Catalytic Conversion CCl$_3$F and CCl$_2$F$_2$ over Metal Supported Catalysts

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Abstract

A comparison of the catalytic properties of metals (Pt, Pd and Ru) supported on carbon in the process of catalytic hydrogenolysis of the C-halogen bond in CCl$_2$F$_2$ (CFC-12) and CCl$_3$F (CFC-11) was made. The mechanism of the halogen substitution in the catalytic conversion of CCl$_3$F was found to differ from that proposed for CCl$_2$F$_2$. The catalysts with Ru as the active phase were characterized by much lower activity than those with Pt or Pd, and the main products of conversion in the two reactions were CHClF$_2$ and CHCl$_2$F, so the products of substitution of only one chlorine atom in the molecule were obtained, in contrast to the case when Pt or Pd were used.

Keywords: metal catalysts, CFCs, hydrodehalogenation

Introduction

Saturated fluorohydrocarbons and CFCs[1)] belong to the rare class of compounds whose discovery in the beginning of the 1930's (XX-century) was the actual response of scientists to the needs of society. Widespread application of these compounds was a result of their very high chemical inertness (they are among the most inert substances) [1], high stability and low toxicity. Their inertness – the very property that has led to their common use, has also become the feature responsible for the necessity of their elimination. The turning point in the history of CFCs was the hypothesis put forward by Rowland and Molina [2] stating their destructive effect on the ozone layer, experimentally verified by ozone layer measurements over Antarctica [3]. The discovery of this effect and the contribution of these compounds in the so-called hothouse effect have initiated efforts towards their withdrawal from the market. At present production of CFCs is forbidden (since 1996). However, devices using freon as well as halon still work. In this situation it seems highly relevant to find methods of their withdrawal and utilization by transforming them into environmentally friendly compounds.

The choice of a compound alternative to CFCs is difficult [4] as it must take into account not only the requirements and possibilities of current technology, but first of all the world must unilaterally recognize the need for their replacement. Moreover, taking into account the unique properties of CFCs and the variety of their applications, we cannot expect that a single substitute would be able to replace all CFCs in all fields of their use. At present CFCs

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[1)]CFCs- chlorofluorocarbons; HCFCs-hydrochlorofluorocarbons; HFCs-hydrofluorocarbons;

are being replaced by HCFCs and in perspective by HFCs, before better replacements are found. The conversion of CFCs into HCFCs and further to HFCs is performed by catalytic hydrogenolysis of the C-Cl bond. The catalysts used for the process of hydrodechlorination are mostly noble metals (Pt, Pd, Ru) supported either on oxides [5-7] (with some modifications) or on activated carbon [8-10].

The thermodynamic stability of CFCs is the most important property, which has to be considered in analysis of the CFC conversion to HCFC. However, the catalytic processes including adsorption, desorption, etc., can completely alternate the picture of CFC stability. In such a case it is questionable to compare and correlate directly C-Cl and C-F dissociation energy with kinetics of hydrogenation, although the catalytic process might proceed through the radical mechanism.

B. Coq [7] concluded that the kinetics of CCl_2F_2 hydrogenation can be described by halogenation/dehalogenation of the Pd surface by CCl_2F_2 and H_2 respectively, or by a classical Langmuir-Hinshelwood mechanism, which implies that the competitive adsorption of the halogen derivative and hydrogen molecule on the metal will determine not only the activity but also the selectivity of the system. On the basis of the observations reported [11-13], it can be surmised that in the case of CCl_2F_2 hydrogenolysis, the strength of bond with metal decreases in the series: Me-F>Me-Cl>Me-C>Me-H. The range of products appearing not only as a result of the hydrogenolysis but also e.g. the process of dismutation, as well as the presence of side products HCl and HF, proves that the adsorption of these species competitive towards adsorption of CFC's, may affect the selectivity and deactivation of the catalysts. It seems that the recognition of this complex catalytic problem may be facilitated by results of a comparative study of chloro-fluoro-derivatives with quantitatively and qualitatively different contributions of the halogen.

Regarding the fact that the conversion of chloro-fluoro-hydrocarbon molecules must start from the attack on the electronegative halogen and knowing the energies of the C-halide bond, design of the catalyst of CFCs conversion meets a few problems. The hydrogenolysis requires reaction of some electronegative reagent, which might be quite challenging since halogens are highly electronegative themselves. This is the case in a simple hydrogenolysis of the C-Cl bond in the hydrodehalogenation but also in the catalytic processes in which the splitting of the C-halogen bond is achieved in the reaction with basic character molecules, e.g. NH_3 [14]. The fact that an effective catalyst of CFC conversion has not been developed yet means that the problem is much more complex.
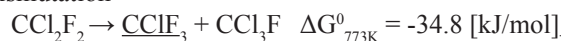
There are two groups of factors, which impede the picture of catalytic hydrogenolysis of CFCs. One of them is the realization that a simple transfer of certain thermodynamic properties of the molecule, e.g. energies of C-halogen bonds, to the catalytic considerations can be risky. The fact that the C-Cl bond is much weaker than the C-F bond does not mean that the hydrogenolysis of the former must be easier. In catalytic hydrodehalogenation the main process is dissociative chemisorption rather than simple bond splitting. Therefore, from the point of view of the hydrogenolysis of the C-halogen bond, a certain equilibrium between F and Cl may be reached, depending on the kind of species involved in the process. Moreover, from the point of view of the HSAB theory, F will prefer the hard proton over soft C, more than Cl does.

Therefore, in the addition of CH_3X to ethylene, the enthalpy of the reaction in the gas phase is –96.0 kJ/mol for X=Cl and –99.2 for X=F. However, if CH_3X is replaced by HX, the corresponding values are –72 kJ/mol for HCl and only –47.7 kJ/mol for HF. It should also be remembered that fluorine as the most electronegative element will be the most powerful electron-attracting group leading to many anomalous effects.

The other group of factors obstructing the design of a selective catalyst of hydrogenolysis of the C-halogen bond in chlorofluorocarbon molecule are related to the monitoring of the experiment, i.e. the course of the competitive reactions and drastic (relative to the other catalytic processes) changes of the catalyst surface (especially when oxide supports are used). These competitive reactions include the coupling reactions, leading to the derivatives comprising a greater number of carbons in a molecule, and the Cl-F exchange reactions. The latter can occur either through catalytic dismutation or as a result of secondary reactions, e.g. hydrofluorination, which leads to additional difficulties in interpretation as it is not always possible to identify the source of a particular product (see below):

Dismutation

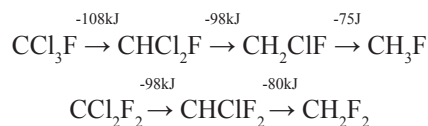$$CCl_2F_2 \rightarrow \underline{CClF_3} + CCl_3F \quad \Delta G^0_{773K} = -34.8 \text{ [kJ/mol]}$$

Hydrofluorination

$$CCl_2F_2 + HF \rightarrow \underline{CClF_3} + HCl \quad \Delta G^0_{773K} = -51.7 \text{ [kJ/mol]}$$

To sum up, the reason for this complex picture of the catalytic conversion of CFCs is the fact that for chloro-fluoro-methanes both hydrogenolysis of the C-X bond as well as the Cl-F exchange process have negative values of free enthalpy [15], so are thermodynamically possible.

As an example two series of reactions of CFC-11 and CFC-12 can be considered:

$$\overset{-108kJ}{CCl_3F \rightarrow} \overset{-98kJ}{CHCl_2F \rightarrow} \overset{-75J}{CH_2ClF \rightarrow} CH_3F$$

$$\overset{-98kJ}{CCl_2F_2 \rightarrow} \overset{-80kJ}{CHClF_2 \rightarrow} CH_2F_2$$

Some work on the influence of halogen substitution was performed by Chan and Gellman [16], who provided convincing evidence that Cl substitution increases the reactivity of C-Cl for hydrogenolysis, whereas the F substitution decreases it on Pd(111).

As follows from our earlier studies of the process of catalytic conversion of CCl_2F_2 [10], the qualitative and quantitative differences in product distribution depend on the kind

and amount of the active phase (Pt, Pd, Fe, Ni), the degree of its dispersion and type of support [17].

This paper reports results of a study on the hydrogenolysis of the C-Cl bond in the CCl_3F molecule, and is a continuation of our earlier studies on the catalytic conversion of CCl_2F_2 [5, 9, 10] with the use of the same metal catalysts supported on activated carbon.

Experimental

Preparation of Catalysts

The support used for preparation of the metal catalysts was Activated Carbon (Darco-acid washed, 20-40 mesh, with surface area 638 m^2/g) from American Norit Co., Inc. Precursors of the metal phases were acetone solutions of H_2PtCl_6 x $6H_2O$, $PdCl_2$ and $RuCl_2$, introduced onto the support surface by the impregnation technique (incipient wetness). The materials obtained were dried at 100^0C and reduced in hydrogen atmosphere for 5 hours at 350^0C. The loading of the preparations with the metal phase was the same for each metal and equal to 0.026, 0.052 and 0.12 %mol Me/C, for Pt, Pd and Ru, respectively. The preparations have been partly characterized in our previous paper (XRD, SAXS and textural studies) [9].

Apparatus for Catalytic Studies

The catalytic tests were performed in a standard flow-through system in which the desired composition of the reaction mixture – the ratio of CCl_2F_2 to H_2 – was maintained by the thermal gas-mass-flow control system. In the case of CCl_3F conversion the desired composition was maintained by passing H_2 at a certain rate through a saturator containing CFC-11, at a certain temperature. The fluctuations of the composition of the reaction mixture were below 0.2%. The reactor of the catalytic system was incorporated into the flow system, and all components where analyzed on a gas chromatograph /mass spectrometer Hewlett Packard G.C.M.S. model G1800A system fitted with a GS-Q (J&W Scientific) column, length 30m., id. 0.53 mm, He flow 5 ml/min with programmed temperature from 35 to 200^0C. The construction details were described in our earlier works [10,13]. In the majority of experiments the ratio of CFC to H_2 was kept at the level of 1:6, the total flow rate of the mixture was 47 cm^3/min, the catalyst mass was 4.00 g, and the tests were carried out in the temperature range from 200 to 350^0C.

Results and Discussion

The study reported in this paper has been undertaken to determine the changes in the reaction of the C-halogen bond hydrogenolysis effected by different catalysts (Pt, Pd and Ru supported on activated carbon) and different freons (F-11 and F-12).

The influence of the hydrogen to CFC feed ratio on the catalytic process is depicted in Fig. 1a-d. It would seem that using very similar substrates as CCl_2F_2 and CCl_3F, a change in the concentration of other reagent (hydrogen) should produce similar effects in the course of the relevant catalytic conversions. Taking into regard the fact that in both cases the process was run with the same catalyst and in the same conditions, and that the stoichiometry of the reaction (full hydrogenolysis of the C-X bond) requires 4 moles of H_2 per mole of a freon, it was reasonable to assume that an increase in the hydrogen concentration in the reaction mixture would lead to an increased degree of conversion and a greater contribution of higher hydrogenated molecules in the reaction products.

The experimentally observed changes depicted in Fig. 1 do not always confirm the validity of all the above reasoning. As expected, an increase in the contribution of hydrogen in the reaction mixture in the two cases have brought about an increase of the freon conversion degree, but it should be noted that the conversion was somewhat greater for CCl_3F. As in all experiments the catalyst loading with the reaction mixture was constant, this means that by increasing the ratio H_2:Freon we actually decreased the amount of the freon getting in contact with the catalyst. Therefore, a more adequate presentation of these data would be in the convention mol·centrum^{-1}·s^{-1} so TOF (*turnover frequency*). The character of these curves (Fig. 1a and b) clearly indicates a competitive adsorption of hydrogen and freon at the metallic centers, which leads to a decreasing amount of the molecules undergoing conversion per single metallic center. In the case of CCl_2F_2, although the degree of conversion almost linearly increases with increasing concentration of hydrogen (Fig. 1a) this is not reflected in considerable changes in the distribution of the reaction products (Fig. 1c). Irrespective of the feed composition, the main reaction products were CH_2F_2 (~45 mol%) and CH_4 (~30 mol%), similar to the study reported by B. Coq [7]. However, in contrast to the above work, we also observed significant amounts of $CHClF_2$ – about 15 mol% on the Pt/C catalyst, (while on the Pd/C catalyst only ~1.5 mol% [7]), and CH_3Cl - ~8 mol% also on the Pt/C catalyst. It seems that much greater amounts of $CHClF_2$ observed in our experiment can be a result of changes in the kinetics of the reaction due to other relations between CCl_2F_2 and H_2 in the competing adsorption on the active centers on Pd and Pt. In the system with Pd/C [7] the interactions between Pd and CCl_2F_2 or hydrogen are of the same order of magnitude. Keeping in mind that the strength of bonds between the surface metal and metal-adsorbed species decreases when going from 3d to 5d metals, it is rational to suppose that the conversion of $[CClF_2^-]^*$ (suggested by Coq [7] as the first species formed as a result CCl_2F_2 adsorption on Pd) will be much faster on Pt. Most probably the presence of CH_3Cl in our experiment (the product not observed on Pd/C [7]) may be a direct result of the interaction between the HCl forms adsorbed on Pt and the radical precursor of CH_4, which in the mechanism proposed by Coq is $(CH_2^-)^*$. There is no doubt that during this catalytic conversion, on the surface of metal clusters, volatile metal halides, removable by

hydrogen, are formed. As mentioned earlier, metal-halogen bond strength depends on the position of the metal in the periodic system, so it could be expected that the Pt-Cl bond should be weaker than Pd-Cl, leading to the appearance of CH_3Cl in considerable amounts among the products.

The occurrence of changes in the relations between the strength of bonding the substrates and transition forms is to some extent manifested in the course of CCl_2F_2 conversion on the two kinds of catalysts. Coq and coworkers observed that the rate of the hydrogenolysis goes through the maximum value for the feed composition about 1:1, which is consistent with our TOF data. In conclusion, it seems that the differences in the course of the catalytic conversion of CCl_2F_2 on the catalysts with Pt and Pd do not contradict the mechanism proposed by Coq, but are

a consequence of differences in the relations among the chemisorptive forces appearing for the catalysts with these two metals. We have to keep in mind that on the basis of our results (conversion higher than 50%) any wider discussion of the kinetics is pointless.

The situation is different for the CCl_3F conversion, especially in respect to product distribution. The curves illustrating the degree of conversion as well as distribution of the reaction products as functions of the feed composition indicate that "full hydrogenolysis" of the C-halogen bond is in this compound much easier than in CCl_2F_2. This observation is in agreement with the values of dissociation energies of both C-Cl and C-F in these two compounds; in CCl_3F they are 305 and 426 kJ/mol, while in CCl_2F_2 – 318 and 460 kJ/mol, respectively [18] as well as with the above-mentioned results of Chan and Gellman
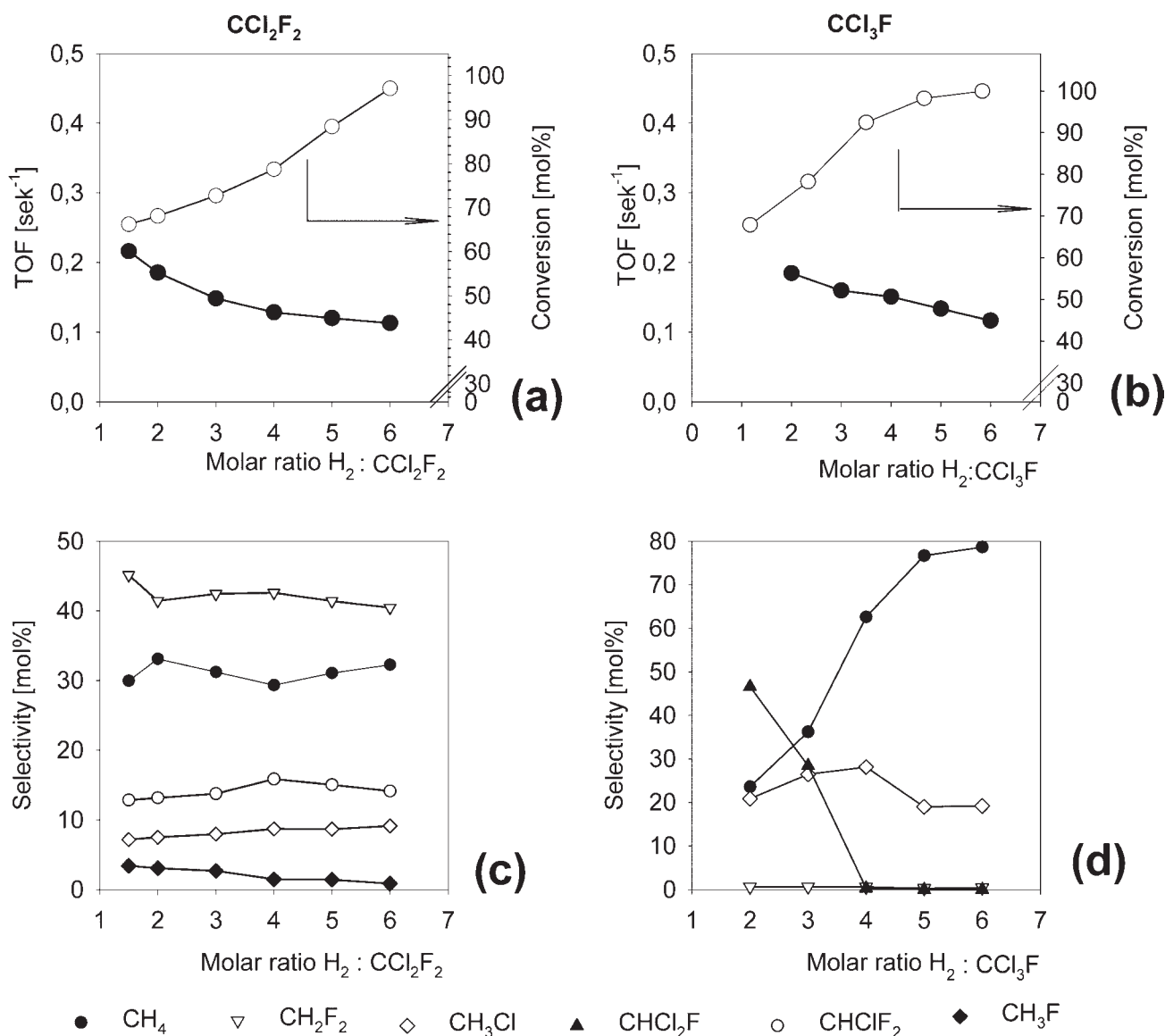

Fig.1. Values of TOF for conversion of CCl_2F_2 (a) and respectively for CCl_3F (b) as a function of molar ratio of H_2 : CCF's for 0.12 mol% Pt/C catalyst (at 300°C) and selectivities (c, d) for the above reactions.
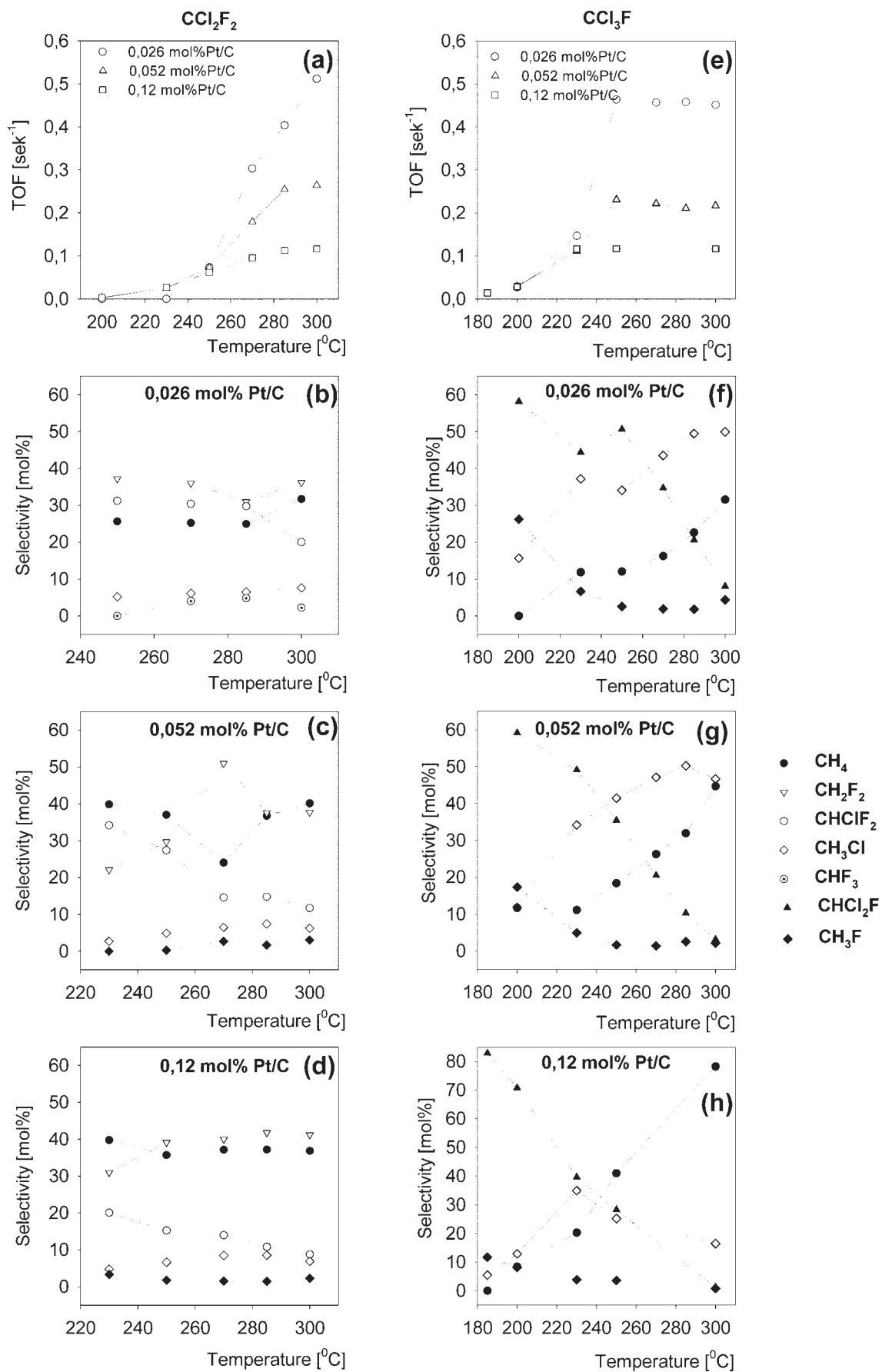
Fig.2. Values of TOF and selectivities for Pt/C catalyst with different loading of metal phase as a function of temperature.

[16]. It was assumed that similarly as for CCl_2F_2 the presence of CH_3Cl among the reaction products is a consequence of a secondary process between the metal-halogen species on the surface and the intermediate products. The presence of only $CHCl_2F$, besides the main product - CH_4, whose contribution very fast decreases with increasing access of hydrogen, could suggest that in this case the reaction can be described by a simple consecutive scheme; however, only traces of CH_3F and no traces of CH_2ClF were detected in the effluents:

$$CCl_3F \rightarrow CHCl_2F \rightarrow CH_2ClF \rightarrow CH_3F \rightarrow CH_4.$$

On the basis of the above experiments we have chosen for further investigation the feed composition of H_2 to freon at the molar ratio of 6:1. Figs. 2a and 2e present results of the catalytic conversion (in terms of TOF) of CCl_2F_2 and CCl_3F over a Pt/C catalysts with different metal loadings as functions of the conversion temperature.

It seems that the main reason responsible for the differences observed is the change in the degree of dispersion of Pt. The difference in the size of crystallites between the preparations of the lowest (2 nm) and greatest (41nm) loading is of about 38 nm. As described in [10], changes in the size of the crystallites are reflected in the process of conversion as well as in deactivation of the catalyst by its coking. It seems that the size of Pt clusters, for our preparations growing with the metal loading, is the reason for significant qualitative and quantitative changes in distribution of the products of catalytic hydrogenolyses of CCl_2F_2 and CCl_3F, which has been illustrated in Fig. 2, b,c,d,f,g,h.

In the case of the CCl_2F_2 conversion, one of such changes is the presence of $CHClF_2$ among the reaction products. For the catalyst with the smallest crystallites, the amount of $CHClF_2$ is close to that of the main reaction products – CH_4 and CH_2F_2, in the whole temperature range (Fig. 2b) while for the catalyst with the largest one (Fig.2d) the contribution of $CHClF_2$ almost linearly decreases with temperature, and at the final stage (at 300^0C) it appears in the amount 4 times lower than the other products. It is also worth noting the presence of small amounts ~2-5 mol% of CHF_3 – (the product not observed for the samples with 0.052 and 0.12 mol% Pt/C), whose presence may be a result of the dismutation reaction as suggested by trace amounts of $CHCl_2F$ among the reaction products,

$$2CHClF_2 \rightarrow CHF_3 + CHCl_2F$$

The distribution of the products of the CCl_3F conversion also significantly depend on metal loading and the temperature of the process. However, there are a few similarities between the two conversions. First of all, irrespective of the degree of metal loading and temperature of conversion, we observed in all cases the presence of the same spectrum of products. Another characteristic common feature is an almost linear decrease in

the contribution of the first product of hydrogenolysis of the C-Cl bond – that is $CHCl_2F$, accompanied by a parallel increase in the contribution of the fully hyrogenated product CH_4. This is particularly visible for the catalyst with maximum metal loading (Fig. 2h). A somewhat surprising feature was the presence of significant amounts of CH_3Cl among the reaction products; for catalysts 0.026 and 0.052 mol%Pt/C at 300^0C this was a dominant product. The contribution of this product as a function of temperature, parallel to the contribution changes in CH_4, was the feature considerably different for these two catalytic processes, as the contribution of CH_3Cl in the CCl_2F_2 conversion significantly decreased with increasing temperature. This situation changed and became similar to that in hydrogenolysis of CCl_2F_2 only when using the catalyst with the greatest metal loading and thus the greatest size of Pt crystallites. It seems that this behavior can be explained by a greater concentration of HCl in the environment of the reaction with higher Cl substituted CCl_3F, as well as by an easier process of chlorination of smaller metal groups relative to their 20-times greater analogues. This rule has been also observed for CCl_2F_2 conversion, in which the contribution of $CHCl_3$ in the reaction products decreases with increasing size of Pt crystallites.

From the point of view of prospective applications, the catalyst with 0.12 mol%Pt/C appears the most promising as the presence of only two reaction products: CH_4 (~80mol%) and CH_3Cl (~20mol%) makes it relatively highly selective for this kind of process.

Figs. 3 and 4 show the results of the catalytic conversions of both freons on the catalysts with Pd and Ru of the metal loading of 0.052mol%/C. Similarly as for the Pt catalyst, the Pd one reached the maximum activity in CCl_3F conversion at temperatures much lower than those of the maximum activity in the CCl_2F_2 conversion. Moreover, this process was detected at temperatures not much higher than 100^0C, whereas the first products of CCl_2F_2 hydrogenolysis were observed above 200^0C. A common feature of these two catalysts in the CCl_2F_2 conversion was the presence of the same main products – CH_2F_2 and CH_4, although, an increase in the temperature of conversion led to a strong decrease in the contribution of CH_4 and an increase in those of CH_2F_2 and C_2H_6, in contrast to the situation when the Pt catalyst was used. It should be noted that the products of conversion performed with the use of the Pd catalyst contained much less $CHClF_2$ when compared to the case of the Pt catalyst, which as already mentioned, may be a result of the difference in the strength of bonding the initial substrate with a given metal surface.

Much greater differences between the Pt and Pd catalysts appear as far as the distribution of the products of CCl_3F conversion is concerned. Although for the Pd catalyst a radical decrease of $CHCl_2F$ among the reaction products is observed, similarly as for the Pt catalyst, this decrease is not accompanied with an increase in CH_4 but its analogues C_2H_6 and C_3H_8 appear.
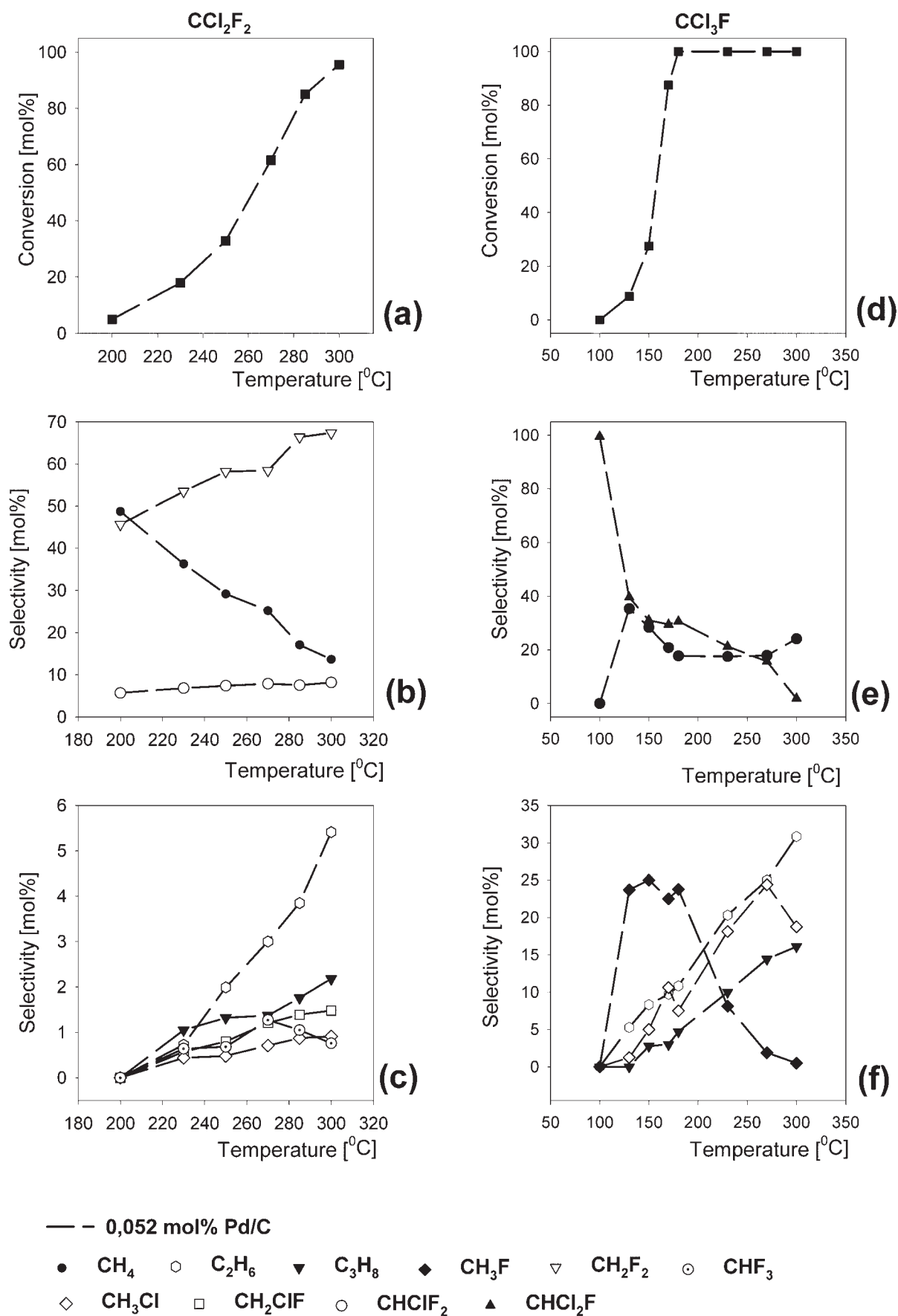
Fig.3. Results of the catalytic conversion of CCl$_2$F$_2$ (a, b, c) and CCl$_3$F (d, e, f) over Pd/C catalyst.

The Ru catalyst is much less active in both conversions, Fig. 4a,c, and the main products of CCl_2F_2 and CCl_3F conversions are $CHClF_2$ and $CHCl_2F_2$, respectively, so the products of hydrogenolysis of the first C-Cl bond.

At present it is difficult to suggest an unambiguous interpretation of this difference. It may be related to the change in the process of chemisorption (different d-character of transition metals) and to a different geometry of the active metal center. The latter explains the similarity of the catalytic properties of Pt and Pd (both metals crys-

tallize in the face-centered cubic lattice) and the different properties of Ru (hexagonal closest packed-based) catalysts.

Conclusions

1. The number of fluorine atoms in a molecule of fluorochloromethane strongly affects the mechanism of catalytic hydrodehalogeniation.

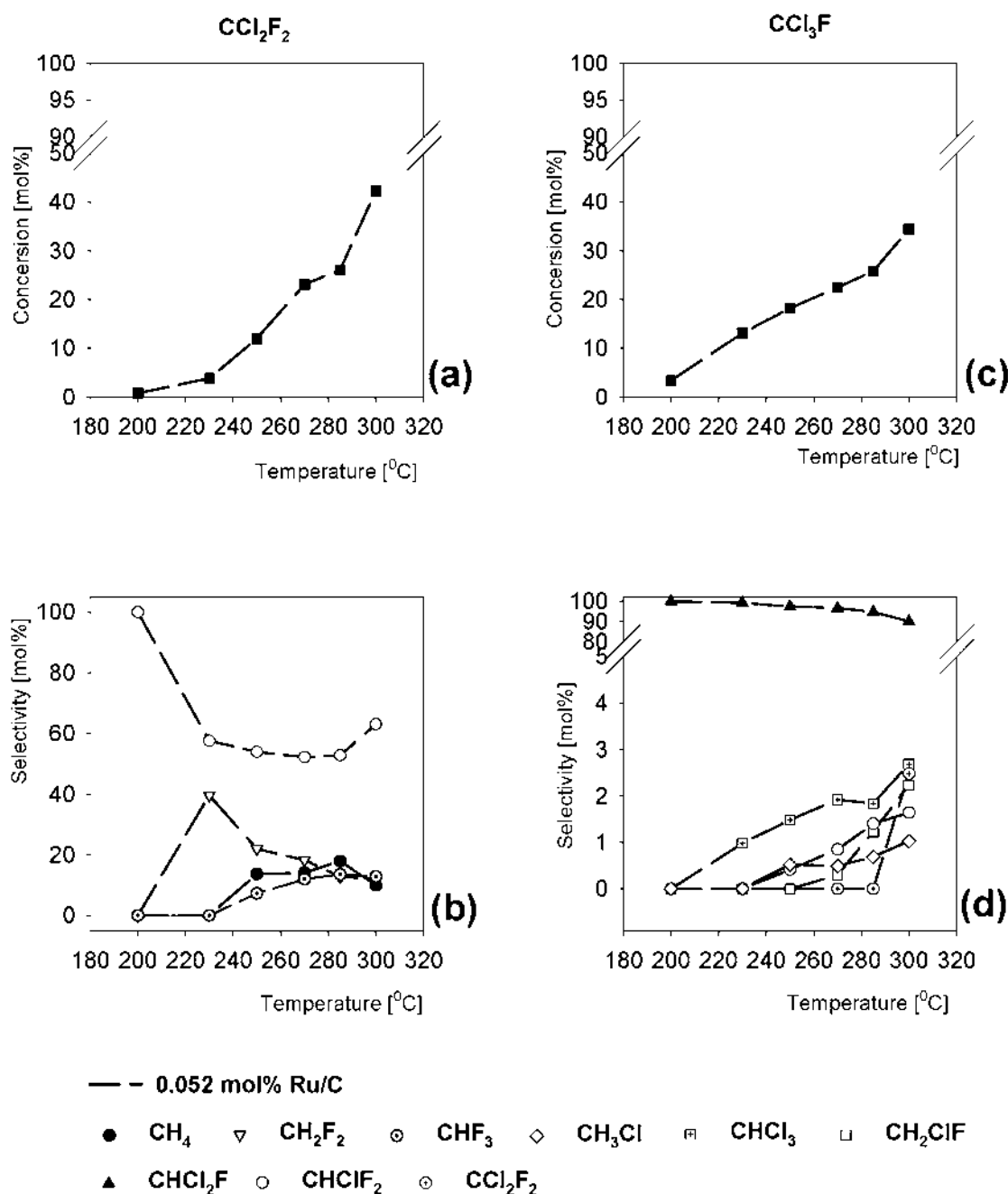2. In the case of freon higher substituted by F atoms,

Fig.4. Results of the catalytic conversion of CCl_2F_2 (a, b,) and CCl_3F (c, d) over Ru/C catalyst.

e.g. CC_2F_2, the conversion on Pt/C as well as Pd/C catalysts, occur according to the mechanism proposed by B. Coq [7], i.e. reactions favored are those allowing the removal of two halogen atoms during one sojourn at the surface. However, this could not be generalized for all metal catalyst. As an example, an exception to the above rule can be the Ru/C catalyst, in reaction on which the main product was $CHClF_2$.

3. For freon with only one fluorine atom in the molecule, the formal reaction scheme is similar to that proposed by Weiss [19] for hydrodechlorination of CCl_4, e.g. a consecutive rake scheme mechanism.

4. In the case of Ru/C catalyst in both kinds of substrate (CCl_2F_2 and CCl_3F) the consecutive scheme mechanism seems to be valid.

Acknowledgements

References

1. KIPLINGER J.L., RICHMOND T.G., OSTERBERG C.E., Chem.Rev. **94**, 373, **1994**.
2. MOLINA M.J., ROWLAND F.S., Nature **810**, 249, **1974**.
3. Scientific Assessment of Stratospheric Ozone: 1989, World Meterological Organization Global Ozone Research and Monitoring Project, Report No.20, 1 and 2 **1989**
4. MANZER L.E., RAO V.N.M., Adv. Catal., **39**, 329, **1993**.
5. BELL T.N., KIRSZENSZTEJN P., CZAJKA B., React. Kinet. Catal. Lett. **56**, 221,**1995**.
6. OHNISHI R., WANG W-L, ICHIKAWA M., Appl. Catal. A: General **113**, 29, **1994**.
7. COQ B., COGNION J.M., FIGUERAS F., TOURNIGANT D., J. Catal. **141**, 21, **1993**.
8. WIERSMA A., van de SANDT E.J.A.X, MAKKE M., LUTEIN C.P., van BEKKUN H., MOULIJN J.A., Catal. Today **27**, 257, **1996**.
9. CZAJKA B., KIRSZENSZTEJN P., WACHOWSKI L., ŁOPATKA R., BELL T.N., BECALSKI A., Archiwum Ochrony Środowiska **23** (3-4), 47, **1997**.
10. CZAJKA B., KIRSZENSZTEJN P., J. Therm. Anal. Cal. **55**, 619, **1999**.
11. AHN B.S., LEE S.C., MOON D.J., LEE B.G., J. Mol. Catal. **106**, 83, **1996**.
12. van de SANDT E.J.A.X., Catalytic Hydrogenolysis of CCl_2F_2 into CH_2F_2, Chapter 2, Catalyst selection, PhD-thesis, Delf University of Technology, p.26, **1997**.
13. CZAJKA B., KIRSZENSZTEJN P., WACHOWSKI L., in Proceedings of the II International Scientific Conference "Air Protection in Theory & Application" Zabrze, Poland, pp. 161-169, **1998**.
14. TAKITA Y., IMAMURA T., MIZUHARA Y., ISHIHARA T., J. Catal. **136**, 617, **1992**.
15. KEMNITZ E., KOHNE A., LIESKE E., J. Fluorine Chem. **81**, 197, **1997**.
16. CHAN CH.W., GELLMAN A.J., Catal. Lett., **53**, 139, **1998**.
17. BELL T.N., KIRSZENSZTEJN P., CZAJKA B., Catal. Lett. **30**, 305, **1995**.
18. BARIN I., Thermochemical data of pure substances, 3th Ed.VCH, Weinheim **1995**.
19. WEISS A.H., GAMBHIR B.S.AND LEON R.B., J. Catal. **22**, 245, **1971**.