Stable and Active $AlPO_4$ Catalyst for Decomposition of CCl_2F_2

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CCl_2F_2 was decomposed to CO_2 at 350-450 °C in the presence of water vapor and O_2 over $AlPO_4$ calcined at 1000 °C. CCl_2F_2 conversion slightly decreased at initial 50 h and then took a steady value. $AlPO_4$ was not fluorinated during 1000 h reaction at 400 °C.

Decomposition of CCl_2F_2 is of importance in a viewpoint of preservation of grobal enveronment. Catalytic decomposition of spent CFCs, especially hydrolysis of spent CFCs, is thought to be an excellent method because it seems to form no toxic compounds such as dioxines. Since metal fluorides are thermodynamically much stable, metal or matal oxide catalysts are gradually changed into the corresponding fluorides, which are less active, during CFC reactions. So one of the most important target of the research was to find out the stable catalyst against formed HF or F_2. It has been reported that many catalysts are effective for CFC reactions,[1-6] however, catalyst life was generally not examined or not reported.

Authors have been studied catalytic destruction of CCl_2F_2[7] and $CHClF_2$[8] and reported that ZrO_2-Cr_2O_3 is very active catalyst, however, the activity of this catalyst gradually decreases.

Currently, authors found out that $AlPO_4$ is effective for decomposition of CCl_2F_2 in the presence of water vapor and air and the catalytic activity lasts for long time. We will report briefly the catalysis of $AlPO_4$ for decomposition of CCl_2F_2 which has been used for a refrigerant of automobile air conditioner.

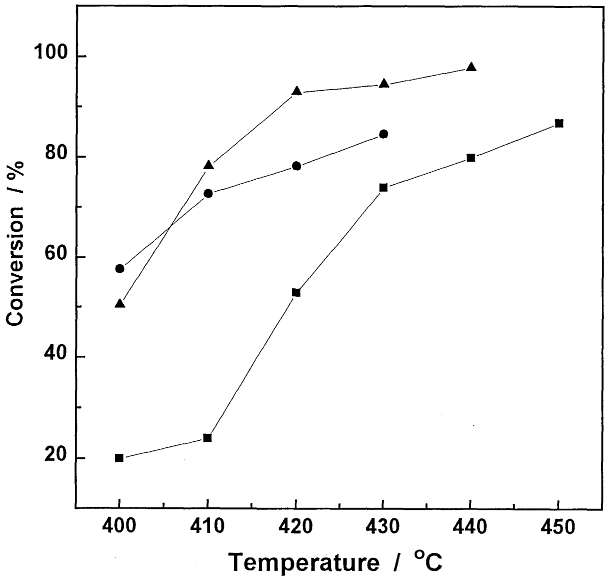

Figure 1. Decomposition of CCl_2F_2 over the $AlPO_4$ catalysts. Catalyst: 4.5 g (ca 10 cm^3); Feed gas composition (mol%): CCl_2F_2 1.52, H_2O 51.7, O_2 8.3, N_2 balance; Flow rate 36.0 cm^3/min; Calcination temperature: □ 600 °C, ○800 °C, △ 1000 °C.

The $AlPO_4$ catalyst was prepared by adding an NH_4OH aqueous solution into an aqueous solution containing equimolar $Al(NO_3)_3$ and H_3PO_4 until the pH of the solution became 7. The precipitate formed was well washed by pure water, filtrated, and dried at 70 ℃ overnight. The obtained powder was pressed, crashed, and sieved. The 14-32 mesh granules of the catalyst was finally calcined at 600-1000 ℃ for 5h in an air flow. Catalytic reaction was carried out with an ordinally flow type reaction system with vertical tubelar reactor (16 ϕ i.d.,SUS 304). Mixture of CCl_2F_2, water vapor, oxygen, and nitrogen was fed into the top of the reactor. The products were analyzed by GC with DB624, molecular sieve 5A, and SiO_2 gel columns.

Catalytic performance of the $AlPO_4$ catalysts calcined at some temperatures is shown in Figure 1. The calcination temperature affected the catalytic activity. The catalyst calcined at 1000 ℃ showed the highest activity and the CCl_2F_2 conversion reached to 50% at 400 °C and exceeded 90% at 420 ℃. The activity of the catalyst calcined at 600 ℃ was lower than that calcined at 1000 °C and the conversion was 88% at 450 ℃. The products containing carbon were CO_2 and 2-5% $CClF_3$ in every catalyst. The catalyst calcined at 600 ℃ has very large specific surface area , 147 m^2/g. The specific surface area (SSA) of $AlPO_4$ calcined at 1000 ℃ was also large (135 m^2/g), however it was somewhat smaller than that at 600 ℃. After the reaction up to 450 °C, SSA of these catalysts was slightly decreased to 142 and m^2/g and 124 m^2/g, respectively. It is clear that the conversion is independent of SSA of the catalysts.

The acid amounts of the catalysts were examined by

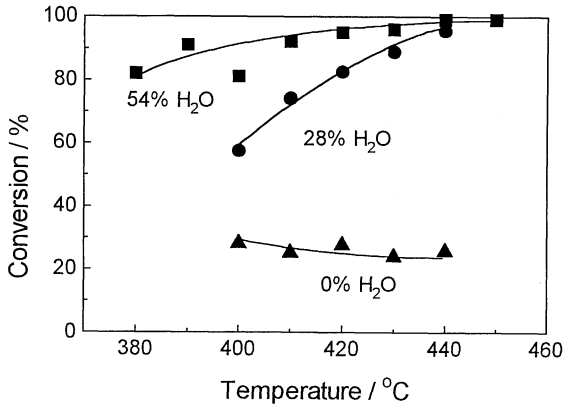

Figure 2. The effects of water vapor concentration on the CCl_2F_2 conversion. Reaction conditions are the same as in Figure 1. Balance N_2.

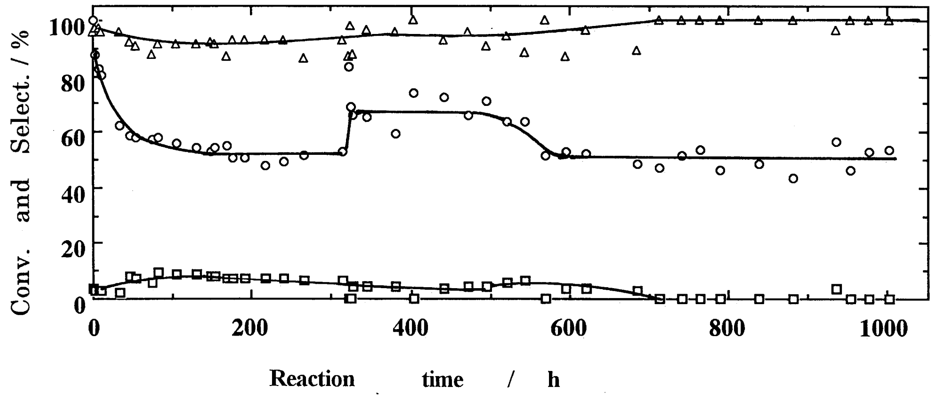

Figure 3. The effect of reaction time. Catalyst: $AlPO_4$(1000 °C) 4.50g; Feed gas (mol%): CCl_2F_2 1.25 (0-315 h) 0.80 (315-1000h), O_2 7.5, H_2O 57.6, N_2 balance, 40 cm^3/min, 400°C; ○ Conversion, △ CO_2 selectivity, □ $CClF_3$ selectivity.

temperature rogrammed desorption (TPD) of NH_3. Sole large desorption peak appeared at 180°C and no NH_3 desorption was observed above 400 °C in the spectrum of $AlPO_4$ calcined at 1000 °C, suggesting no strong acid sites on the surface. So that the relatively weak acid sites are thought to be active for the decomposition of CCl_2F_2.

The effect of water vapor on the reaction was examined and the results are shown in Figure 2. The presence of water vapor strongly affected the catalytic activity. When no water vapor was fed to the reactor, CCl_2F_2 conversion decreased to 1/4 at 400-440 ℃ and equimolar CO_2 and $CClF_3$ were formed. An optimum concentration of water vapor may be larger than 54%. It is of interest that the presence of a large amount of water vapor does not depress the reaction. On the contrary, absence of molecular oxygen in the feed gas gave a small effect on the CCl_2F_2 conversion, that is, the conversion reduced by 20% at 375-400 °C, and did not affect the selectivity. In the case of the ZrO_2-Cr_2O_3 catalyst,[7] CCl_2F_2 conversion increased and disproportionation was much promoted in the absence of water

$$2CCl_2F_2 \rightarrow CCl_3F + CClF_3$$

vapor. No observation of retardation by water vapor over the $AlPO_4$ catalyst may imply that CCl_2F_2 initially interacts with surface hydroxyls. The results of the effects of water vapor and oxygen concentration lead to a tentative conclusion that the basic reaction of the decomposition can be written by the hydrolysis of CCl_2F_2.

$$CCl_2F_2 + 2\,H_2O \rightarrow CO_2 + 2HCl + 2HF$$

Stability of the $AlPO_4$ catalyst was examined. The catalytic reaction was carried out over $AlPO_4$ calcined at 1000 ℃ for about 1000 h and the results are shown in Figure 3. The temperature adopted to the reaction was 400 °C because the CCl_2F_2 conversion did not reach to 100%, in order to clarify the changes in the activity. The conversion decreased by 30% for initial 50 h, but the conversion seems to take a steady value for the following 265 h. The CO_2 selectivity was kept at about 95% until 315 h and the other product was $CClF_3$.

Since it has been known from separate experiments that the $CClF_3$ selectivity increases with the CCl_2F_2 concentration in the feed gas, CCl_2F_2 concentration decreased from 1.25% to 0.80% to improve the CO_2 selectivity at 315 h. After the CCl_2F_2 concentration change, the conversion increased to 70% immedeately and then gradually decreased. The CCl_2F_2 conversion, however, approached to a new steady value at 600 h. The reason for the temporary increment of conversion at around 400 h is not clear at the present stage. The CO_2 selectivity showed some scatter after CCl_2F_2 concentration change but it incresed and reached to near 100% at 700 h as expected.

The many kinds of adsorbed species such as Cl^-, F^-, CCl_nF_m, CCl_nF_mO and so on will be present on the catalyst surface during the decomposition of CCl_2F_2, $CClF_3$ will be formed from the reaction between F^- and $CClF_2$ or CCl_2F_2 on the surface. The decrease of CCl_2F_2 concentration in the feed gas will lead to the reduction of the surface concentrarion of F^- species. The disapperance of $CClF_3$ at 700-1000 h may reflect this situation.

The catalyst before reaction was amorphous. The XRD pattern of the catalyst after reaction for 1000 h consisted of small peaks due to $AlPO_4$, but no diffraction peaks derived from AlF_3 were appeared. This clearly shows that no fluorination of the catalyst takes place.

It is clear that $AlPO_4$ is an effective catalyst for decomposition of CCl_2F_2 with sufficiently long catalyst life. Studies on the reaction mechanism and the origin of the stability against HF are now in progress.

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