CHEMISTRY LETTERS, pp. 1545-1546, 1993.

Oxidative Decomposition of Chlorofluorocarbon (CFC-115) in the Presence of Butane over γ-Alumina Catalysts

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The catalytic oxidative decomposition of chlorofluorocarbons (CFC's) was carried out in the presence of butane. The reactivity of CFC's was the following order: CFC-113 > CFC-114 > CFC-115. The reactivity decreased as the content of fluorine in the CFC's increased. γ-Alumina was an effective catalyst among silica and various acidic oxides. Vanadium(V) oxide and tungsten(VI) oxide were found to exhibit a higher activity than the other metals and metal oxides when supported on γ-alumina.

Molina and Rowland1) reported in 1974 that chlorofluorocarbons (CFC's) diffused to the stratosphere, and destroyed the ozone layer. So, recently it becomes very important to develop an economic and reasonable treatment technique for used CFC's.2) In this work, the catalytic oxidative decomposition in the presence of hydrocarbons was proposed as a new treatment method for CFC's, and several acidic oxides and γ-alumina-supported metals and metal oxides were investigated as a catalyst. CFC-113, CFC-114, and CFC-115 were adopted as a CFC reactant.

Silica, γ-alumina, silica-alumina (S-A), mordenite (M), ferrierite (F), Y-type zeolite (Y), L-type zeolite (L), and ZSM-5 zeolite (Z) were employed as a catalyst, and in addition, γ-alumina-supported metals and metal oxides were employed. γ-Alumina-supported metal and metal oxide catalysts were prepared with a conventional impregnation method. The decomposition of CFC's was carried out using a conventional flow reaction apparatus. The reaction conditions were as follows: feed gas, CFC 1.0 ml/min, butane 1.2 ml/min, air 150 ml/min; catalyst weight, 2.0 g; reaction temperature, 573 - 873 K; total pressure, 0.1 MPa.

The reactivity of CFC's including two carbon atoms was examined over γ-alumina catalyst. CFC-113 was completely decomposed at 773 K, and CFC-114 at 723 K, though CFC-115 was not completely decomposed at temperatures as high as 823 K. The order of reactivity of CFC's was as follows:

CFC-113 > CFC-114 > CFC-115.

In the case of CFC-113, the degradation products such as CFC-11 and CFC-12 were observed in the temperature range of 527 to 627 K, while those products were not observed with respect to CFC-114 and CFC-115.

The oxidative decomposition of CFC-115 was investigated over silica and several acidic oxides in the presence of butane. The products including carbon atoms were carbon monoxide and carbon dioxide. All the catalysts were observed to be gradually deactivated with passage of time on stream. γ-Alumina catalyst was deactivated from 96% to 45% during the oxidative decomposition of 4 h. According to the measurement of acidity of the γ-alumina catalyst, the acidity after the oxidative decomposition was less than before the oxidative decomposition. The activity after 4 h on stream is shown in Fig. 1. γ-Alumina catalyst exhibited the highest activity. Silica was not considered to catalyze the oxidative decomposition because its activity was almost the same as when no catalyst was present. Figure 1 suggests that the acidic properties of the catalysts are important for the oxidative decomposition.

All the zeolite catalysts were less active than γ-alumina catalyst though zeolites had stronger acidity than γ-alumina, and accordingly, it was concluded that the oxidative decomposition activity was not necessarily dependent upon the strength of the acidity. ZSM-5 zeolite and mordenite catalysts, which were relatively hydrothermostable, had a high activity among the zeolites employed here. Accordingly, the deactivation of zeolite catalysts might be attributed to the dealumination of zeolite caused by water formed during the oxidative decomposition and the fluorination of aluminum hydroxide by hydrogen fluoride formed likewise.[3]

The metal and metal oxide catalysts were supported on γ-alumina which was the most active as a carrier, and those catalytic performances were examined for the oxidative decomposition. The catalysts which were more active than γ-alumina are shown in Fig. 2. Tungsten(VI) oxide and vanadium(V) oxide catalysts exhibited a very high activity. Butane conversion was more than 90% over the catalysts listed in Fig. 2. The ratios of carbon dioxide to carbon monoxide in the product were various in the different catalysts. In the case of chromium(III) oxide, copper(II) oxide, and the noble metals, the ratios were 100%, while the ratios were between 45% and 75% in the case of the other metal oxides.

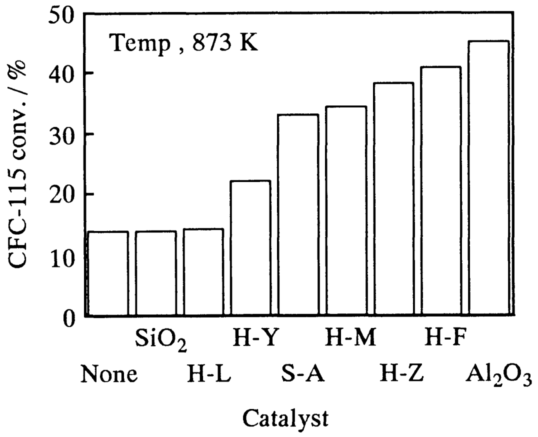

Fig. 1. Activity of silica and acidic oxides for decomposition of CFC-115.

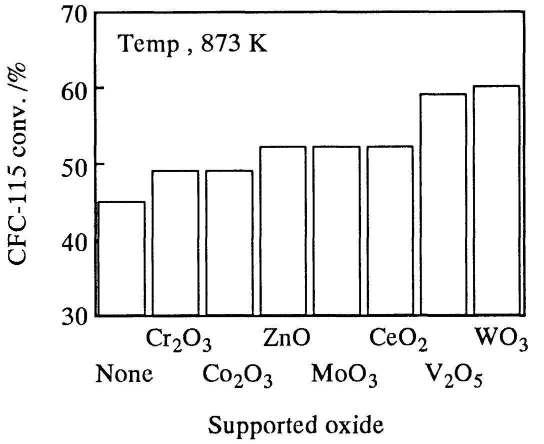

Fig. 2. Activity of γ-alumina-supported catalysts for decomposition of CFC-115.

References

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2) S. Imamura, *Shokubai(Catalyst)*, 34, 464 (1992) and references therein.
3) K. Mizuno, Y. Fujii, M. Tajima, Y. Koinuma, R. Aizawa, S. Kushiyama, S. Kobayashi, and H. Ohuchi, Proc. Fukuoka Int. Symp. '90, Fukuoka, 1990.

(Received June 7, 1993)