

# Conversion of dichlorodifluoromethane with hydrogen over Pd/AlF<sub>3</sub> and Ru/AlF<sub>3</sub> prepared by sol–gel method

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## Abstract

The reaction of dichlorodifluoromethane and hydrogen has been studied in the gas phase at temperatures 438–538 K and atmospheric pressure over Pd and Ru supported AlF<sub>3</sub> catalysts prepared by sol–gel method. For the hydrogenation of CF<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>F<sub>2</sub> and CH<sub>4</sub> represented more than 97% of the products. The catalytic properties of the catalysts are unchanged with time and they showed no significant difference in their activities. At the steady state, the kinetics of the reaction described by a mechanism of a halogenation/dehalogenation of the Pd and Ru surfaces by CF<sub>2</sub>Cl<sub>2</sub> and H<sub>2</sub>, respectively. The values of the respective rate constants were then determined. It was concluded that at 448 K, the interaction between the Pd and Ru surfaces with CF<sub>2</sub>Cl<sub>2</sub> or H<sub>2</sub> is of the same order of magnitude. The conversion ratio on Ru/Pd supported catalysts within the temperature range used was increased from 1.5 to 4.1, while the selectivity of CH<sub>2</sub>F<sub>2</sub>/CH<sub>4</sub> ratio was decreased from about 17.4 to 1.8 on the surfaces of both catalysts. This leads to the proposition that the high dispersion of Pd and Ru over the support are responsible for the high activity and high selectivity in CH<sub>2</sub>F<sub>2</sub>.

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## 1. Introduction

Chlorofluorocarbons (CFCs) are industrially important compounds which are extremely stable. With the recent international restrictions on the production and deployment of CFCs, much effort is currently taking place to search for suitable ozone-friendly replacements. Owing to their chemical and physical properties, CFCs are largely used as propellants for domestic use, solvents, blowing, and refrigerants. For the latter applications, hydrochlorofluorocarbons (HCFCs), which have a limited effect on the ozone layer [1], and hydrofluorocarbons (HFCs), a non-ozone depleting compounds, are excellent candidates as substitutes for CFCs.

The catalytic conversion of CFCs by hydrogen to HCFCs and HFCs is a challenging task for heterogeneous catalysis [2–7]. One important industrial process is the hydrodechlorination of CF<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>F<sub>2</sub>, which are considered a good substitute for CF<sub>2</sub>Cl<sub>2</sub> in refrigerant applications [8]. All of these reactions require selective cleavage of C–Cl bonds

which in turn require highly selective catalysts. It appears that hydrogenolysis of the C–Cl bonds occur more readily than hydrogenation of the C=C bonds, which in turn is faster than hydrogenolysis of C–F bonds.

Numerous examples of hydrodechlorination catalysts are described in [9–16], many of which emphasize on the superior performance of platinum and palladium supported catalysts. Several factors have been found to influence the activity and selectivity of hydrodechlorinating catalysts. These factors include support material, metal particle size, and reaction conditions. Palladium supported on carbon or AlF<sub>3</sub> seems to be the best catalysts in order to obtain fluoroalkanes [4–6,14–16]. Coq et al. [14] reported that Pd supported on AlF<sub>3</sub> had higher initial activity than Pd supported on either carbon or Al<sub>2</sub>O<sub>3</sub>.

All previous hydrodechlorination of CFCs, focused on the use of Pd over different supports prepared by conventional impregnation methods. This study focuses on the hydrodechlorination of CF<sub>2</sub>Cl<sub>2</sub> catalyzed by Pd/AlF<sub>3</sub> and Ru/AlF<sub>3</sub> prepared by a sol–gel method. This method gives a very large BET surface area for supported metal catalysts, high metallic dispersion, and higher thermal stability [17,18]. The catalyst of Ru/SiO<sub>2</sub> prepared by sol–gel

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method produced a stable microporous solid with very large surface area which did not sinter or volatilize following treatment with O<sub>2</sub> at high temperatures [19]. The influence of high dispersion of the metallic phase (high surface area) on the catalytic properties was studied in details. The effect of time-on-stream on the catalytic activity and selectivity, the effect of reactant concentrations, and temperature on the selectivity and reaction rate were carefully studied. The results of both catalysts were analyzed and compared with previous published results of hydrodechlorination of CFCs compounds.

## 2. Experimental

### 2.1. Materials

All chemicals used were of reagent grade and used as received without further purification. Hydrogen (high purity grade, 99.99%), helium and nitrogen (both 99%) gases (International Industrial and Medical Liquid-Gas Co.). Dichlorodifluoromethane, CF<sub>2</sub>Cl<sub>2</sub> (purity >99.9%, was checked by GC and dried over molecular sieve 5 Å, Mafron), PdCl<sub>2</sub> and RuCl<sub>3</sub> (Janssen Chemica, both 99%), absolute ethanol (99.99%, Baker Analyzed). Analysis of the reactions was followed by gas chromatography (Chrompack Packard, model 437 A, connected with FID detector using 5% Fluorocol, 60/80 carboxpack B column, 10 ft × 1/8 in. (Supelco)). The data was collected on SP thermoseparation electronic integrator (Spectraphysics Product, Data Jet). The temperature of the oven, injector and detector were maintained at 318, 433 and 473 K, respectively. The temperature of the reaction was controlled using a variable AC transformer as a power supply and a temperature controller (AntinessControls, TCE). The gas flow was controlled by using a mass flow controllers (Cole Parmer) and a two-channel manual flow meter controller (Gilmont, Model 150 MM).

### 2.2. Catalysts preparation

The supported catalysts Pd/AlF<sub>3</sub> and Ru/AlF<sub>3</sub> of 0.50% (w/w) metal loading used in this study were prepared by the sol-gel method. A calculated mass of anhydrous aluminium chloride salt (AlCl<sub>3</sub>) which is needed to prepare the desired AlF<sub>3</sub> support was dissolved in a sufficient amount (about 30 ml) of absolute ethanol in a crucible. The mixtures was stirred and heated in a water bath to 333 K for 20 min [ethoxy derivatives are formed immediately, i.e. Al(OEt)<sub>3</sub>]. The pH of the solution was adjusted to 1 by the addition of HCl solution, then the required weight of PdCl<sub>2</sub> or RuCl<sub>3</sub> (needed to prepare the 0.50% metal sol-gel supported catalyst) was suspended in a minimum amount of absolute ethanol and added to the solution. A specific volume of hydrofluoric acid solution (HF, 40% (v/v)) was then added slowly over 30 min period in which a gel starts to appear after the second drop. The reaction solution was then heated at 343 K for

3–4 h with a thorough stirring to maintain the formed gel homogeneous (metal salt over AlF<sub>3</sub>). In order to evaporate the ethanol and the moisture, the temperature of the water bath was increased to a suitable temperature. The gel formed was then stirred from time-to-time in order to get homogeneous dispersion, and left over night to complete drying. Calcination and hydrogenation procedure were followed under air at 473 K for 1 h and hydrogen for 4 h at 723 K.

### 2.3. Catalysts characterization

Total surface area of both Pd/AlF<sub>3</sub> and Ru/AlF<sub>3</sub> were measured by N<sub>2</sub> physisorption at its saturation pressure using BET method. The surface area for both catalysts are 519 and 829 m<sup>2</sup>/g, respectively. FT-IR analyses (solid samples in KBr disks) were done for Pd/AlF<sub>3</sub> and Ru/AlF<sub>3</sub> catalysts. Spectra of both catalysts possess all the features expected for those catalysts. Pd and Ru dispersion were measured by chemisorption of hydrogen in a conventional volumetric apparatus at 523 K in the 0–30 kPa pressure range. The sample was first reactivated in situ in a hydrogen stream at 523 K overnight and then evacuated to  $1.3 \times 10^{-3}$  Pa at the same temperature for 2 h. The double isotherm method proposed by Benson et al. [20] was used to measure the amount of hydrogen chemisorbed on the surface of both catalysts. The first isotherm consist of both adsorbed and absorbed hydrogen; outgassing at room temperature for 40 min removes adsorbed hydrogen on the surfaces. The second (back-sorption) isotherm represents the amount of hydrogen absorbed into the bulks of Pd and Ru since hydrogen chemisorbed on the Pd and Ru surfaces has not been removed by evacuation at room temperature. The difference between the two curves represents the isotherm of adsorption of hydrogen. The metal dispersion (%) was calculated as  $D = (H/Pd \text{ or } H/Ru \text{ ratio}) \times 100$  with the assumed surface stoichiometry of one adsorbed hydrogen molecule per Pd or Ru atom.

### 2.4. Catalytic experiments

The reaction of CF<sub>2</sub>Cl<sub>2</sub> with hydrogen was carried out at atmospheric pressure in a glass fixed-bed reactor. Reaction rates are expressed as micromole of reactant (CF<sub>2</sub>Cl<sub>2</sub>) converted per unit of contact time (min) and mass (g) of catalyst. Product selectivities are defined as  $S_i (\%) = 100C_i / \sum C_i$ , where  $C_i$  is the moles of the detected product  $i$ . Hydrogen chloride and hydrogen fluoride formed during the reaction were not taken into account as reaction products. They were adsorbed on a precolumn filled with the mixture of ZnCl<sub>2</sub>, NaF and Cu [14]. The pressure ratio of CF<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub> used in this study for both catalysts and for all reactions is 0.33.

Usually some catalysts suffer changes of activity and selectivity with time-on-stream, therefore, a protocol was developed which allowed the catalyst to reach constant catalytic activity. The protocol used for catalytic tests was: (1) the reaction conditions were fixed at reaction

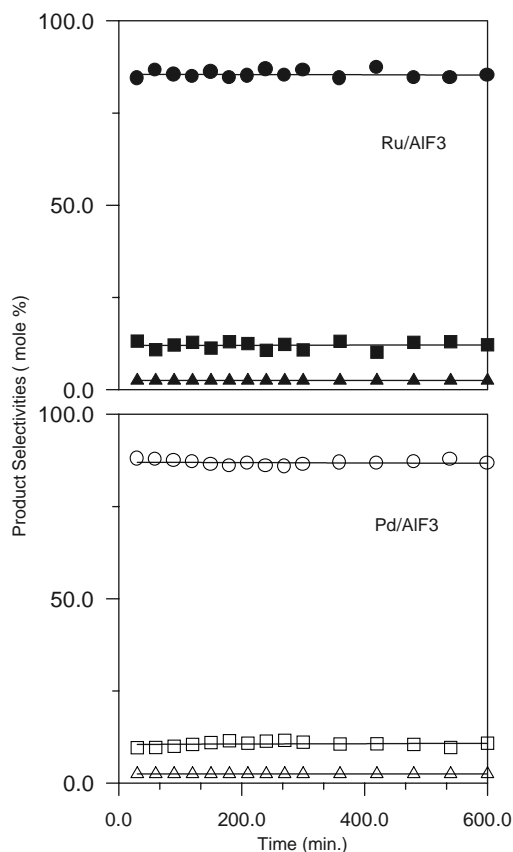


Fig. 1. Product selectivities for the hydrogenation of  $\text{CF}_2\text{Cl}_2$  over Pd and Ru supported catalysts as a function of time during a 10h duration on stream, temperature = 473 K, pressure ratio ( $\text{CF}_2\text{Cl}_2/\text{H}_2$ ) = 0.33. (○)  $\text{CF}_2\text{H}_2$ , (□)  $\text{CH}_4$ , (▲) (△) by-products.

temperature = 475 K, pressure ratio  $\text{CF}_2\text{Cl}_2/\text{H}_2 = 0.35$ , and space velocity =  $2200 \text{ h}^{-1}$  (flow rate = 20 ml/min, sample volume = 0.54 ml) for 15 h which corresponds to the passivation of the catalyst (attainment of constant activity and selectivity); (2) the reaction temperature was varied in sequence of (475, 430, 455 and 416 K) with pressure ratio  $\text{CF}_2\text{Cl}_2/\text{H}_2 = 0.30$  and space velocity between 2100 and  $1400 \text{ h}^{-1}$ ; (3) at a reaction temperature of 455 K, the feed composition was varied in the range between  $0.05 < \text{CF}_2\text{Cl}_2/\text{H}_2 > 3$  with space velocity in the range between 2100 and  $1400 \text{ h}^{-1}$ . With these conditions of test and after the passivation period, the catalytic activity was stable as a function of time-on-stream (Fig. 1). Each fresh catalyst sample was activated before using it in any reaction by flowing hydrogen at 723 K for 1 h, then cooling the catalyst to room temperature under helium gas flow. The catalyst must be placed in the same glass fixed-bed reactor to continue the hydrogenation reaction on it.

### 3. Results

The hydrogenation of dichlorodifluoromethane catalyzed by Pd/AlF<sub>3</sub> and Ru/AlF<sub>3</sub> resulted in the formation of two

main products:  $\text{CH}_2\text{F}_2$  and  $\text{CH}_4$ , which usually represent more than 97% of the products. Trace amounts of  $\text{CHF}_2\text{Cl}$ ,  $\text{CHFCl}_2$ ,  $\text{CH}_3\text{F}$  and  $\text{CF}_3\text{Cl}$  were detected and grouped cumulatively as “by-products” in selectivity measurements. The amount of  $\text{CHF}_2\text{Cl}$  and  $\text{CHFCl}_2$  decreased with time-on-stream during the passivation of the catalysts.  $\text{CF}_3\text{Cl}$  product (very probably) was formed by F/Cl exchange between  $\text{CF}_2\text{Cl}_2$  and HF, since AlF<sub>3</sub> is considered a good catalyst to prepare  $\text{CF}_3\text{CFCl}_2$  from  $\text{CFCl}_2\text{CF}_2\text{Cl}$  at 673 K [21].  $\text{CF}_2\text{Cl}_2$  was hydrogenated on the surface of both catalysts under various reaction conditions to study at steady states the effect of time, concentration, feed composition and temperature on the catalysts activity and selectivity. This will lead to the kinetic study of the reactions rate and activation energies.

Fig. 1 shows the effect of time-on-stream on the product selectivity for both catalysts at 473 K. The selectivities towards formation of major products showed linear and insignificant variations. Figs. 2 and 3 illustrates the dependence of the product selectivities and rate of reaction at

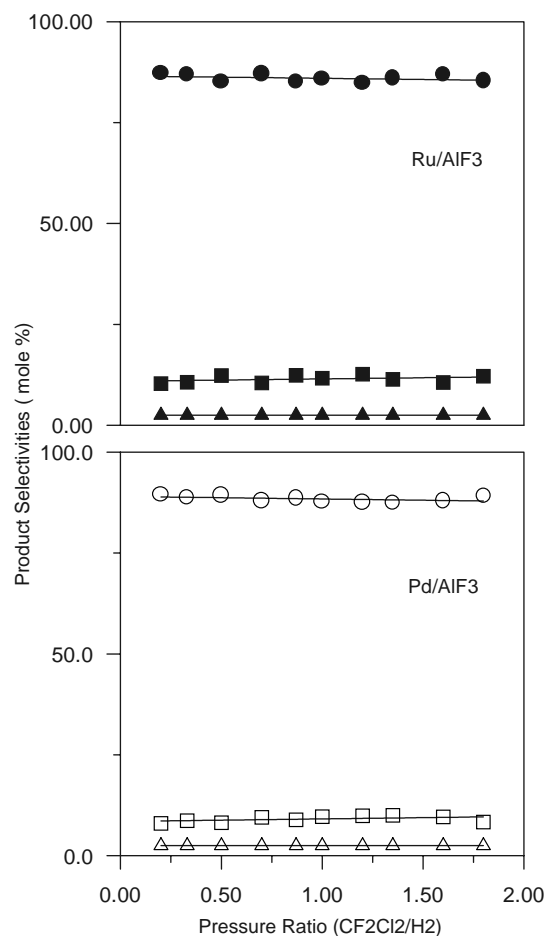


Fig. 2. Product selectivities for the hydrogenation of  $\text{CF}_2\text{Cl}_2$  over Pd and Ru supported catalysts as a function of feed composition during the first 2–3h on stream, temperature = 448 K, pressure ratio  $0 < (\text{CF}_2\text{Cl}_2/\text{H}_2) > 2$ . Symbols as in Fig. 1.

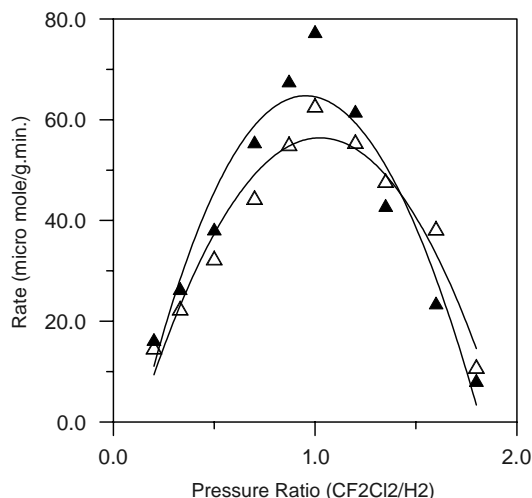


Fig. 3. Reaction rate for the hydrogenation of CF<sub>2</sub>Cl<sub>2</sub> over Pd/AlF<sub>3</sub> and Ru/AlF<sub>3</sub> catalysts as a function of feed composition during the first 2–3 h on stream, temperature = 448 K, pressure ratio  $0 < (CF_2Cl_2/H_2) > 2$ . Pd ( $\Delta$ ), Ru ( $\blacktriangle$ ).

temperature = 448 K on the feed composition (pressure ratio:  $0 < CF_2Cl_2/H_2 > 2$ ) for both catalysts. In the range studied, the feed composition had little influence on the product selectivities for both Pd and Ru supported catalysts, while the effect on the activities goes through a maximum (62.4 μmol/(g min) for Pd and 77.1 μmol/(g min) for Ru) then decreased. This behaviour indicates that there is a competition of adsorption between H<sub>2</sub> and CF<sub>2</sub>Cl<sub>2</sub> for adsorption on active sites [15]. The same trend of feed composition on product selectivities and rate of reaction was also reported by [14–16] for the hydrogenation of CF<sub>2</sub>Cl<sub>2</sub> using different Pd catalysts. Fig. 4 shows the effect of increasing conversion on product selectivity for both catalysts at temperature = 538 K. When the conversion increases the

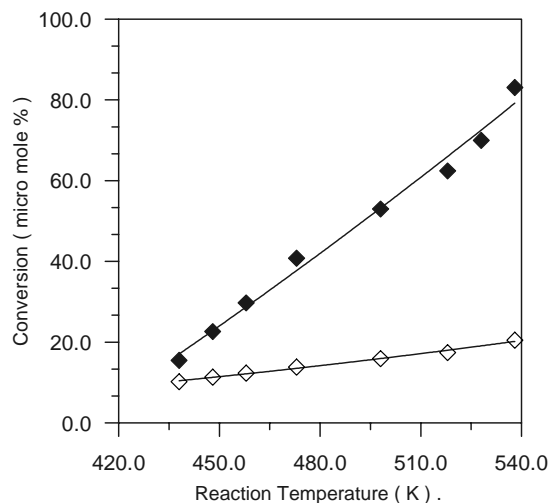


Fig. 5. Reactant conversion for the hydrogenation of CF<sub>2</sub>Cl<sub>2</sub> over Pd/AlF<sub>3</sub> and Ru/AlF<sub>3</sub> supported catalysts as a function of reaction temperature during a 10 h duration on stream, temperature = 438–538 K, pressure ratio (CF<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>) = 0.33. ( $\diamond$ ) Pd, ( $\blacklozenge$ ) Ru.

ratio of CH<sub>4</sub>/CH<sub>2</sub>F<sub>2</sub> increases also, suggesting that a formation consecutive reactions: CF<sub>2</sub>Cl<sub>2</sub> → CH<sub>2</sub>F<sub>2</sub> → CH<sub>4</sub>. Figs. 5 and 6 illustrate the effect of increasing temperature, for both catalysts, on the degree of percentage conversion and product selectivity, respectively, in temperature range = 438–538 K and during 10 h duration on stream. Conversion on Pd/AlF<sub>3</sub> increased from 10 to 20 mol% while the conversion on Ru/AlF<sub>3</sub> increased from 15 to 83 mol% within the temperature range used, selectivity on CH<sub>4</sub> increased from about 5 to 34 mol% and decreased on CH<sub>2</sub>F<sub>2</sub> from about 92 to 63 mol% on the surfaces of both catalysts. The effects of increasing temperature on both the selectivity ratio CH<sub>2</sub>F<sub>2</sub>/CH<sub>4</sub> and rate of reaction are summarized in Table 1.

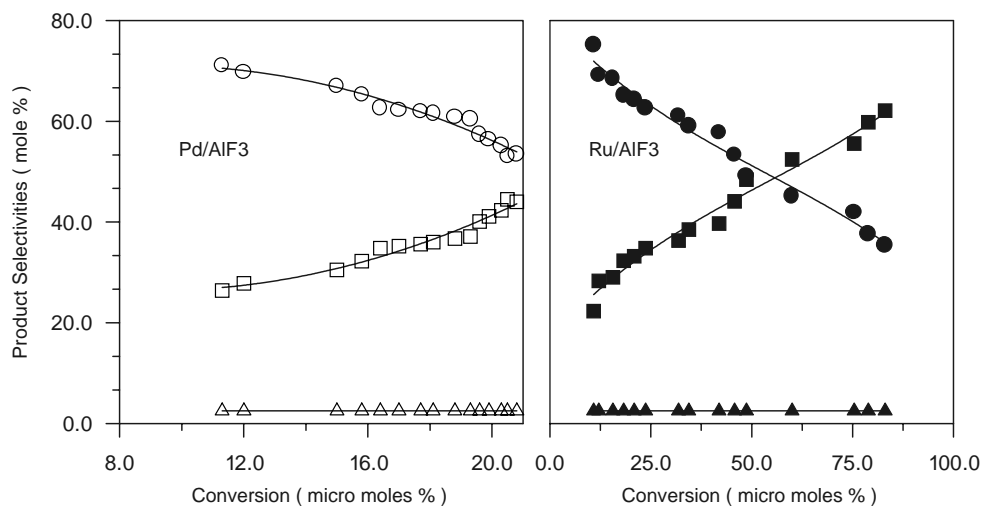


Fig. 4. Product selectivities for the hydrogenation of CF<sub>2</sub>Cl<sub>2</sub> over Pd and Ru supported catalysts as a function of reactant conversion during 10 h duration on stream at temperature = 538 K, pressure ratio (CF<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>) = 0.33. Symbols as in Fig. 1.

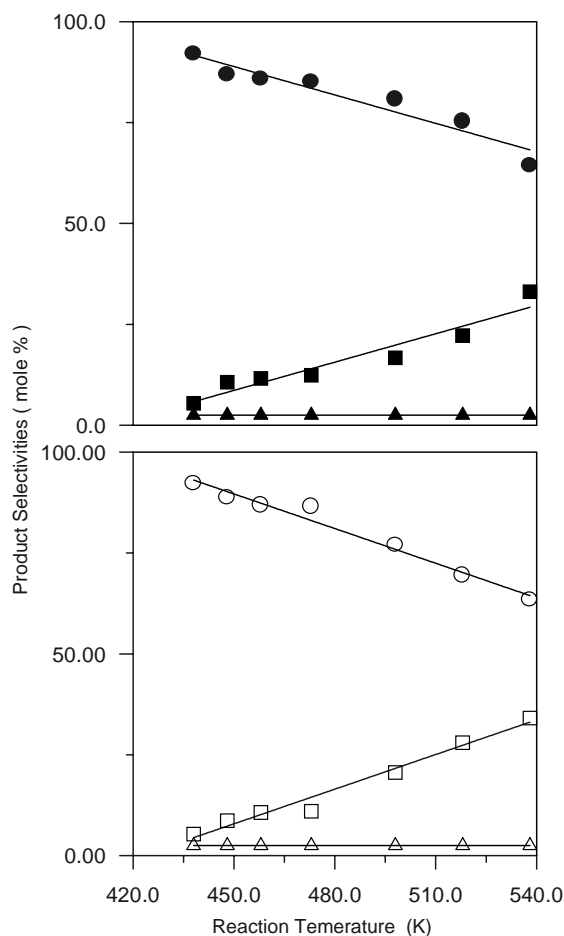


Fig. 6. Product selectivities for the hydrogenation of  $\text{CF}_2\text{Cl}_2$  over Pd and Ru supported catalysts as a function of reaction temperature during a 3 h duration on stream, temperature = 438–538 K, pressure ratio ( $\text{CF}_2\text{Cl}_2/\text{H}_2$ ) = 0.33. Symbols as in Fig. 1.

Table 1  
Change of catalytic properties of Pd/ $\text{AlF}_3$  and Ru/ $\text{AlF}_3$  catalysts during 2–3 h on stream;  $\text{CF}_2\text{Cl}_2/\text{H}_2 = 0.33$

Temperature (K)	Pd/ $\text{AlF}_3$		Ru/ $\text{AlF}_3$	
	$\text{CH}_2\text{F}_2/\text{CH}_4$	Reaction rate <sup>a</sup>	$\text{CH}_2\text{F}_2/\text{CH}_4$	Reaction rate <sup>a</sup>
438	17.4	14.0	17.1	7.9
403	4.0 <sup>b</sup>	–	–	–
448	10.2	22.1	8.1	26.1
448 <sup>c</sup>	10.5	24.2	8.3	26.9
	10.6	24.5	7.8	28.1
458	8.1	42.3	7.4	45.0
473	7.9	57.8	6.7	66.0
473	3.8 <sup>d</sup>	–	–	–
498	3.7	81.6	4.8	100.0
518	2.5	96.0	3.4	123.4
538	1.9	109.5	1.9	154.0

<sup>a</sup> Expressed in  $\text{mol}/(\text{g min}) \times 10^6$ .

<sup>b</sup> The catalyst prepared by impregnation method, Pd metal load (%) = 3.45, [16].

<sup>c</sup> Mechanical mixture of each Pd and Ru supported catalysts and  $\text{AlF}_3$  in proportions 1:3 and 1:5, respectively.

<sup>d</sup> The catalyst prepared by impregnation method, Pd metal load (%) = 0.39, [14].

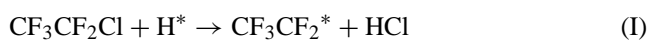
#### 4. Discussion

It was reported that some acidic supports can remove chlorine or fluorine atoms from CFCs [22]. To confirm that the removal of halogen was catalyzed by Pd and Ru sites and not catalyzed by the support  $\text{AlF}_3$ . Two mechanical mixture of each Ru and Pd supported catalysts and  $\text{AlF}_3$  in proportions 1:3 and 1:5 were tested. It was found that adding  $\text{AlF}_3$  either to supported Pd or Ru catalysts does not modify significantly the activities of both catalysts (Table 1). Therefore, we can assume that the hydrodehalogenation of  $\text{CF}_2\text{Cl}_2$  takes place for the main part on the Pd and Ru surfaces. As stated previously,  $\text{CH}_4$  and  $\text{CH}_2\text{F}_2$  are the main products formed during  $\text{CF}_2\text{Cl}_2$  conversion. Moreover, the selectivity in  $\text{CH}_2\text{F}_2$  decreases when the conversion increases on both Pd and Ru supported catalysts (Fig. 4), which suggests a possible consecutive reaction scheme. Coq et al. [14] showed in the hydrogenation of  $\text{CF}_2\text{Cl}_2$ , that the molecules of  $\text{CHF}_2\text{Cl}$  and  $\text{CH}_2\text{F}_2$  exhibit a much lower reactivity for the Pd surface with respect to  $\text{CF}_2\text{Cl}_2$ . A similar behaviour observed in the hydrodechlorination of  $\text{CCl}_4$ ,  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  over supported Pt catalysts [23]. Weiss et al. [23] found  $\text{CHCl}_3$  and  $\text{CH}_4$  as main products with  $\text{CHCl}_3/\text{CH}_4$  ratio remaining roughly the same (four to six) depending on the catalyst, whatever the conversion level of  $\text{CCl}_4$ . Moreover,  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  exhibited very low reactivities under the same reaction conditions. In the same way, in the hydrodechlorination of  $\text{CF}_3\text{CFCl}_2$  over different structure of Pd catalysts [5],  $\text{CF}_3\text{CFClH}$ ,  $\text{CF}_3\text{CFH}_2$  and  $\text{CF}_3\text{CH}_3$  were detected, with  $\text{CF}_3\text{CFH}_2/\text{CF}_3\text{CH}_3$  average ratio is about 12. Riberio et al. [5] mentioned that the hydrodechlorination of  $\text{CF}_3\text{CFCl}_2$  is insensitive to the structure of Pd catalysts and the rate of the reaction will be proportional to the total Pd surface area. Karpinski et al. [4] showed that in the hydrogenation of  $\text{CF}_3\text{CFCl}_2$  over Pd/ $\text{Al}_2\text{O}_3$  under high hydrogen pressure ( $\text{H}_2/\text{CFC}$  feed ratio = 20) the  $\text{CF}_3\text{CFH}_2/\text{CF}_3\text{CH}_3$  ratio at 474 K is 6.8 and the kinetics results are consistent with a reaction which occurs via the participation of a stable adsorbed carbon  $\text{CF}_3\text{CF}$ . For the same class of reactants, Coq et al. [14] indicated that the favoured reactions are those allowing the removal of two halogen atoms during one sojourn at the surface:  $\text{CF}_2\text{Cl}_2 \rightarrow \text{CH}_2\text{F}_2$ ;  $\text{CHF}_2\text{Cl} \rightarrow \text{CH}_3\text{F}$ ;  $\text{CH}_2\text{F}_2 \rightarrow \text{CH}_4$ . Similar conclusions can be applied for the conversion of  $\text{CF}_2\text{Cl}_2$  on both catalysts reported here in. The ratio  $\text{CH}_2\text{F}_2/\text{CH}_4$  is about 8 on Pd/ $\text{AlF}_3$  and about 7 on Ru/ $\text{AlF}_3$  at 473 K during 10 h duration on stream. The  $\text{CH}_2\text{F}_2/\text{CH}_4$  ratio obtained at the same temperature on Pd/ $\text{AlF}_3$  by Coq et al. [14] is 3.8, while the maximum ratio ( $\text{CH}_2\text{F}_2/\text{CH}_4$ ) obtained on the same catalyst [16] at 403 K is about 4.0 (Table 1).

The selectivity for the two main products,  $\text{CH}_2\text{F}_2$  and  $\text{CH}_4$  is mainly determined by the ratio between the desorption rate of the:  $\text{CF}_2$  radical and the rate of the surface reaction leading to  $\text{CH}_4$ . Indeed, the readsorption of the product  $\text{CH}_2\text{F}_2$  and the very low reactivity of  $\text{CH}_2\text{F}_2$  in the gas phase, can explain clearly the formation of  $\text{CH}_4$ . In the

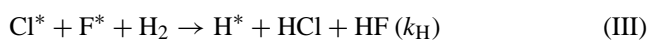
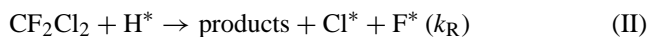
hydrodehalogenation of  $\text{CF}_2\text{Cl}_2$ , the ratio  $\text{CH}_2\text{F}_2/\text{CH}_4$  decreases when the conversion level increases (Fig. 4), whereas the ratio  $\text{CHCl}_3/\text{CH}_4$  in the hydrodechlorination of  $\text{CCl}_4$  does not [23]. Very probably, when  $\text{CF}_2\text{Cl}_2$  conversion increases, the surface coverage in  $\text{CF}_2$  species is changed and different kinetic dependences of the reactions lead either to  $\text{CH}_2\text{F}_2$  or to  $\text{CH}_4$ . However, due to the high exothermicity of the halogen removal [24], some heat-transfer limitations can occur which modify the selectivity between surface reactions exhibiting different Arrhenius parameters.

Fig. 3 illustrates the dependence of reaction rate on the feed composition (pressure ratio  $\text{CF}_2\text{Cl}_2/\text{H}_2$ ) for the two catalysts. The activity goes through a maximum, then decreases. This observed behaviour for both Pd and Ru catalysts led us to speculate that there is a competition of adsorption between hydrogen and  $\text{CF}_2\text{Cl}_2$  for the active sites. The order of reaction with respect to each of  $\text{CF}_2\text{Cl}_2$  and  $\text{H}_2$  are calculated from the rates in Fig. 3 within feed composition,  $\text{CF}_2\text{Cl}_2/\text{H}_2 = 0.20\text{--}1.00$  and ranged from 0.85 to 0.95 and 0.90 to 1.00 on Pd and Ru supported catalysts, respectively. In order to understand the kinetics of the reactions, several mechanisms which differ only slightly have been postulated [14,23,25,26]. Campbell and Kembal [27] provided evidence for the inhibiting effect of chlorine during the reaction between alkyl chlorides and hydrogen. The regeneration of the active surface is reached by removal of adsorbed chlorine by hydrogen. Previous studies [25,26] proposed that the chlorination/dechlorination of metallic surface respectively for  $\text{CFCl}_2\text{CF}_2\text{Cl}$  over different metal catalysts and chlorobenzene over supported Pd and Ru catalysts, could be the key step controlling the reaction rate. On similar basis Gervasutti et al. [10] proposed a rapid dissociation-adsorption/associative-desorption mechanism for  $\text{CF}_3\text{CF}_2\text{Cl}$  of the type:



where the asterisk (\*) refers to an adsorbed species.

By considering the findings in the literature and our experimental results, the following halogenation/dehalogenation mechanism was proposed:



where  $k_R$  is the rate constant for the halogenation of the Pd and Ru surfaces, and  $k_H$  the rate constant for the regeneration of the Pd and Ru surfaces. The expression of the rate equation is:

$$\text{rate} = \frac{k_R P_R}{[(k_R P_R / k_H P_H) + 1]} \quad (1)$$

Assuming a first-order dependence with respect to  $\text{CF}_2\text{Cl}_2$  and  $\text{H}_2$  pressures [14,15] (which is very near to the experimental results) for the halogenation and regeneration of the Pd and Ru surfaces. As we worked at atmospheric pressure

Table 2

Calculated values of the kinetic parameters in the halogenation/dehalogenation mechanism for the hydrogenation of  $\text{CF}_2\text{Cl}_2$  at 448 K over Pd and Ru supported catalysts

Catalyst	$(P_R/P_H)_{\text{max}}$	$r_{\text{max}}^a$	$k_H^b$	$k_R^b$	$E_a$ (kJ/mol)	Dispersion (%)
Pd/AlF <sub>3</sub>	1.0	58	232	232	55.7	68
Ru/AlF <sub>3</sub>	0.95	64	250	277	53.6	71
Pd/AlF <sub>3</sub> <sup>c</sup>	0.90	74	267	330	63.5	10
Pd/AlF <sub>3</sub> <sup>d</sup>	1.10	20	88	73	75	17

<sup>a</sup> Expressed in  $\text{mol}/(\text{g min}) \times 10^6$ .

<sup>b</sup> Expressed in  $\text{mol}/(\text{g min}) \times 10^{11}$ .

<sup>c</sup> Metal load of Pd (%) = 3 at 453 K [14].

<sup>d</sup> Metal load of Pd (%) = 0.39 at 453 K [14].

( $10^5$  Pa), the rate law takes the form:

$$\text{rate} = \frac{10^5 k_R k_H}{[k_R (P_R/P_H) + (k_R + k_H) + (k_H/P_R P_H)]} \quad (2)$$

When the  $P_R/P_H$  ratio varies from zero to infinity, the reaction rate goes through a maximum value ( $r_{\text{max}}$ ) for  $\partial r/\partial (P_R/P_H) = 0$ , the rate constants  $k_R$  and  $k_H$  can then be determined from the values of the coordinates ( $r_{\text{max}}$ ) and  $(P_R/P_H)_{\text{max}}$  of that point:

$$\left(\frac{P_R}{P_H}\right)_{\text{max}} = \left(\frac{k_H}{k_R}\right)^{0.50} \quad (3)$$

$$(r_{\text{max}}) = \frac{10^5 k_H}{[1 + (k_H/k_R)0.50]^2} \quad (4)$$

The values of  $k_R$  and  $k_H$  were then determined for both catalysts and are reported with dispersion (%) results in Table 2. It is clear that the values of  $k_H$  and  $k_R$  are close to each other for both catalysts. Hence, the strength of interaction between each of Pd and Ru surfaces and  $\text{CF}_2\text{Cl}_2$  or  $\text{H}_2$  is of the same order of magnitude. For comparison purposes, we have also included in the table some other values [14]. When comparing the values of  $r_{\text{max}}$  and activation energy obtained from this study on Pd/AlF<sub>3</sub> with the respective values on Pd/AlF<sub>3</sub> for nearly the same metal load catalyst (d) [14], a conclusion could be proposed that: the catalytic activity of the supported Pd catalyst prepared by sol-gel method are improved. There is no significant difference between the activity of Pd and Ru supported catalysts. This argument could be proved by comparing the results in Table 1, and by knowing from the table that the ratio between the two rates of Ru and Pd does not change greatly and equal to 1.2 and 1.4, respectively; at respective temperatures of 448 and 538 K at pressure ratio  $\text{CF}_2\text{Cl}_2/\text{H}_2 = 0.33$ .

## 5. Conclusion

The conversion under hydrogen of  $\text{CF}_2\text{Cl}_2$  over Pd and Ru supported catalysts on AlF<sub>3</sub> prepared by sol-gel method, yield two main products,  $\text{CH}_2\text{F}_2$  and  $\text{CH}_4$ . Stable catalytic

activity can be obtained for the hydrogenation of  $\text{CF}_2\text{Cl}_2$  over both catalysts. Under the reaction conditions, they show no significant difference in their activities. The selectivity to the desired product  $\text{CH}_2\text{F}_2$  reach 92% for both catalysts at 438 K. The conversions on Pd/ $\text{AlF}_3$  and Ru/ $\text{AlF}_3$  catalysts reached 20 and 83%, respectively at 538 K. The distribution of products can be explained by the formation of carbenoid surface species. The kinetics of the reaction showed evidence for a competition of adsorption between  $\text{CF}_2\text{Cl}_2$  and hydrogen for the active sites. The interaction between Pd and Ru and  $\text{CF}_2\text{Cl}_2$  or hydrogen are of the same order of magnitude. It is proposed that the high dispersion of Pd and Ru over the support is responsible for the high activity and also high selectivity in  $\text{CH}_2\text{F}_2$ .

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