Kinetics and Catalysis, Vol. 45, No. 2, 2004, pp. 183–188. Translated from Kinetika i Kataliz, Vol. 45, No. 2, 2004, pp. 199–204.
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CATALYTIC REACTION MECHANISMS

Hydrodechlorination of Tetrachloromethane in the Vapor Phase in the Presence of Pd–Fe/Sibunit Catalysts

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Received December 25, 2002

Abstract—The hydrodechlorination of CCl_4 in the presence of Pd–Fe/Sibunit catalysts of different composition was studied. An optimum concentration of the metals (2.5% at the ratio Pd/Fe = 1 : 4) was determined, which corresponds to the highest stability of catalysts and selectivity of C_2–C_4 olefin and paraffin formation. With the use of TPR and magnetic measurements, it was found that the metals occurred in an oxidized state in the course of the reaction; it is likely that this resulted in the formation of C_2–C_4 hydrocarbons.

INTRODUCTION

Chlorinated hydrocarbons are important chemical products and intermediates; however, the majority of them are environmentally hazardous substances. At the same time, the production of tetrachloromethane in the course of organochlorine waste processing by exhaustive chlorination exceeds the industrial demand for this compound [1]. Moreover, CCl_4 is a by-product of some commercial processes, for example, the production of chloroform. Combustion is currently of considerable use for organochlorine waste treatment. However, in this case, carbon-containing raw materials are lost and highly toxic compounds, such as dioxins, are formed. The use of catalytic combustion techniques exhibits the same disadvantages. Catalytic hydrodechlorination is a promising way to process organochlorine compounds with the formation of useful products at comparatively low temperatures.

Palladium-containing catalysts are most frequently used in hydrodechlorination reactions [2]; however, their commercial applications are restricted by their high costs, although they are highly active. To decrease the cost of these catalysts, less expensive metals such as iron or nickel are introduced into the system. Thus, the hydrodechlorination of tetrachloromethane [3], trichloroethylene [4, 5], and polychlorinated biphenyls [6] was efficiently performed with the use of iron catalysts. The modification of palladium catalysts by adding a second metal, which is active in hydrodechlorination, often changed the selectivity and conversion of reaction [7]. In particular, after the treatment of Fe powders with Pd, Ni, Pt, and Cu, their activity in the hydrodechlorination of pentachlorophenol decreased [8]. In contrast, the introduction of Pd or Ni into a system containing Fe exerted a promoting effect in the reaction of tetrachloroethane decomposition [9]. The rapid and exhaustive hydrodechlorination of polychlorobiphenyls occurred in the presence of palladinized iron in an aqueous methanol solution [10]. Bimetallic Pd–Fe catalysts supported onto magnesium oxide [11], aluminum oxide [12], or a carbon composite material [13] exhibited considerable activity in the vapor-phase hydrodechlorination of chlorobenzene. The treatment of catalysts in a microwave oven before reduction resulted in a greater increase in the activity.

The activity of Pd–Fe catalysts depends on the nature of the support, the particle size, and the degree of interaction between the active components [7, 14]. In this context, it is a topical issue to study in detail the behavior of such systems in catalysis with the use of currently available physicochemical techniques for determining the dispersity and electronic state of active components.

In this work, we studied the physicochemical and catalytic properties of the Pd–Fe systems supported on a Sibunit carbon support. The hydrodechlorination of tetrachloromethane in the vapor phase at 150–270°C was chosen as a model reaction. In the course of the reaction, the formation of C_2–C_4 hydrocarbons along with hydrodechlorination products can occur. This allowed us to compare the selectivity of the catalytic action of Pd–Fe systems.

EXPERIMENTAL

Catalysts with total metal contents of 1.25, 1.7, 2.5, 5, and 10% (Pd/Fe = 2 : 3, 3 : 7, and 1 : 4) were used in this study. They were prepared by the impregnation of Sibunit (specific surface area of 370 m^2/g, pore volume of 0.4 cm^3/g, micropore volume of 0.15 cm^3/g, and particle size of 0.5 mm [15]) with palladium chloride and iron chloride followed by the evaporation of the solvent and the reduction of the metals with $NaBH_4$ in an aque-

Catalysts used in the hydrodechlorination of CCl_4

Metal content, %		Pd : Fe	S_{sp}, m^2/g
Pd	Fe		
0.5	0.75	2 : 3	374
0.5	1.2	3 : 7	360
0.5	2	1 : 4	358
1	4	1 : 4	342
2	8	1 : 4	337

ous ethanol solution at the ratio metal/$NaBH_4$ = 1 : 3. The prepared catalysts were kept in ethanol.

The vapor-phase hydrodechlorination of CCl_4 was performed in a flow system. An air-dried catalyst (0.1 g) was placed in a quartz flow reactor, heated to the reaction temperature in a flow of H_2, and kept at this temperature for 2 h. Hydrogen was passed through a bubbler with CCl_4 (chemically pure grade, distilled); next, a CCl_4/H_2 mixture was supplied to the reactor (molar ratio $H_2/CCl_4 = 6.5$). Gaseous reaction products were sampled immediately after the reaction with the use of a syringe.

The reaction products were analyzed by GLC under the following conditions: column with Porapak Q (1 m); carrier gas, N_2 (30 ml/min); FID; and column temperature, 100°C.

The gaseous reaction products were analyzed by gas chromatography–mass spectrometry (GC–MS) on a Finnigan MAT 112S instrument with the use of an ion trap and an HP-PLOT/Al_2O_3 capillary column (30 m) in the temperature range 20–200°C; argon was the carrier gas.

The catalytic properties of the catalysts were compared using the selectivity of reaction product formation for 100% conversion of CCl_4 (S_{CH_4}, S_{C_2}, S_{C_3}, S_{C_4}, and S_{CHCl_3}).

The specific surface areas of the catalysts were determined from the low-temperature adsorption of nitrogen. As a reference sample, Al_2O_3 (83 m^2/g) was used.

The temperature-programmed reduction (TPR) was performed on heating a catalyst (0.1 g) in a flow of H_2/Ar (10 vol % H_2 in Ar) at a rate of 13 K/min. The release and consumption of hydrogen were monitored with the use of a thermal-conductivity detector.

Magnetic measurements (the temperature dependence of magnetization) were performed on a vibration magnetometer on heating in a controlled gas atmosphere of a specified composition.

X-ray diffraction patterns were obtained on an HZG-Y apparatus using CuK_α radiation. A monochromator (graphite, flat) filtered δ-radiation of a diffraction beam, an optimum ratio between diffraction peak and background intensities, and a minimum fluorescence intensity. The operating conditions of the X-ray tube were as follows: $V = 35$ kV; $J = 35$ mA; diffractometer slits of 1 : 2 : 0.35 mm. The diffraction patterns were recorded on a recorder at a meter speed of 1 deg/min and a paper feed rate of 60 mm/h.

RESULTS AND DISCUSSION

The test catalysts are characterized by an insignificant increase in the specific surface area with increasing total metal content (see the table). Even at a 10% metal content, the surface area of the catalysts decreased by 10 rel. %.

According to the GC–MS data, $CHCl_3$, CH_3Cl, and C_1–C_4 hydrocarbons (methane, ethane, propene, propane, isobutane, *n*-butane, 1-butene, *trans*-2-butene, and *cis*-2-butene) were the products in the presence of all the catalysts. In the course of the reaction, three periods were characteristic of all the catalysts: a short initial period of development, a period of stable operation (during which the composition of reaction products remained unchanged and conversion was 100%), and a period of decreasing activity because of deactivation. Note that the selectivity of C_4 hydrocarbon formation was sometimes as high as 70% before the period of stability. The time of stable operation (t_{st}) depended on the reaction temperature, and the character of this dependence changed in catalysts with different compositions (Fig. 1). For catalysts with high total metal contents of 5 and 10% (Pd/Fe = 1 : 4), the value of t_{st} increased from a few minutes to 3–5 h as the reaction temperature was increased (Fig. 1a). A catalyst containing 2.5% metals (Pd/Fe = 1 : 4) exhibited maximum stability at 220°C. Not only the total metal content but also the Pd/Fe ratio, which was varied by changing the Fe content at a constant concentration of Pd (0.5%), affected the stability of the catalysts. A sample containing 2.5% metals was most stable in this series of catalysts.

The selectivity of CCl_4 conversion also depended on metal contents and catalyst composition. In a comparison of selectivity, it is reasonable to distinguish two reaction pathways: hydrodechlorination and the formation of C_2–C_4 hydrocarbons. Because these pathways are interdependent under the conditions of the test reaction, this comparison is relative; however, it provides an opportunity to evaluate the selectivity of catalysts with different compositions of active components. Figure 2 diagrammatically illustrates changes in the selectivity of CCl_4 conversion in the presence of various catalysts during the period of stable operation at 220°C. Note that product distributions over the test temperature range differed only slightly. The selectivity of formation of the products of CCl_4 conversion on catalysts containing 5 and 10% metals (Pd/Fe = 1 : 4) was equal. The degree of hydrodechlorination decreased as the total metal content was decreased to 2.5%. The total selectivity of C_2–C_4 hydrocarbon formation remained practically unchanged, except for a small increase in S_{C_2}. In addition to the dependence on the total metal content, the selectivity depended on the ratio Fe/Pd in the catalyst. As the iron content was decreased, S_{CH_4} increased and S_{CHCl_3} and the total yield of C_2–C_4 products simultaneously decreased.

Thus, an increase in the iron content of the catalysts resulted in an increase in the selectivity of CCl_4 conversion into C_2–C_4 hydrocarbons and in a small decrease in the degree of hydrodechlorination. Analogously, Lingaiah *et al.* [13] observed a decrease in the degree of chlorobenzene dechlorination by a factor of four as the iron content of a Fe–Pd/C catalyst was increased from 50 to 80%. Lingaiah *et al.* [13] explained this decrease by the segregation of iron on the catalyst surface in the course of the *in situ* reduction of hematite to magnetite and further to iron metal.

From a comparison of stability and selectivity, it follows that, at high total metal contents (5 and 10%), the catalysts were practically equal both in selectivity and the values of t_{st} as a function of temperature. However, as the metal content was decreased to 2.5%, the properties of the catalyst changed, although the ratio between the metals remained unchanged (Pd/Fe = 1 : 4). It is believed that hydrodechlorination is a structure-sensitive reaction [16]. It is likely that an increase in the amount of metals resulted in the formation of coarse particles on the catalyst surface, whereas the formation of smaller particles was more probable at low metal concentrations. In addition, electron effects began to play a more important role. Both the selectivity and the temperature dependence of the period of stable operation were different as the ratio between metals in a given catalyst was changed. A change in catalytic properties can be related to different interactions between metals in an active component and to the formation of finely dispersed particles.

To study the electronic structure of the metals in Pd–Fe catalysts, the TPR of samples before and after the reaction was performed, and it was accompanied by magnetization measurements.

Figure 3 demonstrates the temperature dependence of the magnetization of catalysts. The initial catalysts were fully nonmagnetic; consequently, iron in a catalyst occurred in an oxidized state by the time of the onset of the reaction. Magnetization appeared on heating in hydrogen above 300°C, and its value was proportional to the amount of iron in the catalyst. It is likely that the presence of oxidized iron is responsible for the high selectivity of C_4 hydrocarbon formation at the onset of the reaction. A change from the initial period to the period of stable operation was due to the reduction of iron in the catalyst to the metal. A decrease in conversion after the period of stable operation was due to catalyst deactivation by liberated HCl, as well as due to the possibility of the formation of a hydrocarbon film on the catalyst surface.

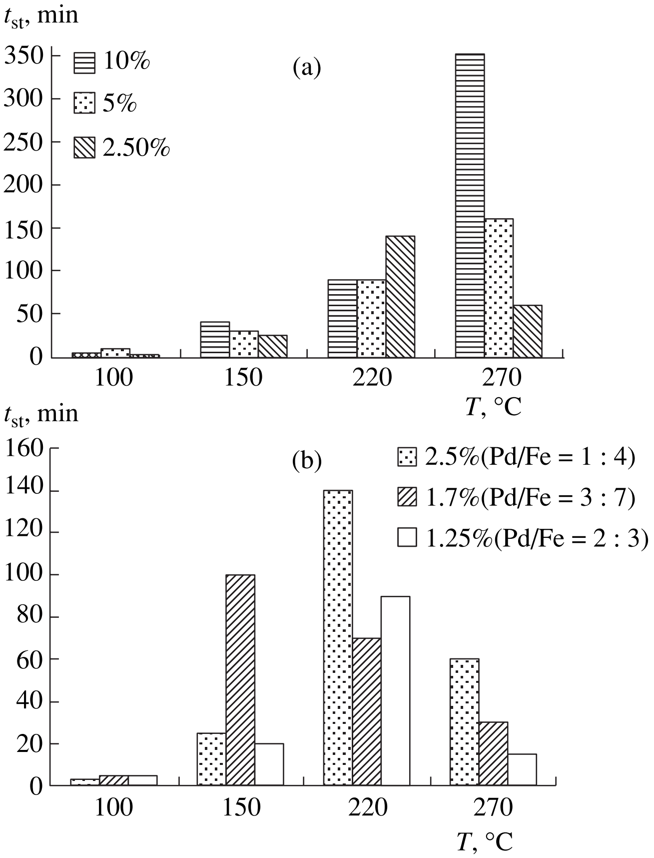

Fig. 1. The temperature dependence of the period of stable operation (t_{st}) for catalysts (a) with different total metal contents at Pd/Fe = 1 : 4 and (b) with different iron contents at 0.5% Pd.

Figure 4 demonstrates the TPR spectra of catalysts. The shapes of spectra for catalysts before and after the reaction are strongly different. The TPR spectra of all the initial catalysts (Fig. 4a) represent a set of peaks with different intensities. In spite of the complex composition of the spectra, several groups of peaks can be distinguished in these spectra. It is likely that low-temperature peaks (100–120°C) belong to the reduction of palladium. A group of peaks at higher temperatures corresponds to the reduction of iron and the support. It is most likely that the peaks of hydrogen absorption at temperatures higher than 600°C correspond to the hydrogenation of the support. A further increase in the temperature resulted in the methanation of Sibunit. Methane was detected in the exit gases by chromatography.

Unresolved peaks at close temperatures can correspond to the reduction of the groups of iron atoms in the same oxidation state but with different energies of binding to the support surface. This can be explained by the adsorption of metal atoms in support regions different in energy characteristics (defects and coordinatively unsaturated atoms of the support).

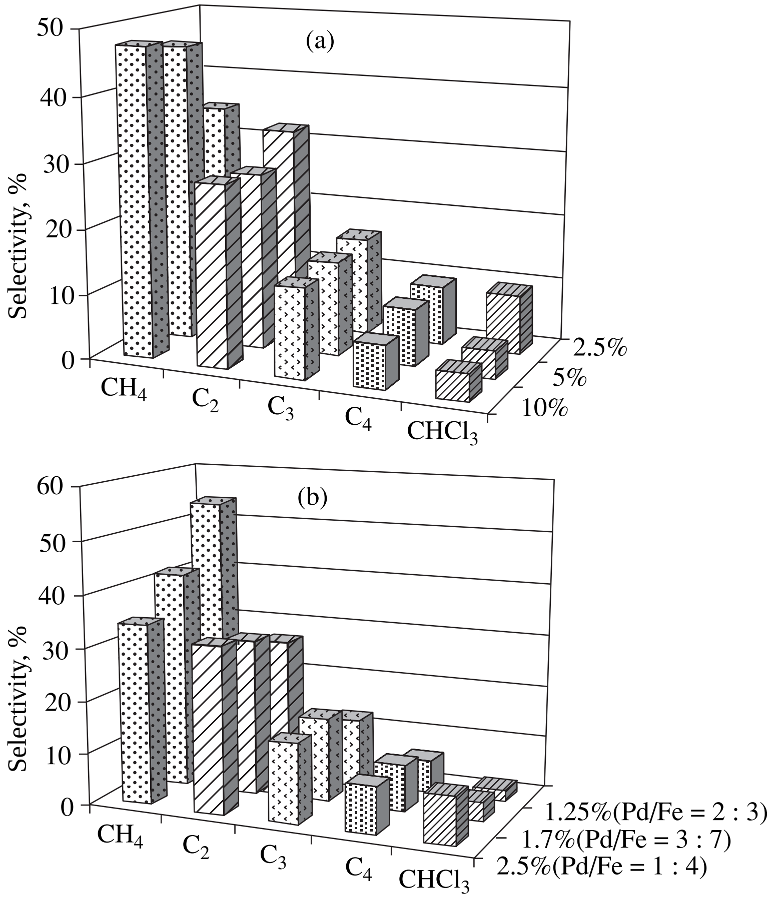

Fig. 2. Selectivity of the hydrodechlorination of CCl_4 in the presence of catalysts (a) with different total metal contents at Pd/Fe = 1 : 4 and (b) with different iron contents at 0.5% Pd.

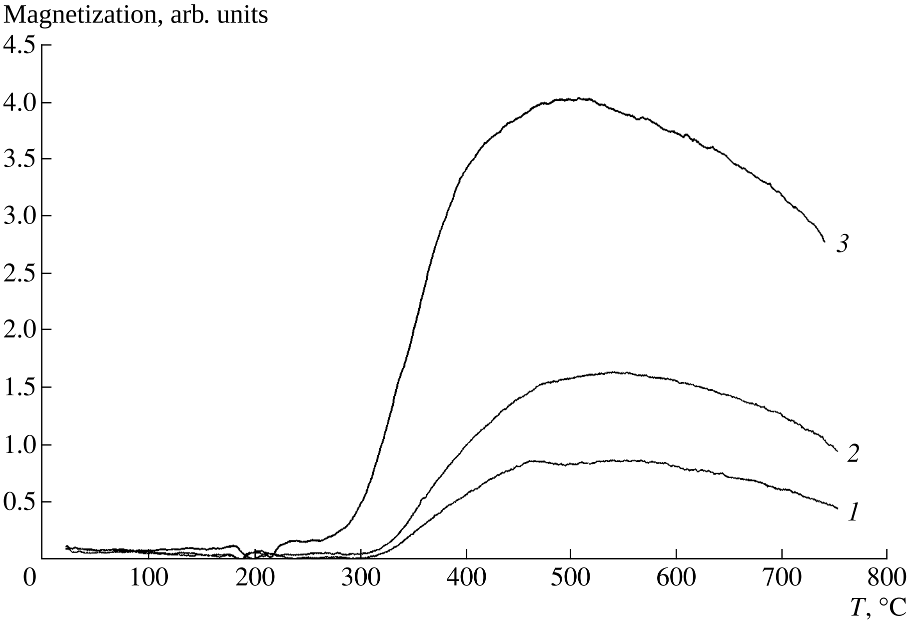

Fig. 3. The temperature dependence of the magnetization of Pd–Fe/Sibunit catalysts in the course of TPR: (*1*) 1.25% (Pd/Fe = 2 : 3), (*2*) 1.7% (Pd/Fe = 3 : 7), and (*3*) 2.5% (Pd/Fe = 1 : 4).

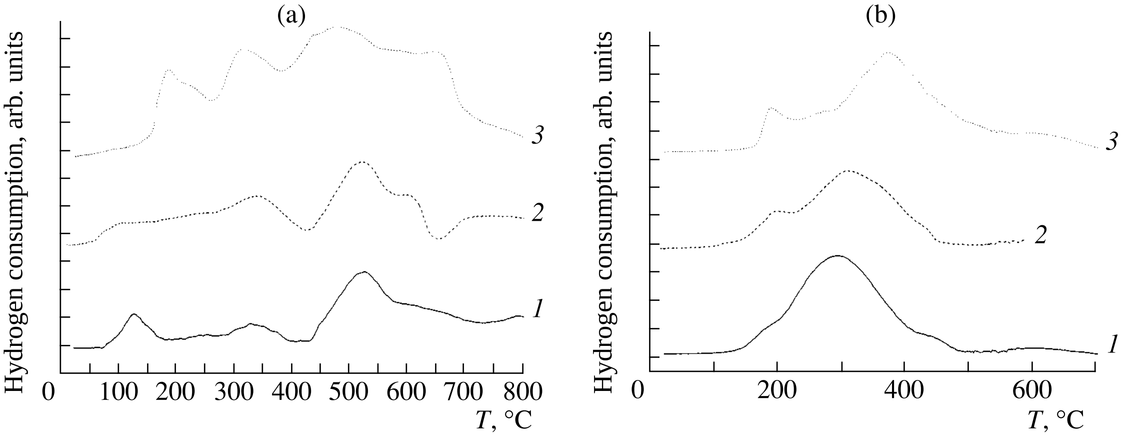

Fig. 4. TPR spectra of Pd–Fe/Sibunit catalysts (a) before the hydrodechlorination reaction and (b) after the hydrodechlorination reaction: (*1*) 1.25% (Pd/Fe = 2 : 3), (*2*) 1.7% (Pd/Fe = 3 : 7), and (*3*) 2.5% (Pd/Fe = 1 : 4).

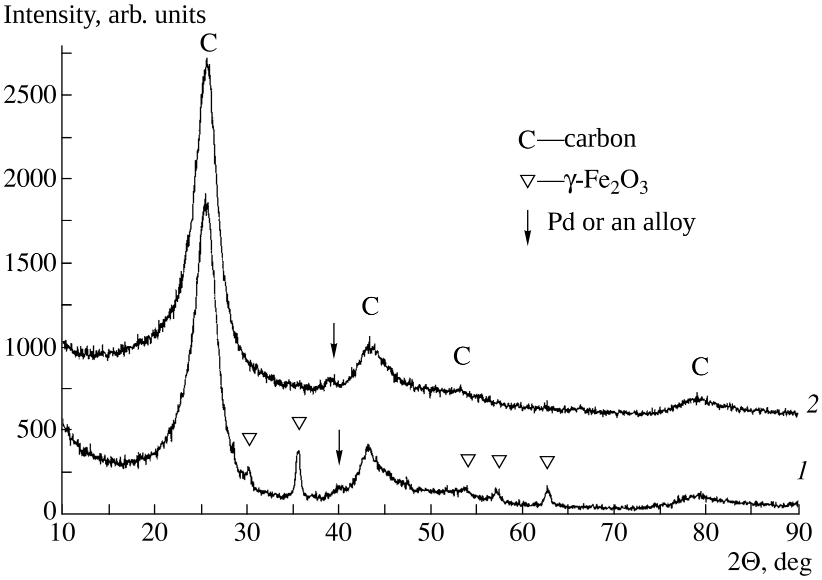

Fig. 5. XRD spectra of 3%Pd–Fe/Sibunit (Pd/Fe = 1 : 4) (*1*) before and (*2*) after the hydrodechlorination of CCl_4.

The TPR spectra of samples after the reaction were noticeably simplified. First, the high-temperature reduction peaks ($T_r > 500°C$) disappeared. Moreover, the number of peaks in the spectra noticeably decreased. However, the peak corresponding to T_r = 180°C was present in the TPR spectra of all the catalysts. It is believed that peaks at T_r = 300 (2.5%, Pd/Fe = 1 : 4), 330 (1.7%, Pd/Fe = 3 : 7), and 380°C (1.25%, Pd/Fe = 2 : 3) correspond to the reduction of atoms with similar electronic states.

An XRD study of a 3% sample (Pd/Fe = 1 : 4) demonstrated that FePd alloy and γ-Fe_2O_3 phases occurred in the initial catalyst (Fig. 5). A shift of the initial peak due to the FePd alloy was observed after the reaction; the phase of γ-Fe_2O_3 was absent. It is most likely that the occurrence of iron oxide in the initial catalysts resulted from the oxidation of surface atoms in storage.

Thus, the physicochemical studies of catalysts before and after the reaction demonstrated that the iron in the initial samples had a nonzero oxidation number. It is likely that the occurrence of oxidized iron in the active component of a catalyst results in the high selectivity of C_4 hydrocarbon formation at the onset of the reaction.

ACKNOWLEDGMENTS

We are grateful to Doctor of Chemistry P.A. Chernavskii for his assistance in performing the magnetization measurements. This work was supported by the Russian Foundation for Basic Research (grant no. 01-03-33127) and INTAS (grant no. 2000-00710). Golubina acknowledges the support of Haldor Topsøe.

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