CHEMISTRY LETTERS, pp. 2247-2250, 1990.

Decomposition of Freon-12 and Methyl Chloride over Supported Gold Catalysts

Takashi AIDA, Reiji HIGUCHI, and Hiroo NIIYAMA[+*]
Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152
[+]International Cooperation Center for Science and Technology,
Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

Decomposition of Freon-12 (CCl_2F_2) and methyl chloride (CH_3Cl) over gold catalysts were studied. Au/Co_3O_4 showed a high activity for CH_3Cl but a lesser activity for CCl_2F_2 while Au/Al_2O_3 showed moderate activities for the both reactants. The first step of the reactions over Au/Al_2O_3 was considered as substitution of Cl by surface OH group on support surface.

Recently, Freons(chlorofluorocarbons) has been claimed to be notorious on destruction of the ozon layer[1)] and on "greenhouse effect".[2)] Many efforts have been made on cutting down of the total amount of Freon wasted, but few studies are available on Freon decomposition. Catalytic decomposition[3)] is expected as one of the promising method to decompose Freons because it may work in a moderate temperature and give a higher efficiency than other methods such as non-catalytic thermal decomposition.

In these days, it is suggested to use hydrogen containing Freons as alternatives to the Freons of current use because they decompose more easily than the latter. For example, Freon-22($CHCl_2F$) is able to use as an alternative to CCl_2F_2.

Over all decomposition of CCl_2F_2 is described as Eq. 1 and this is considered as hydrolysis. In contrast, decomposition of $CHCl_2F$ may proceed under oxidative atmosphere (Eq. 2).

$$CCl_2F_2 + 2H_2O \longrightarrow CO_2 + 2HCl + 2HF \qquad (1)$$
$$CHCl_2F + H_2O + (1/2)O_2 \longrightarrow CO_2 + 2HCl + HF \qquad (2)$$

In order to decompose a variety of Freons and other halogenated organic compounds as well, catalysts should have both hydrolysis and oxidation activities. Another problem to employ catalysts for the decomposition of

Freons is that highly corrosive halogenated compounds are produced which may cause degradation of catalysts.

Supported gold catalysts is reported to have very high oxidation activity[4)] and it might be possible to donate a hydrolysis function by choosing an appropriate support. Furthermore, gold, known as the most "noble" metal in chemical sense, may be an anti-corrosive material.

In this study, we will report the results of decomposition of CCl_2F_2 and CH_3Cl over the supported gold catalysts. CH_3Cl was employed as a representative of halogenated organic compounds which is expected to decompose through oxidation, though it is not a serious contaminant by itself. We will also discuss about the mechanism of decomposition of the two reactants in a comparative manner.

Supported gold catalysts were prepared by a coprecipitation method reported by Haruta et al.[4)] Reactions were conducted by using a conventional flow system. Runs were done in the presence of water unless otherwise stated. Analysis of the products were done by gas chromatography (TCD). Out gas was passed through an alkali trap, and trapped HCl and Cl_2 were quantified by titration.

Oxidative decomposition of CH_3Cl was carried out to test activities and stabilities of the catalysts. Table 1 summarizes the results for the reaction over various gold catalysts. The temperature giving 50%-conversion, T_{50}, represents the activity of the catalysts. The reaction

Table 1. Temperature and products distribution at 50%-conversion of CH_3Cl for the oxidative decomposition over various gold catalysts

Catalyst	T_{50} /K	Product distribution at T_{50} /%[a)]
11.4 wt% Au/Co_3O_4	580	CO_2(100), HCl[68], Cl_2[32]
Co_3O_4	624	CO_2(100), HCl[78], Cl_2[22]
10.0 wt% Au/Al_2O_3	686	CO_2(24), CO(76), HCl[100]
11.5 wt% Au/Fe_2O_3	735	CO_2(100), HCl[99.7], Cl_2[1.3]
12.0 wt% Au/Cr_2O_3	745	CO_2(94), CO(6), HCl[100]
6.4 wt% Au/SnO_2	745	CO_2(82), CO(18), HCl[100]
14.7 wt% Au/SiO_2[b)]	5%-conversion at 773 K	CO_2(100), HCl[100] at 773 K
Al_2O_3[c)]	17%-conversion at 713 K	CH_4(63), C_2H_4(20), C_3H_6(9), CH_3OH(8), $(CH_3)_2O$(tr.), HCl[100] at 713 K

Feed: 1 vol% CH_3Cl, 16 vol% O_2, balance He. W/F = 3.73 g-cat h/mol.

a) values in ( ) are %-distribution in C-containing products.
values in [ ] are %-distribution in Cl-containing products.

b) prepared by a conventional impregnation.

c) feed: 1 vol% CH_3Cl, 8.5 vol% O_2, 1 vol% H_2O, balance He.
W/F = 1.86 g-cat h/mol.

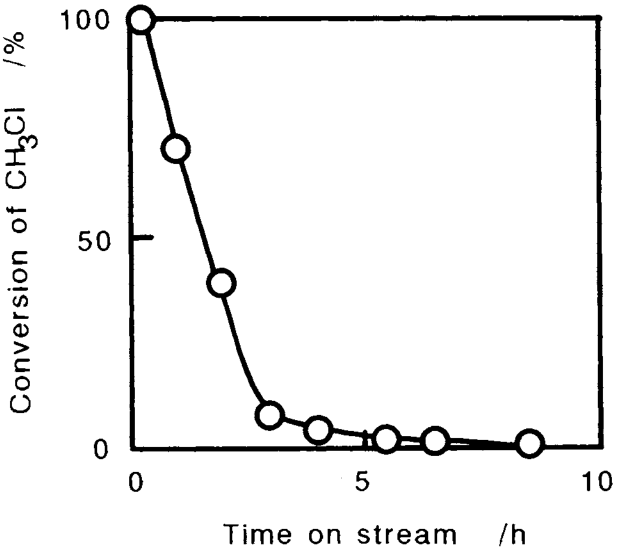

Fig.1. Deactivation of 5 wt% Au/Al_2O_3 for the decomposition of methyl chloride at 573 K as a function of time on stream.
Feed gas: 100 mlNTP/min
(1 vol% CH_3Cl, 2 vol% H_2O, balance air)
Catalyst: 1 g
Pretreatment: none.

was accelerated by the presence of water, and oxidation to CO_2 and CO could not proceed without oxygen. Au/Co_3O_4 and Au/Al_2O_3 showed the highest activity and stability for the reaction. Au/Al_2O_3 showed a steady activity for the reaction at higher temperatures than 700 K. But it declined to zero within several hours when the reaction was conducted at 573 K (Fig.1) and it is regenerated when raising the temperature up to 700 K. The integrated amount of reacted CH_3Cl in the latter case was 4.9 mmol/g-cat, which lies in the some order of magnitude to the amount of OH-groups determined by thermogravimetry (TG). These results might indicate that the reaction was initiated by substitution of Cl by surface OH. The overall scheme of the catalytic reaction may be written as follows:

$$CH_3Cl + HO\text{-}M \longrightarrow CH_3OH + Cl\text{-}M \quad (3)$$

$$Cl\text{-}M + H_2O \longrightarrow HO\text{-}M + HCl \quad (4)$$

$$CH_3OH + O_2 \longrightarrow CO_2 + H_2O \quad (5)$$

where, M means Al or metal atom of support material. At high temperature, steps of Eq. 3 and Eq. 4 proceed easily, completing a catalytic cycle. But at low temperature as 573 K, the reaction becomes stoichiometric, probably due to slow desorption of HCl from the surface. TG measurement indicated that desorption of HCl obviously occurs at higher than 700 K.

Decomposition of CCl_2F_2 were conducted by using Au/Co_3O_4 and Au/Al_2O_3, whose supports showed quite different behaviors. These results were summarized in Fig.2 together with the results for CH_3Cl. Traces of COF_2 and COClF were observed by mass spectroscopy. The curve for CCl_2F_2 was similar to that for CH_3Cl in the case of Au/Al_2O_3. In contrast, Au/Co_3O_4 showed a very high activity for CH_3Cl but very low for CCl_2F_2. These indicated that the rate controlling step (probably the first step) for CCl_2F_2 over Au/Al_2O_3 was similar to that for CH_3Cl.

These are interpreted as follows. There are two possible initiation steps for the decomposition of CH_3Cl; Eq. 3 and Eq. 6. Equation 6 is considered as an oxidation-type, and Eq. 3 as a hydrolysis-type. On the other hand, only hydrolysis-type initiation (Eq. 7) is possible for CCl_2F_2. Au/Al_2O_3 which has many OH-groups being effective for hydrolysis showed high activities for both reactants, while Au/Co_3O_4 has less hydrolysis activity.

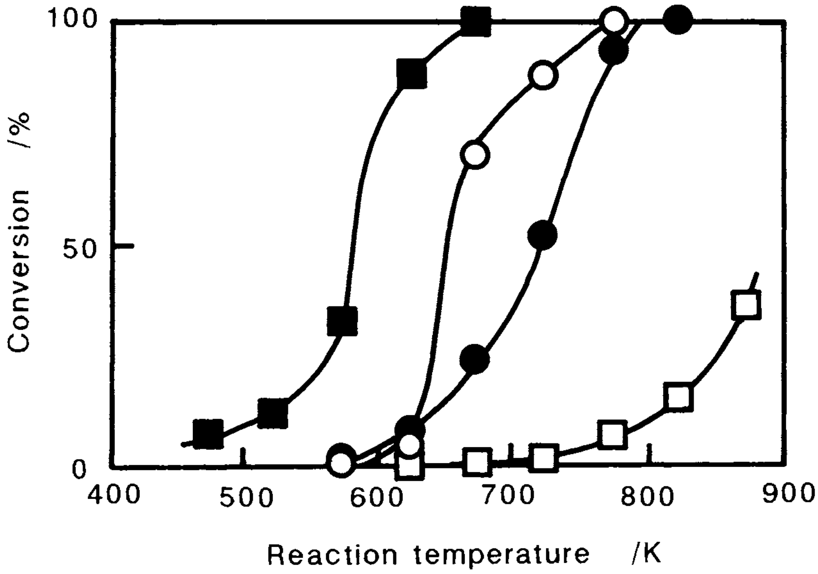

Fig.2. Activity of the catalysts for the decomposition of methyl chloride and Freon-12 as a function of reaction temperature.
Catalyst: 1 g
Oxidative decomposition of CH_3Cl
Feed gas: 100 mlNTP/min, (1 vol% CH_3Cl, balance air)
(●) 5 wt% Au/Al_2O_3, (■) 5 wt% Au/Co_3O_4
Decomposition of CCl_2F_2
Feed gas: 100 mlNTP/min,
(1 vol% CCl_2F_2, 2 vol% H_2O, balance air)
(○) 5 wt% Au/Al_2O_3, (□) 5 wt% Au/Co_3O_4.

$$CH_3Cl + O\text{-}M \longrightarrow CH_2Cl(a) + HO\text{-}M \qquad (6)$$

$$CCl_2F_2 + HO\text{-}M \longrightarrow CClF_2OH + Cl\text{-}M \qquad (7)$$

These assumptions suggest that Al_2O_3 itself also has an activity for the decomposition. In fact, CCl_2F_2 could be decomposed over Al_2O_3. But Al_2O_3 could not complete the oxidative decomposition of CH_3Cl, producing methanol and dimethylether. Supported metals such as gold may be important for an overall decomposition of a variety of halogenated compounds.

References

1) M.J.Molina and F.S.Rowland, Nature, 249, 810(1974).
2) J.R.Hummel and R.A.Reck, Atmos. Environ., 15, 379(1982).
3) S.Okazaki and A.Kurosaki, Chem. Lett., 1989, 1901.
4) M.Haruta, N.Yamada, T.Kobayashi,and S.Iijima, J. Catal., 115, 301(1989).

(Received August 13, 1990)