>2</sub> decreased with increasing temperature. The yields of COF<sub>2</sub> and CF<sub>3</sub>OF had the highest values. In addition, CF<sub>3</sub>OOCF<sub>3</sub> was detectable at temperatures higher than 498 K. The yields of COF<sub>2</sub> and CF<sub>3</sub>OF become larger in the presence



Fig. 6. Mass chromatogram and MS spectra of the products in the presence of CsF. (a) Mass chromatogram at m/z = 69, 66 and 47, (b) mass spectra at the retention time of 9.04 min, (c) at the retention time of 9.17 min and (d) at the retention time of 9.17 min.  $CO_2:F_2 = 76$  kPa:76 kPa, reaction temperature 498 K, reaction time 50 h, and GC oven temperature 223 K.

of CsF than in the direct reaction at temperatures of 373-473 K. Furthermore, the yields of CF<sub>3</sub>OOCF<sub>3</sub> appeared at the high-temperature range over 473 K. However, CF<sub>4</sub> was only slightly observed in the presence of CsF, as shown in Fig. 11. Total yields of the reaction products were equal, about 23%, for both reactions at 498 K.

On the other hand, in the presence of 0.25 g  $(1.65 \times 10^{-3} \text{ mol})$  CsF, the reaction product was similar to the direct reaction. The different yields of COF<sub>2</sub> and CF<sub>3</sub>OF can be explained using the reaction mechanism.

In the presence of 0.35 g  $(1.65 \times 10^{-3} \text{ mol})$  EuF<sub>3</sub> under the condition of CO<sub>2</sub>/F<sub>2</sub> = 76 kPa/76 kPa at the reaction time of 50 h, the yields of COF<sub>2</sub>, CF<sub>3</sub>OF, CF<sub>4</sub> and CF<sub>3</sub>OOCF<sub>3</sub> are shown in Fig. 12. Those yields were identical to those of the direct reaction. It appears that the amount of EuF<sub>3</sub> was insufficient to hasten the reaction.

Fig. 13 shows the yield of the direct reaction under the condition of  $CO_2/F_2 = 76 \text{ kPa}/76 \text{ kPa}$  at 498 K. In this case, it

seemed that the yields of  $COF_2$ ,  $CF_3OF$  and  $CF_4$  at the direct reaction increased with increasing reaction time, as shown in Table 1.

In summary, the best yield of  $COF_2$  was 11.1% under the reaction condition of  $CO_2/F_2 = 76$  kPa/76 kPa, with reaction temperature of 498 K and reaction time of 72 h. In the presence of CsF, the best yield of  $COF_2$  was 6.5% under the reaction conditions of  $CO_2/F_2 = 76$  kPa/76 kPa, with reaction temperature of 473 K and reaction time of 50 h.

# 2.4. Reaction rate

The reaction of  $COF_2$  generation can be written as  $CO_2 + F_2 = COF_2$ . For the reaction rate, *v* is  $k[CO_2][F_2]$ , where *k* is a rate constant.

The whole amount of  $COF_2$  produced during the reaction process was calculated as the amount of the products that were produced through  $COF_2$  pathways such as  $COF_2$ ,  $CF_3OF$ ,  $CF_4$ 



Fig. 7. Mass chromatograms of the products obtained in the presence of CsF at (a) 303 K, (b) 423 K, (c) 473 K and (d) 498 K.  $CO_2$ :F<sub>2</sub> = 76 kPa:76 kPa, reaction time 50 h, and GC oven temperature 243 K.

and  $CF_3OOCF_3$  in the direct reaction. However, under the existence of CsF (3 g) it was calculated as the total of  $COF_2$ ,  $CF_4$  and  $CF_3OOCF_3$ .

The  $COF_2$  formation rates and rate constants are shown in Table 2. The  $COF_2$  formation rates in the presence of CsF were five times larger than those without any catalyst.

# 2.5. Activation energy of COF<sub>2</sub> formation

The activation energy of  $COF_2$  is estimated according to the following reaction. The relation between the rate constant *k* and the temperature *T* is usually expressed as an Arrhenius reaction:

$$k = A e^{-E/RL}$$

The value of the activation energy *E* was determined from the gradient of the plots of  $\ln k$  versus -1/T.

The values of the activation energy are shown in Table 2. The activation energy in case of using CsF was the smallest among all that were obtained.

#### 2.6. Reaction mechanism

The radical reaction probably takes place, especially in the gas phase between  $CO_2$  and  $F_2$ . The reaction mechanism will be considered as follows:

$$F_2 \xrightarrow{\Delta} F^{\bullet} \tag{1}$$

$$\operatorname{CO}_2 + \operatorname{F}^{\bullet} \to \operatorname{CF}(\operatorname{O})\operatorname{O}^{\bullet}$$
 (2)

$$CF(O)O^{\bullet} + F_2 \rightarrow COF_2 + OF^{\bullet}$$
 (3)

$$OF^{\bullet} + F_2 \to OF_2 + F^{\bullet} \tag{4}$$

$$COF_2 + F^{\bullet} \to CF_3O^{\bullet}$$
(5)

$$CF_3O^{\bullet} + F_2 \to CF_3OF + F^{\bullet}$$
(6)

$$CF_3OF + F^{\bullet} \to CF_3^{\bullet} + OF_2 \tag{7}$$

$$CF_3^{\bullet} + F_2 \to CF_4 + F^{\bullet} \tag{8}$$

$$CF_3O^{\bullet} + CF_3O^{\bullet} \to CF_3OOCF_3 \tag{9}$$

$$CF_3O^{\bullet} + CF_3O^{\bullet} \rightarrow CF_3OF + COF_2$$
 (10)

$$OF^{\bullet} + OF^{\bullet} \to F_2 + O_2 \tag{11}$$

The fluorine radical ( $\mathbf{F}^{\bullet}$ ) is produced by the dissociation of  $F_2$  in reaction (1); subsequently,  $\mathbf{F}^{\bullet}$  might go on to react with  $CO_2$ . In this case, the  $\mathbf{F}^{\bullet}$  formation is hastened by heating in the initiation step (reaction (1)). The reaction (1) proceeds very slowly at room temperature; it proceeds remarkably faster at 473 K.

Some subsequent steps are shown in reactions (2)–(8), and  $COF_2$ ,  $CF_3OF$  and  $CF_4$  are produced. These products were detected as described above. Many other subsequent steps are possible; they might proceed in parallel.

Similarly, the termination steps are shown in reactions (9)–(11), and CF<sub>3</sub>OF and CF<sub>3</sub>OOCF<sub>3</sub> are produced. Thus, this direct reaction process, including the reactions (1)–(11), involves a free radical chain reaction [16]. In our present experiment, it seemed that reaction (9) proceeded only slightly.

On the other hand, another reaction between  $CO_2$  and  $F_2$  can occur. Hohorst and Shreeve report that when the reaction temperature is near room temperature and the  $F_2$  amount is sufficient under the existence of CsF, the reaction product between  $CO_2$  and  $F_2$  is  $CF_2(OF)_2$  [12]. However,  $CF_3OF$  and  $OF_2$  are formed when the reaction temperature rises and the  $F_2$ amount is insufficient. Identical results were confirmed through our experiments.

In the first step, the adsorption of  $F_2$  on the CsF surface must take place. The first ionization energy of Cs is 3.89 eV. In addition, fluorine has the largest electronegativity. Therefore, CsF is the material that has the highest ionic bond. This highly ionic bond apparently causes the larger polarization of  $F_2$ molecule adsorbed on CsF. This polarization of the  $F_2$  molecule might promote the reaction between CO<sub>2</sub> and  $F_2$ .

It has also been reported that atomic fluorine [17] must be generated easily at the CsF interface. The atomic fluorine might



Fig. 8. Mass chromatogram of the products in the presence of CsF at the reaction temperature of 303 K. (a) Mass chromatograms at m/z = 69, 66 and 47 after (a)-10 days and (a)-2 4 days. (b) Mass spectra of the sample in (a)-1 having the retention time of (b)-1 9.01 min, (b)-2 9.16 min, (b)-3 9.23 min and (b)-4 9.37 min. CO<sub>2</sub>:F<sub>2</sub> = 76 kPa:76 kPa, reaction time 50 h, and GC oven temperature 223 K.



Fig. 9. XPS F 1s spectrum of CsF before and after the reaction. (a) Before reaction: (a)-1 non-etching and (a)-2 after etching; (b) after reaction: (b)-1 non-etching and (b)-2 after etching.

Table 1 Yields of the products

Temperature	Time (h)	Yield (%)							
(K)		COF <sub>2</sub>	CF <sub>3</sub> OF	CF <sub>4</sub>	CF <sub>3</sub> OOCF <sub>3</sub>	CF <sub>2</sub> (OF) <sub>2</sub>			
(a) Direct read	ction								
$CO_2/F_2 = 76 \text{ kPa}/76 \text{ kPa}$									
303	5	0	0.7	0	0	0			
373	5	0	0.7	0	0	0			
373	50	0	0.8	0	0	0			
423	5	0	1.4	0.1	0	0			
423	50	0.8	8.5	0.1	0	0			
473	5	0.5	10	0.1	0	0			
473	49	2.6	17	0.5	0	0			
498	2	0.2	3.5	0.2	0	0			
498	5	0.8	8	0.3	0	0			
498	10	0.4	6.6	0.1	0	0			
498	20	1.3	9.5	0.6	0	0			
498	30	1.3	13.8	0.3	0	0			
498	40	2.5	16.4	0.7	0	0			
498	50	2.2	20	1.1	0	0			
498	60	4.5	19.1	1.9	0	0			
498	72	11.1	32.1	4.6	0	0			
525	50	3.4	26.7	2.6	0	0			
$CO_2/F_2 = 50$	).7 kPa/1	01.3 kPa							
498	2								
498	5								
498	10								
498	20	2.4	30.8	0.8	0	0			
498	30								
498	40								
498	50	6	51.5	1.5	0	0			
498	60	4.3	45.2	1.9	0	0			
498	72	5.3	43.4	1.8	0	0			
(b) In the pres	sence of	CsF (3 g)							
$CO_2/F_2 = 76$	6 kPa/76	kPa							
303	5	0.3	0	0	0	19.4			
303	50	0.6	0	0	0.1	36.6			
373	5								
373	50	2.7	31.5	0	0	9			
423	5								
423	50	4	30.1	0	0	5			
473	5								
473	50	6.5	23.3	0.1	0.1	0			
498	2								
498	5	3.7	11.1	0	0.4	0			
498	10								
498	20	2.5	27.4	0	0.2	0			
498	30			-		-			
498	40								
498	50	2.9	17.2	0	1.5	0			
498	60	2.7	17.4	0	1.0	v			
498	72								

proceed to react with CO<sub>2</sub> as well as fluorine radical:

 $F_2 \xrightarrow{CsF} 2F$ 

In many reactions, the reaction intermediates should be postulated. The XPS analyses of the CsF surface give some information about the organic compounds as intermediates.

In the second step, it seems to form  $CF_2(OF)_2$  by passing through reactions (12)–(14). The possible reaction intermediates



Fig. 10. Yields of products in the direct reaction at various temperatures.  $CO_2$ :  $F_2 = 76$  kPa:76 kPa and reaction time 50 h. ( $\bigcirc$ )  $CF_2O$ , ( $\triangle$ )  $CF_3OF$ , ( $\square$ )  $CF_4$ , ( $\diamond$ )  $CF_3OOCF_3$  and ( $\times$ )  $CF_2(OF)_2$ .

of  $[CF(O)O^{\delta-} Cs^{\delta+} F]$  and  $[CF_2(OF)O^{\delta-} Cs^{\delta+} F]$  [18–20] shown in the following reactions must be formed:

$$CO_2 + F_2 + CsF \rightarrow [CF(O)O^{\delta-}Cs^{\delta+}F], CsF(CF(O)OF)$$
(12)

$$[CF(O)O^{o^{-}}Cs^{o^{+}}F] + F_{2} \to [CF_{2}(OF)O^{o^{-}}Cs^{o^{+}}F]$$
(13)

$$[CF_2(OF)O^{\delta-} Cs^{\delta+} F] + F_2 \rightarrow CF_2(OF)_2 + CsF$$
(14)

At temperatures higher than 303 K or under low fluorine gas pressure,  $CF_3OF$  seems to form, leaving  $OF_2$  by reaction (15) instead of proceeding to reaction (14):

$$[CF_2(OF)O^{\delta-}Cs^{\delta+}F] + CsF \rightarrow CF_3OF + OF_2 + Cs_2O$$
(15)

$$Cs_2O + F_2 \rightarrow CsF + OF_2 \tag{16}$$

The concentration of  $F_2$  adsorbed on the surface must decrease with increasing temperature. Therefore, it seems to be difficult for the intermediate compound to react with



Fig. 11. Yields of products in the presence of CsF at various temperatures. CO<sub>2</sub>:F<sub>2</sub> = 76 kPa:76 kPa and reaction time 50 h. ( $\bigcirc$ ) CF<sub>2</sub>O, ( $\triangle$ ) CF<sub>3</sub>OF, ( $\square$ ) CF<sub>4</sub>, ( $\diamond$ ) CF<sub>3</sub>OOCF<sub>3</sub> and ( $\times$ ) CF<sub>2</sub>OF)<sub>2</sub>.



Fig. 12. Yields of products in the presence of EuF<sub>3</sub> at various temperatures. CO<sub>2</sub>:F<sub>2</sub> = 76 kPa:76 kPa and reaction time 50 h. ( $\bigcirc$ ) CF<sub>2</sub>O, ( $\triangle$ ) CF<sub>3</sub>OF, ( $\square$ ) CF<sub>4</sub>, ( $\diamond$ ) CF<sub>3</sub>OOCF<sub>3</sub> and ( $\times$ ) CF<sub>2</sub>OF)<sub>2</sub>.

the  $F_2$  molecule. The possible reaction intermediate [CF<sub>2</sub>(O-F)O<sup> $\delta$ -</sup> Cs<sup> $\delta$ +</sup> F] reacts with CsF, and CF<sub>3</sub>OF must be formed by reactions (15) and (21). In fact, Cs<sub>2</sub>O reacts immediately with F<sub>2</sub>, as in reaction (16), and it will return to CsF. The low F<sub>2</sub> concentration on the CsF surface induced by the low F<sub>2</sub> pressure yields the similar result to that shown above.

Fig. 11 shows the temperature dependence of the yield of  $COF_2$ . It seems that pathways (17)–(21) are considered to form  $COF_2$  and  $CF_3OF$  [21–23]. With rising temperature,  $OF_2$  would be similarly produced as follows;  $OF_2$  would remain in the products at higher temperature like in case of  $CF_3OF$ :

$$[CF(O)O^{\delta-}Cs^{\delta+}F] + F_2 \rightarrow COF_2 + OF_2 + CsF$$
(17)

$$[CF(O)O^{\delta-}Cs^{\delta+}F] + CsF \rightarrow COF_2 + Cs_2O$$
(18)

$$[CF_2(OF)O^{\delta-}Cs^{\delta+}F] + F_2 \rightarrow COF_2 + OF_2 + CsF$$
(19)

$$CF_2O + CsF \rightarrow [CF_3O^{\delta-}Cs^{\delta+}F]$$
(20)

$$[CF_3O^{\delta-}Cs^{\delta+}F] + F_2 \rightarrow CF_3OF + CsF$$
(21)



Fig. 13. Yields of products in the direct reaction at 498 K with various reaction times.  $CO_2:F_2 = 76$  kPa:76 kPa and reaction time 50 h. ( $\bigcirc$ ) CF<sub>2</sub>O, ( $\triangle$ ) CF<sub>3</sub>OF, ( $\square$ ) CF<sub>4</sub>, ( $\diamondsuit$ ) CF<sub>3</sub>OOCF<sub>3</sub> and ( $\times$ ) CF<sub>2</sub>O(F)<sub>2</sub>.

Fig. 11 shows that the yield of CF<sub>3</sub>OF increased with rising reaction temperature in the temperature range of 373-473 K. The formation and stability of the possible intermediates such  $[CF(O)O^{\delta-} Cs^{\delta+} F],$  $[CF_2(OF)O^{\delta-}Cs^{\delta+}F]$ as and  $[CF_3O^{\delta-}Cs^{\delta+}F]$  must be examined to explain the change in CF<sub>3</sub>OF yield. This situation will be estimated from XPS analysis of the CsF used for the reaction. The binding energy of the F 1s electron on the CsF surface was analyzed using XPS (Fig. 9). After the reaction, the XPS profile of F 1s electron shows a peak at 687.1 eV that corresponds to the C-F bond. The XPS profile after etching has a peak at 684.3 eV that corresponds to CsF. Results showed that the organic compounds including C-F bond were adsorbed onto the CsF surface. These organic compounds must be intermediates.

On the other hand, it is considered that the radical [24] reaction must contribute to the increased CF<sub>3</sub>OF yield at temperatures of 373–473 K. However, comparing Fig. 10 with Fig. 11 at 498 K, the radical reaction must only slightly contribute to the increase of the CF<sub>3</sub>OF yield. Fig. 11 shows that the yields of COF<sub>2</sub> and CF<sub>3</sub>OF decreased over 473 K. That is, they have a maximum value around 473 K. With the change of the reaction temperature, it seems that the kinds of the reaction intermediates change on the CsF surface. At low temperatures, the possible reaction intermediates of  $[CF(O)O^{\delta-}Cs^{\delta+}F]$  and  $[CF_2(OF)O^{\delta-}Cs^{\delta+}F]$  must be formed by reactions (12)–(14);  $CF_2(OF)_2$  is formed dominantly at room temperature. The COF<sub>2</sub> and CF<sub>3</sub>OF must be formed dominantly from the reaction intermediates by reactions (15)-(21) at temperatures of 373-473 K. The formation of CF<sub>3</sub>OF becomes dominant. At temperatures greater than 498 K, the reaction through the possible intermediate  $[CF_3O^{\delta-}Cs^{\delta+}F]$  will become dominant. Furthermore, some reactions exist in which the possible reaction intermediates of  $[CF(O)O^{\delta-}Cs^{\delta+}F]$ ,  $[CF_2(O FO^{\delta^{-}}Cs^{\delta^{+}}F$  and  $[CF_{3}O^{\delta^{-}}Cs^{\delta^{+}}F]$  might undergo competing reactions to give different products such as COF<sub>2</sub>, CF<sub>3</sub>OF, CF<sub>4</sub> and CF<sub>3</sub>OOCF<sub>3</sub>.

CF<sub>3</sub>OOCF<sub>3</sub> is formed by the following reaction:

$$2[CF_3O^{\delta-}Cs^{\delta+}F] \to CF_3OOCF_3 + CsF$$
(22)

As inferred from the results shown in Fig. 11, reaction (22) must take place significantly at temperatures greater than 473 K. Yields of  $CF_3OF$  might decrease because of the consumption of  $[CF_3O^{\delta-}Cs^{\delta+}F]$  by reaction (23). Table 1 shows that  $CF_3OOCF_3$  was also produced at 303 K in 0.1%. This fact can not be explained using the reaction scheme described above. There is probably a reaction path way through which  $CF_3OOCF_3$  is produced from  $CF_2(OF)_2$ , which is the major product at 303 K.

The formation of  $CF_4$  described by reaction (23) scarcely occurred, as shown in Fig. 11:

$$[CF_3O^{\delta-}Cs^{\delta+}F] + F_2 \rightarrow CF_4 + O_2 + CsF$$
(23)

As described above, it became the possible major intermediate instead of  $[CF_2(OF)O^{\delta-}Cs^{\delta+}F]$  at temperatures greater than 473 K. It is easily converted to CF<sub>3</sub>OF and CF<sub>3</sub>OOCF<sub>3</sub> because  $[CF_3O^{\delta-}Cs^{\delta+}F]$  must react with F<sub>2</sub> to

Table 2			
Formation rate of COF <sub>2</sub> and	d rate constant and ad	ctivation energy of	COF <sub>2</sub> formation

Catalyst	Pressure (kPa)		Temperature,	Formation rate,	Rate constant,	Activation
	CO <sub>2</sub>	F <sub>2</sub>	<i>T</i> (K)	$v \pmod{\operatorname{dm}^{-3} \operatorname{h}^{-1}}$	$k (\mathrm{dm}^{-3}\mathrm{mol}^{-1}\mathrm{h}^{-1})$	energy (kJ mol <sup>-1</sup> )
None	50.7	101.3	498	$2  imes 10^{-4}$	1.63	
	76	76	373	$0.4 imes 10^{-5}$	0.00594	45.7
	76	76	423	$0.5  imes 10^{-4}$	0.0859	
	76	76	473	$1 \times 10^{-4}$	0.208	
	76	76	498	$1  imes 10^{-4}$	0.232	
CsF (3 g)	76	76	303	$6 \times 10^{-6}$	0.00966	24.2
	76	76	373	$2 \times 10^{-5}$	0.0402	
	76	76	498	$5  imes 10^{-4}$	1.88	
EuF <sub>3</sub> (0.35 g)	76	76	373	$0.5 imes 10^{-5}$	0.00629	38.9
	76	76	423	$0.8 imes 10^{-5}$	0.00932	
	76	76	473	$0.6 imes 10^{-4}$	0.0789	
	76	76	498	$0.8 imes 10^{-4}$	0.121	



Scheme 1. Scheme of competitive reaction processes. Blanketed compounds are the possible intermediates.

generate  $CF_4$ . The reactions (21) and (22) proceed rapidly more than reaction (23), thereby giving low  $CF_4$  yield.

The competitive reaction processes mentioned here are summarized in Scheme 1.

## 3. Conclusion

By the reaction between  $CO_2$  and  $F_2$ ,  $COF_2$  was obtained at high yield in conditions of 473 K during 50 h in a direct reaction. The by-products were CF<sub>3</sub>OF and CF<sub>4</sub>. All of NaF, CaF and EuF<sub>3</sub> were tested as catalysts. Results showed that CsF can play a role as the catalyst. The COF<sub>2</sub> formation rates in the presence of CsF were five times larger than that without catalyst. Using CsF, the yields of COF<sub>2</sub> and CF<sub>3</sub>OF become higher than that in the direct reaction for temperatures of 373– 473 K. In addition,  $CF_2(OF)_2$  was produced at 303 K and its yield decreased with increasing temperature; CF<sub>3</sub>OOCF<sub>3</sub> was detected more at 473 K. Yields of COF<sub>2</sub> and CF<sub>3</sub>OF become higher than that in the direct reaction at temperatures of 373-473 K. The slightly lower amount of CF<sub>4</sub> less than 0.1% was produced in this case. The CsF affected the reaction pathways. For the reaction without CsF, the F<sup>•</sup> formation plays an important role in the products' composition. Considering that  $COF_2$  is converted into  $CF_3OF$ , the best yield of  $COF_2$  was 11.1% under the reaction conditions of  $CO_2/F_2 = 76$  kPa/ 76 kPa, with temperature of 498 K and 72 h reaction time in the direct reaction. The reaction mechanism in the presence of CsF can be explained using the formation of possible reaction intermediates  $[CF_2(OF)O^{\delta-} Cs^{\delta+} F]$  and  $[CF_3O^{\delta-} Cs^{\delta+} F]$  at each temperature. The best yield of  $COF_2$  was 6.5% under the reaction conditions of  $CO_2/F_2 = 76$  kPa/76 kPa with 473 K reaction temperature and 50 h reaction time.

# 4. Experimental

Fig. 14 shows a gas line made of SUS 316L for the reaction between  $CO_2$  and  $F_2$ , which was originally designed to control and monitor reaction pressures and temperatures precisely. This apparatus has three separate parts: a gas–gas reaction line, a trap-to-trap separation line, and a vacuum line.

The reactor was filled with  $F_2$  gas at 20 kPa; it was kept at 523 K for 1 day to passivate the inner wall of the line before use. The  $F_2$  gas in the exhaust was eliminated by passing it through the activated alumina column. The reactor vessel capacities were 59.6 ml. The amount of  $F_2$  gas that was fixed to the activated alumina was about 300 dm<sup>3</sup>/450 g Al<sub>2</sub>O<sub>3</sub>.

The CO<sub>2</sub> was introduced into the reactor and the reactor was cooled to 77 K (liquid N<sub>2</sub>). Then,  $F_2$  gas was introduced into the reactor. The reaction temperature was controlled at 303–523 K. Residual  $F_2$  in the product was eliminated by vaporization at 77 K.

For the reaction with the metal fluorides, the metal fluoride (1 equiv. mol or 3 g) was first put into a nickel container. Before use, the metal fluorides were kept all through the night in  $F_2$  gas at 503 K to eliminate trace amounts of water and oxides.

After mixing  $CO_2$  and  $F_2$ , the temperature at the surface of the reactor was measured. The relation between the lapse of time and pressure change was measured to monitor the reaction progress. The total pressure was fixed at 152 kPa.

The reaction product after eliminating  $F_2$  was introduced into the 10 cm path length IR cell having  $BaF_2$  or  $CaF_2$  window



Fig. 14. Apparatus for the reaction between  $CO_2$  and  $F_2$ . (a) Gas–gas reaction line, (b) trap-to-trap separation line and (c) vacuum line. (1)  $CO_2$  gas storage, (2)  $F_2$  gas storage, (3) reactor (SUS 316L), (4) constant volume container, (5) reactor pressure gauge, (6)  $CO_2$  gas pressure gauge, (7)  $F_2$  gas pressure gauge, (8) Pirani gauge, (9) Ar or He gas cylinder, (10) gas sampler, (11) activated alumina, (12) trap (liquid  $N_2$ ), and (13) vacuum pump (oil rotary).

at 2 or 0.4 kPa (FT-IR 8960 PC; Shimadzu Corp.). Moreover, the product was analyzed by GC/FT-IR (Nexus; Thermo Nicolet Japan Inc.) with a sample amount 20  $\mu$ l, split-less and GC/EI–MS, CI–MS: for EI (6890/5970 GC/MDS; Hewlett Packard Co.), *m*/*z* 15–300, with a sample amount 20  $\mu$ l, splitless; for CI with methane (QP 5000A; Shimadzu Corp.), *m*/*z* 45–300, with a sample amount 1 ml, split. The capillary column

for the GC was 100 m (for GC/FT-IR, 200 m)  $\times$  0.25 mm  $\times$  0.5  $\mu m$  (DB-PETRO; J&W Scientific Inc.). The oven temperature was controlled at 223, 243 and 303 K. Before GC/MS analysis, helium gas was introduced into the reactor so that the total pressure was set at 202.6 kPa.

The calibration line of the reaction product was prepared with IR data and MS intensity.



Fig. 15. Calibration lines of CO<sub>2</sub> (a), COF<sub>2</sub> (b), CF<sub>3</sub>OF (c) and CF<sub>4</sub> (d). (b)-1 and (b)-2 correspond, respectively, to data at 1930 cm<sup>-1</sup> in Ref. [25] and Ref. [26]. (c)-1, (c)-2 and (c)-3 correspond to data at 1282 cm<sup>-1</sup> in Ref. [27], at 1282 and at 945 cm<sup>-1</sup> measured in this study.

Fig. 15(a) portrays a  $CO_2$  calibration line in which the absorbance was plotted against the pressure. Into the IR cell, CO<sub>2</sub> gas was introduced at a proper pressure; the IR spectra were measured at resolution of  $4 \text{ cm}^{-1}$ . The absorption peak at 2360  $\text{cm}^{-1}$  was chosen for the calibration line of CO<sub>2</sub>. For COF<sub>2</sub>, CF<sub>3</sub>OF, CF<sub>2</sub>(OF)<sub>2</sub> and CF<sub>3</sub>OOCF<sub>3</sub> [2], the relations between the pressure and the absorbance were referred from the literature [4,11,13,14,25–27]. The calibration line was obtained by plotting the absorbance against the pressure. Fig. 15(b) shows the  $COF_2$  calibration line. Line 1 in Fig. 15(b) was drawn using the absorbance at 1930  $\text{cm}^{-1}$  in the literature [25]. The corrected calibration line, line 2 in Fig. 15(b) was obtained by plotting the absorbance against the pressure measured by Central Glass Co. Ltd. [26]. The slopes of line 1 and line 2 were approximated, respectively, as 1803 and 1254. Fig. 15(c) shows the CF<sub>3</sub>OF calibration line. Line 1 in Fig. 15(c) was drawn using the absorbance at  $1282 \text{ cm}^{-1}$  in the literature [27]. However, the sum of CO<sub>2</sub> residual pressure and pressure of CF<sub>3</sub>OF was greater than 2 kPa, which was the total pressure at the measurement, when the pressure of CF<sub>3</sub>OF was estimated using line 1 in Fig. 15(c). The corrected calibration line 2 was determined by considering the effect of IR spectrum resolution against line 1. The slopes of line 1 and line 2 were, respectively, approximately 366 and 153. The pressures evaluated using these corrected calibration lines were about 50% lower than those by calibration lines with plotting the values in the literature [4,11,13,14,25,27]. In this case, the resolution greatly affected the absorption intensity. Line 3 in Fig. 15(c) was obtained by plotting the absorbance at 945 cm<sup>-1</sup> against the pressure. Line 3 was used instead of line 2 when the absorbance at  $1282 \text{ cm}^{-1}$  could not be used for the calculation.

Fig. 15(d) is the CF<sub>4</sub> calibration line. This line plotted the MS intensity against concentration of CF<sub>4</sub>. The concentration of CF<sub>4</sub> and its MS intensity were measured using GC/MS with the standard sample. The CF<sub>4</sub> concentration was measured as a volume percentage of the GC injection gas. It was assumed that the MS intensities of COF<sub>2</sub> and CF<sub>3</sub>OOCF<sub>3</sub> were equal to that of CF<sub>4</sub> to draw the calibration line of COF<sub>2</sub> and CF<sub>3</sub>OOCF<sub>3</sub>.

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