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Bi-Pd Catalyst for Selective Hydrodechlorination of 1,1,2-Trichlorotrifluoroethane to Trifluoroethene, a Key Intermediate to 1,1,1,2-Tetrafluoroethane as a CFC Replacement for Refrigeration

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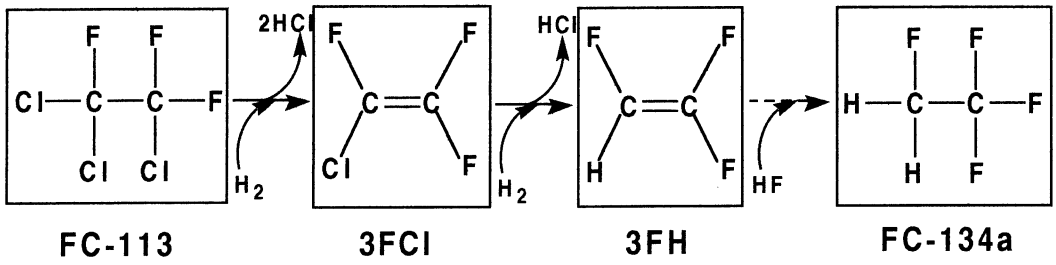
Trifluoroethene, a key intermediate to 1,1,1,2-tetrafluoroethane (FC-134a), was catalytically synthesized with 80 - 90% selectivity at 80 - 100% conversion in the hydrodechlorination of 1,1,2-trichlorotrifluoroethane(FC-113) at 200 - 250 °C under an atmospheric pressure over Bi-Pd (Bi/Pd = 0.4 - 0.6) supported on metal oxides.

Chlorofluorocarbons(CFCs) are widely used for refrigeration, air-conditioning, propellants, form-blowing, and cleaning agents due to its nontoxic, stable, condensable, and incombustible characters. However, the usage of CFCs has to be discontinued by the year of 2000 because of the global environmental problems, *e.g.*, destructive effect on the stratospheric ozone layer promoted by chlorine atom dissociated from CFCs.[1] There are several candidates for the alternatives to the CFCs, bearing no chlorine atom in a molecule and matching the physical properties. FC-134a[2] has been chosen by the most of the CFC manufacturers as a replacement of dichlorodifluoromethane(FC-12) for refrigeration and could be synthesized from a number of materials.[3] FC-113, one of the CFCs, could be converted to chlorotrifluoroethene(3FCl) and to trifluoroethene(3FH) *via.* hydrodechlorination and to FC-134a *via.* hydrofluorination (see Scheme 1).



Scheme 1. A Route to FC-134a from FC-113.

Table 1. Product Selectivities[a] of Hydrodechlorination of FC-113 on Pd Catalyst modified by various Metal Additives

Pd content /wt%	Modifier	M/Pd[b]	Support	Temp /°C	Conv. /%	Selectivity[c]/%		
						3FCl	3FH	123a
0.5	none	0	Al_2O_3	150	25	0	11	8
0.5	$TlNO_3$	4	Al_2O_3	250	15	97	2	0
5.0		4	Al_2O_3	200	13	100	0	0
				250	40	**99**	1	0
		0.5	Al_2O_3	200	60	1	**72**	6
0.5	$SnCl_2$	4	Al_2O_3	250	14	**87**	8	0
5.0		1	Al_2O_3	250	21	70	24	1
0.5	$Cu(NO_3)_2$	4	Al_2O_3	250	14	78	19	3
5.0		4	Al_2O_3	200	31	58	32	6
0.5	$InCl_3$	4	Al_2O_3	250	13	61	24	3
5.0		1	Al_2O_3	230	15	**90**	0	1
0.5	$CdCl_2$	4	Al_2O_3	200	8	64	10	7
				250	21	54	27	3
5.0	$AgNO_3$	1	Al_2O_3	200	44	59	33	1
				230	64	62	31	1
0.5	$Pb(NO_3)_2$	4	Al_2O_3	250	14	54	39	4
5.0		1	Al_2O_3	200	24	51	43	4
0.5[d]	$HgCl_2$	4	Al_2O_3	250	45	8	**83**	5
5.0[d]		2	Al_2O_3	200	31	17	80	1
0.5	$BiCl_3$	2	Al_2O_3	200	<2	-	-	-
5.0		0.4	Al_2O_3	200	46	12	**86**	1
				230	**82**	11	**82**	1
2.0	$BiCl_3$	0.5	SiO_2	200	59	8	78	5
				230	81	11	80	5
2.0[e]	$BiCl_3$	0.5	SiO_2	230	96	2	85	3
				250	**99**	2	**90**	2
2.0	$BiCl_3$	1.0	SiO_2	200	1	32	68	0
				250	13	43	56	0

a) At the steady state. b) Atomic ratio. c) 3FCl, 3FH, and 123a are abbreviation for chlorotrifluoroethene, trifluoroethene, and 1,2-dichloro-1,1,2-trifluoroethane, respectively. d) Activity fell down gradually. e) Ratio of flow rate of H_2 to FC-113 is 2.4.

It has been reported that 3FCl was formed from FC-113 on charcoal,[4] Ni, Fe, Co, and Cr[5] catalysts with high selectivity of more than 90% at a high temperature between 400 - 500 °C. In

contrast, there has not found an efficient catalyst to promote the direct reaction of FC-113 to 3FH.[6] In this communication, we report that palladium catalysts modified with selected metals such as Bi, Hg, and Tl promote the hydrodechlorination of FC-113 with very high selectivity to 3FH at a mild temperature between 200 - 250 °C under an atmospheric pressure.

Palladium catalysts used were 0.5 and 5 wt%Pd/Al_2O_3 purchased from N.E.Chemcat Co. and 2 wt%Pd/SiO_2 prepared by the conventional impregnation of $PdCl_2$ with silica gel. The Pd catalysts were successively impregnated with various metal salts. A catalyst was placed on a fixed bed in a reactor and reduced in a hydrogen stream at 300 °C for 2 h prior to the reaction. The reaction was carried out under an atmospheric pressure by using a continuous flow reactor system. The flow rate of FC-113 and the weight of catalyst were 7 ml/min and 4 g, respectively, in the case of 0.5 wt%Pd/Al_2O_3 and its derived catalysts. In other cases, these were 9 - 10 ml/min and 1 - 1.3 g, respectively. A ratio of flow rate of H_2 to FC-113 was 2. Products were analyzed by a GC with a packed column. The molar conversion of FC-113 and the selectivity for each component were calculated as fractional parts of the reactant converted and of each component in the converted, respectively.

Hydrodechlorination of FC-113 over 0.5 wt%Pd/Al_2O_3 catalyst gave a mixture of 1,1,2-trifluoroethane(FC-143) and 1,1-dichloro-2-fluoroethane with 44 and 41% selectivities, respectively, in addition to a small amount of a desired product, 3FH, and 1,2-dichloro-1,1,2-trifluoroethane(FC-123a) at 150 °C. Twenty four additives of metal salts were examined for impregnating 0.5 and 5 wt%Pd/Al_2O_3 catalysts. The conversions of FC-113 were apparently suppressed by the impregnation. The selectivities for the formation of 3FH and 3FCl were markedly enhanced by the addition of the selected metals such as Tl, Sn, Cu, In, Cd, Ag, Pb, Hg, Bi, which were classified in the late Ib - IIIb metals in the periodic table (see Table 1). In particular, 3FH was formed in 83, 86, and 72% selectivities on Hg-, Bi-, and Tl-Pd (Tl/Pd=0.5) /Al_2O_3, while 3FCl was in 87, 90, and 99% on Sn-, In-, and Tl-Pd (Tl/Pd=4) /Al_2O_3, respectively. An yield of 3FH on the Bi-Pd/Al_2O_3 catalyst was calculated to be 67% at 230 °C.

To improve the yield and selectivity of 3FH, the 2 wt%Pd/SiO_2 catalyst was successively impregnated with various amount of Bi (see the lower part of Table 1). It was found that there was an optimum content of Bi in the Pd catalyst to promote the reaction with high selectivity of 3FH and with high conversion of FC-113. The highest yield of 3FH was observed to be 90% on 2 wt%Pd/SiO_2 modified by Bi of Bi/Pd = 0.5. This high selectivity at the high conversion was maintained for at least 10 h, as

shown in Fig. 1. This figure also suggested that the increase in selectivity of 3FH came from the expense of 1,1,2-trifluoroethane(FC-143).

In summary, FC-113 which is named as a malignant chemical to global environment was selectively converted to 3FCl, a raw material for polymer, with more than 87% selectivity on Sn-Pd/Al_2O_3, In-Pd/Al_2O_3, and Tl-Pd/Al_2O_3 (Tl/Pd>1) catalysts. More importantly, FC-113 was selectively transformed to 3FH, a key intermediate to FC-134a and a raw material for polymer, with more than 80% selectivity on Hg-, Bi-Pd/Al_2O_3, and Bi-Pd/SiO_2 catalysts at mild temperatures between 200 - 250 °C. It was noteworthy that 3FH was produced in 90% selectivity at 99% conversion on 2 wt%Pd/SiO_2 modified by bismuth of Bi/Pd = 0.5.

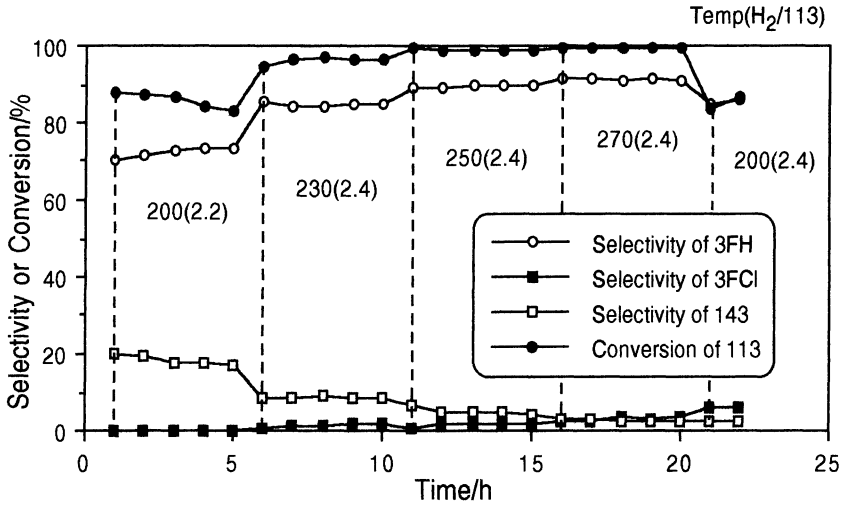


Fig. 1. Hydrodechlorination of FC-113 over Bi-2wt%Pd/SiO_2 (Bi/Pd = 0.5).

References

1)*Chem. Brit.*, **26**, 731(1990).

2)Refer to PCR catalog with respect to numbering for fluorocarbons.

3)*Chem. Eng. News*, **July 24**, 7(1989): *Chem. Brit.*, **26**, 406(1990).

4)T.Morimoto, S.Morikawa, and T.Funayama, *Jpn. Patent* 60185734(1985); *Chem. Abstr.*, **104**, 109005x(1986).

5)M.Ueda, S.Tomioka, Y.Morikawa, M.Sudo, and T.Ikawa, *Chem. Lett.*, **1990**, 870; Y.Takita, H.Yamada, M.Hashida, and T.Ishihara,*ibid.*,**1990**,715.

6)W.J.Cunningham, R.F.Piskorz, and A.M.Smith, *Eur. Patent* 53657; *Chem. Abstr.*, **97**, 162332q(1982); C.Gervasulli, *Eur. Patent* 253410; *Chem. Abstr.*, **109**, 8377i(1988); S.Sato and M.Ogura, *Jpn. Patent* 02178238.

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