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Reactivating Effect of Water on Freon 12 Decomposition Catalysts

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Effect of water was investigated on the durability of titania-silica (TiO_2/SiO_2), phosphate-supported zirconia (PO_4/ZrO_2), and boron phosphate (BPO_4) catalysts in the vapor phase decomposition of dichlorodifluoromethane (Freon 12). Water helped to maintain their catalytic activity by eliminating inorganic fluorines produced during the reaction. No deactivation nor configuration change was observed for BPO_4 catalyst even after 35 h. Thus the way is open to the development of practical process for catalytic detoxification of chlorofluorocarbons (Freon's).

Detoxification of Freon's is an important assignment to protect the global environment of the earth related to the ozone layer destruction by them. Catalytic decomposition seems to be one promising method for destroying Freon's.$^{1-3)}$ One of the authors has investigated the catalytic decomposition of Freon 12 and found that many solid acids act as effective catalysts.$^{4-7)}$ However, inorganic fluorines produced during the reaction attacked these catalysts and deactivation occurred very rapidly. Fluorine atom is highly reactive and combines with almost all elements shown in the periodic table since it is the most electronegative among all the elements and reacts with metallic elements more easily than with non-metallic ones. Thus it is very difficult to design robust catalysts against fluorine, and to prolong the life of the catalysts is the critical point in developing catalytic Freon decomposition process. Extensive investigation reached the conclusion that phosphate based solid acids (e.g. BPO_4 and PO_4/ZrO_2) are the only possible catalysts owing to the inertness of phosphate group toward fluorine. Especially BPO_4 had an excellent performance because its constituent elements are all non-metallic. However, boron also reacted with inorganic fluorine even slowly, and elimination of boron as BF_X gave rise to the deactivation of BPO_4 in prolonged use. It is known that metal-halogen bond is very easily hydrolyzed at elevated temperatures, releasing hydrogen halides.$^{8)}$ Therefore, water or other hydrogen sources may react with fluorines on the catalyst surface and eliminate them in the form of HF even if fluorine is combined with non-metallic elements of the catalysts. Based on this assumption the effect of water was investigated on the durability of three catalysts (TiO_2/SiO_2, PO_4/ZrO_2, and BPO_4) which were developed for the decomposition of Freon 12 in our past studies.

The methods of the preparation of TiO_2/SiO_2 with a Ti to Si molar ratio of 1, PO_4/ZrO_2 with a P to Zr molar ratio of 0.005, and BPO_4 were described elsewhere.4–7) Freon 12 was used as a model compound. Reactions were carried out with an ordinary flow reactor under atmospheric pressure. The reaction mixture (Freon 12 0.60%, O_2 21.2%, He 78.2%) was introduced into the reactor at a space velocity (SV) of 5900 h^{-1} or 6000 h^{-1} at prescribed temperatures. Details of the reaction procedure are described elsewhere.4–7)

Figure 1 shows the time course of the decomposition of Freon 12 on the three catalysts in the presence or absence of 1% water. The data obtained in the absence of water are from the previous studies.4–7) In the absence of water, all catalysts deactivate during the reaction. TiO_2/SiO_2 lost its activity quite rapidly, and deactivation of PO_4/ZrO_2 also occurred after 5 h. Although BPO_4 had the highest durability among the three, its activity also decreased after 10 h; however, the deactivation was not so rapid. The causes for the deactivation were a loss of silica for TiO_2/SiO_2,4) ZrF_4 formation for PO_4/ZrO_2,7) and a loss of boron as BF_x for BPO_4.5,6)

In the presence of 1% water, lives of all catalysts were prolonged. The conversion of Freon 12 was 100% on BPO_4 even after 35 h. Although a slight decrease in the conversion of Freon 12 occurred within 20 h on PO_4/ZrO_2, 100% of conversion was recovered in the later stage. TiO_2/SiO_2 maintained 97% conversion after 33 h, although it tended to further lose its activity.

Selectivities of the carbon part of Freon 12 to CO and CO_2 at a reaction time of 25 h were 4.7% CO and 74.9% CO_2 for TiO_2/SiO_2, 51.5% CO and 46.9% CO_2 for BPO_4, and 57.5% CO and 48.7% CO_2 for PO_4/ZrO_2, respectively. The CO plus CO_2

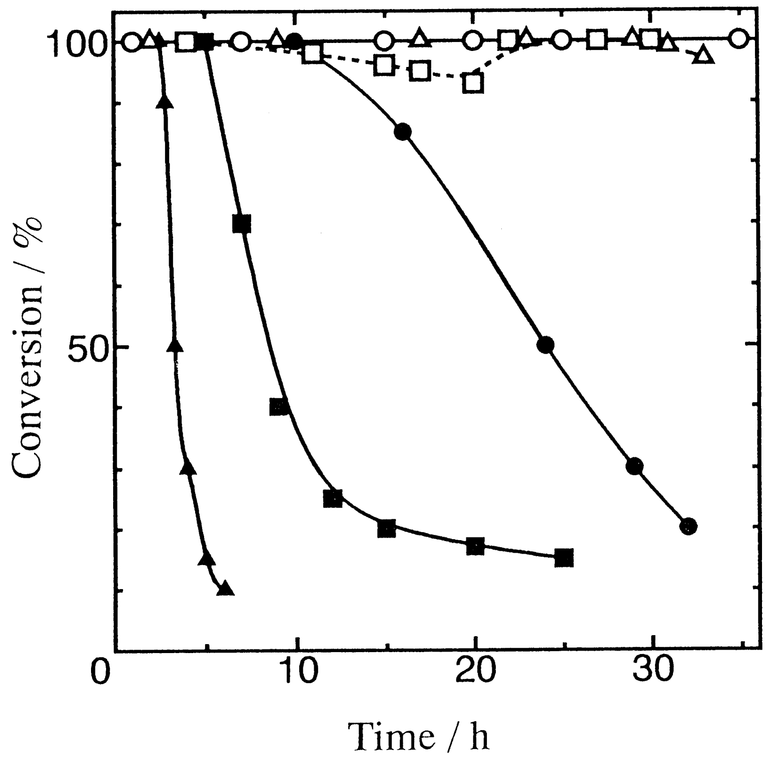

Fig. 1. Decomposition of Freon 12.

Catalyst	Reaction temp (°C)	SV (h^{-1})	H_2O (%)
▲ TiO_2/SiO_2	550	5900	0
△ TiO_2/SiO_2	550	6000	1
■ PO_4/ZrO_2	500	6000	0
□ PO_4/ZrO_2	550	6000	1
● BPO_4	550	5900	0
○ BPO_4	500	6000	1

selectivity higher than 100% on PO_4/ZrO_4 would be an experimental error. Complete material balance for carbon could not be attained, especially, on TiO_2/SiO_2, which indicated that other products were formed: this point needs further investigation.

Figure 2 shows the X-ray patterns of TiO_2/SiO_2 before and after the reaction (33 h) in the presence of water. TiO_2/SiO_2 did not show any peak before the reaction, while diffraction peaks due to TiO_2 (anatase type) were clearly observed after the reaction as in the case of the reaction in the absence of water,[4)] showing that elimination of silica occurred. X-ray diffraction analysis of PO_4/ZrO_2 also indicated the presence of fluorinated zirconium species after the reaction (30 h) in the presence of water. These results show that water can not completely protect these two catalysts although it has a remarkable protecting effect. The configuration of BPO_4 was exactly the same before and after the reaction (35 h) in the presence of water (Fig. 3). As shown in Fig. 1, BPO_4 retained its activity until 10 h even in the absence of water, and, in addition, the deactivation was not so rapid compared with other two catalysts. In addition to the stability of BPO_4 itself against fluorine, it seems that water eliminates the F atoms of the B-F bond long before the BPO_4 reaches the fragile state (i.e. the state after 10 h). Thus the activity of BPO_4 will possibly remain unchanged for a time-scale of practical use.

On the basis of the result obtained in this study, it is concluded that the most strong barrier to the realization of the catalytic detoxification of Freon's has been cleared by the combined use of BPO_4 and water or other hydrogen sources. The details of the effect of hydrogen sources on the BPO_4 assisted decomposition of Freon's are under active investigation now.

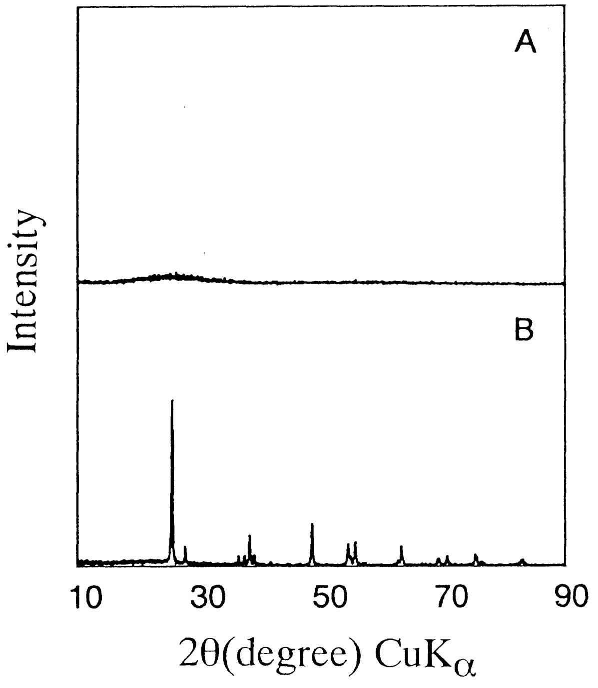

Fig. 2. X-Ray pattern of TiO_2/SiO_2.
A: before reaction, B: after reaction (33 h) in the presence of 1% of water.

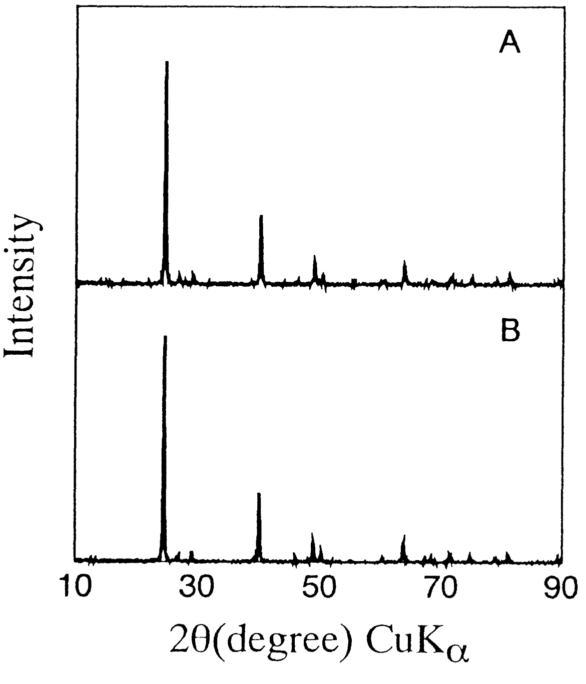

Fig. 3. X-Ray pattern of BPO_4.
A: before reaction, B: after reaction (35 h) in the presence of 1% of water.

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