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Catalytic hydrodehalogenation of halon 1211 ($CBrClF_2$) over γ-alumina-supported Ni, Pd and Pt catalysts

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Abstract

The hydrodehalogenation of halon 1211 over Ni, Pd and Pt supported on γ-alumina was studied. The effect of reaction temperature and hydrogen/halon 1211 input ratio was examined. Steady state catalytic activities of Pd and Pt are very similar, and much higher than that of Ni. Hydrodehalogenation over Pd favours the formation of CH_2F_2, while Pt and Ni produce primarily CH_4 and CH_3F, respectively. Product profiles suggest that the hydrodehalogenation of halon 1211 over Pd and Pt follows a reaction mechanism which is similar to hydrodehalogenation of CFC-12. Over Ni catalysts, the primary hydrodehalogenation reactions are those which first remove one halogen (Cl or Br) and then remove two halogens (one F and either Br or Cl). The higher mobility of hydrogen atom on the surface of Pt is consistent with the observation that only trace amounts of C_{2+} hydrocarbons were detected when Pt was used compared with Pd and Ni. Increasing selectivity to CH_2F_2 with time on stream over Pd and Pt is mainly ascribed to the transformation of support alumina to partially fluorinated alumina.

Keywords: Halon; CFC; $CBrClF_2$; CH_2F_2; Nickel; Palladium; Platinum; γ-Alumina; Fluorinated alumina; Catalytic hydrodehalogenation

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1. Introduction

Chlorofluorocarbons (CFCs) and halons (bromine-containing fluorocarbons and CFCs) are responsible for the depletion of the ozone layer in the stratosphere [1]. International efforts aimed at reducing the manufacturing, use and emission of these chemicals led to the signing of *The Montreal Protocol on Substances that Deplete the Ozone Layer* in 1987. This legislation, with its later amendments, required signatory nations to phase out the production of CFCs and halons [2]. The recovery and treatment of these chemicals presents a growing trans-national problem.

Treatment technologies can be classified as either destructive or transforming depending on the products formed. In destructive processes, CFCs and halons are usually converted into species such as CO_2, HX or X_2 ($X = F$, Cl and Br). Transforming processes, of which catalytic hydrodehalogenation is the most extensively studied, aim at converting the CFC or halon to a product with some intrinsic value, such as hydrofluorocarbons (HFCs). During hydrodehalogenation, in which CFCs or halons react with a hydrogen donor, CFCs and halons are transformed into a mixture of hydrocarbons, halocarbons and mineral acids. Some of the halogenated hydrocarbons produced in these processes, such as HFCs, are environmentally benign and can be used directly either as CFC or halon replacements or as chemical feedstocks. Catalytic hydrodehalogenation of CFCs and halons to HFCs has been intensively studied because it is energy efficient,

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and, in many cases, it selectively forms products of economic value.

Most research has focused on the catalytic hydrodehalogenation of CFCs, CCl_2F_2 (CFC-12) in particular. Supported group VIII noble metal catalysts have generally been the catalysts of choice for most of this research. Makkee and coworkers [3,4] reported the hydrodehalogenation of CCl_2F_2 and CCl_3F over carbon-supported noble metal catalysts. They found that Pd is especially 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), which make it an ideal CFC replacement in refrigeration applications. Selectivity to CH_2F_2, intrinsic catalytic activity and catalyst durability during hydrodehalogenation of CFC-12 over supported palladium catalysts are strongly influenced by many factors, including reaction conditions and nature of support. van de Sandt et al. [5,6] suggested that activated carbon is the most suitable support. A detailed assessment of the process for conversion of 10 000 t per year of CCl_2F_2 into CH_2F_2 by catalytic hydrodehalogenation over carbon-supported Pd catalysts suggests that, the process is both technically and economically feasible [5].

Conversely, little work has been done on the catalytic hydrodehalogenation of halons, especially halon 1211, which remains a major contributor to the depletion of the ozone layer [7,8]. Halon 1211 ($CBrClF_2$) is similar to CCl_2F_2 in terms of molecular composition except that a chlorine atom is replaced by a bromine atom. The difference in the bond dissociation energies between C and Br (265.7 kJ/mol) and C–Cl (323.0 kJ/mol) is much smaller than the difference between C and F (460.2 kJ/mol for CCl_2F_2) and C–Cl or C–Br [9,10]. This suggests that the selective removal of both Br and Cl atoms by catalytic hydrodehalogenation to produce CH_2F_2 would be feasible. Recently we reported the catalytic hydrodehalogenation of halon 1211 over carbon-supported Pd catalysts and found that Pd is active in the hydrogenolysis of halon 1211 [11]. Li et al. [12,13] investigated the catalytic hydrodehalogenation of halon 1301, which contains C–Br and C–F bonds only, over metal exchanged zeolite catalysts, and found that Ni-exchanged catalysts showed the highest activity for C–Br bond cleavage compared with other metal catalysts investigated. Supported Ni catalysts have also been reported to be active in the hydrodehalogenation of CFCs and brominated aromatic compounds [14,15].

In this research, we report the hydrodehalogenation of halon 1211 over γ-alumina-supported Ni, Pd and Pt catalysts. Pt was selected for study because it is often used in hydrogenation reactions and is known to cleave C–halogen bonds [16,17]. One of the primary aims of the present research was to compare the product selectivity of these three metals during the hydrodehalogenation of halon 1211. Our preliminary experimental work using alumina-supported Pd catalyst showed that the selectivity to CH_2F_2 increases dramatically with time on stream. The steady state selectivity is higher than that obtained when carbon-supported Pd catalysts were used at a similar halon 1211 conversion level and thus γ-alumina was used as support in the present investigation. Indeed, Coq et al. [18–23] and others also observed a similar trend (increasing selectivity to CH_2F_2 with time on stream) when working on the catalytic hydrodehalogenation of CCl_2F_2 over Pd/alumina catalysts. In this paper, we also study the effect of the alumina support on the catalytic activity and selectivity, and determine whether similar phenomena occurs when alumina-supported Pt and Ni are used as catalysts.

2. Experimental

2.1. Catalyst preparation

The catalyst support used in this study, γ-alumina, is commercially available (Mizusawa Chemicals, Japan) with a specific surface area of 120 m^2/g. Supported catalysts were prepared by impregnation with an aqueous solution of $Pd(NO_3)_2 \cdot 2H_2O$ (Sigma-Aldrich), $H_2PtCl_6 \cdot 6H_2O$ (Sigma-Aldrich) and $Ni(NO_3)_2 \cdot 2H_2O$ (Ajax Chemicals) to obtain nominal loading of 0.5 wt.% Pd, 0.5 wt.% Pt, as well as 0.5 and 5 wt.% Ni, respectively. 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 charged into an alumina microreactor and calcined in flowing air (60 cm^3/min) while being heated at a rate of 10 K/min to 773 K. The temperature in the reactor was held at this temperature for 3 h. After cooling down of the reactor to room temperature, the sample was reduced in flowing H_2 (12 cm^3/min) at a heating rate of 10 K from room temperature to 673 K and held at this temperature for 3 h for Pd and Pt catalysts and 16 h for Ni catalysts, respectively.

2.2. Catalytic experiments

All hydrodehalogenation experiments were conducted in a high purity (99.99%) alumina reactor (i.d. = 6.8 mm). A three zone electrically heated furnace, surrounding the alumina tube, was used to control the reaction temperature. A blank reaction using alumina chips was undertaken 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). In a typical run, the flow rate of the reacting gas mixture was 40 cm^3/min (STP), while the amount of catalyst used was 1.2 g. With a bulk density of the catalyst of 0.76 g/cm^3, this corresponds to a gas hourly space velocity (GHSV) of 1524 h^{-1}.

Directly after exiting the reactor tube, the product gas stream passed through a three-way valve. One branch of the stream was directed through a liquid trap (273 K) and subsequently through a caustic scrubber (0.1 M NaOH solution) to remove acid products HF, HCl and HBr before reaching an online Micro GC (Varian CP-2003) for quantification of gaseous carbon-containing products. The Micro GC is equipped with dual columns: 5A Molsieve column (343 K) to separate nitrogen, methane and hydrogen, and PoraPLOT Q column (373 K) used to separate hydrocarbons and halogenated hydrocarbons. An offline gas chromatograph–mass spectrometer (GC/MS-QP5000, Shimadzu) equipped with an AT-Q column was used for identification of gaseous product.

The alternative branch of the three-way valve directed the product gases to a transportable acid scrubber which contained 100 cm^3 of 0.1 M NaOH solution. The halogen halides (HF, HCl and HBr) formed during reaction combine with NaOH to form soluble sodium halides. Analysis of the effluent past the acid scrubber confirmed that halogen halides can be absorbed completely. The scrubber was removed and the concentration of halides was determined by an ion chromatograph (IC) (Dionex-100) equipped with an IonPac AS14A column (4 mm × 250 mm).

2.3. Catalyst characterisation

Spent catalyst samples for characterisation were taken after the catalytic hydrodehalogenation reactions reached a relatively steady state (typically after approximately 14 h on stream) at temperatures 443 K for Pd and Pt and 483 K for Ni, with an input ratio of N_2:H_2:halon 1211 of 25:9:1.

X-ray diffraction (XRD) patterns of the fresh and spent catalysts were obtained on a Philips Powder X-ray diffractomer (PW 1710). Halogen content on the surface of used catalysts 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) at a rate of 10 K from ambient temperature to 773 K and held at this temperature for 3 h. Hydrogen halides leaving the surface were trapped in the 0.1 M NaOH solution. Further increasing treatment time (up to 8 h) only slightly increased the amount of halogens trapped. Following this relatively high temperature hydrogenation treatment, the fluorinated alumina phase, as observed in XRD patterns of spent catalysts, disappeared. 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. The concentration of halides in the NaOH trap was then analysed by IC and the amount of halogen on the catalyst surface was estimated.

3. Results

Alumina support alone has been reported to be able to catalyse the dismutation of CFCs following activation [24–26]. Dismutation of CFC-12 over alumina involves the following reaction:

$$2CCl_2F_2 \xrightarrow{\gamma\text{-alumina},523\,K} CClF_3 + CCl_3F$$

Under all conditions investigated in this research, the γ-alumina support did not show any discernible activity for either hydrodehalogenation or dismutation of halon 1211. Blank experiments were also conducted to

Table 1
Steady state halon 1211 conversion, catalytic activity and selectivity to major carbon containing products (GHSV = 1524 h^{-1})

Catalyst	T (K)	H_2/halon ratio	Halon conv. %	Rate (μmol $(g_{metal}{}^{-1})\,s^{-1}$)	Selectivity (%)										
					$CHClF_2$	$CHBrF_2$	CH_2F_2	CH_3F	CH_3Cl	CH_3Br	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
0.5% Pd/Al_2O_3	443	2/1	5.9	9.3	0.3	0.8	52.3	5.5	3.5	11.9	3.2	0.7	15.8	0.3	4.4
	443	9/1	10.3	16.3	0.4	0.2	63.1	2.2	0.7	10.2	10.5	0.5	9.1	0.2	1.8
0.5% Pt/Al_2O_3	443	2/1	6.1	9.7	5.4	0.5	11.9	1.2	1.6	13.5	63.5	0.5	<0.1	<0.1	<0.1
	443	9/1	9.4	14.9	9.2	0.3	16.1	0.8	1.2	20.1	49.5	0.3	<0.1	<0.1	<0.1
5% Ni/Al_2O_3	483	2/1	4.7	0.7	10.8	7.3	1.0	71.5	0.7	0.2	2.1	1.5	0.4	3.2	<0.1
	483	9/1	9.0	1.4	6.9	12.8	1.7	65.0	0.1	0.3	3.5	4.8	0.4	2.9	<0.1

ascertain that the reaction did not take place in the absence of catalysts over the temperature range investigated. Since 0.5 wt.% Ni/alumina catalysts show only very minor catalytic activity under the conditions studied, a higher nickel loading catalyst (5% Ni/alumina) was used instead to obtain a comparable conversion level with the 0.5% Pd and Pt catalysts.

Catalytic hydrodehalogenation of halon 1211 over Ni, Pd and Pt catalysts show different catalytic performance. As shown in Table 1, the steady state catalytic activities of Pd and Pt (μmol_{CBrClF_2} (g^{-1}_{metal}) s^{-1}) are quite similar and much higher than that of Ni. For Ni catalysts, a higher Ni loading (5 wt.%) and reaction temperature (483 K) are required to obtain a similar halon 1211 conversion level with Pd and Pt catalysts (0.5 wt.% and 443 K, respectively). Steady state is taken when the change in catalyst activity and product selectivity varies by less than 1% over a 1 h period.

Cleavage of carbon–halogen bonds in the presence of hydrogen leads to the formation of hydrogen halides, which were removed from the gas stream with 0.1 M NaOH solution present in the acid scrubber. The concentration of halides in the scrubber solution was determined by IC and subsequently the amount of halogen halides in the effluent was estimated. The extent of C–halogen bond cleavage (the removal efficiency of halogens) during the catalytic hydrodehalogenation of halon 1211 is expressed as the ratio of the total number of moles of halogens trapped (per unit time) in the NaOH solution to the number of moles of halon 1211 converted, normalised for halogen content (per unit time). The removal efficiency of halogens at steady state is presented in Table 2. For all three catalysts, the removal efficiency of Br and Cl is much higher than that of F, consistent with C–Br and C–Cl bonds being more labile than C–F bonds, as suggested by C–halogen bond dissociation energies. At a similar halon 1211 conversion level, the extent of C–F bond cleavage over different catalysts increases in the following order: Pt > Ni > Pd. This result is consistent with the gas-phase analysis: Pt favours the formation of CH_4, Ni produces CH_3F at high selectivity and Pd displays high selectivity to CH_2F_2.

Fig. 1 shows the conversion of halon 1211 and selectivity of major carbon-containing product as a function of time on stream over different catalysts. Pd catalysts favour the formation of CH_2F_2, while Pt catalysts mainly produce the completely hydrogenated product

Table 2
Steady state removal efficiency of halogen and the amount of halogen retained on the used catalysts (100 mg) (GHSV = 1524 h^{-1}, volumetric input ratio of N_2:H_2:halon 1211 = 25:9:1)

Catalyst	T (K)	Removal efficiency of halogen (%)			The amount of halogen on the spent catalysts (100 mg) (mmol)		
		F	Cl	Br	F	Cl	Br
0.5% Pd/Al_2O_3	443	28.9	94.2	86.7	0.039	0.016	0.009
0.5% Pt/Al_2O_3	443	55.4	88.6	80.3	0.133	0.014	0.009
5% Ni/Al_2O_3	483	38.1	90.0	80.0	0.043	0.008	0.019

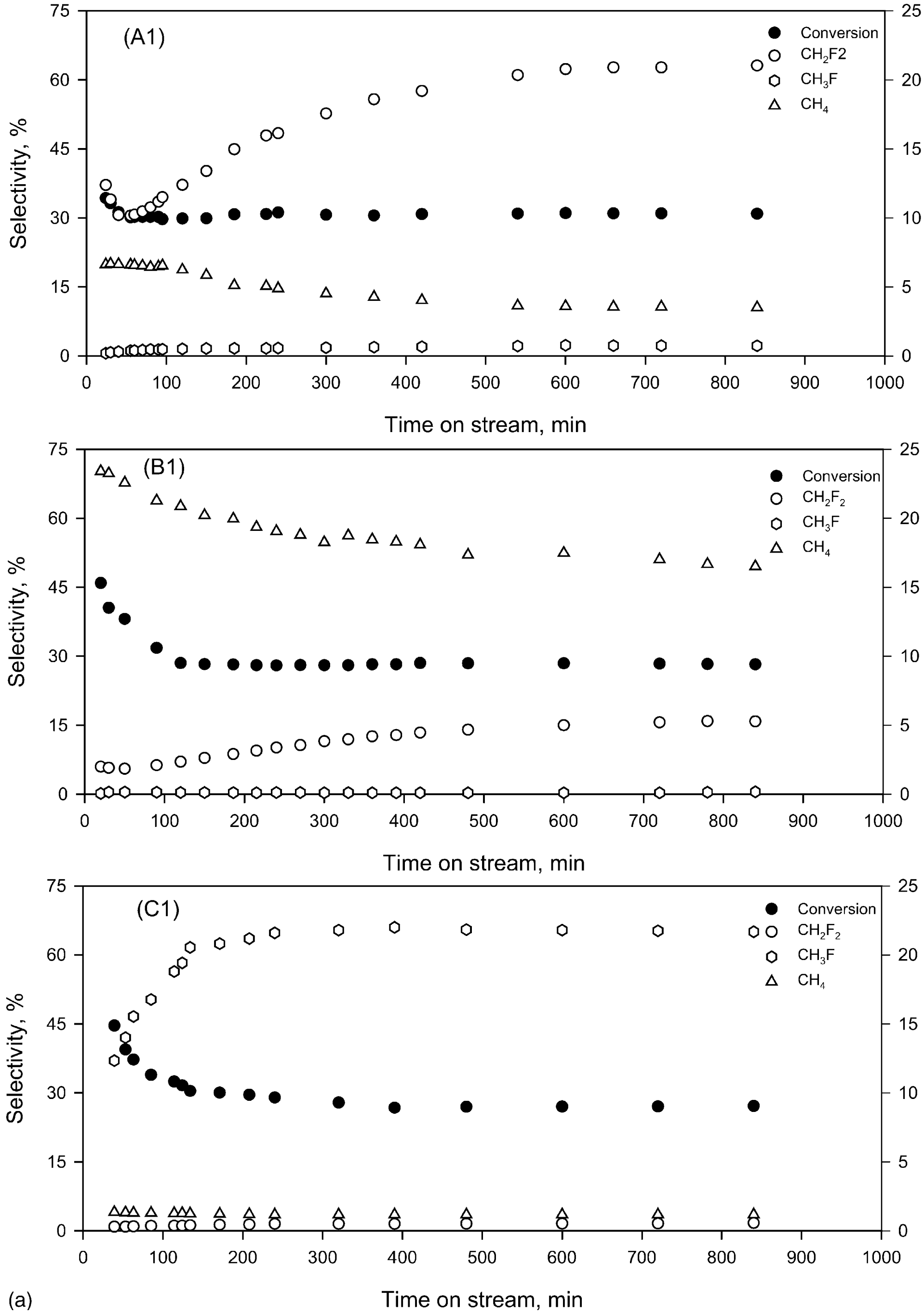

Fig. 1. (a) Conversion of halon 1211 and product selectivity (CH_2F_2, CH_3F and CH_4) as a function of time on stream; GHSV = 1524 h^{-1}; volumetric input ratio of N_2:H_2:halon 1211 = 25:9:1. (b) Selectivity to other major products (except CH_2F_2, CH_3F and CH_4) as a function of time on stream; GHSV = 1524 h^{-1}; volumetric input ratio of N_2:H_2:halon 1211 = 25:9:1. (A1, A2) 0.5% Pd/Al_2O_3, $T = 443$ K; (B1, B2) 0.5% Pt/Al_2O_3, $T = 443$ K; (C1, C2) 5% Ni/Al_2O_3, $T = 483$ K.

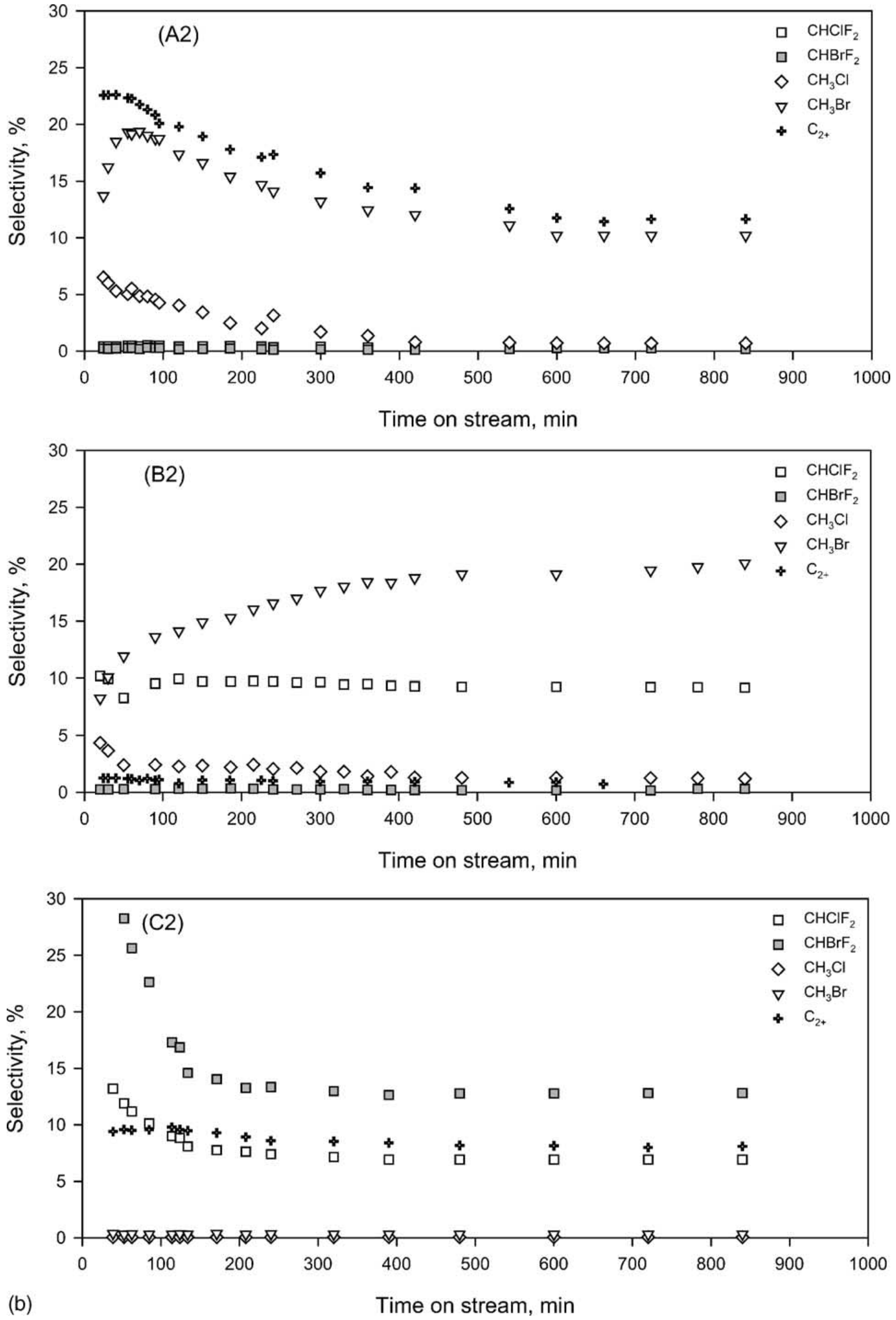

Fig. 1. (*Continued*).

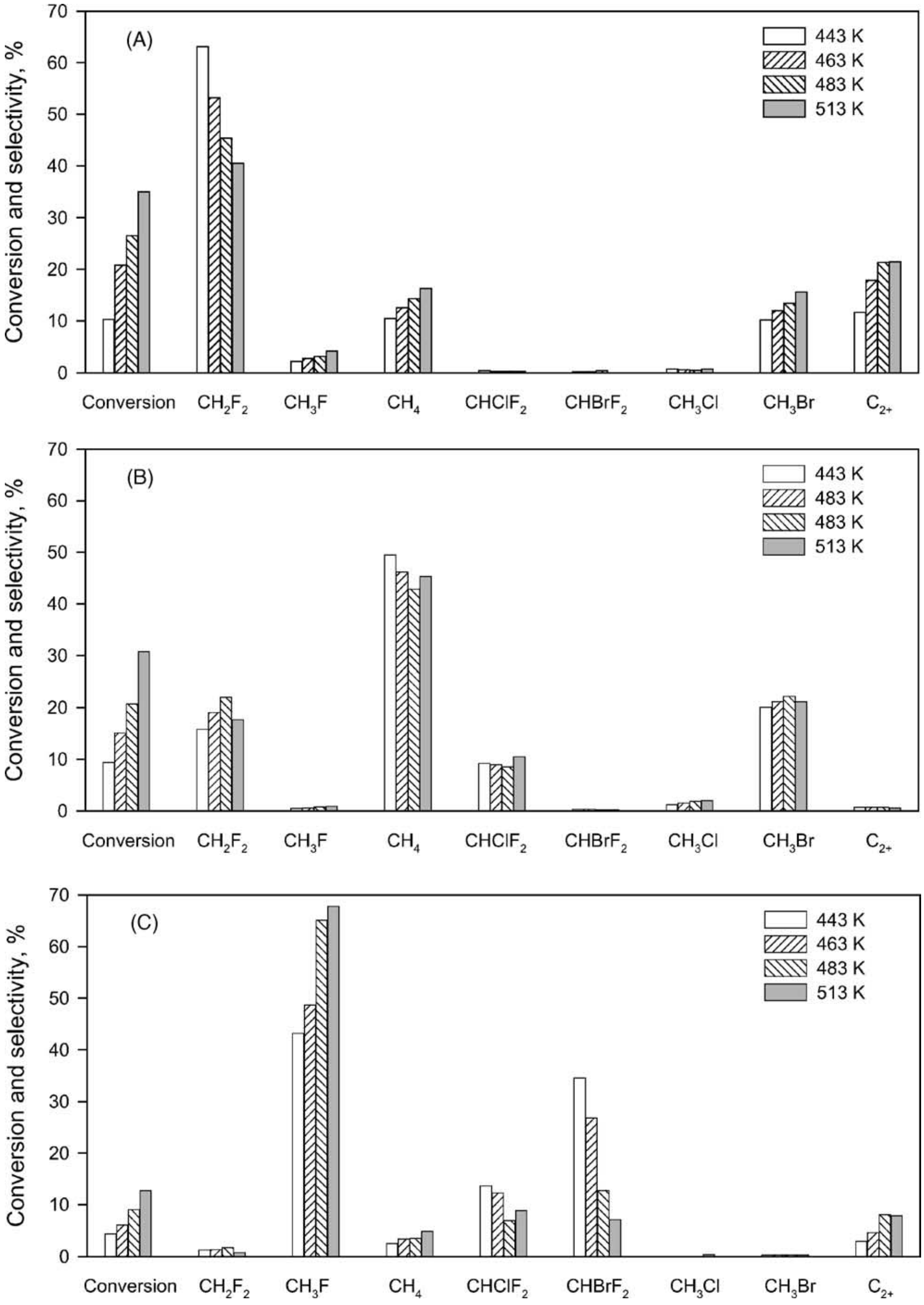

Fig. 2. Steady state conversion of halon 1211 and selectivity of the major products as a function of temperature; GHSV = $1524\,h^{-1}$; volumetric input ratio of N_2:H_2:halon 1211 = 25:9:1. (A) 0.5% Pd/Al_2O_3; (B) 0.5% Pt/Al_2O_3; (C) 5% Ni/Al_2O_3.

CH_4. For Ni catalysts, CH_3F is the dominant product while selectivity to CH_4 and CH_2F_2 is relatively low. Other major carbon containing products are also produced including CH_3F, CH_3Cl, CH_3Br, $CHClF_2$, $CHBrF_2$ and C_{2+} hydrocarbons (C_2H_4, C_2H_6, C_3H_6 and C_3H_8). The quantities of these products vary, according to the catalysts employed and reaction conditions. Also worth noting is that Pd and Ni catalysts show a higher selectivity to coupling products (C_{2+} hydrocarbons) than Pt catalysts. Only trace amounts of C_{2+} species are detected when a Pt catalyst is used.

All alumina-supported catalysts underwent an initial deactivation period. Ni and Pt displayed a greater magnitude of deactivation than Pd and more than 50% of their initial activities (after 20 min on stream) were lost. Following this deactivation period, all catalysts attained a steady state activity level. During and after this initial deactivation period, the selectivity to major products changed dramatically with time on stream. For Pd and Pt catalysts, selectivity to major product CH_2F_2 generally increases while selectivity to CH_4 decreases. For nickel catalyst, selectivity to CH_3F increases while selectivity to $CHBrF_2$ and $CHClF_2$ (less dehalogenated species) decreases.

Fig. 2 illustrates the effect of temperature on the steady state conversion and selectivity at a GHSV of $1524\,h^{-1}$ over a temperature range of 443–513 K. With an increase in temperature, the conversion of halon 1211 increases over all three catalysts, as expected. For Pd catalysts, increasing temperature leads to a lower selectivity to CH_2F_2 and a higher selectivity to hydrogenated products such as C_1–C_3 hydrocarbons and CH_3F. Ni catalysts follow a similar trend. Selectivity to C_1–C_3 hydrocarbons and CH_3F increase, while selectivity to $CHBrF_2$ and $CHClF_2$ decrease. In case of Pt catalysts, the effect of temperature on product selectivity does not follow a straightforward trend. For example, selectivity to CH_2F_2 increases at temperatures 443–483 K and then drops at 513 K.

The effect of hydrogen/halon 1211 molar ratio on the halon 1211 conversion level and major product selectivity is shown in Table 1 (the concentration of halon 1211 in the feed was kept constant). Halon 1211 conversion level increases with hydrogen/halon 1211 ratio. For Pd catalysts, higher hydrogen/halon 1211 ratio leads to a higher selectivity to CH_2F_2, CH_4 and lower selectivity to CH_3F, CH_3Cl, C_2H_6 and C_3H_8 while for Pt catalysts, with increase in hydrogen/halon 1211 ratio, selectivity to CH_2F_2, $CHClF_2$ and $CBrH_3$ increases and selectivity to CH_4 decreases. Over Ni catalysts, hydrogen/halon 1211 ratio has little effect on product selectivity over the ratio range investigated.

4. Discussion

Nickel, palladium, and platinum are all widely used hydrogenation catalysts [27,28]. However, significant differences exist in their hydrodehalogenation properties, as reported by those studying hydrodehalogenation of CFCs. For example, during the hydrodehalogenation of CCl_2F_2 over carbon-supported noble metal catalysts, Wiersma et al. [3] found that Pd is more active and selective to the formation of CH_2F_2 than Pt. Conversely, Kulkarni et al. [29] found that Pt is much more active than Pd, and primarily produces fully hydrodehalogenated C_1 species whereas Pd favours the formation of coupling products. In comparison with Pd catalysts for the hydrogenolysis of CCl_2F_2, Ni catalysts show a lower activity and the reaction mechanism involved is different from Pd, resulting in a different product profile [14].

The product profiles obtained in our study suggest that catalytic hydrodehalogenation of halon 1211 over alumina-supported Pd and Pt catalysts follows a similar reaction mechanism to CFC-12 reactions. Based on the studies of the hydrogenolysis of CCl_2F_2 and our previous research on the catalytic hydrodehalogenation of halon 1211 over Pd/C catalysts [3,11,17,21,30], the following mechanism (Fig. 3) could be used to explain the pathways to formation of major products.

Two major intermediates are CF_2 and CH_2 carbenes on the surface of catalysts. Selectivity to CH_2F_2 or more highly hydrogenated species such as CH_4 is mainly determined by the concentration of CF_2 and CH_2 on the surface of catalysts. Pt seems to cleave C–F more readily than Pd, leading to a higher concentration of CH_2 species on the surface of catalysts. As a result, selectivity to CH_2F_2 is much lower than when Pd catalyst is used under the same reaction conditions.

In the case of Ni catalysts, the dominant product is CH_3F, which retains only one C–F bond. Selectivity to CH_4 or CH_2F_2 is very low, which seems to suggest that hydrogenation of halon 1211 over Ni catalysts may follow a different reaction mechanism to that over Pd and Pt. Morato et al. [14] investigated the catalytic

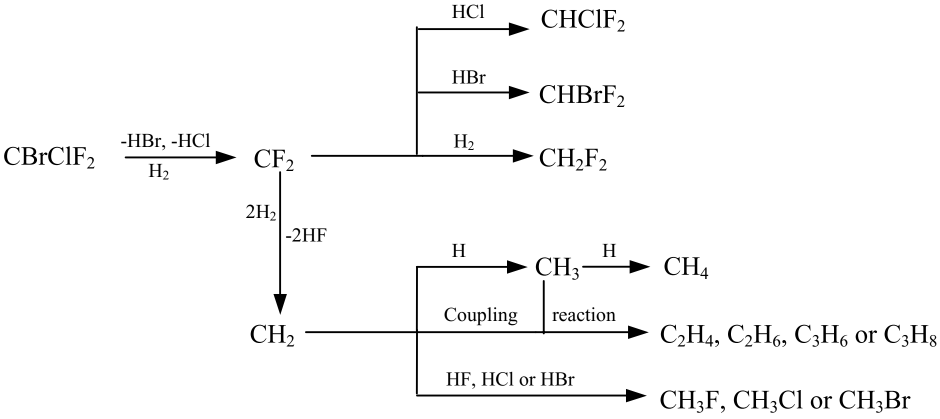

Fig. 3. Reaction scheme for halon 1211 hydrodehalogenation over alumina-supported Pd and Pt catalysts.

hydrodehalogenation of CCl_2F_2 over Ni catalysts, in which the major products were $CHClF_2$, CH_3F and coupling species. This product profile is very different from that obtained using Pd catalysts. Morato et al. suggested that the most common reactions (excluding the formation of coupling products) are those which allow first the removal of one chlorine atom during initial reaction on the surface of the catalysts, followed by the subsequent removal of the two remaining halogen atoms. They proposed the pathway for the conversion of CCl_2F_2 over Ni catalysts in which coupling products are not included:

$$CCl_2F_2 \rightarrow CHClF_2 \rightarrow CH_3F$$

In our experiments, CH_3F, $CHClF_2$ and $CHBrF_2$ were produced as major carbon-containing products, which suggests that hydrodehalogenation of halon 1211 over Ni catalysts follow a very similar reaction pathway to that suggested by Morato et al. [14]. Since C–Br and C–Cl bond dissociation energies are very close in comparison to C–F bond dissociation, either Br or Cl can be removed first and then two additional halogens Cl and F or Br and F are removed. The reaction scheme is illustrated below:

$$CBrClF_2 \rightarrow CHClF_2 \quad \text{or} \quad CHBrF_2 \rightarrow CH_3F$$

The different catalytic behaviour of Ni, Pd and Pt catalysts could be ascribed to many factors, including the interaction of halon 1211, hydrogen and intermediate species with metal or catalytic support. Clearly, the activation of hydrogen on the metal will play an important role in the observed difference in selectivity among these metals. Hydrogen is a chemically reactive gas that absorbs dissociatively on most transition metal surfaces, including Ni, Pd and Pt. The absorbed hydrogen atom can either reside on different adsorption (coordination) sites of metal surface or diffuse from one site to another [27,28,31,32]. Watson et al. [33] investigated the adsorption and diffusion of hydrogen on the {1 1 1} surface of Ni, Pd and Pt, based on density functional theory calculations. Their computational results show that the adsorption energies on the surface of Ni and Pd vary as a function of hydrogen coordination, with the 3-fold hollow sites being the most stable and the 1-fold atop site being considerably less stable. For Pt, the adsorption energies for all the adsorption sites are similar. Further investigation on the energy barriers to hydrogen diffusion across the {1 1 1} surfaces on Ni, Pd and Pt indicate that diffusion of hydrogen on the Pt{1 1 1} surface will occur more rapidly than on the Pd{1 1 1}and Ni{1 1 1} crystal faces. These differences in diffusion rate could explain the degree of coupling during the catalytic hydrodehalogenation of halon 1211 observed over Ni, Pd and Pt catalysts. Higher hydrogen mobility on Pt surface will allow hydrogen atoms to diffuse to the reaction sites to inhibit coupling reactions taking place. As a result, mainly hydrogenated C_1 species are produced and selectivity to CH_4 is correspondingly higher. Over Ni and Pd catalysts, however, a lower rate of hydrogen diffusion enhances the lifetime of C_1 species, facilitating the formation of coupling products. This phenomena will be more pronounced when H_2 partial pressures are lower (lower hydrogen/halon 1211 ratio), as shown in Table 1. A lower hydrogen/halon 1211 input ratio (2:1) leads to a higher selectivity to C_2H_6 and C_3H_8, while an increase in hydrogen/halon 1211 ratio results in a higher selectivity to C_1 products.

One striking feature of catalytic hydrodehalogenation of $CBrClF_2$ over all three alumina-supported catalysts is that product selectivity changes with time on stream, especially over Pd and Pt catalysts, even after the halon 1211 conversion level reaches a steady state. The changing catalytic performance (conversion and selectivity) with time on stream has been reported on the catalytic hydrodehalogenation of CFCs [18–23]. Deshmukh and d'Itri [30] speculated that the most active sites on the catalyst are responsible for cleavage of C–F bonds. After these active sites are blocked by carbonaceous deposits, the extent of C–F breakage decreases and formation of fully hydrogenated and coupling products is suppressed. Consequently, the selectivity to CH_2F_2 increases. A change in metal dispersion during reaction could either lead to an increase or a decrease in catalytic activity. Furthermore, it could lead to change in the observed selectivity. Wiersma et al. [3] reported that noble metals could undergo redispersion under the reaction conditions for hydrodehalogenation of CFCs. Conversely, the sintering of Pd catalysts in the hydrodehalogenation of CFCs was reported by several researchers [23,34,35], leading to a lowering of catalytic activity. Moon et al. [35] suggested that the sintering of Pd is the primary reason for the deactivation of Pd in the hydrodehalogenation of CF_2ClCF_3. However, it is not clear how the sintering of Pd affects product selectivity.

Our preliminary investigation of halon 1211 hydrodehalogenation, together with previous work on hydrodehalogenation of CCl_2F_2 over alumina-supported catalysts, seems to suggest that formation of metal carbide and interaction of support with metal are two major reasons for the changing selectivity during the hydrogenation of halon 1211.

The transformation of Pd to palladium carbide has been reported by many authors who studied the hydrodehalogenation of CFCs over Pd catalysts, including Pd black and Pd catalysts supported on carbon or alumina [19,23,34,36]. Juszczyk et al. [19] and Ahn et al. [23] suggested that Pd carbide is more selective for formation of CH_2F_2 during CCl_2F_2 hydrodehalogenation. However the experiments conducted by van de Sandt et al. [34] indicated that formation of palladium carbide takes place rapidly and thus a steady state activity and selectivity should be observed after a relatively short period on stream. Morato et al. [14] investigated the hydrodehalogenation of CCl_2F_2 and $CHClF_2$ over various nickel catalysts. They found that Ni supported on alumina was totally transformed into nickel carbide, which, they suggest, is more active than nickel metal. The effect of this transformation on product selectivity is not clear. There has been no report on the formation of platinum carbide during the hydrodehalogenation of CFCs over Pt catalysts.

In our research, the formation of metal carbide is difficult to detect by XRD, due to the interference of alumina pattern and the relatively low content of metal on the support. XRD analysis of 3% Pd/C catalysts, which were used in our previous investigation on the hydrogenation of halon 1211 [11], clearly showed the transformation of Pd to Pd carbide (Fig. 4). Although selectivity to CH_2F_2 increases initially in that case, it remains steady after the conversion level becomes constant. It seems that, during the hydrodehalogenation of halon 1211 over Pd/alumina catalysts, the transformation to palladium carbide also takes place. But this transformation probably occurs during the initial deactivation period. As mentioned previously, selectivity to CH_2F_2 over Pd and Pt catalysts continues to increase even after the halon 1211 conversion level is constant, and this seems to suggest that other factors play an additional role in the observed changing selectivity once activity is constant.

The support has a strong influence on hydrodehalogenation selectivity and activity. Many authors report an increasing selectivity to CH_2F_2 with time on stream during hydrodehalogenation of CCl_2F_2 over Pd/alumina catalysts [18–23]. One important finding of their work is the transformation of alumina to aluminium fluoride or partially fluorinated alumina during reaction. Coq et al. [20,21] suggested that AlF_x ($x < 3$) was formed at the periphery of and on the Pd particles during the course of CCl_2F_2 hydrogenation, and that these species are able to absorb fluorine atoms, hence effectively scavenging the surface and "protecting" the Pd particles against the diffusion of fluorine into the bulk. Moreover, the strong Lewis acidity of the fluoride species could induce electron

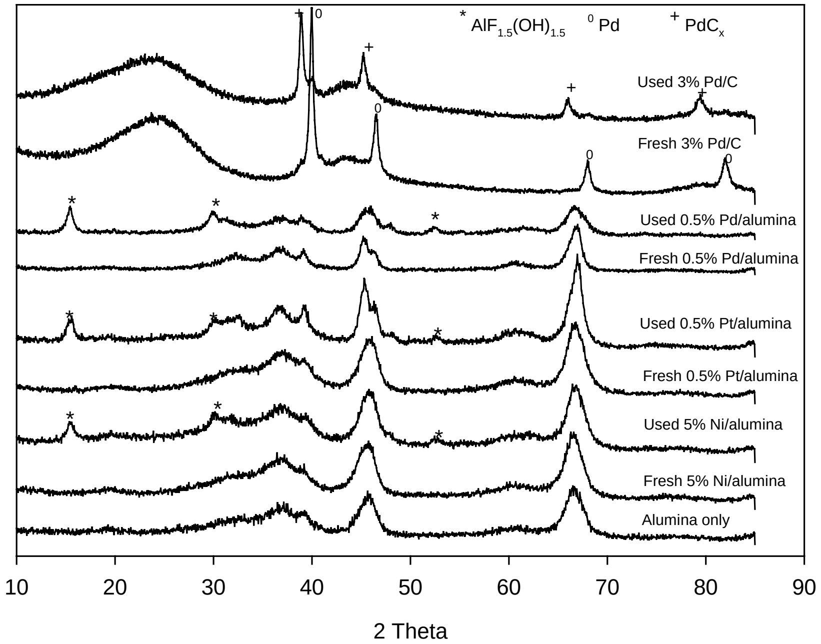

Fig. 4. XRD pattern of alumina (support) and used catalysts. Fresh and used 3% Pd/C catalysts are also included in the figure for reference, although they were not used in this study.

deficiency ($Pd^{\delta+}$) in Pd atoms located in the vicinity of the support. The electron deficient state of Pd should bind CF_2 radicals less strongly, and, as a result, CF_2 would tend to be more easily hydrogenated to CH_2F_2 with this species desorbing from the surface, leading to a higher selectivity to CH_2F_2 with time (the extent of fluorination of alumina increases with time). On ZrO_2 support [20], which cannot be fluorinated under conditions investigated or on alumina which has been fluorinated prior to hydrodehalogenation experiments [22,23], the selectivity to CH_2F_2 remains relatively stable.

Our experimental results support Coq's argument that the interaction between alumina and metal is the main reason for an increasing selectivity to CH_2F_2. IC analysis of used alumina-supported catalysts show that a large amount of fluorine exists on the spent catalysts. XRD analysis of used catalysts clearly shows the transformation of alumina to partially fluorinated alumina-$AlF_{1.5}(OH)_{1.5}$ (Fig. 4). As suggested, Pd and Pt follow a similar reaction mechanism during halon 1211 hydrodehalogenation. Thus it is very likely that the formation of fluorinated alumina will affect the catalytic performance of Pd and Pt in a similar way. This seems to be the case in our investigation. For Pd and Pt catalysts, the selectivity to CH_2F_2 increases while selectivity to CH_4 and other hydrogenated species such as coupling products decreases (Fig. 2). Compared with the amount of fluorine on the different metals (Table 2), it has been found that a much higher level of fluorine exists on the surface of Pt than on that of Pd, which suggests that Pt impregnated alumina undergoes a greater degree of fluorination. This fluorination becomes more pronounced at higher temperatures, inducing a stronger interaction between the support and metal. On the other hand, increasing temperature favours the cleavage of C–F bonds. So, the competing effect of fluorination of support and the cleavage of C–halogen bonds at higher temperatures would lead to a CH_2F_2 selectivity trend with temperature, which is different from Pd, as shown in Fig. 2(B).

5. Conclusions

Marked differences in catalytic performance for γ-alumina-supported Ni, Pd and Pt catalysts were observed during the hydrodehalogenation of halon

1211. The steady state catalytic activities of Pd and Pt are similar, and much higher than that of Ni. Product profiles suggest that hydrodehalogenation of halon 1211 over Pd and Pt follows a similar reaction mechanism, in which Pd favours the formation of CH_2F_2 while Pt mainly produces CH_4. Over Ni catalysts, the primary hydrodehalogenation reactions are those which first remove one halogen (Cl or Br) and then remove two halogens (one F and the remaining Br or Cl atoms), resulting in the formation of $CHClF_2$, $CHBrF_2$ and CH_3F as major C_1 products. The higher mobility of hydrogen atoms on the surface of Pt could explain the result that only trace amounts of coupling products were detected when Pt was used. Increasing selectivity to CH_2F_2 with time on stream over Pd and Pt is mainly ascribed to the transformation of alumina to the fluorinated alumina, which is pronounced for Pt impregnated alumina.

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