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Catalysis Today 88 (2004) 111–120

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Hydrodechlorination of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) over supported ruthenium and other noble metal catalysts

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Abstract

The hydrodechlorination of $CCl_2F–CClF_2$ (CFC-113) was studied using silica- and activated carbon-supported Ru, Rh, Pd, and Pt catalysts. The activity of the catalysts changed with time-on-stream. Ru was most stable among the four noble metals and gave a simple product distribution yielding $CClF{=}CF_2$ (CFC-1113) and $CHClF–CClF_2$ (HCFC-123a) as main products. Over silica-supported Ru, CFC-1113 yield decreased gradually with time-on-stream but HCFC-123a yield did not change throughout the reaction, suggesting that these products were formed on different sites of Ru. XRD studies and temperature-programmed reduction of the spent catalyst revealed that the deactivation was caused by halogen-containing carbonaceous species accumulated on the Ru surface during the reaction. The carbonaceous species seemed to be formed on the active site for CFC-1113 formation. Because CFC-1113 selectivity was higher over the catalyst having higher Ru dispersion, it was assumed that the hydrodechlorination of CFC-113 is structure-sensitive and CFC-1113 formation is promoted by Ru having highly unsaturated coordination sphere.

Keywords: Hydrodechlorination; Trichlorotrifluoroethane; Chlorofluorocarbon; Ru catalyst; Noble metal catalyst

1. Introduction

Catalytic hydrodechlorination is one of the options for the safe disposal of chlorofluorocarbon (CFC) waste and involves the substitution and abstraction of halogen atoms in CFCs with hydrogen. The substitution of chlorine atoms in C_2 CFCs with hydrogen produces hydrofluorocarbon (HFC) available for CFC replacements, e.g.

$$CCl_2F–CF_3\ (\text{CFC-114a}) + 2H_2 \rightarrow CH_2F–CF_3(\text{HFC-134a}) + 2HCl \quad (1)$$

The abstraction of chlorine atoms from two halogen-substituted methyl groups of C_2 CFCs produces halogen-substituted ethylene available for fluorinated polyethylene syntheses, e.g.

$$CCl_2F–CClF_2\ (\text{CFC-113}) + 1.5H_2 \rightarrow CHF{=}CF_2\ (\text{HFC-1123}) + 3HCl \quad (2)$$

For the disposal of C_1 CFCs, complete degradation seems to be rather realistic because it is not easy to convert them into valuable chemicals by halogen substitution with hydrogen. The degradation is usually conducted by the reaction of CFC with water vapor and oxygen using acidic catalysts. The reaction corresponds mechanistically to the hydrolysis-initiated oxidation and produces corrosive compounds in-

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doi:10.1016/j.cattod.2003.11.004

cluding hydrogen fluoride that damages the catalyst seriously. Takita et al. [1–4] have investigated the degradation of CFCs extensively and found that metal phosphates show the high activity and high stability for the reaction. They have predicted the high corrosion resistibility of metal phosphates by calculating the thermodynamic equilibria of reactions between various acidic compounds and hydrogen fluoride.

It has been known that small amounts of C_{2+} products are formed during the hydrodechlorination of CCl_2F_2 (CFC-12) over Pd [5] and Pd alloy [6] catalysts. Morato et al. [7] reported that the hydroconversion of $CHClF_2$ (HCFC-22) and CFC-12 over Ni catalysts yielded both halogen/hydrogen substitution and hydrodechlorinative dimerization products. Kulkarni et al. [8] investigated the hydrodechlorination of CFC-12 over noble metal catalysts and showed that the selectivity to C_{2+} oligomerization products varied widely depending on the type of metal. Recently, Kulkarni et al. [9] found that the selectivity to C_2–C_3 hydrocarbons attained ca. 50% during the hydrodechlorination of CFC-12 over an activated carbon-supported Pt–Co catalyst. The hydrodechlorinative oligomerization is interesting for the transformation of C_1 CFCs into useful chemicals.

CCl_2F–$CClF_2$ (CFC-113) makes up major portion of C_2 CFC wastes. The hydrodechlorination of CFC-113 gives a variety of products by halogen/hydrogen substitution, and dehalogenative olefin formation. The isomerization, Eq. (3), disproportionation, Eq. (4), of the reactants, and subsequent hydrodehalogenation are also possible to take place.

$$CCl_2F\text{–}CClF_2\ (\text{CFC-113}) \rightarrow CCl_3\text{–}CF_3\,(\text{CFC-113a}) \tag{3}$$

$$2CCl_2F\text{–}CClF_2(\text{CFC-113}) \rightarrow CClF_2\text{–}CClF_2(\text{CFC-114}) + CCl_2F\text{–}CCl_2F\ (\text{CFC-112}) \tag{4}$$

This complexity seems to be a reason why the reaction of CFC-113 has not been investigated extensively comparing to that of C_1 CFC such as CFC-12. CFC-113 is hydrodechlorinated selectively into $CClF{=}CF_2$ (CFC-1113) over transition metal oxide catalysts including Cr, Fe, Co, and Ni oxides [10]. The catalytic activity of noble metal catalysts is different depending on the metal species and supports. The hydrodechlorination activity of Pd catalysts is very high and the reaction of CFC-113 at 200 °C over Pd/Al_2O_3 [11] and Pd/C [12] yields a completely hydrogenated product, CH_2F–CHF_2 (HFC-143), at 40 and 60% selectivities, respectively. The selectivity reaches 100% when MnF_2 is used as a support [13]. The modification of Pd/Al_2O_3 with Bi or Tl reduces the hydrogenation activity of Pd and results in the selective formation of unsaturated compounds, CFC-1113 and $CHF{=}CF_2$ (HFC-1123) [11]. ZnO-modified Pd/Al_2O_3 gives CH_3–CF_3 (HFC-143a) through the isomerization (Eq. (3)) and subsequent Cl/H substitution [14]. Pt usually catalyzes Cl/H substitution but Pt/TiO_2 shows high selectivity toward HFC-1123 [12]. The activity of Rh and Ru for CFC-113 hydrodechlorination has not been studied extensively.

2. Experimental

Silica-supported Ru, Rh, Pd, and Pt catalysts were prepared by an incipient wetness method. An aqueous solution (70 ml) containing a precalculated amount of metal salt ($RuCl_3{\cdot}2.5H_2O$, $[Rh(NH_3)_6]Cl_3$, $[Pd(NH_3)_4]Cl_2{\cdot}0.68H_2O$, and $[Pd(NH_3)_4]Cl_2{\cdot}0.90H_2O$) was added dropwise to 70 g of silica aerosol (Nippon Aerosil, 200 m^2/g) while stirring well, allowed to stand overnight, dried in an oven at 110 °C for 24 h, and finally calcined at 450 °C for 6 h. The material was pressed at 300 kg/cm^3, crushed, and sieved to get 32–64 mesh granules.

Activated carbon-supported Ru, Rh, Pd, and Pt catalysts were prepared by conventional impregnation of activated carbon (Kanto Chemicals, 1030 m^2/g) with the aqueous solution of metal salts employed in the preparation of silica-supported catalysts. Before the impregnation, the active carbon was degassed in water using an ultrasonic vibrator.

The metal loadings on silica and activated carbon were confirmed by using an X-ray fluorescence analyzer (Horiba MESA-1130) and shown on the top of catalyst designation like $1Ru/SiO_2$ for the silica-supported 1.0 wt.% Ru catalyst.

The reaction was conducted at atmospheric pressure in a fixed-bed flow reaction system consisting of a down-flow quartz reactor (13 mm i.d.). An amount of 1.0 g of catalyst was loaded in the reactor and reduced in flowing hydrogen (30 ml/min) while being heated at a rate of 2.5 °C/min to 450 °C and held at the final temperature for 2 h. After the reduction, the catalyst was cooled to the reaction temperature, usually 200 °C, and the hydrogen flow was switched to the reaction mixture consisting of Ar (30 ml/min), H_2 (30 ml/min), and CFC-113 (5 ml/min). The reactor effluent was analyzed with a gas chromatograph (Shimadzu GC-9A) equipped with a Gaskuropack 54 packed column (GL Sciences, 3 mm × 2 m). The reaction products were identified with a GC-mass spectrometer (Hitachi M-80A) equipped with the same column.

Temperature-programmed reduction (TPR) was carried out for spent silica-supported catalysts. After the reaction, the catalyst was cooled in argon flow and stored in a closed vessel. An amount of 100 mg of the spent catalyst was loaded in a sample tube (4 mm i.d.) made of quartz and connected to the separator of GC-MS instead of the Gaskuropack column. The catalyst sample was treated in a hydrogen stream (30 ml/min) for 2 h at 200 °C and then heated at a rate of 10 °C/min storing the MS spectrum of every scan in a computer.

3. Results and discussion

3.1. Catalytic activity of supported noble metal catalysts

Table 1 summarizes the results of CFC-113 hydrodechlorination at 200 °C over various catalysts. The values of conversion and selectivity were obtained at 8 h of time-on-stream. Ru catalysts gave a simple product distribution. Over $5Ru/SiO_2$, the dechlorination product, CFC-1113, and the Cl/H substitution product, HCFC-123a, were produced as main products in approximately equal amounts. When $1Ru/SiO_2$ was employed for the reaction, the conversion level decreased to 8.2% but the values of selectivity were not changed appreciably (CFC-1113, 60.7%; HCFC-123a, 39.2%). 1Ru/C showed higher activity and selectivity for CFC-1113 formation (96.1% selectivity) than silica-supported Ru catalysts and produced a completely hydrodechlorinated olefin, $CHF{=}CF_2$. Ohnishi et al. [11] reported that the defluorination also took place over Ru/Al_2O_3 to form ethene. However, we did not observe ethene formation and detected a trace amount of ethane over uncalcined $1Ru/SiO_2$.

With $1Rh/SiO_2$, a broad product distribution was observed, which consisted of olefins, three Cl/H substitution products, i.e. HCFC-123a, HCFC-133 ($CH_2F–CClF_2$), and HFC-143, and the products of further F/H substitution, i.e. HFC-152a ($CH_3–CHF_2$) and ethane. 1Rh/C was more active than $1Rh/SiO_2$ and gave multiple Cl/H substitution products preferentially, suggesting that Rh has higher hydrodechlorination ability than Ru. Pt catalysts showed low selectivity for olefin formation and yielded a variety of Cl/H and/or F/H substitution products. Besides the products listed in Table 1, HFC-143a ($CH_3–CF_3$), -152 ($CH_2F–CH_2F$), and -161 ($CH_3–CH_2F$) were formed with selectivity 3–10% each. The formation of these HFCs and the high selectivity toward ethane suggest that C–F bond scission takes place over Pt catalysts considerably. Some discrepancies are found in the product identifications reported by other research groups, although products formed over supported noble metal catalysts are different by the supports. Takita et al. [12] observed the predominant

Table 1
Hydrodechlorination of $CCl_2F–CClF_2$ (CFC-113) over supported noble metal catalysts at 200 °C

Catalyst	Conversion (%)	Selectivity (%)						
		$CClF{=}CF_2$ CFC-1113	$CHF{=}CF_2$ HFC-1123	$CHClF–CClF_2$ HCFC-123a	$CH_2F–CClF_2$ HCFC-133b	$CH_2F–CHF_2$ HFC-143	$CH_3–CHF_2$ HFC-152a	$CH_3–CH_3$
$5Ru/SiO_2$	21.3	58.0	0	42.0	0	0	0	0
$1Rh/SiO_2$	15.6	49.2	3.2	4.5	1.5	10.0	5.8	1.3
$0.1Pd/SiO_2$	13.8	0	39.5	5.1	0	29.0	6.9	0.9
$1Pt/SiO_2$	30.2	0	0	41.6	0	2.3	3.9	21.8
lRu/C	33.5	96.1	0.9	2.1	0	0	0	0
lRh/C	30.3	7.2	8.5	5.9	18.3	25.7	16.0	1.4
0.1Pd/C	13.7	28.1	58.8	3.9	5.0	3.0	0	0.3
1Pt/C	13.7	1.3	0.6	13.8	19.4	19.6	5.0	8.2

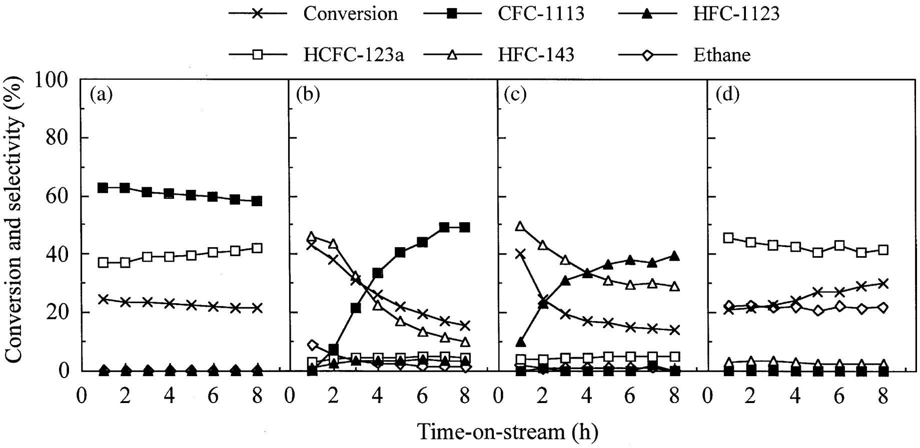


Fig. 1. Time-on-stream behavior of $CCl_2F–CClF_2$ (CFC-113) hydrodechlorination over $5Ru/SiO_2$ (a), $1Rh/SiO_2$ (b), $0.1Pd/SiO_2$ (c), and $1Pt/SiO_2$ (d) at 200 °C.

formation of $C_2F_2Cl_2$ (the structure was not shown) and $CH_2Cl–CHF_2$ over Rh/C and Pt/C, respectively. Ohnishi et al. [11] reported the formation of HCFC-141a ($CHCl_2–CH_2F$) over Rh/ and Pt/Al_2O_3. Those products result from the F/H substitution of Cl-containing species formed from CFC-113. However, it is unlikely that F/H substitution is preferential to Cl/H substitution, because the bond energy of C–F is much larger than that of C–Cl.

Pd is most active for the hydrodehalogenation among the four noble metals. The conversion levels observed with Pd catalysts were comparable with those with the other noble metal catalysts although the loading amount of Pd was one-tenth of those of the other metals. The relatively high selectivity to completely dechlorinated olefin (HFC-1123) is the characteristic activity of Pd catalysts as reported in literatures [11,13].

3.2. Time-on-stream behavior

The catalytic activity of noble metal catalysts changed with time-on-stream differently depending on the metal employed. Fig. 1 illustrates the activity changes of silica-supported noble metal catalysts during the reaction at 200 °C. $5Ru/SiO_2$ was most stable among the four noble metal catalysts. The similar stability was observed with $1Ru/SiO_2$ (not shown). The decrease of conversion was only 3% after 8 h of time-on-stream, while the selectivity to CFC-1113 decreased from 63.0 to 58.0% and the selectivity to HCFC-123a increased from 37.0 to 42.0%. Time-on-stream behaviors observed with $1Rh/SiO_2$ and $0.1Pd/SiO_2$ were not quite different. The conversion of CFC-113 decreased considerably in the first 6 h of time-on-stream. The increase in the selectivity to olefin (CFC-1113 over $1Rh/SiO_2$ or HFC-1123 over $0.1Pd/SiO_2$) and the decrease in the selectivity to triple Cl/H replacement product (HFC-143) were remarkable in the same period of time-on-stream. The activity change of $1Pt/SiO_2$ was completely different from those of the other catalysts. The conversion of CFC-113 increased with time-on-stream almost linearly and the selectivities to all products were not changed appreciably during the reaction. The increasing activity with time-on-stream has been observed with Pt/C [5] and Pd/Al_2O_3 [15–17] in the hydrodechlorination of CFC-12 and explained by increasing dispersion of Pt particles and Pd carbide formation, respectively.

Fig. 2 shows the time courses of conversion and product selectivities over active carbon-supported noble metal catalysts. Kulkarni et al. [8] observed initial increase followed by decrease in the conversion with time-on-stream during the hydrodechlorination of CFC-12 over carbon-supported noble metal catalysts. However, as seen in Fig. 2, the conversion decreased monotonously in the reaction of CFC-113 over all catalysts. The conversion over 1Ru/C decreased from 41.0 to 33.5% in 8 h of time-on-stream but the prod-

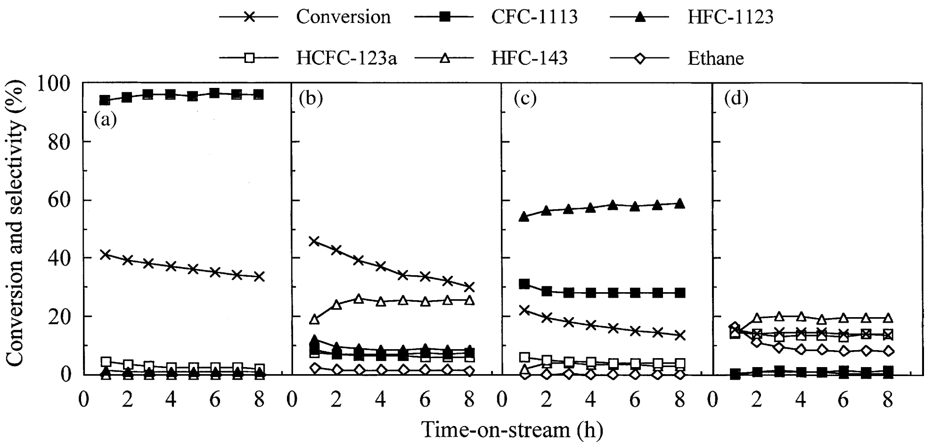


Fig. 2. Time-on-stream behavior of $CCl_2F–CClF_2$ (CFC-113) hydrodechlorination over 1Ru/C (a), 1Rh/C (b), 0.1Pd/C (c), and 1Pt/C (d) at 200 °C.

uct selectivity did not change appreciably. 1Rh/C and 0.1Pd/C deactivated gradually with time-on-stream but the degree of deactivation was smaller than that observed with $1Rh/SiO_2$ and $0.1Pd/SiO_2$. Considering that the hydrodefluorination products, HFC-152a and ethane, were formed over the catalysts (Table 1), the smaller deactivation of activated carbon-supported catalysts seems to be caused by the low reactivity of the support for HF formed during the reaction. The selectivity of 1Pt/C varied largely in the initial 4 h of time-on-stream. The selectivity to ethane at the steady activity was twice lower than that observed at 1 h of time-on-stream. In order to estimate the degree of activity change, the value of halogen conversion was calculated on the basis of reacted halogen atoms in CFC-113. When CFC-113 is converted completely to ethane or HFC-143, the value should be 100 or 50%, respectively. The values were 7.7 and 7.4% at 2 and 8 h of time-on-stream, respectively, suggesting that the hydrodehalogenation activity of 1Pt/C did not change during the reaction.

3.3. Regeneration of spent catalyst

The regeneration of silica-supported catalysts was studied by H_2 treatment of spent catalysts. After the reaction had been carried out at 200 °C for 8 h, the reaction feed was switched to flowing H_2 and the catalyst was heated at 300 or 450 °C for 2 h. The H_2-treated catalyst was cooled to 200 °C and the H_2 stream was switched back to the reaction feed. The effect of H_2 treatment was studied by comparing the

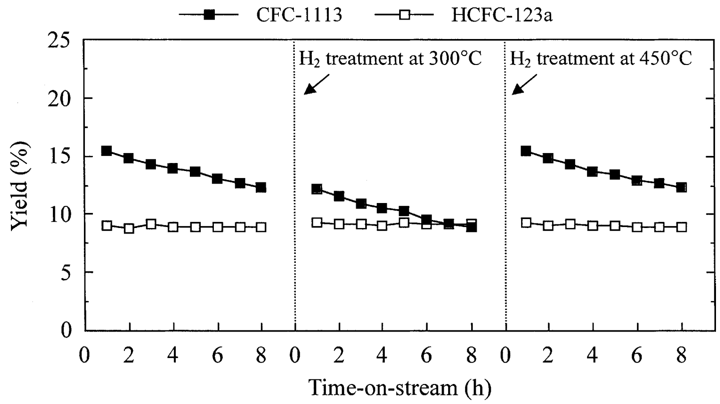


Fig. 3. Effect of hydrogen treatment on deactivated $5Ru/SiO_2$ (reaction temperature, 200 °C).

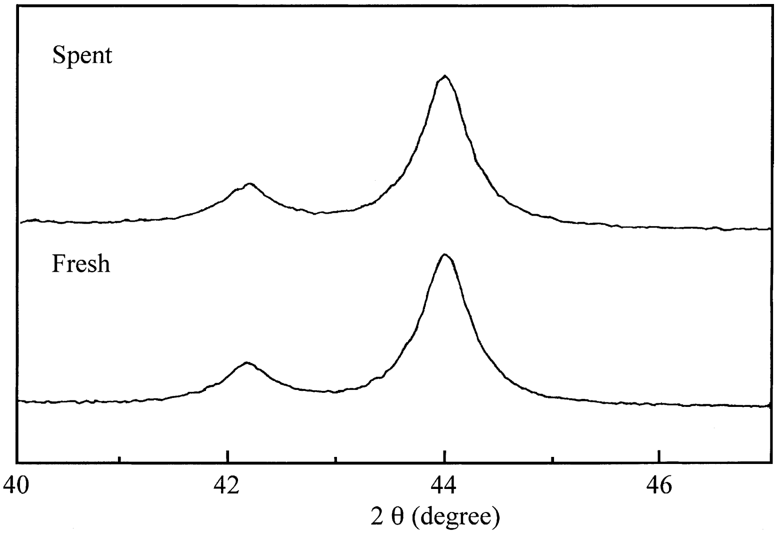


Fig. 4. XRD profiles of ruthenium supported on silica before and after the reaction of 8 h time-on-stream.

time-on-stream behaviors of the reactions before and after the H_2 treatment. The results with $5Ru/SiO_2$ are shown in Fig. 3, which illustrates the time-on-stream behaviors of product yields during the reaction. HCFC-123a yield did not change at all throughout the reaction, while CFC-1113 yield decreased with time-on-stream gradually regardless of the H_2 treatment at 300 °C. The time-on-stream behaviors of product yields over fresh $5Ru/SiO_2$ were reproduced completely after the H_2 treatment at 450 °C. Considering that the product yield is a linear function of the rate of product formation, the results strongly suggest that Ru has two kinds of hydrodechlorination sites, namely, one for Cl/H substitution, which is not deactivated throughout the reaction, and the other for Cl abstraction, which is deactivated and is responsible for the decline of conversion level shown in Fig. 1a. The deactivation was not thought to be due to the structural change of Ru particles supported on silica, because no difference was found between the XRD patterns of fresh and spent $5Ru/SiO_2$ (Fig. 4). The particle size was calculated from the diffraction profile broadening to be 17 nm for both of the catalyst samples. TPR profile obtained with used $5Ru/SiO_2$ is shown in Fig. 5. The assignment of each MS-chromatogram was performed carefully by the analysis of MS spectrum changing in every scan. Broad peaks assigned to CCl_2F^+, $CHClF^+$, CHF_2^+, SiF_3^+, and H_2O^+ were observed in the temperature range of 250–400 °C. Although the parent peak of SiF_3^+ fragment was not found in the MS spectra, a small amount of HF formed in the TPR would react with silica support to produce the parent compound of the fragment. $5Ru/SiO_2$ deactivated seriously during the reaction at 250 °C and the spent catalyst evolved CH_4 in the TPR at around 400 °C. Because of the low efficiency of CH_4 ionization, its small evolution seemed to be not counted during the TPR shown in Fig. 5. The TPR

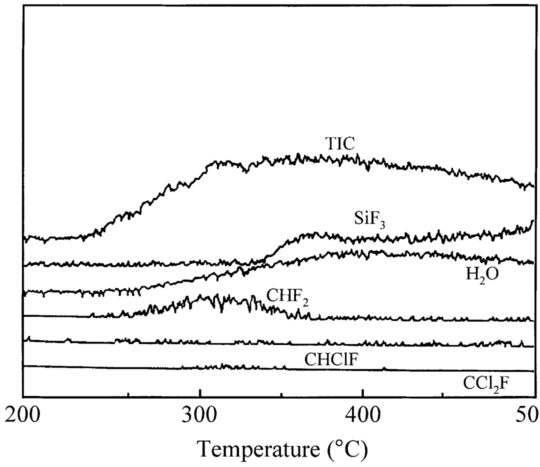


Fig. 5. TPR profile obtained with spent $5Ru/SiO_2$ (total ion current, TIC).

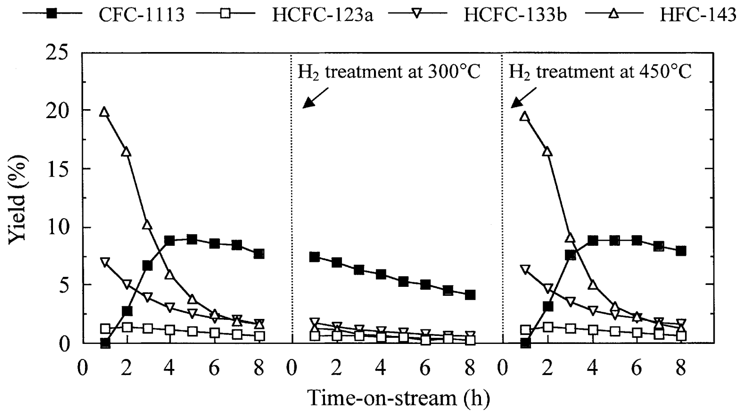


Fig. 6. Effect of hydrogen treatment on deactivated $1Rh/SiO_2$ (reaction temperature, 200 °C).

profiles suggest that F- and Cl-containing species are deposited on the surface of spent catalyst. The deposited species undergo hydrogenolysis including hydrodehalogenation and degradation during the H_2 treatment at 300 °C to leave carbonaceous residue, which is removed as methane for the most part by the H_2 treatment at 450 °C. From the time-on-stream dependency of CFC-1113 yield, the carbonaceous species seems to sit on the active site for CFC-1113 formation. Minor part of CFC-1113 precursors formed on the active sites would polymerize before desorption and the resultant polymer would hinder the reuse of active sites.

Fig. 6 shows the effect of H_2 treatment on the regeneration of spent $1Rh/SiO_2$. A variety of products were formed over $1Rh/SiO_2$ and the yields of main products were plotted for clarity. With fresh $1Rh/SiO_2$, the yield of triple Cl/H substitution product, HFC-143, decreased drastically with time-on-stream and CFC-1113 yield increased during the initial 4 h of time-on-stream. The yields of the other products decreased with time-on-stream monotonously. The catalytic activity was not regenerated by the H_2 treatment at 300 °C and the product yields decreased with time-on-stream on the extension of their time courses observed with fresh catalyst. The activity of fresh $1Rh/SiO_2$ was recovered completely by the H_2 treatment at 450 °C, suggesting that the damage of silica support by HF formed during the reaction was not serious after the time-on-stream scale of this study. Fig. 7 illustrates the MS-chromatograms recorded during the TPR of spent catalyst. The MS-chromatograms show that F rich species are deposited on the used catalyst and not hydrogenolyzed completely by the treatment at 300 °C. In general, successive Cl/H substitution through the desorption and readsorption of product does not take place substantially because every Cl/H substitution lowers the reactivity of Cl containing molecule remarkably [18,19]. From the low selectivity to the single Cl/H substitution product, HCFC-123a, it is deduced that CFC-113 adsorbs on Rh releasing more than one Cl atoms predominantly. The adsorbed species, most likely $*CClF–CF_2*$, would be desorbed or hydrogenated to give various hydrodechlorination products (Scheme 1). The hydrogen coverage of Rh surface is assumed to be high at the initial period of

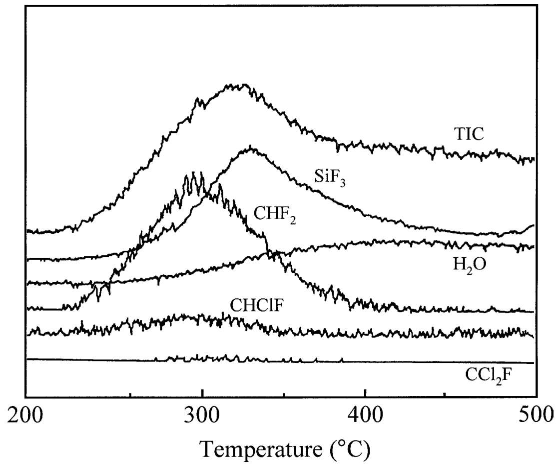
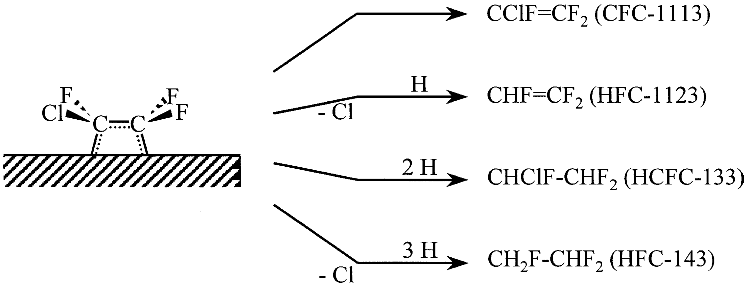


Fig. 7. TPR profile obtained with spent $1Rh/SiO_2$ (total ion current, TIC).



Scheme 1.

reaction and decrease with time-on-stream by competitive adsorption of Cl and F formed by the dissociative adsorption of CFC-113. It is likely that high hydrogen coverage results in high HFC-143 yield and decrease in the hydrogen coverage causes remarkable decrease in the HFC-143 yield accompanied by preferential formation of CFC-1113, because the formation of HFC-143 and CFC-1113 from the same precursor is, respectively, strongly dependent and independent on the hydrogen coverage. The accumulation of F rich carbonaceous species is considered to give rise to the gradual decrease in the number of working sites, hence CFC-1113 yield after 4 h of time-on-stream.

Over 0.1Pd/SiO_2, HFC-143 yield decreased rapidly from 19.8 to 4.0% in 6 h of time-on-stream and was not raised from the low value by the H_2 treatment at 450 °C (Fig. 8). HFC-1123 yield did not change largely throughout the reaction. The difference in the time-on-stream dependency between HFC-143 and HFC-1123 yields might be explainable by the concentration of adsorbed hydrogen as described above. Over 1Pt/SiO_2, all of the product yields increased gradually with time-on-stream (Fig. 9). The yields dropped to their initial levels after the H_2 treatment and then increased with time-on-stream drawing the same curves observed with the fresh catalyst.

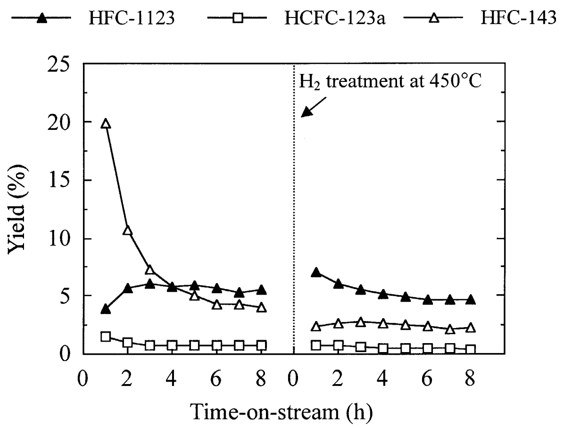


Fig. 8. Effect of hydrogen treatment on deactivated 0.1Pd/SiO_2 (reaction temperature, 200 °C).

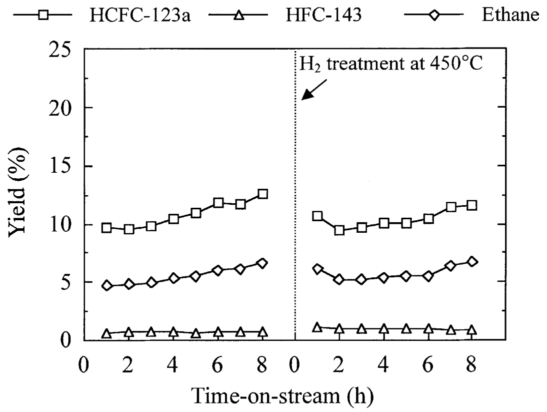


Fig. 9. Effect of hydrogen treatment on deactivated 1Pt/SiO_2 (reaction temperature, 200 °C).

3.4. Selectivity of silica-supported Ru catalyst

As mentioned in Section 2, 1Ru/SiO_2 were prepared by the calcination of the catalyst precursor at 450 °C and used for the reaction after the reduction in H_2 at the same temperature. In addition to this 1Ru/SiO_2, the catalyst designated to 1Ru/SiO_2–HD was prepared without the calcination. Fig. 10 shows the results of the reaction at 200 °C over 1Ru/SiO_2–HD. The figure includes the results with 5Ru/ and 1Ru/SiO_2 for comparison. 1Ru/SiO_2 gave 8.2% conversion at 8 h of time-on-stream and showed slightly higher selectivity

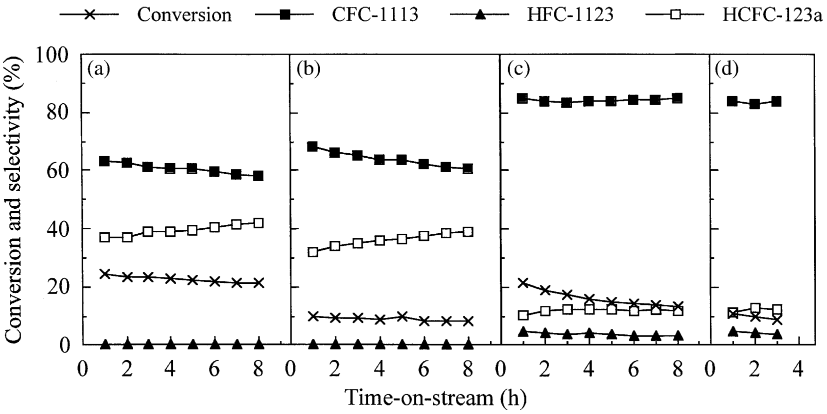


Fig. 10. Hydrodechlorination of $CCl_2F–CClF_2$ (CFC-113) over silica-supported Ru catalysts at 200 °C: (a) $5Ru/SiO_2$ (1.0 g); (b) $1Ru/SiO_2$ (1.0 g); (c) $1Ru/SiO_2$–HD (1.0 g); (d) $1Ru/SiO_2$–HD (0.3 g).

to CFC-1113 than $5Ru/SiO_2$. Much higher selectivity to CFC-1113 was obtained with $1Ru/SiO_2$–HD (Fig. 10c). The selectivity was as high as 83%. The activity was higher and declined more rapidly than $1Ru/SiO_2$, giving 21.3% conversion at early time-on-stream. When the catalyst amount was reduced to 0.3 g (Fig. 10d), the initial conversion dropped to 10.7% but the selectivity did not change significantly. The facts indicate that the selectivity is determined by the calcination in the catalyst preparation and is independent on the conversion level. From the XRD analysis of the catalysts, Ru particle size was calculated to be 17 nm for both $1Ru/SiO_2$ and $5Ru/SiO_2$. No diffraction lines assigned to Ru metal were observed with $1Ru/SiO_2$–HD. The results of the reaction and XRD studies suggest that the hydrodechlorination of CFC-113 is structure-sensitive and Ru having a highly unsaturated coordination sphere promotes the CFC-1113 formation. The high selectivity of 1Ru/C toward CFC-1113 formation is understandable by the high Ru dispersion that comes from the high surface area of activated carbon and the preparation without the calcination. Structure sensitivity of hydrodechlorination has been reported for the reactions of CFC-12 over Pd/Al_2O_3 [17] and chlorobenzene over Pd/Al_2O_3 and Rh/Al_2O_3 [20].

The conversion level over $5Ru/SiO_2$ was only twice higher than that over $1Ru/SiO_2$ in spite of five times higher Ru loading. The conversion level obtained with 1.0 g of $1Ru/SiO_2$ was less than twice higher than that with 0.3 g of the same catalyst. The results show that the conversion is not a linear function of catalyst amount even at the relatively lower conversion level. This suggests that the higher conversion, namely, the higher product concentration, causes the more retardation of hydrodechlorination rate because of negative dependency of reaction rate on the product. HCl formed during the reaction seems to be responsible for the kinetic retardation as suggested by Ribeiro and coworkers [18,21,22] for the hydrodechlorination of CFCs over Pd catalysts.

4. Conclusions

The hydrodechlorination of CFC-113 was studied using silica- and activated carbon-supported Ru, Rh, Pd, and Pt catalysts. The Ru catalysts gave a simple product distribution yielding CFC-1113 and HCFC-123a preferentially, whereas the other catalysts gave various products including differently F- and/or Cl-substituted ethenes and ethanes. The silica-supported Ru, Rh, and Pd deactivated with time-on-stream, but the activity of silica-supported Pt increased. The smaller time-on-stream dependencies were observed with activated carbon-supported catalysts.

With Ru supported on silica, CFC-1113 yield decreased gradually with time-on-stream but HCFC-123a yield was constant during the reaction. The activity of fresh catalyst was completely regenerated by treating the spent catalyst with hydrogen at 450 °C. Because

XRD profile of fresh catalyst did not change after the reaction and temperature-programmed reduction of the spent catalyst showed the deposition of carbonaceous species on Ru surface, it was concluded that CFC-1113 and HCFC-123a were formed on different sites and a part of the CFC-1113 precursors polymerized to form the carbonaceous species.

The catalyst having high Ru dispersion showed the high selectivity toward CFC-1113 formation, suggesting that the hydrodechlorination of CFC-113 is sensitive to the surface structure of Ru particles.

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