CHEMISTRY LETTERS, pp. 17-20, 1988.

Preparation of Hexafluoroacetone by Vapor Phase Oxidation of Hexafluoropropene

Akito KUROSAKI and Susumu OKAZAKI*
Department of Industrial Chemistry, Faculty of Engineering,
Ibaraki University, Nakanarusawa, Hitachi, Ibaraki 316

Hexafluoroacetone was readily formed by circulating a gaseous mixture of hexafluoropropene and oxygen over platinum group metals supported on carbon. Reaction temperatures, ranging from 130 to 170 °C, gave both high selectivity and conversion for the hexafluoroacetone formation using a Pd/C catalyst.

Hexafluoroacetone(HFA) is becoming widely used as a modifier for a copolymer of ethylene and tetrafluoroethylene[1)] and as a cross-linking agent of fluoroelastmer.[2)] It is also utilized as an industrial solvent[3)] and an intermediate for the preparation of certain organofluorine compounds.[2)]

HFA is produced by various reactions[4)] such as fluorination of hexachloroacetone with anhydrous HF, isomerization of hexafluoropropylene oxide, or oxidations of octafluoroisobutylene and hexafluoropropene(HFP) with O_2. Among these reactions, the oxidation of HFP is considered to be the simplest and the most convenient. We have therefore studied on the HFP oxidation catalyzed by platinum group metals, which are known to be generally capable of catalyzing oxidations at lower reaction temperatures.

Various platinum group metals, supported on carbon, were commercially obtained (Nihon Engerhart Co.). Some catalysts were prepared by impregnation method at room temperature. The HFP oxidation was carried out by circulting gaseous HFP (Mitsui-Du Pont Fluorochemical Co., purity $>$ 99.9%) mixed with O_2 over a catalyst (0.5 g, 16-20 mesh) at 110-190 °C in a circulating reactor(volume, 0.32 dm^3). The reaction start and progress were followed by observing the decrease in pressure due to addition of O_2 to the fluoroolefin. The reaction products were analyzed by infrared spectroscopy and gas chromatography using a 8 m column packed with Porapak R.

When V_2O_5, MoO_3,or Ag_2O was used as a catalyst, the reaction proceeded at temperatures higher than 250 °C. No HFA was found at all as an oxidation product. A fair amount of HFA was formed, however, after an induction period when Pd, dispersed on several supports such as carbon, SiO_2 and TiO_2. Besides HFA, a small amount CO_2 was found in the reaction product of the Pd-catalyzed oxidation. Among the supported Pd catalysts, Pd dispersed on carbon gave the most favorable results regarding conversion and selectivity of HFA formation.

Then, catalytic activities of Pt group metals supported on carbon were compared with each other. As is shown in Table 1, the Pt/C catalyst was particularly effective in shortening the induction period. The commercial catalysts in general showed higher activities even when they contained a smaller amount, such as 0.5%, of an active metal component.

Table 1. Oxidation of hexafluropropene over carbon-supported Pt group metals

Catalyst[a)]	Reaction time /min	Induction period/min	Conversion of HFP/mol%	Selectivity for HFA formation/mol%
0.5%Pd/C(Com.)[b)]	150	120	54.7	87.4
2.0%Pd/C(Com.)	120	55	55.1	83.3
5.0%Pd/GC-1(450)	120	60	48.4	86.7
2.0%Pt/C(Com.)	60	30	42.5	82.1
5.0%Pt/GC-1(500)	60	10	54.4	96.8
0.5%Rh/C(Com.)	120	50	51.4	82.8
5.0%Rh/GC-1(500)	120	80	21.5	94.8
0.5%Ru/C(COm.)	120	50	63.2	80.9
5.0%Ru/GC-1(500)	150	100	30.2	67.1
2.0%Ir/C(Com.)	60	25	47.5	85.1

a) Unless otherwise noted by numbers in parenthese, the reduction in H_2(400 Torr) was carried out at 450 °C. Reaction conditions were the same as those described in Table 1. b) Com. denotes the catalyst sample was a commercial product.

The reaction temperatures had a significant effect as is exhibited in Fig.1 which shows the results of the reaction promoted by the Pd/C catalyst. The catalyzed reaction proceeded well at 130 °C or above, but temperatures higher than 170 °C were unsuitable because of the activation of CO_2 formation. The molar ratio of O_2 to HFP, P_{O_2}/P_{HFP}, in the range of about 0.8 to 1.5 was preferable to obtain high selectivity of the HFP formation together with high HFP conversion(Fig.2).

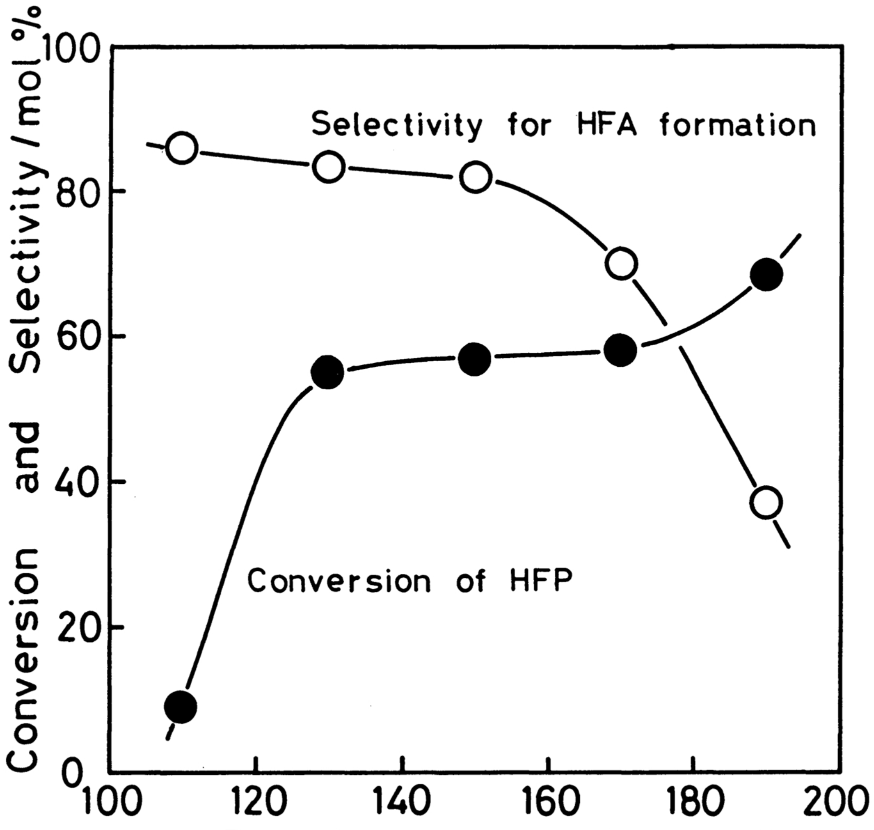

Fig.1. Effect of reaction temperature on catalytic activity.

Reaction conditions
Catalyst : 2%Pd/Carbon (0.5 g), Time: 2 h ,
Initial pressure : 258 Torr (O_2/HFP = 1).

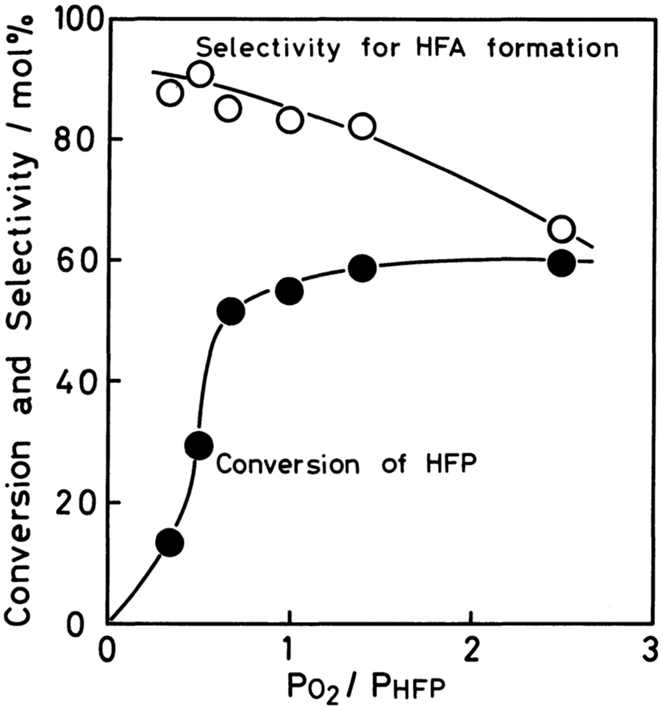

Fig. 2. Effect of O_2 pressure on catalytic activity.

Reaction conditions
Catalyst : 2%Pd / Carbon(0.5 g) , Time : 2 h,
Temperature : 130 °C ,
Initial pressure : 150−414 Torr (P_{HFP} = 129 Torr)

The authors are grateful to Mitsui-Du Pont Fluorochemical Company for financial support extended to this study.

References

1) E.G.Howard and Jr.H.Del, U.S.Patent 3 322 721(1967).

2) Kirk-Othmer, Encyclopedia of Chemical Industry, 3rd ed, Wiley Interscience, New York(1979), Vol.8, p.508 and p.881.

3) W.J.Middleton, U.S.Patent 3 418 337(1968).

4) C.G.Krespan and W.J.Middleton, Hexafluoroacetone, in Fluorine Chemistry Reviews, ed by P.Tarrant, Marcel Dekker, New york(1967), p.145.

(Received September 9, 1987)