Hydrodechlorinative dimerization of 1,1,1-trifluorohaloethanes over Ru/SiO_2 catalyst

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The hydrodechlorination of CCl_3–CF_3 (CFC-113a) was studied over silica-supported metal catalysts. Pd/SiO_2 and Pt/SiO_2 catalysts showed high activity for the replacement reaction of the chlorine atoms in CFC-113a with hydrogen. On the other hand, Ru/SiO_2 selectively catalyzed the dimerization and gave CF_3–CCl=CCl–CF_3 and CF_3–CCl_2–CCl_2–CF_3. $CHCl_2$–CF_3 (HCFC-123) and CCl_2F–CF_3 (CFC-114a) also dimerized into the corresponding C_4-dimers over the catalyst. The reactivity of CF_3-having haloethanes on the Ru/SiO_2 decreased in the order of CFC-113a $\gg$ HCFC-123 > CFC-114a $\gg$ HCFC-124. The selectivity of dimerization decreased with decreasing the reactivity of substrates.

Keywords: ruthenium catalyst; hydrodechlorination; dimerization; chlorofluoroethanes; hydrochlorofluoroethanes

1. Introduction

Various technologies have been proposed for the recovery and the decomposition of chlorofluorocarbons (CFCs). Hydrodechlorinations of CFCs have been studied to obtain hydrochlorofluorocarbons, hydrofluorocarbons and fluoroolefins, which are valuable as CFC alternatives and monomers of fluorine-containing polymers. The hydrodechlorinations are known to be catalyzed by noble metals [1–8]. In particular, Pd is very active for the Cl/H replacement, replacement of chlorine atoms in CFC with hydrogen atoms, for example, from CCl_2F–CF_3 (CFC-114a) to CH_2F–CF_3 (HFC-143a) [4]. Besides noble metals, Ni is active for the hydrodechlorinations and it promotes the hydrodechlorination giving fluoroolefins instead of Cl/H replaced products [10–12].

We have studied the hydrodechlorination of CCl_2F–$CClF_2$ (CFC-113) over supported metal catalysts and reported that Ni/SiO_2 catalyzes the conversion of CFC-113 to CClF=CF_2 (CFC-1113) with high selectivity (above 95%) [11]. Recently, we have found that CFC-113a (CCl_3–CF_3), an isomer of CFC-113, dimerized in the hydrodechlorination over the Ni/SiO_2 catalyst [13]:

$$2CCl_3-CF_3+2H_2 \rightarrow CF_3-CCl=CCl-CF_3+4HCl \quad (1)$$

The dimerization of halogenated alkanes is known to proceed thermally [14] or photo-chemically [15,16] and stoichiometrically with metallic zinc [17]. However, the catalytic dimerization of CFCs has been only dealt with as a side reaction [8]. In the present work we wish to report the catalytic properties of supported metal catalysts and the reactivity of the halogenated methyl group in the hydrodechlorinative dimerization of CF_3-having haloethanes.

2. Experimental

2.1. Catalyst preparation

Four silica-supported metal catalysts, 0.5 wt% Pd/SiO_2, 5 wt% Pt/SiO_2, 5 wt% Ru/SiO_2 and 10 wt% Ni/SiO_2, were used in this study. These catalysts were prepared by the incipient wetness impregnation of Aerosil 200 (Japan Aerosil, surface area 200 m^2 g^{-1}) with an aqueous solution of $[Pd(NH_3)_4]Cl_2$, $[Pt(NH_3)_4]Cl_2$, $RuCl_3 \cdot nH_2O$, or $Ni(NO_3)_2 \cdot 6H_2O$. The water was allowed to evaporate with continuous stirring at 343 K in air. The resulting paste was dried overnight at 383 K, and was calcined at 723 K in air for 6 h. The catalysts were tableted under 300 kg cm^{-2}, then crushed and sieved. A fraction of 32–62 mesh was used for reactions.

2.2. Catalytic reaction

All CFCs and HCFCs were special grade reagents supplied from Daikin Industries, Ltd. and used without further purification. The reactions of CCl_3–CF_3 (CFC-113a), $CHCl_2$–CF_3 (HCFC-123), CCl_2F–CF_3 (CFC-114a), and $CHClF$–CF_3 (HCFC-124) with hydrogen were carried out under atmospheric pressure using a conventional flow-type reaction system with a quartz glass reactor (12 mm i.d.). The catalyst samples were heated in a H_2 stream (30 cm^3 min^{-1}) from room temperature to 723 K at the heating rate of 2.5 K min^{-1} and kept at the final temperature for 2 h. They were cooled in the H_2 stream to reaction temperatures and exposed to a premixed feed gas. The reactions were carried out under the following conditions: temperature, 303–623 K; feed composition (molar ratio), Ar : H_2 : CFC = 6 : 6 : 1;

total flow rate, 65 $cm^3\ min^{-1}$; catalyst amount, 1 g. The compositions of the feed and effluent gases were analyzed with a gas chromatograph (Shimadzu GC-9A) equipped with a TCD detector and a Gaskuropack 54 column. The products were identified with a GC-MS (Hitachi 663-30 GC and Hitachi M-80 MS) using the same column.

3. Results and discussion

3.1. Hydrodechlorination of CFC-113a

Pd, Pt, Ru, and Ni/SiO_2 differed widely in their catalytic activities as shown in fig. 1. The hydrodechlorination of CCl_3–CF_3 (CFC-113a) took place even at room temperature over Pd/SiO_2 and at temperatures higher than 423 K over Ni/SiO_2. The reaction gave a variety of products but no compounds resulted by the reaction on the CF_3 group of CFC-113a. Chlorine atoms in CFC-113a were replaced with hydrogen over all catalysts employed here to give $CHCl_2$–CF_3 (HCFC-123), CH_3–CF_3 (HFC-143a), and CH_2Cl–CF_3 (HCFC-133a). In addition, hydrodechlorinative dimerization took place over Ru/SiO_2 and Ni/SiO_2 to form C_4 compounds.

Pd/SiO_2 catalyzed the Cl/H replacement reaction and showed no activity for the dechlorinative dimerization. The Cl/H replacement reaction predominantly gave the tri-replaced product HFC-143a even at a low conversion level (10%). Because the reactivities of the mono-replaced and di-replaced products (HCFC-123 and HCFC-133a) are, respectively, lower and probably much lower than that of CFC-113a, as described in the next section this paper, the product distribution seems not to result from the consecutive Cl/H replacement through the readsorption of desorbed molecules. Similar observations were reported for the hydrodechlorinations of other CFCs [4,5]. Gervasutti et al. [4] investigated the reaction of CCl_2F–CF_3 (CFC-114a) with hydrogen over Pd/C and found that CH_2F–CF_3 and

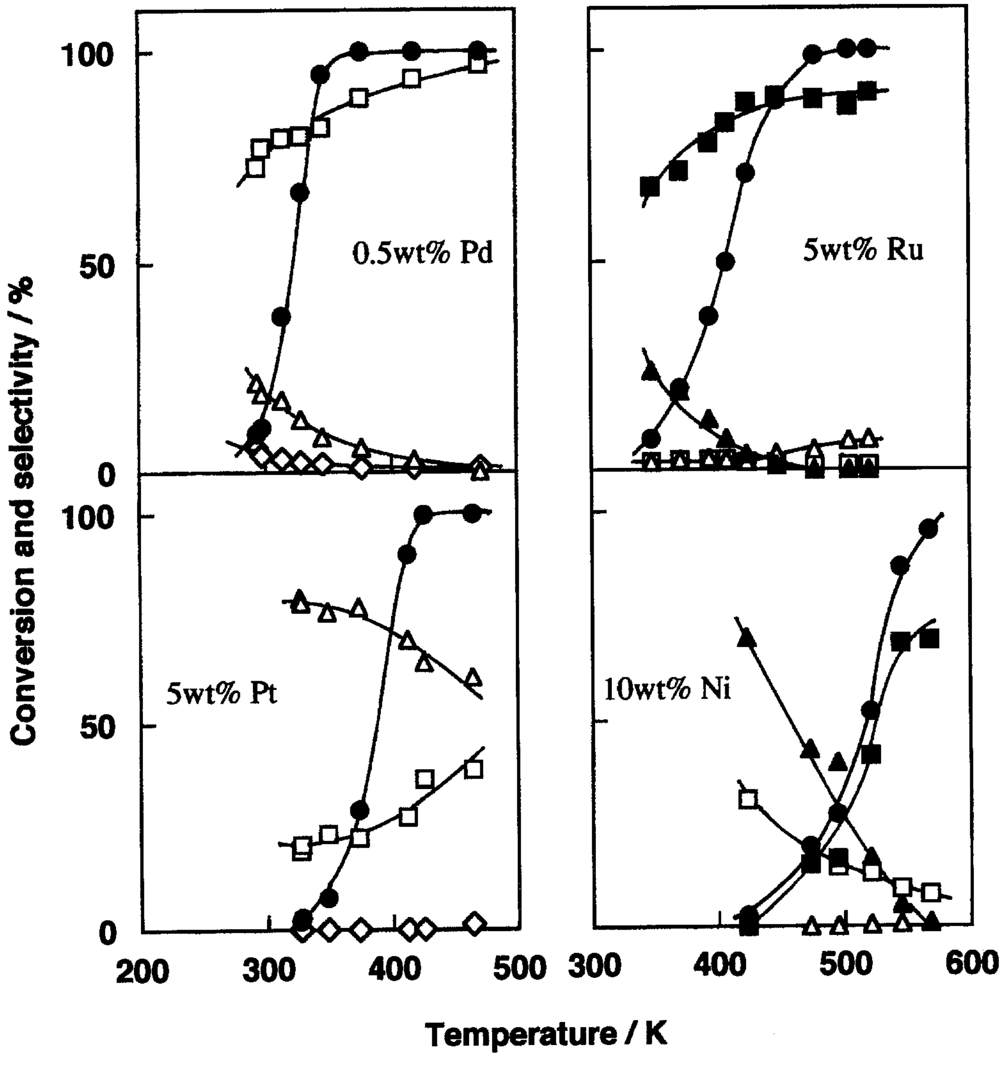

Fig. 1. Hydrodechlorination of CFC-113a over silica-supported metal catalysts. (●) Conversion and selectivity to (△) HCFC-123, (◇) HCFC-133a, (□) HFC-143a, (▲) CFC-316, (■) CFC-1316.

CH_3-CF_3 were produced as main products without mono-replaced product $CHClF-CF_3$. Coq et al. [5] reported that over supported Pd catalysts CCl_2F_2 (CFC-12) converted into CH_2F_2 and CH_4 predominantly and scarcely into $CHClF_2$, and that $CHClF_2$ and CH_2F_2 were much less reactive than CCl_2F_2 on the Pd surface.

The activity of Pt/SiO_2 was much lower than that of Pd/SiO_2 although the loading of Pt was 10 times as high. Pt/SiO_2 also catalyzed the Cl/H replacement reaction but the product distribution was different from that observed with Pd/SiO_2. The selectivity for HCFC-123 formation was as high as 70–80% at relatively lower temperatures and decreased gradually with increasing the reaction temperature. The rest of products consisted of HFC-143a for the most part and only a trace amount of HCFC-133a was detected. The results that the two extreme (single and total Cl/H replacement) products were formed predominantly over Pd/SiO_2 agree with the observations for Pt/C [6]. Weiss et al. [7] have reported similar product distributions for the hydrodechlorination of CCl_4 over Pt/η-Al_2O_3 and Pt wire, that is, the mono-replaced product $CHCl_3$ and the total replacement product CH_4 are predominant.

The catalytic activity of Ru/SiO_2 was completely different from those of Pd/SiO_2 and Pt/SiO_2. Ru/SiO_2 catalyzed the hydrodechlorinative dimerization selectively to give cis- and trans-$CF_3-CCl{=}CCl-CF_3$ (CFC-1316) and $CF_3-CCl_2-CCl_2-CF_3$ (CFC-316). The selectivity for dimerization was as high as 90% and the Cl/H replaced products, HCFC-123 and HFC-143a, were formed in only small quantities at all reaction temperatures. Ni/SiO_2 also catalyzed the dimerization as reported previously [13], but the catalytic activity was so poor that the reaction temperature giving the same conversion level was 120 K higher with Ni/SiO_2 than with Ru/SiO_2. Deposition of carbonaceous materials was observed especially at higher temperatures and Ni/SiO_2 was accordingly deactivated with reaction time.

As seen in fig. 1, the selectivity for the saturated dimer CFC-316 decreased and that for the unsaturated dimer CFC-1316 increased with reaction temperature. Similar changes of the selectivities with increasing contact time were observed in a supplemental study using the same catalyst. CFC-316 has vic-dichlorine atoms, two Cls bonded separately to two adjacent carbon atoms, and $CCl_2F-CClF_2$ (CFC-113) as well. CFC-113 readily reacts with hydrogen over supported Ru and Ni catalysts to give $CClF{=}CF_2$ (CFC-1113) [7,11]. These facts suggest that CFC-316 is a primary product of the dimerization and is consecutively dechlorinated to CFC-1316.

Although the mechanisms of hydrodechlorination of CFC-113a over metal catalysts are not well understood at this stage of investigation, the first step of the reaction is considered to be the dissociative adsorption to form $\cdot CCl_2-CF_3$ species on the catalyst surface. It is of special interest that the $\cdot CCl_2-CF_3$ reacts with hydrogen over Pd and Pt catalysts to give Cl/H replaced products and undergoes coupling over Ru and Ni catalysts to give C_4-dimers.

3.2. Hydrodechlorination of CF_3-having haloethanes over Ru/SiO_2

The reactions of haloethanes composed of CF_3 and variously halogenated methyl groups were conducted using the Ru/SiO_2 catalyst. The comparative results are shown in table 1, which summarizes the temperature giving 30% conversion of the haloethane (T_{30}) and the selectivity at T_{30}. $CHClF-CF_3$ (HCFC-124), which has only one chlorine atom, was most inactive giving the low conversion of 8.5% even at the relatively high temperature of 573 K. The table shows that the reactivity of CF_3-having haloethanes for a Ru catalyst decreases in the order of CFC-113a $\gg$ HCFC-123 $>$ CFC-114a $\gg$ HCFC-124, that is, the reactivity of the halogen-substituted methyl group lowers markedly with decreasing the number of chlorine atoms in it. Gervasutti et al. [4] conducted the hydrodechlorinations of CCl_2F-CF_3 (CFC-114a) and $CClF_2-CClF_2$ (CFC-114) and observed that CFC-114 was more inactive compared to CFC-114a. Their studies also indicate that $CClF_2-$ is more inactive than CCl_2F-.

In the hydrodechlorination of CF_3-having haloethanes other than CFC-113a, a Cl/H replacement reaction proceeded predominantly. The main products were mono-replaced products shown as 1(Cl/H) in table 1, that is, CH_2Cl-CF_3 (HCFC-133a), $CHClF-CF_3$ (HCFC-124), and CH_2F-CF_3 (HFC-134a) formed from HCFC-123, CFC-114a, and HCFC-124, respectively.

Table 1
Hydrodechlorination of CF_3-having haloethanes over 5 wt% Ru/SiO_2

Reactant	T_{30} [a] (K)	Selectivity [b] (%)				
		SD	USD	1(Cl/H)	2(Cl/H)	3(Cl/H)
CCl_3-CF_3	386	12	77	4	0	3
$CHCl_2-CF_3$	491	7	4	56	27	–
CCl_2F-CF_3	514	4	1	87	1	–
$CHClF-CF_3$	8.5% at 573 K	0	0	73	–	–

[a] Reaction temperature giving 30% conversion of the reactant.

[b] SD and USD are saturated and unsaturated dimer, respectively. 1(Cl/H), 2(Cl/H) and 3(Cl/H) are mono-, di- and tri-replaced products of the reactants, respectively.

The dimers formed as minor products were a couple of CF_3–CHCl–CHCl–CF_3 (HCFC-336) and CF_3–CH=CH–CF_3 (CFC-1336) in the reaction of HCFC-123 and a couple of CF_3–CHF–CHF–CF_3 (HFC-318) and CF_3–CF=CF–CF_3 (FC-1318) in the reaction of CFC-114a. The saturated and unsaturated dimers seem to be formed through a reaction pathway similar to the dimerization of CFC-113a, which includes the coupling of dissociatively adsorbed species to form a saturated dimer and subsequent dechlorination of the desorbed species to form a double bond. Because the coupling rate is determined by the surface concentration of the dissociative species, the observed difference in the selectivity might be explainable by the difference in the reactivity of haloethanes, assuming the competitive adsorption of haloethane and hydrogen. It is likely that haloethanes of lower reactivity adsorb on Ru at the lower surface coverage, resulting in the higher coverage of adsorbed hydrogen, and hence the adsorbed species do not dimerize appreciably and are attacked by hydrogen to form the Cl/H replacement products.

4. Conclusions

Ru supported on silica is a highly selective and effective catalyst for the hydrodechlorinative dimerization of CFC-113a to C_4-dimers, CFC-1316 and CFC-316. Pd/SiO_2 and Pt/SiO_2 catalysts showed high activity for the replacement reaction of the chlorine atoms in CFC-113a with hydrogen, but were not active for the dimerization. The reactivity of CF_3-having haloethanes for the hydrodechlorination over Ru catalyst decreased in the order of CFC-113a $\gg$ HCFC-123 $>$ CFC-114a $\gg$ HCFC-124. Thus the reactivity is attributable to the number of chlorine atoms in the halogen-substituted methyl group. The hydrodechlorinative dimerization also proceeded when HCFC-123 and HCFC-124 were reacted as a substrate. However, the selectivity to dimerization decreased with decreasing the reactivity of substrates.

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