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Conversion of halon 1211 ($CBrClF_2$) over supported Pd catalysts

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Abstract

Conversion of halon 1211 has been studied over γ-Al_2O_3 and supported 0.5% Pd catalysts (Pd/Al_2O_3, Pd/fluorinated Al_2O_3, Pd/AlF_3, Pd/Al_2O_3 pretreated with CH_4 and $CHClF_2$). The experiments were performed in the temperature range of 443–523 K, in a tubular alumina reactor. The temperature of the reactor was maintained uniformly by a three zone furnace. The reaction products were quantified with a micro gas chromatograph and identified with a gas chromatograph–mass spectrometer. The catalysts were characterised with XRD diffractometry and the content of halogen on the catalysts was determined with an ion chromatograph. The measurements were presented in terms of the conversion of halon 1211 and product selectivity, as functions of catalyst type, catalyst time on stream and composition of inlet gases. Transformation of Pd to Pd carbide is observed in the CH_4 treated Pd/Al_2O_3, but not in the $CHClF_2$ treated Pd/Al_2O_3 in which case Al_2O_3 was partially fluorinated. In the absence of hydrogen, the conversion of halon 1211 over Al_2O_3 and Pd/Al_2O_3 gives a similar product profile and the reactions follow a heterogeneous halogen exchange reaction pathway, which takes place on the positively charged aluminum ions. Introduction of hydrogen has no apparent effect on either halon 1211 conversion level or the product profile during the conversion of halon 1211 over Al_2O_3. Over supported Pd catalysts, major products are hydrogenated species which include CH_2F_2, CH_4, C_2H_6, C_3H_8, CH_3Br and CHF_3. The most striking feature of the hydrodehalogenation reactions is the increasing CH_2F_2 selectivity with time on stream, especially on Pd/Al_2O_3 and the CH_4 treated Pd/Al_2O_3. The changing selectivity during the catalytic hydrodehalogenation reactions is mainly ascribed to the interaction of support with Pd.

Keywords: Halon; CFC; $CBrClF_2$; CH_2F_2; Palladium; γ-Al_2O_3; Fluorinated alumina; AlF_3; Catalytic hydrodehalogenation

1. Introduction

Research into the development of disposal techniques for CFCs and halons has intensified as a result of *The Montreal Protocol on Substances that Deplete the Ozone Layer* [1]. Catalytic hydrodehalogenation is a promising technique for converting these substances into environmentally benign products. Intensive research has focused on the catalytic hydrodehalogenation of CFCs, in particular CCl_2F_2, on supported noble metal catalysts. Pd is the most widely applied noble metal due to its selective cleavage of C–Cl bonds and resistance to catalyst poisoning by halide ions. For example, Makkee and coworkers reported the hydrodehalogenation of CCl_2F_2 and CCl_3F over carbon-supported noble metal catalysts [2,3]. They found that, especially, Pd was active in the selective removal of chlorine atoms from the parent CFC, resulting in the selective production of HFCs (CH_2F_2 and CH_3F).

CH_2F_2 has good cooling properties and is environmentally benign with zero ozone depleting potential (ODP) and low global warming potential (GWP), and its thermodynamic properties make it suitable as a CFC replacement in refrigeration applications. Selectivity to CH_2F_2, intrinsic catalytic activity and catalyst durability during hydrodehalogenation of CCl_2F_2 over Pd catalysts are strongly

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influenced by many factors, especially the nature of the support. Coq et al. [6,7] and others [4,5,8,9] observed increasing selectivity to CH_2F_2 with time on stream when working on the catalytic hydrodehalogenation of CCl_2F_2 over Pd/Al_2O_3 catalysts. Possible reasons for this observation can be ascribed to either the conversion of Pd to Pd carbide or the transformation of Al_2O_3 to partially fluorinated Al_2O_3 or AlF_3 during the hydrodehalogenation reactions. For example, Ahn et al. [9] reported that the pretreatment of Pd/Al_2O_3 catalysts with $CHClF_2$ prior to the hydrodehalogenation of CCl_2F_2 significantly improved the catalytic activity and the catalyst lifetime. The formation of Pd-carbide and AlF_3 was observed on the $CHClF_2$ treated catalyst, and the presence of the Pd carbide was thought to enhance the selectivity to CH_2F_2. Juszczyk et al. [5] reported that poorly dispersed Pd catalysts facilitate the formation of Pd carbide during the hydrodehalogenation of CCl_2F_2 over alumina supported Pd catalysts, resulting in a higher selectivity to CH_2F_2 in comparison with a well dispersed Pd catalyst. Coq et al. [6,7], on the other hand, suggested that the fluorination of Al_2O_3 during the hydrodehalogenation process modified the Pd–Al_2O_3 interface via the formation of fluoride and oxifluoride species on the catalyst. Due to the highly electronegative nature of fluorine, such a transformation induced an electron deficiency in Pd atoms located in the vicinity of the fluorinated support. The electron-deficient Pd species could bind CF_2 carbene (the most abundant intermediates during the hydrodehalogenation of CCl_2F_2) less strongly, resulting in a higher selectivity to CH_2F_2.

Compared to the intensive research efforts on the hydrodehalogenation of CFCs, little attention has been paid to the catalytic hydrodehalogenation of halons, especially halon 1211 ($CBrClF_2$), which remains a major contributor to the depletion of the ozone layer [10,11]. Halon 1211 is similar to CCl_2F_2 in terms of molecular composition except that one chlorine atom is replaced by a bromine atom. The difference in the bond dissociation energies between C–Br (265.7 kJ mol^{-1}) and C–Cl (323.0 kJ mol^{-1}) is much smaller than the difference between C–F (460.2 kJ mol^{-1} for CCl_2F_2) and C–Cl or C–Br [12,13]. This suggests that, the selective removal of both Br and Cl atoms by catalytic hydrodehalogenation to produce CH_2F_2 should be feasible. Recently, we reported the catalytic hydrodehalogenation of halon 1211 over Pd catalysts supported on activated carbon and Al_2O_3 [14,15]. Our results suggest that the reaction mechanism is similar to that operating during the hydrodehalogenation of CCl_2F_2 over Pd catalysts. During the hydrodehalogenation of halon 1211 over Pd catalysts supported on Al_2O_3, we also observed a dramatic increase in selectivity to CH_2F_2 with time on stream. The steady-state selectivity is higher than that obtained when carbon supported Pd catalysts were used at a similar conversion level of halon 1211. However, reaction mechanisms involved during the hydrodehalogenation of halon 1211 over Pd catalysts have not been fully elucidated.

In this study, we report the catalytic conversion of $CBrClF_2$ over γ-Al_2O_3 and Pd/γ-Al_2O_3 in the absence and presence of hydrogen. Hydrodehalogenation of halon 1211 was also conducted over Pd/Al_2O_3 catalysts pretreated with CH_4 and $CHClF_2$, respectively, as well as over Pd catalysts supported on fluorinated Al_2O_3 and AlF_3. Since Al_2O_3, fluorinated Al_2O_3 and AlF_3 have been reported to be able to catalyse the exchange reactions between Cl and F in CFCs, it is possible that, these phases could play a role during the hydrodehelogenation of halon 1211. Treating Pd catalysts with CH_4 will convert Pd into Pd carbide prior to the hydrodehalogenation reactions [16] while treating Pd/Al_2O_3 with $CHClF_2$ will possibly convert Pd into Pd carbide and partially fluorinate Al_2O_3 support [9]. In the present study, we investigate the effect of support (Al_2O_3, fluorinated Al_2O_3 and AlF_3) and the formation of Pd carbide on the catalytic hydrodehalogenation of halon 1211.

2. Experimental

2.1. Preparation of catalysts

Three different supports were used in this study. γ-Al_2O_3 and $AlF_3{\cdot}3H_2O$ having surface areas of 120 and 30 $m^2\,g^{-1}$, respectively, were obtained from Mizusawa Chemicals (Japan) and Sigma–Aldrich. Partially fluorinated Al_2O_3 (identified as F-Al_2O_3) was prepared in our lab by treating γ-Al_2O_3 in an alumina (α-type) microreactor with a mixture of nitrogen and $CHClF_2$ flowing (10:1 (v/v), 30 $cm^3\,min^{-1}$) at the temperature of 623 K for 3 h, followed by calcination in nitrogen, flowing at 60 $cm^3\,min^{-1}$, at the temperature of 773 K for 3 h.

Supported catalysts were prepared by impregnation with an aqueous solution of $Pd(NO_3)_2{\cdot}2H_2O$ (Sigma–Aldrich) to obtain a nominal loading of 0.5 wt.% Pd. The solvent (H_2O) was removed using a rotary evaporator at 318 K under vacuum. The supported metal catalyst was placed in an air oven at 373 K overnight and then placed into an α-Al_2O_3 microreactor and calcined in flowing air (60 $cm^3\,min^{-1}$), with the microreactor temperature increased to 773 K at a rate of 10 K min^{-1}. This temperature was held for 3 h. After cooling of the microreactor to room temperature, the sample was reduced in flowing H_2 (12 $cm^3\,min^{-1}$) by heating it to 673 K, at a rate of 10 K min^{-1}, and holding this temperature for 3 h. Pd supported on fluorinated Al_2O_3 is identified as Pd/F-Al_2O_3.

Some of the fresh Pd/Al_2O_3 catalysts (reduced with hydrogen) were treated in flowing CH_4 at the temperature of 623 K for 2 h. These catalysts are identified as Pd/Al_2O_3 (CH_4). The pretreatment aims to convert Pd supported on Al_2O_3 into Pd carbide prior to hydrodehalogenation reactions [16].

Some fresh Pd/Al_2O_3 catalysts (after reduction with hydrogen) were treated in a mixture of N_2 and $CHClF_2$ flowing (10:1 (v/v), 30 $cm^3\,min^{-1}$) at the temperature of

623 K for 3 h. These catalysts are identified as Pd/Al_2O_3 ($CHClF_2$). This pretreatment aims to partially fluorinate Al_2O_3 and possibly convert Pd into Pd carbide prior to hydrodehalogenation reactions [9,17].

2.2. Catalytic experiments

Both decomposition (in the absence of hydrogen) and hydrodehalogenation (in the presence of hydrogen) of halon 1211 were conducted in a temperature-controlled high purity (99.99%) alumina reactor. A three zone electrically heated furnace, surrounding the alumina reactor, was used to control reaction temperature. Alumina surface reaction (blank) was investigated and found to have no activity under all reaction conditions investigated. Three gases N_2 (BOC Gases, 99.99% purity), H_2 (BOC gases, 99.97% purity) and halon 1211 (99.7% purity) were metered with electronic mass flow controllers (Brooks).

After exiting the reactor tube, the product gas stream was directed through an ice cooled liquid trap (273 K) and subsequently through a caustic scrubber (0.1 M NaOH solution) to remove acid products, HF, HCl and HBr, and halogens produced during the conversion of halon 1211 in the absence of hydrogen, before reaching an online μGC (Varian CP-2003) for quantification of gaseous carbon-containing products. The μGC was equipped with dual columns: 5A Molsieve column (343 K) to separate nitrogen, methane and hydrogen, and PoraPLOT Q column (373 K) to separate hydrocarbons and halogenated hydrocarbons. An offline gas chromatograph–mass spectrometer (GC/MS-QP5000, Shimadzu) equipped with an AT-Q column was used to identify gaseous products.

Conversion of halon 1211 in the absence of hydrogen over Al_2O_3 and 0.5% Pd/Al_2O_3 was performed within the temperature range of 443–523 K. Hydrogenolysis of halon 1211 over various Pd catalysts was conducted at the temperature of 443 K and a gas hourly space velocity (GHSV) of 1520 h^{-1} with an input molar ratio of N_2:H_2:halon 1211 equal to 25:9:1. Blank experiments were conducted to ascertain that, the reaction did not take place thermally in the absence of catalysts at temperatures below 623 K. The conversion of halon 1211, X_h, and selectivity of product *i*, S_i, were calculated on the basis of product formation according to the following equations:

$$X_h = \frac{\sum_{i=1}^{z} n_i C_i}{C_{uh} + \sum_{i=1}^{z} n_i C_i}$$

$$S_i = \frac{n_i C_i}{\sum_{i=1}^{z} n_i C_i}$$

where z is the number of detectable carbon-containing products, n_i the number of carbon atoms in a molecule, C_i and C_{uh} the mole concentration of the product i and unreacted halon 1211 in the effluent gas, respectively. The carbon balances for the hydrodehalogenation reactions over supported Pd catalysts are ca. 97%, while for the conversion of halon 1211 over Al_2O_3 and Pd/Al_2O_3, in the absence of hydrogen, the carbon balances are ca. 90%.

The reaction conditions for the catalytic conversion of halon 1211 over Pd and supported Pd catalysts are summarised in Table 1.

2.3. Catalyst characterisation

X-ray diffraction patterns of the fresh and spent catalysts were obtained on a Philips powder X-ray diffractometer (PW 1710). Halogen content on the surface of used catalysts or fluorinated alumina were determined according to the following procedure: The spent catalysts (100 mg) were charged into an alumina tube and heated in flowing hydrogen (12 $cm^3 min^{-1}$) at a rate of 10 K min^{-1} from ambient temperature to 773 K and held at this temperature for 3 h. Further increasing the treatment time (up to 8 h) resulted in a relatively small increase in the amount of halogens trapped in the NaOH solution. Following this relatively high temperature hydrogenation treatment, the phase for the fluorinated alumina disappeared, as observed in XRD patterns of spent catalysts. This indicates that, most of halogen associated with the AlF_x phase, formed on the spent catalyst, was hydrogenated to hydrogen halides, which subsequently desorbed into the gas stream. All hydrogen halides produced during this process were trapped with NaOH solution (0.1 M). The concentration of halide was subsequently analysed by ion chromatography (IC) (Dionex-100) equipped with an IonPac AS14A column (4 × 250 mm), allowing the estimation of the amount of halogen on the catalyst surface.

Table 1
Reaction conditions for the catalytic conversion of halon 1211 over support Al_2O_3 and supported Pd catalysts

Reaction no.	Catalyst	Input molar ratio of reactants	Temperature (K)	GHSV (h^{-1})
1	Al_2O_3	N_2:halon = 32:1 (without H_2)	443–523	4310
		N_2:halon:H_2 = 32:1:2 (with H_2)		4570
2	Pd/Al_2O_3	N_2:halon = 25:1	443–523	1400
3	Pd/Al_2O_3	N_2:halon:H_2 = 25:1:9	443	1520
4	Pd/Al_2O_3 ($CHClF_2$)	N_2:halon:H_2 = 25:1:9	443	1520
5	Pd/Al_2O_3 (CH_4)	N_2:halon:H_2 = 25:1:9	443	1520
6	$Pd/F\text{-}Al_2O_3$	N_2:halon:H_2 = 25:1:9	443	1520
7	Pd/AlF_3	N_2:halon:H_2 = 25:1:9	443	1520

3. Results

3.1. Catalyst characterisation

XRD patterns of fresh and spent catalysts are presented in Fig. 1a and b. The transformation of Pd to Pd carbide was found in the spent Pd/Al_2O_3 and Pd/F-Al_2O_3 after hydrodehalogenation of halon 1211. After Pd/Al_2O_3 was treated with CH_4 (sample Pd/Al_2O_3 (CH_4)), Pd was converted to Pd carbide. Pretreatment of Pd/Al_2O_3 with $CHClF_2$ (sample Pd/Al_2O_3 ($CHClF_2$)) failed to convert Pd to Pd carbide but, after hydrodehalogenation of halon 1211, the transformation of Pd to Pd carbide was observed. Probably due to the presence of AlF_3 and Pd carbide, PdC_x phase was not detected in the used Pd/AlF_3 catalyst. There is no formation of Pd carbide observed in Pd/Al_2O_3 which was used in the conversion of halon 1211 in the absence of hydrogen.

During the conversion of halon 1211 over Al_2O_3 and Pd/Al_2O_3 (with and without hydrogen) as well as over Pd/Al_2O_3 (CH_4), the Al_2O_3 support was partially fluorinated, and a new phase ($AlF_{1.5}(OH)_{1.5}$) was detected by the XRD analysis, as shown in Fig. 1a and b. This phase was also detected in Pd/Al_2O_3 catalysts which were treated with $CHClF_2$. XRD spectra of fluorinated Al_2O_3 also disclosed this new phase but, following calcination at 723 K for 3 h,

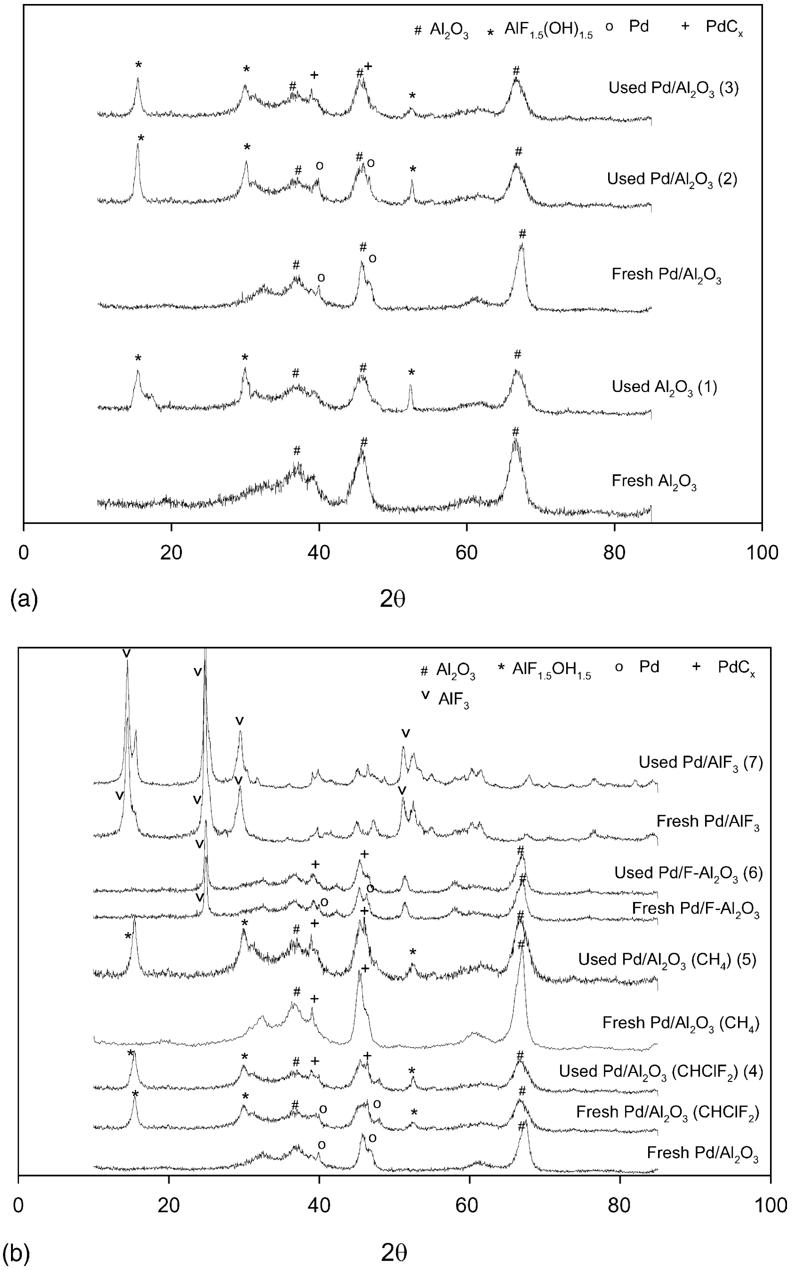

Fig. 1. (a) XRD patterns of Al_2O_3 and 0.5% Pd-Al_2O_3 (fresh and used). Numbers in parenthesis refer to the reaction numbers which are specified in Table 1. (b) XRD patterns of fresh and used catalysts. Numbers in parenthesis refer to the reaction numbers which are specified in Table 1.

Table 2
The amount of halogen retained on the selected samples (100 mg)

Reaction no.	Sample	Amount of halogen on used catalysts (100 mg) (mmol)		
		F	Cl	Br
1	Used Al_2O_3	0.200	0.020	0.016
2	Used Pd/Al_2O_3	0.190	0.019	0.014
3	Used Pd/Al_2O_3	0.039	0.016	0.009
	Fresh F-alumina	0.255	0.024	<0.001
	Fresh Pd/Al_2O_3 ($CHClF_2$)	0.250	0.021	<0.001

The reaction conditions are given in Table 1.

this phase disappeared and another phase was formed. It has been reported [18] that drying of hydroxyfluoride $AlF_x(OH)_{3-x}$ at high temperatures would normally result in two coexisting phases (AlF_3 and Al_2O_3). We identified the new phase as AlF_3, which was formed from $AlF_{1.5}(OH)_{1.5}$ during its calcination.

The amount of halogen retained on the used Al_2O_3 and Pd/Al_2O_3 catalysts, fluorinated alumina and fresh Pd/Al_2O_3 ($CHClF_2$) are presented in Table 2. Large amounts of fluorine were found on Al_2O_3 and Pd/Al_2O_3 which were used in the conversion of halon 1211 in the absence of hydrogen. A large amount of fluorine was also present in the fluorinated alumina and Pd/Al_2O_3 pretreated with $CHClF_2$. For Pd/Al_2O_3 used in the hydrodehalogenation of halon 1211, a relatively small amount of fluorine was detected. For all samples analysed with IC, the amount of halogen deposited on the samples decreases in the following order:

$$F \gg Cl > Br$$

3.2. Conversion of halon 1211 over Al_2O_3 in the absence and presence of hydrogen

Catalytic conversion of halon 1211 over Al_2O_3 was examined over the temperature range 443–523 K in the absence of H_2. At temperatures below 523 K, the conversion of halon 1211 was negligible (<0.5%) after 4 h on stream. However, at 523 K after 40 min on stream, the conversion level of halon 1211 increased dramatically to 80%. Fig. 2 shows the halon conversion and product selectivity as a function of time on stream at 523 K. Major carbon-containing products include $CClF_3$, $CBrF_3$, CCl_2F_2, CBr_2F_2 and CCl_3F. After reactions reached a steady state (4 h time on stream), hydrogen was introduced to the reaction system. It was found that the addition of hydrogen to the reaction system had no apparent effect on either halon conversion level or product profile, and no hydrogenated products were detected, which suggested that H_2 was not participating in the reaction with halon 1211 under the present conditions.

3.3. Conversion of halon 1211 over Pd/Al_2O_3 in the absence and presence of hydrogen

Experiments on the conversion of halon 1211 over Pd/Al_2O_3 were first conducted in the absence of hydrogen under conditions similar to the conversion of halon 1211 over Al_2O_3 in order to investigate the effect of Pd. As with the conversion of halon 1211 over Al_2O_3, reactions over Pd/Al_2O_3 did not reach steady state until approximately 50 min on stream. The steady-state conversion and selectivity to major products are given in Fig. 3 for comparison with reactions over Al_2O_3. Although the conversion level is

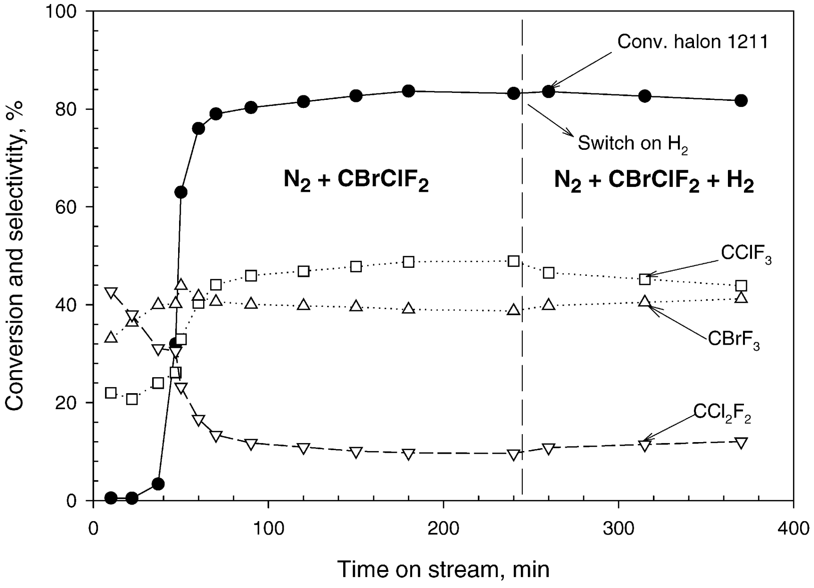

Fig. 2. Conversion of halon 1211 over Al_2O_3 in the absence and presence of H_2; $T = 523$ K. (a) In the absence of H_2, N_2:halon 1211 = 32:1 and GHSV = 4310 h^{-1}. (b) In the presence of hydrogen, N_2:halon 1211:H_2 = 32:1:2 and GHSV = 4570 h^{-1}.

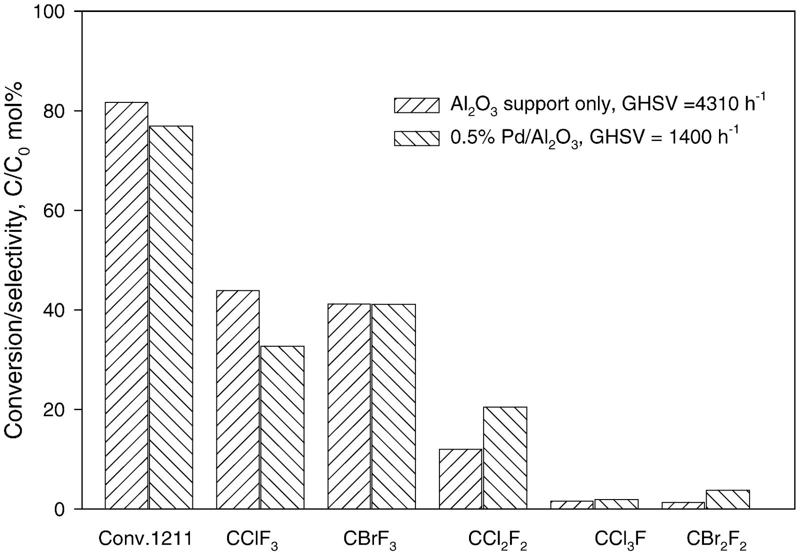

Fig. 3. Conversion of halon 1211 over Al_2O_3 and 0.5% Pd/Al_2O_3 in the absence of H_2; $T = 523$ K. (a) Over Al_2O_3, N_2:halon 1211 = 32:1 and GHSV = 4310 h^{-1}. (b) Over 0.5% Pd/Al_2O_3, N_2:halon 1211 = 25:1 and GHSV = 1400 h^{-1}.

slightly lower than in the case of Al_2O_3, the product profile is very similar.

Once hydrogen was introduced to the feed stream, reactions were observed to occur at much lower temperatures with mainly hydrogenated products in the outlet stream, including CH_2F_2, CH_4, C_2H_6, C_3H_8, CH_3Br and CHF_3 as major products. CH_3Cl, CH_3F, C_2H_4, C_3H_6, $CHClF_2$ and $CHBrF_2$ were detected in small amounts, at a selectivity of <1%. Fully halogenated species such as CCl_2F_2 and $CClF_3$ were detected only in trace amounts. The conversion of halon 1211 and the selectivity to major products as a function of time on stream at 443 K are shown in Fig. 4a. The conversion level of halon 1211 decreased initially in the first few hours, followed by a slight increase with time on stream. Selectivity to CH_2F_2 increased with time on stream, while selectivity to other products decreased.

3.4. Hydrodehalogenation of halon 1211 over other Pd catalysts

Hydrodehalogenation of halon 1211 was also conducted over Pd/Al_2O_3 (CH_4), Pd/Al_2O_3 ($CHClF_2$), Pd/F-Al_2O_3 and Pd/AlF_3, under the same reaction conditions as Pd/Al_2O_3. Conversion and selectivity to major carbon-containing products with time on stream are presented in Fig. 4a and b. Table 3 compares the conversion levels and selectivity to major carbon containing products at 1 and 8 h on stream, respectively.

Similar to Pd/Al_2O_3, hydrodehalogenation over Pd/Al_2O_3 (CH_4) showed a slight increase in the conversion level of halon 1211 after an initial decrease. Pd/Al_2O_3 treated with CH_4 or $CHClF_2$ showed a lower activity, while the activities of Pd/Al_2O_3, Pd/F-Al_2O_3 and Pd/AlF_3 were higher. The

Table 3
Conversion of halon 1211 and selectivity to major products in the hydrodehalogenation of halon 1211 at 1 and 8 h on stream respectively

Reaction no.	Catalyst	Time on stream (h)	Conversion (%)	Selectivity (%)					
				CH_2F_2	CH_4	C_2H_6	C_3H_8	CH_3Br	CHF_3
2	Pd/Al_2O_3	1	10.1	30.7	19.7	16.6	5.3	19.0	1.2
		8	10.3	59.3	11.5	10.0	3.0	11.6	2.1
3	Pd/Al_2O_3 ($CHClF_2$)	1	5.7	53.0	7.5	13.9	7.0	7.7	3.6
		8	5.0	64.1	5.6	10.0	4.9	5.6	3.3
4	Pd/Al_2O_3 (CH_4)	1	6.7	27.4	21.2	23.8	8.2	14.1	0.9
		8	7.0	46.0	15.3	18.3	6.7	9.5	1.7
5	Pd/F-Al_2O_3	1	11.3	46.1	11.6	19.5	10.8	7.9	1.3
		8	10.8	61.8	9.0	11.8	7.7	6.6	1.5
6	Pd/AlF_3	1	9.3	69.4	13.9	8.3	0.7	6.1	0.3
		8	8.8	77.9	8.0	6.3	0.6	4.3	0.3

The reaction conditions are given in Table 1.

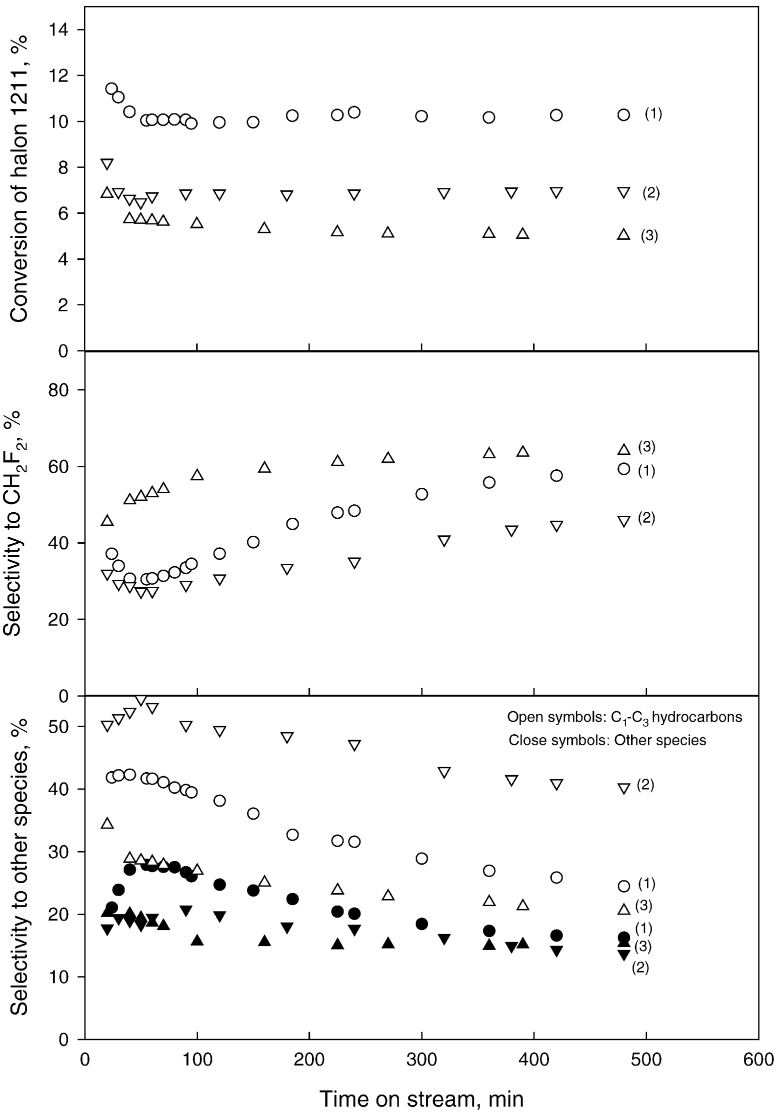

Fig. 4. (a) Conversion of halon 1211 and selectivity to major carbon containing products vs. time on stream in the hydrodehalogenation of halon 1211 over: (1) Pd/Al_2O_3; (2) Pd/Al_2O_3 (CH_4); (3) Pd/Al_2O_3 ($CHClF_2$). The experiments were performed at $T = 443$ K; for GHSV = 1520 h^{-1}; N_2:halon 1211:H_2 = 25:1:9. (b) Conversion of halon 1211 and selectivity to major carbon containing products vs. time on stream in the hydrodehalogenation of halon 1211 over: (1) Pd/Al_2O_3; (2) $Pd/F\text{-}Al_2O_3$; (3) Pd/AlF_3. The experiments were performed at $T = 443$ K; and for GHSV = 1520 h^{-1}; N_2:halon 1211:H_2 = 25:1:9. The measurements for Pd/Al_2O_3 (1) are replotted from (a) for the purpose of comparison.

conversion level of halon 1211 over various Pd catalysts studied at 8 h on streams decrease in the following order:

$$Pd/F\text{-}Al_2O_3 > Pd/Al_2O_3 > Pd/AlF_3 > Pd/Al_2O_3\,(CH_4) > Pd/Al_2O_3\,(CHClF_2)$$

Hydrodehalogenation of halon 1211 over all supported Pd catalysts investigated gave a similar reaction product profile with CH_2F_2, CH_4, C_2H_6, C_3H_8, CH_3Br and CHF_3 as major products.

Over all catalysts studied, selectivity to CH_2F_2 increased while selectivity to other species decreased with time on stream, to some extent, depends on the catalyst employed. Selectivity to CH_2F_2 over Pd/Al_2O_3 and Pd/Al_2O_3 (CH_4) increased dramatically, whereas, over $Pd/F\text{-}Al_2O_3$ and Pd/Al_2O_3 ($CHClF_2$), selectivity to CH_2F_2 increased much more modestly. When Pd/AlF_3 was used, selectivity to CH_2F_2 remained relatively constant.

4. Discussion

All catalytic hydrodehalogenation reactions were conducted at a relatively low temperature (443 K) with a ratio of hydrogen to halon 1211 of (9:1). All catalysts underwent an initial deactivation (in the first several hours) following which the activity and selectivity remained relatively stable. Over Pd/Al_2O_3 and Pd/Al_2O_3 (CH_4), a slight increase in the

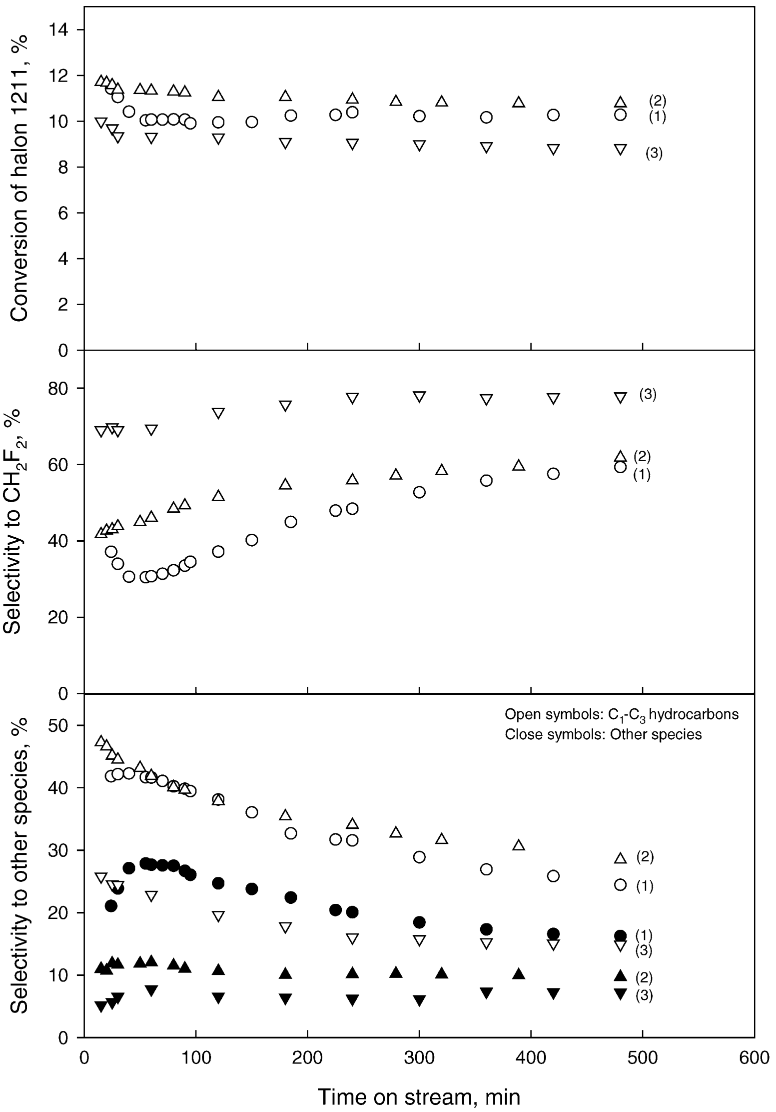

Fig. 4. (*Continued*).

conversion level of halon 1211 with TOS was observed. The most striking feature of catalytic hydrodehalogenation reactions studied is that selectivity to the major product CH_2F_2 increases with time on stream, although the extent to which this occurs depends on the supports used. This phenomenon is observed even when the conversion level of halon 1211 stays constant. At the same time, selectivity to completely hydrogenated species such as C_1–C_3 hydrocarbons decreases. Similar phenomena were reported in the literature [4–9] for the catalytic hydrodehalogenation of CCl_2F_2 over Pd supported on Al_2O_3, fluorinated alumina and AlF_3.

Our previous investigation on the catalytic hydrodehalogenation of halon 1211 over Pd/C and Pd/Al_2O_3 catalysts, along with work conducted on the catalytic hydrodehalogenation of CCl_2F_2 [2,6,19], suggests that the catalytic hydrodehalogenation of halon 1211 over Pd catalysts follows a reaction mechanism similar to the hydrodehalogenation of CCl_2F_2. The most abundant intermediate is believed to be CF_2 which can be further hydrogenated to CH_2 carbenes on the surface of the catalyst. Selectivity to CH_2F_2, or more highly hydrogenated species such as CH_4, is mainly determined by the concentration and reactivity of CF_2 and CH_2 on the surface of catalysts. Given the very limited information on the catalytic hydrodehalogenation of halon 1211, it is very useful to refer to the previous work on the catalytic hydrodehalogenation of CCl_2F_2 over Pd catalysts in order to understand the catalytic behaviour for the hydrodehalogenation of halon 1211 over similar catalysts.

Many factors have been reported to be responsible for the dynamic change of catalytic activities during the hydrodehalogenation of CCl_2F_2, including the formation of coke, transformation of Pd to Pd carbide, the change of Pd dispersion on the support, effect of hydrogen halides formed during the reactions, and the interaction of the support with Pd. Among these factors, more attention has been paid to the transformation of Pd to Pd carbide and the interaction of the support with Pd, which are believed to play essential roles. In this study, we mainly focus on the effect of these two factors on the catalytic hydrodehalogenation of halon 1211.

4.1. Transformation of Pd to Pd carbide

The transformation of Pd to Pd carbide has been reported during the hydrodehalogenation of CCl_2F_2 over Pd black and supported Pd catalysts [5,9,16,20]. Ziemecki et al. [21] determined that the stoichiometry of this carbide is $PdC_{0.15}$, which was confirmed by the measurement of van de Sandt et al. [16]. The mechanism of formation for Pd carbide is not clear. It can be formed by the contact of Pd with methane, ethane, ethylene, acetylene or CO [21–25]. Krishnankutty and Vannice [26] reported that, during the preparation of Pd/C catalysts in which a Pd acetylacetonate was used as precursor and a high surface area carbon black used as support, the formation of Pd carbide was also observed. They believe that carbon atoms, from either the precursor or the carbon support, migrated onto and into Pd crystallites. According to Ziemecki et al. [21], when Pd is heated in atmospheres of ethylene, acetylene, carbon monoxide or other carbon containing molecules, these molecules may absorb molecularly or dissociatively on the Pd surface. If adsorption takes place dissociatively, a carbonaceous overlayer will be deposited on the Pd surface, followed by an activated diffusion of carbon atoms through the metal lattice. Based on thermodynamics of surface segregation of carbon in Pd, Wolf et al. [27] and Hamilton and Blakely [28] suggested that carbon on the surface of Pd is necessary to stabilise carbon in the bulk.

During the catalytic hydrodehalogenation of halon 1211 over Pd catalysts, the carbonaceous materials may deposit on the surface of Pd. The formation of hydrocarbons (CH_4, C_2H_6, etc.) as reaction products clearly suggests that the cleavage of not only C–Cl and C–Br but also C–F bonds takes place during the hydrodehalogenation reactions, which could result in the formation of carbon on the surface of Pd. Carbon could diffuse into the Pd bulk, forming Pd carbide. However, some authors found that the amount of carbon deposited on the clean Pd surface is negligible during incorporation of carbon into the Pd lattice by CO, C_2H_4 decomposition and CCl_2F_2/H_2 reactions. Further investigation is needed to elucidate the route for the formation of Pd carbide.

The properties of Pd carbide are different from those of Pd. It has been reported that, the formation of Pd carbide suppresses hydrogen chemisorption on the Pd surface [22,24,26]. During catalytic hydrodehalogenation, hydrogen needs to be activated by means of dissociative adsorption on Pd. The suppression of hydrogen chemisorption will possibly influence the activity and selectivity of Pd catalysts. In addition, Maciejewski and Baiker [22] reported that carbon deposited in the interstitial position of the Pd lattice is more reactive than carbon in a graphite form deposited on the Pd surface. The interstitial carbon can react with hydrogen to form methane at about 400 K.

Ahn et al. [9] suggested that Pd carbide enhances selectivity to CH_2F_2 and decreases the rate or extent of deactivation of catalysts. This opinion is supported by Juszczyk et al. [5], who reported that poorly dispersed Pd catalysts facilitate the formation of Pd carbide during the hydrodehalogenation of CCl_2F_2 over Al_2O_3 supported Pd catalysts, resulting in a higher selectivity to CH_2F_2 in comparison with a well dispersed Pd catalyst. In our experiments, we deliberately transformed Pd into Pd carbide by treating Pd with CH_4 prior to hydrodehalogenation reactions. However, the catalyst displayed a lower activity as well as a lower selectivity to CH_2F_2 while selectivity to C_1–C_3 hydrocarbons was higher (Fig. 4a and Table 3). The coke formed during the pretreatment may partially cover the surface of Pd, leading to a low catalytic activity, but the effect of Pd carbide on the catalyst deactivation and the lower selectivity to CH_2F_2 cannot be excluded. It is worth noting that, the selectivity to CH_2F_2 still changed dramatically with time on stream although Pd was already converted into Pd carbide. If the formation of Pd carbide was responsible for the changing selectivity to CH_2F_2, the quickly stabilised selectivity to CH_2F_2 should have been expected.

We also adopted a procedure reported by Ahn et al. [9] to produce Pd carbide and fluorinate alumina support simultaneously by treating unreduced or reduced Pd/Al_2O_3 catalysts to investigate the combined effect of formation of Pd carbide and fluorination of support. Fluorination of support was observed but we failed to detect the Pd carbide from the XRD analysis. Our understanding is that, in the absence of hydrogen, contact of Pd/Al_2O_3 (either unreduced or reduced Pd/Al_2O_3) with $CHClF_2$ leads to fluorination of Al_2O_3 support, which subsequently catalyses C/F exchange reactions on the support rather than on the surface of Pd. Since there is only a negligible amount of carbon containing species on the Pd surface, the formation of Pd carbide is unlikely. van de Sandt et al. [16] found that, in the absence of hydrogen, direct contact of Pd black with CCl_2F_2, which has a weaker C–Cl bond than $CHClF_2$, could not convert Pd to Pd carbide. Pd/Al_2O_3 catalysts treated with $CHClF_2$ showed less catalytic activity, which could be ascribed to the inhibition of halogen (migrated onto the surface of Pd from Al_2O_3), but the catalyst displayed a rather stable activity and a higher selectivity to CH_2F_2. This seems to suggest that the fluorination of the Al_2O_3 support plays a more important role.

4.2. Interaction of support with Pd

Al_2O_3, fluorinated Al_2O_3 and AlF_3 can catalyse heterogeneous Cl/F exchange reactions of chlorocarbons for the synthesis of fluorocarbons. The oxide phase itself is not active but can become active via fluorination by a variety of fluorine-containing species including HF (gaseous or aqueous) and fluorocarbons such as $CHClF_2$ and CCl_2F_2. During the reaction of $CHClF_2$ or CCl_2F_2 over Al_2O_3, a sharp transition between a pre-catalytic and a catalytically active state is observed after a certain time of contact with a flow of the gaseous reactants [4,17,18,29,30]. Before this transition state, a heterogeneous reaction between Al_2O_3 and CCl_2F_2 or $CHClF_2$ takes place that is characterised by continual uptake of fluorine by the oxide. Boese et al. [17] suggested that the development of catalytic activity requires a minimal degree of fluorination. Quantitative XPS analysis shows that the fluorination level must exceed 10 atom% of the anions to achieve catalytic activity.

Although C–Cl bond is more labile than C–F bonds, only a small amount of chlorine remains deposited on the catalysts treated with $CHClF_2$. It is suggested that, the formation of aluminium chlorides is thermodynamically much less favorable than the formation of fluoride, so the existence of aluminum chloride is unlikely at the temperature chosen for this reaction (543 K). Boese et al. [17] also suggested that the role of chlorine in the activation process has a negligible influence on the development of catalytic activity.

Hess and Kemnitz [29] proposed the following halogen exchange reaction mechanism for C_1 halocarbons ($CHClF_2$ and CCl_2F_2). In the first step, the positively charged aluminum cations cause weaking of the C–halogen bond of the haloalkane molecule. Further steps involve attacking the positively charged aluminum cations by the nucleophilic group. In the case of a nucleophilic halogen atom of a second molecule of haloalkane, a dismutation reaction takes place, and in the case of a nucleophilic attack by halide ions of the solid surface, a halogen exchange occurs between the solid surface and the adsorbed haloalkane molecules.

In our experiments, Al_2O_3 experienced fluorination in a flow of halon 1211 at the temperature of 523 K (reactions 1 and 2 in Table 2). After more than 40 min on stream, Al_2O_3 became catalytically active and a dramatic increase in the conversion level of halon 1211 was observed (Fig. 2). There has been no report on the conversion of halon 1211 over Al_2O_3 or fluorinated alumina in the literature and the reaction mechanism involved is not clear. Our observations seem to suggest that, the conversion of halon 1211 over Al_2O_3 in the absence or presence of hydrogen follows a similar mechanism to the conversion of CCl_2F_2 or $CHClF_2$ over Al_2O_3. Aluminium cations in Al_2O_3 are not active initially, but the replacement of O or OH groups by fluorine (fluorination of Al_2O_3 support) activates the catalyst. Note, however, that the catalysts are unable to activate hydrogen, at least not at 523 K. This follows from the observation that, the products obtained in the absence and presence of hydrogen are very similar as mentioned earlier (Fig. 2), with no hydrogenated species detected upon the introduction of hydrogen. When Pd was incorporated on the Al_2O_3 support, the conversion level was slightly lower but the product distribution was very similar, which suggests that Pd is not an active site for halogen exchange reactions. It appears that Pd covers the surface of fluorinated Al_2O_3, making some active sites inaccessible to reactant molecules. As a result, the conversion level of halon 1211 is lower even at a lower space velocity of 1400 h^{-1}; that is, at longer contact times (Fig. 3).

When hydrogen is introduced together with halon 1211, the reaction follows a different pathway (hydrodehalogenation), with Pd activating hydrogen. It is well known that Pd can greatly facilitate the dissociative adsorption of hydrogen on Pd, resulting in the generation of active hydrogen adatoms. These adatoms then enhance the cleavage of C–halogen bonds on the surface of Pd, initiating the hydrodehalogenation reactions. In this case, halogen exchange reactions (or dismutation reactions) on the surface of the support become negligible, probably due to the following two reasons: (1) the support needs to be fluorinated to a certain extent before becoming active; (2) halogen exchange reactions require higher temperatures (over 473 K).

During the hydrodehalogenation of halon 1211, fluorination of support can still take place by spillover of fluorine (absorbed on the surface of Al_2O_3) to the neighboring Al_2O_3 or via the reaction of HF with Al_2O_3. Chlorination or bromination of support can also occur but to a much lesser extent as IC analysis suggests in Table 2. Replacement of O and OH groups by F in Al_2O_3 greatly increases the Lewis acidity of the support. Coq et al. [6,7] suggested that, AlF_x ($x < 3$), formed at the periphery of Pd during the course of CCl_2F_2 hydrogenation over Pd/AlF_3, was able to adsorb fluorine atoms, and the strong Lewis acidity of the fluoride species could induce electron deficiency ($Pd^{\delta+}$) in Pd atoms located in the vicinity of the fluorinated support. The electron deficient state of Pd could bind CF_2 radicals less strongly, and, as a result, CF_2 tends to be more readily hydrogenated to CH_2F_2 which desorbs from the surface into the gas phase, resulting in a higher selectivity to CH_2F_2. This also seems to be the case with hydrodehalogenation of halon 1211. With time on stream, Al_2O_3 experiences further fluorination and the interaction between fluorinated alumina and Pd intensifies correspondingly, resulting in an increasing selectivity to CH_2F_2. For Pd/AlF_3 in which, the support has been almost completely fluorinated, selectivity to CH_2F_2 remains relatively steady after an initial increase, while for Pd/F-Al_2O_3 or Pd/Al_2O_3 ($CHClF_2$) in which, Al_2O_3 experienced partial fluorination prior to hydrodehalogenation, the extent of change in selectivity falls between the pure Al_2O_3 and AlF_3. Since CF_2 is bonded loosely due to the effect of the fluorination of the support, the retention time of CF_2 on the surface of Pd will shorten. This could explain why, after the initial deactivation, the conversion level of halon 1211 in the case of Pd/Al_2O_3 and Pd/Al_2O_3 (CH_4) increased slightly with time on stream. Another possible reason is that the support can withdraw halogens from Pd surface, thus reducing the inhibiting effect of halogens. Lower activity of Pd/AlF_3 compared with Pd/Al_2O_3 and Pd/F-Al_2O_3 may be ascribed to the lower dispersion of Pd on

AlF_3 which has a much lower surface area than Al_2O_3 and F-Al_2O_3. In future work, we will conduct a detailed catalyst characterisation study in order to understand the effect of Pd dispersion on the hydrodehalogenation of halon 1211.

5. Conclusions

Conversion of halon 1211 has been studied over γ-Al_2O_3 and supported 0.5% Pd catalysts (Pd/Al_2O_3, Pd/fluorinated Al_2O_3, Pd/AlF_3, Pd/Al_2O_3 pretreated with CH_4 and $CHClF_2$, respectively). In the absence of hydrogen, the conversion of halon 1211 over Al_2O_3 and Pd/Al_2O_3 gives a similar product profile and the reactions follow a heterogeneous halogen exchange reaction pathway. Introduction of hydrogen has no apparent effect on either halon 1211 conversion or product profile during the conversion of halon 1211 over Al_2O_3.

In the presence of hydrogen, conversion of halon 1211 over supported Pd catalysts follows a mechanism that is different from halogen exchange reactions and hydrodehalogenation reactions take place mainly on the surface of Pd. Major products are hydrogenated species which include CH_2F_2, CH_4, C_2H_6, C_3H_8, CH_3Br and CHF_3. The most striking feature of hydrodehalogenation is that selectivity to CH_2F_2 increases with time on stream, especially on Pd/Al_2O_3 and Pd/Al_2O_3 treated with CH_4.

During the hydrodehalogenation of halon 1211 over Pd/Al_2O_3 catalysts, the alumina support experiences a partial fluorination, which is believed to increase the Lewis acidity of the support and induce electron deficiency in Pd atoms located in the vicinity of the fluorinated support. The electron deficient state of Pd could decrease the residence time of CF_2 on Pd, resulting in a higher selectivity to CH_2F_2.

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