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SURFACE STUDY OF SUPPORTED METAL CATALYSTS

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Abstract

The aim of the reported studies was to determine the catalytic behaviour of M–C systems (M=Pt, Pd and Ru) towards hydrogenolysis of the C–X bond (X=Cl and F). The level of noble metal loading is reflected in the size of the metal clusters formed on the surface of the carbon support and affects the product distribution and the amount of carbonaceous deposit formed upon the conversion of CCl_2F_2.

Keywords: catalytic hydrodehalogenation, CFCs, dispersion, supported metals

Introduction

In designing new catalytic systems, we more and more frequently have to resort to high-sensitivity studies, which can be carried out only in high vacuum. Although such studies are not performed under the conditions of catalyst work, they provide important information on the morphology of the catalyst. For instance, from the point of view of application, it seems very important not only to identify the active centres in a given catalyst, but also to know their availability to the reaction mixture. A knowledge of the texture of the carrier and also its changes during introduction of the active phase and then during the catalytic process is indispensable even at the stage of catalytic system design. The information on the carrier texture changes during the catalytic process is particularly meaningful if, in a given process, the catalyst and the products of the catalytic process enter into secondary interactions. An example of such a catalytic reaction is hydrogenolysis of the carbon–halogen bonds in halogen derivatives of paraffins on metal catalysts. In this process, the formation of side-products such as HCl or HF, and the formation of a carbon deposit on the catalyst surface, are the main reasons for the fast deactivation of these catalytic systems, which are applied in the utilization of freons and halons, gases responsible for the disappearance of the ozone layer.

Ozone depletion in the stratosphere is now well documented, and one of the important causative effects is the presence in the troposphere of gaseous halogenated species, including man-made CFCs and halons used for various pur-

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poses. With this recognition, the London (1992) protocol came into effect with the intent of limiting and eventually eliminating the use of these compounds on a world-wide scale.

This could result in the formation of significant stockpiles of CFCs and halons, and the purpose of the present work was to investigate the feasibility of converting these compounds into non-ozone-depleting substances which are themselves useful. To this end, the introduction of hydrogen into the molecules renders the compounds susceptible to free radical attack in the troposphere, and hence their eventual removal from the atmosphere as a result of the conversion of the products into substances which are subject to rain-out.

Processes of conversion of freons are in most cases carried on the basis of catalytic transformation. The most common heterogeneous catalysts used in these processes are well-dispersed noble metals, e.g. Pt, Pd [1], Rh [2, 3] or the bimetallic alloys Pt–Re, Pt–Ir, Pt–Sn and Pt–Au [4].

The methodology chosen to replace halogen by hydrogen involved hydrogenolysis of the carbon–halogen bond using a metal–carbon catalyst system. The partial replacement of halogen atoms in CFCs by hydrogen leads to a class of compounds, e.g. CH_2F_2 (HFC 32), CH_2FCH_3 (HFC 114a) and CHF_2CF_3 (HFC 115), known as HCFCs. From the above list of compounds, CH_2F_2 is most promising as a low-temperature refrigeration agent [5]. The study reported here is a continuation of earlier work on metal–alumina catalyst systems [6, 7], and concerns the platinum–carbon catalyst system. The aim of this work was an investigation of the catalytic behaviour of the Pt–C Pd–C and Ru–C systems, in an attempt to relate the results to the changes observed on the surfaces of these systems.

Experimental

The reaction environment due to the presence of the halogen acids HCl and HF resulting from the hydrogenolysis of halocarbons is particularly hostile, and under the given reaction conditions it can prove particularly destructive to both the catalysts and the reactors. Accordingly, the reactor that was designed was made of graphite, and all connections to it were made of teflon. Details of the technical solution are given in [8]. The reactor was incorporated into a flow system whose components could be evacuated, and the effluent components from the reactor could be sampled with a gas chromatograph/mass spectrometer Hewlett Packard G.C.M.S. model G1800A system fitted with a GS-Q (J&W Scientific) column, length 30 m, i.d. 0.53 mm, He flow 5 ml min^{-1} with temperature programmed from 35 to 200°C. The flow rate of CCl_2F_2 and hydrogen was measured through an electronic mass flow controller, which allowed the reactant ratio and flow rate to be readily varied. Most of the experiments were carried out in the temperature interval 200–300°C, using 4 g catalyst and a reaction mixture with a molar ratio $H_2:CCl_2F_2=6:1$. Prior to catalytic testing, all catalysts were additionally reduced in situ with H_2 at 300°C (1 h).

Catalyst samples

The catalysts were prepared by impregnating a selected activated carbon, acid-washed Darco [granular 20–40 mesh with a surface area of 638 $m^2 g^{-1}$ (American Norit Co., Inc.)]. The Pt–C catalyst was prepared by impregnation of the support with an acetone solution of $H_2PtCl_6 \cdot 6H_2O$. The material was dried at 100°C for 12 h, and then reduced with H_2 for 5 h at 350°C. For all series, the loading of metal was 0.026, 0.052 or 0.12 mol% M–C. $PdCl_2$ and $RuCl_2$ were used as precursors in the cases of Pd and Ru, respectively.

Texture of catalysts

Low-temperature (77 K) nitrogen adsorption measurements were carried out on Micromeritics equipment (ASAP, type 2010 M). Each adsorption isotherm involved 28 measurement points. The pore size distributions were calculated from the desorption branch of the isotherm by the BJH method. As a result of the calculations, plots of the pore volume as a function of the pore diameter *d* were obtained (Fig. 1).

X-ray diffraction study

Structural changes of the catalysts and the carbon support were obtained by using an X-ray diffractometer (Philips model PW 1710) using CuK_α radiation

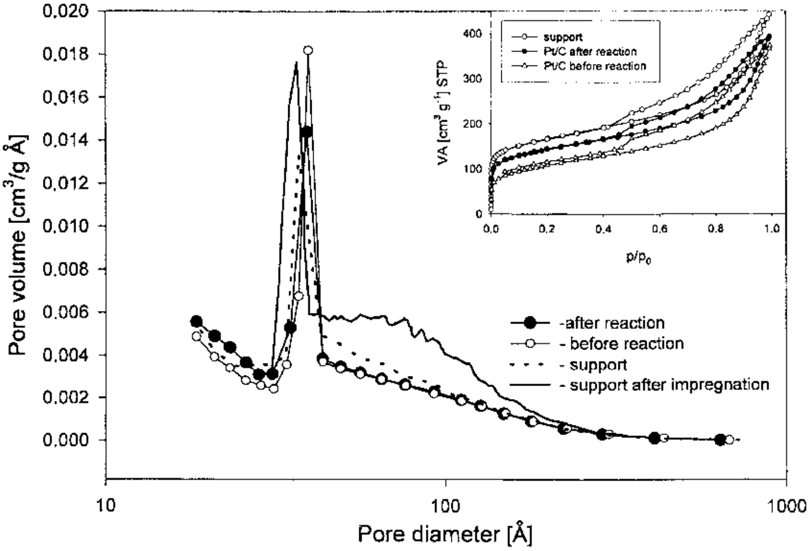

Fig. 1 Nitrogen adsorption-desorption isotherm (a) and pore volume distribution (b) as a function of pore diameter for 0.052 mol% Pt–C catalyst

and an APD (Philips) program for calculations. XRD analysis of some catalysts and the pure support was performed in the 2Θ range 3–70°, and SAXS analysis was carried out on the same apparatus in the 2Θ range 0–5° (Table 1).

Results and discussion

As expected, the changes in the texture of the carrier surface related to the process of impregnation of this carbon carrier with the metal precursor and to the secondary processes taking place during the catalytic reaction (the interactions of HCl and HF with the catalyst, and the coking process) are much smaller than for a similar system in which the metal phase is distributed on the carrier γ-Al_2O_3 [9–11]. Figure 1 presents the pore volume distribution as a function of the pore diameter for the system (0.052 mol% Pt–C), while Table 1 lists some of the texture parameters, e.g. specific surface area and statistical pore diameter.

Table 1 Selected surface parameters for chosen Pt–C catalysts and the support

Sample/ mol% of *M*	C	Pt–C		
		0.026	0.052	0.12
S_{BET}/m^2 g^{-1}				
Before reaction	638	634	370	377
After reaction		540	485	487
D_{av}/Å				
Before reaction	61.8			
After reaction			62.3	
Dispersion of *M*/%			62.0	
Before reaction		39.6		12.2
After reaction		5.8		8.0
Cluster size/Å		<20	~410	~305

Dispersion measurements were performed according to an earlier paper [12]

Introduction of a metal phase onto a carbon carrier in general leads to a decreased specific surface area S_{BET}, although this change is not directly proportional, as could be expected. For the preparation with the lowest load of metal phase, the specific surface area of the catalyst is practically the same as that for the fresh carrier (634 and 638 m^2 g^{-1}, respectively), while for the preparation loaded with twice as much metallic phase (the sample with 0.052 mol% Pt–C) the specific surface area is significantly reduced. Further increase of the metallic phase load does not lead to changes in this parameter. Such a character of changes is probably due to the size of the metal clusters on the carrier surface. On low loading of the metallic phase (0.026 mol% Pt–C), the size of the Pt clusters is below 20 Å, so their presence blocks the carrier pores to only an insignificant degree. For the 0.052 and 0.12 mol% Pt–C preparations, the size of the Pt crystallites formed is one order of magnitude higher (410 and 303 Å, respectively), which most probably leads to the blocking of pores, and thus to a much lower value of S_{BET} (~350 $m^2 g^{-1}$, i.e. roughly half that for 0.026 mol% Pt–C).

No significant changes in the texture of these preparations were observed after catalytic testing. The character of the changes in the specific surface area with increasing loading of the carrier with the metal phase was the same for these samples. Differences in the absolute value of S_{BET} are related to the formation of a carbon deposit on the catalyst surface. In contrast with the case when the metal phase was supported on an oxide carrier such as Al_2O_3, it can hardly be expected that on a carbon carrier the side-product of the hydrodehalogenation reaction (HCl/HF) will lead to considerable destruction in the porous structure of the support. The question arises of why, in the case of the preparation with the least metal phase loading, the carbon deposit formed leads to a decrease in the specific surface area of the system, whereas for the preparations with increased amounts of metal phase the surface area increases. With regard to the mean pore diameter, which is practically the same for the pure carbon carrier, after deposition of the metal phase and after the process of coking, it can be presumed that the carbon carrier may be a matrix for the carbon deposit being formed (Fig. 1). On the other hand, it is also possible that the coke being formed is also deposited on the metal clusters, which could be suggested by a decrease in the degree of dispersion of this phase before and after the catalytic process. It is worth noting that, for the preparation of the least Pt loading (where the size of the metal clusters is of the order of 20 Å), the surface availability of Pt after the catalytic reaction is reduced almost 5 times as compared to that for the preparations with a greater loading with metal phase, in which the size of the clusters is of the order of 300 Å. This would mean that the carbon deposit being formed on the carrier matrix is capable of covering small metal clusters. It could also indicate that metal clusters make a substrate for the carbon deposit and the kinetics of its formation substantially depends on the size of the metal clusters. Almost the same course of the curve illustrating the distribution of pore volume *vs.* pore diameter (Fig. 1) for the sample before and after the catalytic process suggests that the second possibility is highly improbable.

The only curve which deviates from the others in Fig. 1 is the one that illustrates the distribution of the pores in the carrier after deposition of the metal precursor (before reduction). The increased contribution of pores of greater diameter (50–100 Å) is related to the formation of cracking pores, appearing due to cracks in the H_2PtCl_6 crystals. This hypothesis is supported by the course of the curve of pore distribution after its thermal reduction, from which it follows that the cracking pores have disappeared.

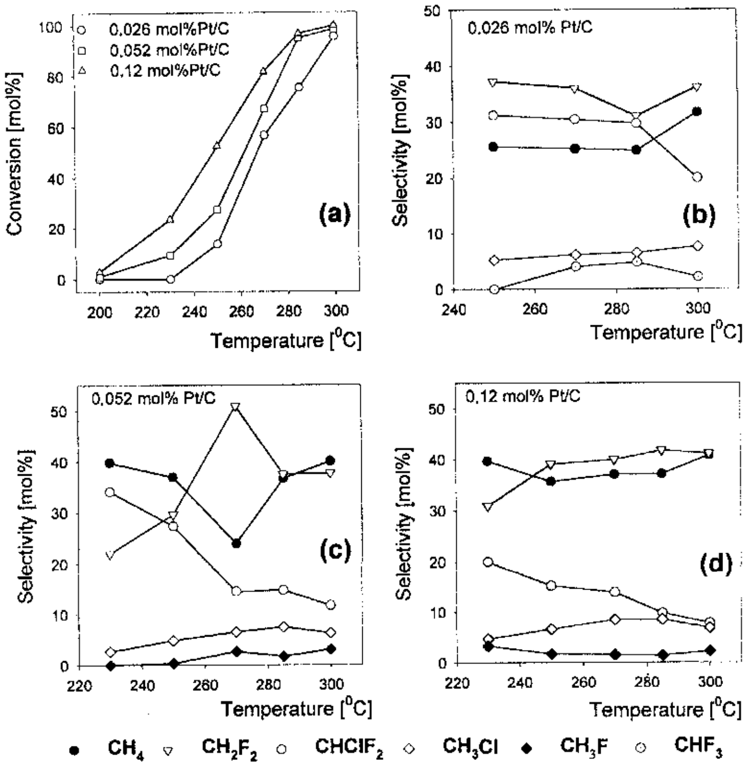

Fig. 2 Catalytic conversion of CCl_2F_2 as a function of temperature for Pt–C catalyst (a) and corresponding selectivities (b), (c), (d)

Results of the catalytic test (CCl_2F_2 conversion) are presented for the Pt catalyst (Fig. 2) and chosen preparations containing Pd or Ru (Fig. 3). The stability of the :CF_2 radical, similarly as in the experiments with Pt supported on Al_2O_3, leads to the formation of CH_2F_2 and CH_4 as the main products of the catalytic conversion of CCl_2F_2. In our opinion, the appearance of relatively large amounts of $CHClF_2$ in the products of hydrodehalogenation of CCl_2F_2 is related to the secondary reaction of (:CF_2+HCl) rather than to the sequential process of hydrodehalogenation.

The cause of the course of this competitive process is most probably directly related to the size of the metal clusters on the carrier surface. Moreover, it seems to us that the change in the size of these clusters leads to the change in the mechanism of the above process. Therefore, in the case of small metal clusters (a high degree of dispersion), the process according to the mechanism of halogenation/dehalogenation is favoured and the amount of $CHClF_2$ in the reaction products is much greater than in the case of a reaction taking place according to the Langmuir-Hinshelwood mechanism on the active sites at relatively close distances. In our reaction, therefore, a catalyst with a high degree of dispersion (0.026 mol% Pt–C, small and relatively distant Pt clusters as compared to those in the sample with 0.12 mol% Pt–C) may favour a secondary reaction. This hypothesis seems to be supported by the initial results of the conversion of CFC-12 on Ru–C (Fig. 3), where the main product proves to be $CHClF_2$. At the present stage, it is difficult to suggest an unambiguous interpretation of this difference.

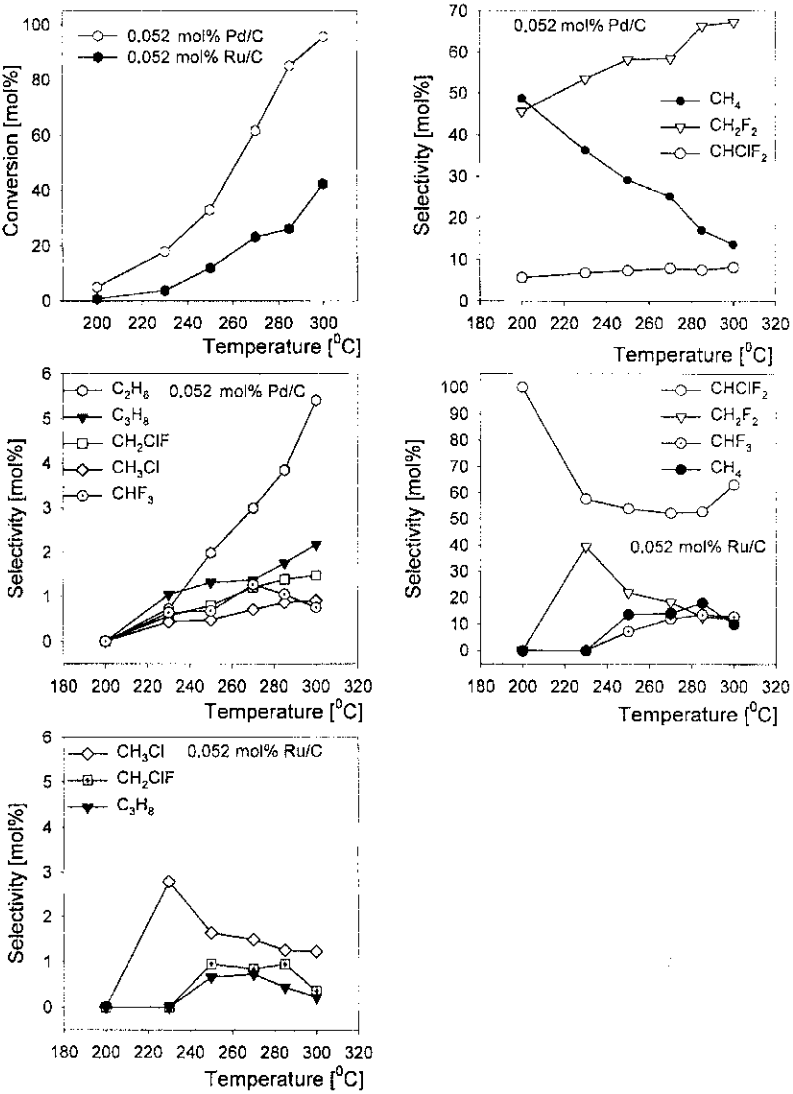

Fig. 3 Results of catalytic conversion of CCl_2F_2 (ratio CCl_2F_2:H_2=1:6) over 0.052 mol% Pd–C and 0.052 mol% Ru–C catalysts

It may be related to the changes in the process of chemisorption (different *d* character of transition metals) and to a different geometry of the active metal centre. The latter explains the similarity of the catalytic properties of Pt and Pd (both metals crystallize in the face-centred cubic lattice) and the different properties of Ru (hexagonal closest packed-based) catalysts.

Conclusions

1. Introduction of the metals onto the carbon support leads to changes in its texture, but the basic structure of the support is preserved:

– low metal loading leads to the formation of small clusters (below 20 Å) and as a consequence small changes in surface area are observed;

– high metal loading leads to the formation of much larger clusters (above 300 Å) and as a consequence a strong reduction of the texture parameters is observed.

2. The metal loading is reflected by the dispersion obtained on the chemisorption of hydrogen.

3. The fact that the carbonaceous deposit formed during the catalytic reaction has the same structure as the carbon support suggests that the support can be a matrix for a 'coke coating'.

4. The activity of the catalyst used in the hydrogenolysis of the carbon–halogen bond decreases in the sequence Pt>Pd>Ru.

5. The product distribution is effected by the nature of the metal applied:

– the conversion of CCl_2F_2 to highly hydrogenated products (CH_4 and CH_2F_2) is most efficient with a Pt catalyst, whereas Ru–C as catalyst leads to $CHClF_2$ as the main product.

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