*Kinetics and Catalysis, Vol. 41, No. 6, 2000, pp. 776–781. Translated from Kinetika i Kataliz, Vol. 41, No. 6, 2000, pp. 855–860.*


# Formation of $C_1$–$C_5$ Hydrocarbons from $CCl_4$ in the Presence of Carbon-Supported Palladium Catalysts

**E. S. Lokteva*, V. I. Simagina**, E. V. Golubina*, I. V. Stoyanova**, and V. V. Lunin***

** Moscow State University, Moscow, 119899 Russia*

*** Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia*

Received July 15, 1999

**Abstract**—Along with hydrodechlorination, the formation of $C_1$ and higher hydrocarbons takes place in a flow system in the presence of catalysts containing 0.5–5.0% Pd supported on a Sibunit carbon carrier at 150–230°C. In the entire range of conditions examined, the reaction products are primarily methane, $C_2$–$C_4$ hydrocarbon fractions, and $C_5$ traces. The catalysts are stable in operation, and a high conversion of $CCl_4$ was retained for a long time interval. The nonselective formation of linear and branched hydrocarbons is indicative of a radical mechanism of the process.

## INTRODUCTION

Palladium catalysts are widely used in the hydrodechlorination reactions of organic compounds [1, 2]. In the presence of hydrogen, successive hydrodechlorination of polychlorinated hydrocarbons usually occurs on these catalysts. Recently, catalytic systems in which various carbon materials are used as a support are of particular interest. Thus, the hydrodechlorination of chlorobenzenes [3] and dichlorodibenzodioxines [4] can efficiently be performed with catalysts containing palladium supported on a Sibunit carbon carrier. Carbon-supported palladium catalysts were also used in the liquid-phase hydrodechlorination of $CCl_4$. The reaction resulted in the formation of a set of completely and partially hydrodechlorinated products [5] and HCl. Hydrogen chloride formed in the reaction is usually considered as a catalytic poison, and alkaline agents are used for its neutralization. At the same time, it is well-known that the presence of acid sites in metal-containing catalysts is a necessary condition for oligomerization and skeletal isomerization reactions. The Brönsted acidity on the surface of alumina dramatically increased in the presence of $Cl^-$ ions. Therefore, in the reforming of crude oil, chlorine-containing organic compounds are added to the starting material to keep the isomerization activity of catalysts at a high level [6]. The formation of oligomer products with chains longer than two carbon atoms in the hydrogenolysis of organochlorine compounds was detected, for example, $CH_nCl_{4-n}$ on Ni, Co, and Fe catalysts [7] or $CH_3Cl$ and $CH_2Cl_2$ on titanium films [8]. We suggested that the oligomerization of hydrodechlorination products would also take place in the presence of carbon-supported palladium catalysts. $CCl_4$ is the most convenient and informative probe. Sugiyama *et al.* [9] used $CCl_4$ to modify methane oxidative dimerization catalysts containing $MgO/MgSO_4$; they considered the formation of Cl in a near-surface region of the catalyst as a reason for an increase in the ethylene yield. A new direction of $CCl_4$ transformations to form higher hydrocarbon products would make it possible to indirectly activate methane in order to involve natural gas in deep conversion processes.

In this work, we studied the hydrodechlorination of $CCl_4$ in a hydrogen flow at atmospheric pressure and temperatures of 150–230°C in the presence of Pd/Sibunit catalysts with different palladium concentrations to experimentally examine the formation of hydrocarbons higher than $C_1$.

## EXPERIMENTAL

The preparation procedure for 0.5–5.0% Pd/Sibunit catalysts (henceforth referred to as Pd/C) used in this study involved the impregnation of a support with a palladium chloride solution followed by the evaporation of the solvent and metal reduction either with sodium borohydride in an aqueous ethanol solution at the ratio $Pd/NaBH_4 = 1/3$ or with molecular hydrogen at 500°C for 4 h. A Sibunit carbon material [2] with the following characteristics was used as a support: $S_s$ = 370 $m^2/g$; pore volume, 0.4 $cm^3/g$; micropore volume, 0.15 $cm^3/g$; and particle size, 0.5 mm.

The catalysts reduced with $NaBH_4$ were stored in ethanol.

The catalytic experiments were performed as described below. After drying in an air flow, a weighed sample (0.2 g) of the catalyst was placed into a quartz reactor and heated in an $H_2$ flow to a reaction temperature and then allowed to stay at this temperature for 1 h. A bubbler with a known amount of $CCl_4$ was heated to 60°C, and hydrogen (2 l/h) was passed through it. Then, a $CCl_4$–$H_2$ mixture was supplied to the reactor. The rate of $CCl_4$ supply was $6 \times 10^{-2}$ g/min. At the reac-

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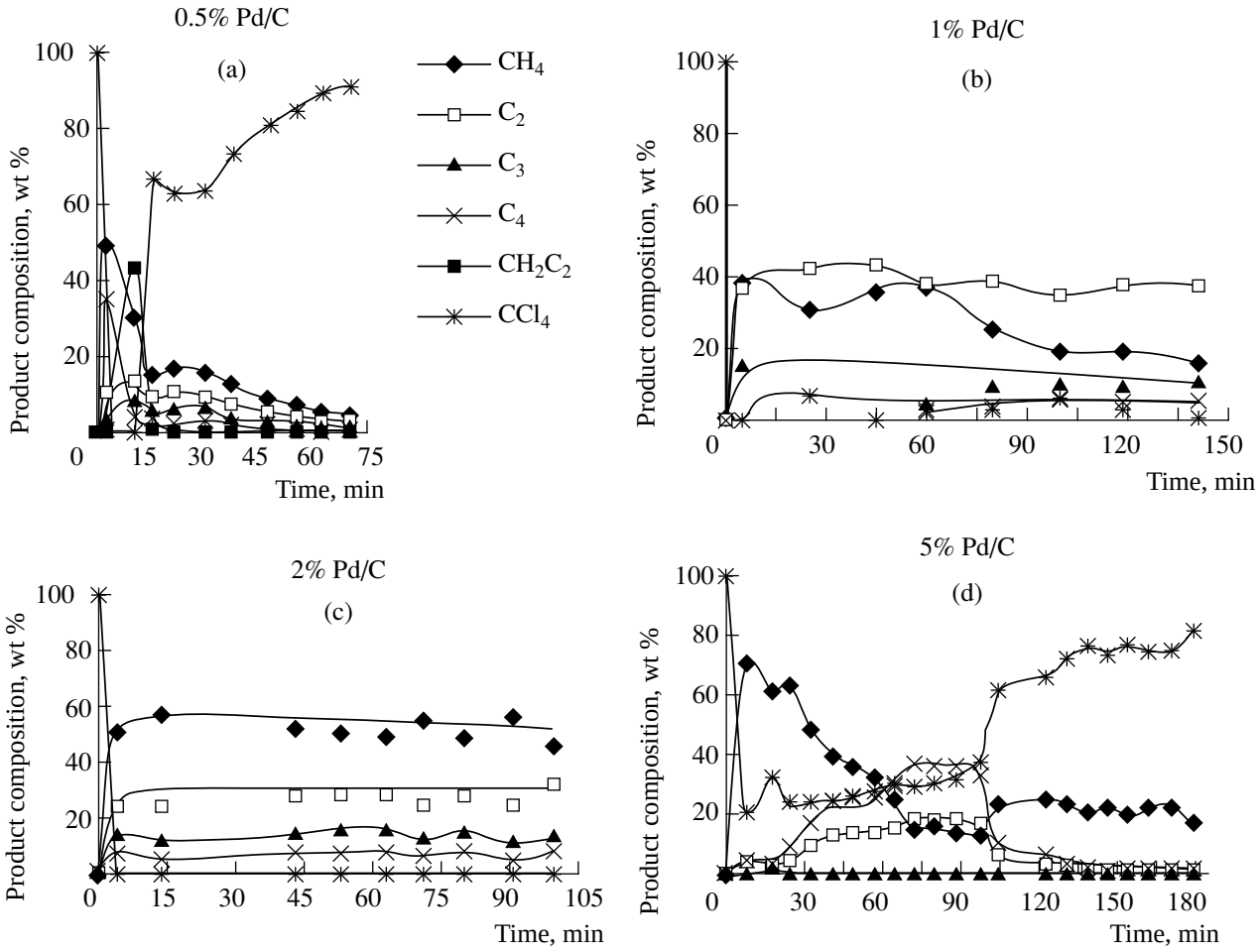



**Fig. 1.** Composition of the products of vapor-phase $CCl_4$ conversion at 150°C in the presence of Pd/C catalysts with the following Pd content: (a) 0.5, (b) 1.0, (c) 2.0, and (d) 5.0%.

tor outlet, samples were taken using a gas-tight syringe. Waste gases were passed through distilled water, which was titrated after the experiment with a 0.25 mol/l NaOH solution in the presence of methyl red to determine the amount of HCl released. In some instances, the products were frozen at the temperature of liquid nitrogen and unfrozen into a gas trap evacuated to $10^{-3}$ torr after the reaction. Then, they were analyzed on a chromatograph coupled with a mass spectrometer.

Mass spectrometric analyses were performed on a Finnigan MAT 112S GC–MS instrument with electron ionization ($E_i$ = 70 eV; ionization chamber temperature, 20–230°C; DB1 column, 60 m; 40–200°C) or using an ion trap ($Al_2O_3$(KCl) capillary column, 30 m; 20–200°C). In both cases, argon was used as a carrier gas. To protect the column from HCl, a syringe was equipped with a tube containing solid KOH.

Gas samples were analyzed by GLC: Porapak Q column, 2 m; carrier gas, $N_2$; detector, FID; column temperature, 100–130°C.

The particle-size distribution of the metal in the catalyst was determined from small-angle X-ray scattering data obtained with a KRM-1 chamber in the 2θ angle range from 7′ to 7° using Cu$K_\alpha$ radiation (Ni filter) and amplitude discrimination.

The particle size in a surface layer was determined by electron microscopy. Electron micrographs were obtained on a JEM-2010 instrument (Japan) with a resolution of 0.14 nm and an accelerating potential of 200 kV. Samples were prepared from a suspension in ethanol; a drop of the suspension was placed onto a copper support coated with a carbon film.

Chemically pure $CCl_4$ was used in this study after distillation.

## RESULTS AND DISCUSSION

The vapor-phase conversion of $CCl_4$ in the presence of hydrogen and 0.5–5.0% Pd/C catalysts reduced using sodium borohydride occurs with the formation of products of partial hydrodechlorination (primarily $CH_3Cl$) and alkanes. Table 1 and Fig. 1 summarize the composition of reaction products at 150°C according to GC–MS (with electron ionization) and GLC data,

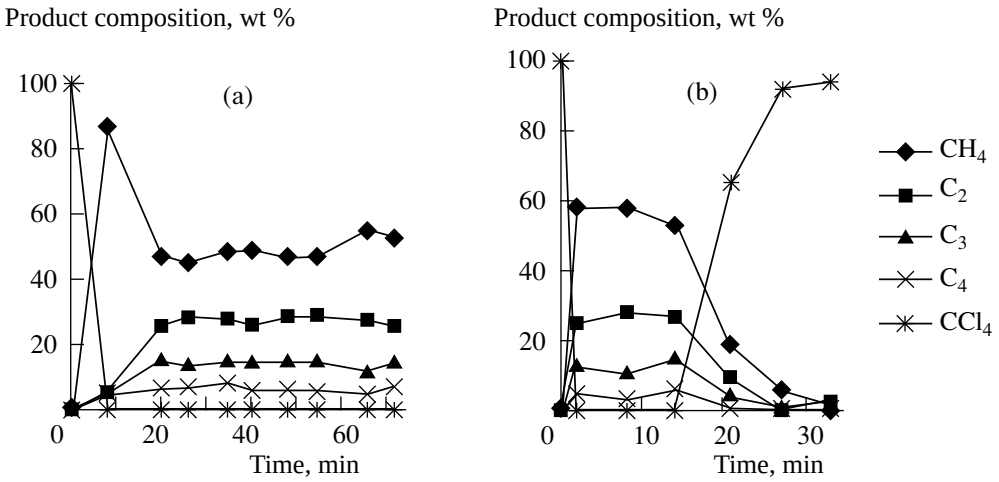



**Fig. 2.** Composition of the products of $CCl_4$ conversion at (a) 150 and (b) 230°C in the presence of a 5.0% Pd/C catalyst reduced in $H_2$ at 500°C.

respectively. It can be seen in Table 1 and Fig. 1 that, of the expected products of partial $CCl_4$ hydrodechlorination, only the products of deep hydrodechlorination—methane and $CH_3Cl$ (in the presence of a catalyst containing 5.0% Pd) or $CH_2Cl_2$ (in the presence of a catalyst containing 0.5% Pd)—were present in the mixture. In addition, considerable amounts of $C_2$–$C_5$ hydrocarbons as isomer mixtures were detected in the products of catalysis. Thus, our hypothesis on the possible oligomerization of tetrachloromethane hydrodechlorination products was supported by experiments.

Data presented in Table 1 were calculated without considering methane formed because it cannot be determined by GC–MS with electron ionization. At the same time, Fig. 1 indicates that methane was a major product in all cases. Its concentration in the products of catalysis varied from ~10 to ~70% depending on the Pd concentration in the catalyst and on the catalyst time-on-stream. Consequently, the real concentration of higher hydrocarbons in the products of catalysis is lower than that given in Table 1.

**Table 1.** The composition of the products of $CCl_4$ conversion averaged over time on 5.0% Pd/C at 150°C (according to GC–MS with electron ionization)

| Products* | Concentration, wt % |
|---|---|
| Fraction $C_2$ | 26.3 |
| Fraction $C_3$ | 37.6 |
| $CH_3Cl$ | 2.7 |
| *n*-Butane | 12.4 |
| Other $C_4$ hydrocarbons | 7.7 |
| *n*-Pentane | 1.9 |
| $CCl_4$ | 11.2 |

* Methane cannot be detected in the products by this technique.

In the presence of catalysts containing 1.0–5.0% Pd, the conversion of $CCl_4$ was rather high (~80–90%), and this value was retained for at least 2 h. The catalyst containing 0.5% Pd rapidly lost its activity. At the initial stage, methane was the major product; subsequently, higher hydrocarbons ($C_3$ and higher) appeared in the products of catalysis. These data are evidence for the fact that the reaction products initially modify the catalyst surface. In the presence of 5.0% Pd/C, methane was formed in considerable amounts at an early stage; then, the formation of higher hydrocarbons began in the reaction mixture. In this process, the total conversion of $CCl_4$ gradually decreased. Thus, simultaneously with the modification, the active surface of the catalyst was somewhat poisoned with reaction products. This effect was noticeable to a small extent for catalysts with lower Pd contents. The highest yields of $C_2$–$C_3$ oligomers were obtained in the presence of a catalyst containing 1.0% Pd/C: the concentration of $C_3$ hydrocarbons in the products of catalysis was as high as ~20%, and the concentration of $C_2$ was ~40%, which is higher than the methane content.

Note that the products of partial hydrodechlorination (chloroform, chloromethane, and methylene chloride) were almost absent from the reaction mixture. Thus, chloromethane was detected in the products of catalysis only in the presence of a 5.0% Pd/C catalyst, whereas in the presence of 0.5% Pd/C, which rapidly lost its activity, up to 40% $CH_2Cl_2$ was formed at the initial period of the reaction when the catalyst was still very active. It is well known [2] that, upon the replacement of chlorine atoms by hydrogen in polychloroalkanes, the energies of the remaining C–Cl bonds considerably increased, and the last chlorine atom is most difficult to abstract. Because of this, of all the products of partial hydrodechlorination, we usually detected only $CH_3Cl$ and rarely $CH_2Cl_2$ in the mixture.

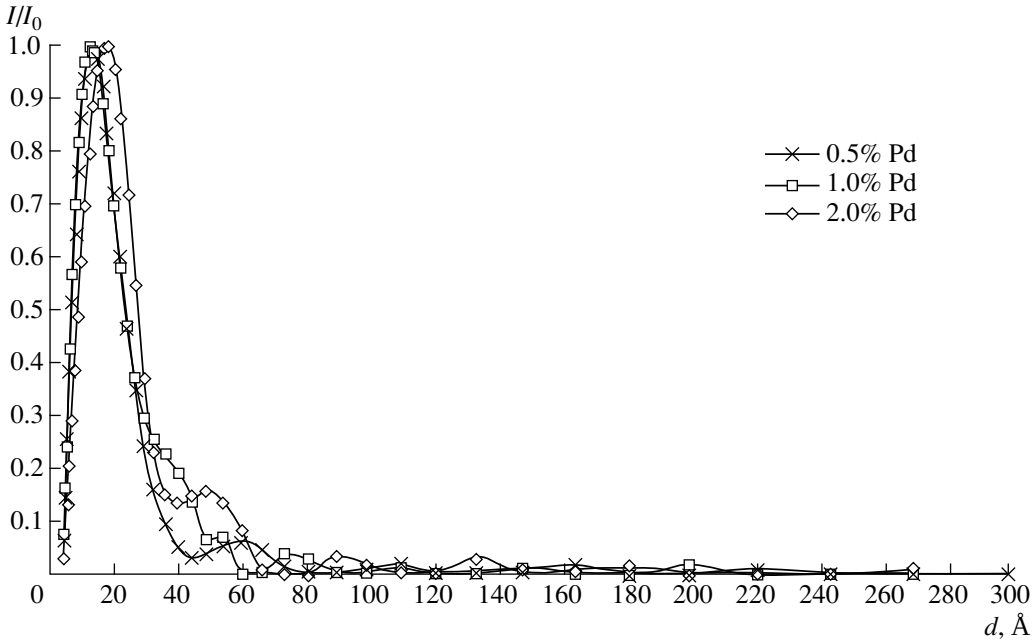



**Fig. 3.** Particle-size distribution of the metal in a Pd/C catalyst reduced with $NaBH_4$ according to small-angle X-ray scattering data.

It was reasonable to suggest that the catalyst surface was modified with boron ions and acid sites appeared at the stage of Pd reduction from the chloride by sodium borohydride. It is well known that boron halides catalyze olefin polymerization and the addition and isomerization reactions of hydrocarbons, and HCl is also a good activator of this process [5]. However, according to elemental analysis, the concentration of boron in the catalyst was as low as 0.005%. Figure 2 demonstrates that a sample of 5.0% Pd/C reduced with hydrogen at 500°C according to a standard procedure also catalyzes oligomerization, although its activity is not higher than the activity of $NaBH_4$-reduced samples with palladium concentrations that are lower by a factor of five or still lower. It is probable that boron interacts with HCl in the course of the reaction, resulting in surface modification with additional acid sites. However, it is unlikely that this contribution is substantial because the boron content is insignificant compared to that of HCl. It is more likely that reduction by $NaBH_4$ under mild conditions affects the dispersity of the active component in the catalyst.

Indeed, we found by small-angle scattering (Fig. 3) and electron microscopy (Fig. 4) that Pd nanoparticles with a size of 15–20 Å were formed in the course of catalyst preparation. The particle-size distribution was very narrow in samples with low Pd contents (0.5 and 1.0%), and particles with a size greater than 40 Å were absent (Fig. 3). Thus, the reduction with $NaBH_4$ is favorable for the formation of a catalyst with a quite uniform surface, which contains Pd nanoparticles.

Table 2 summarizes the initial rates of $CCl_4$ conversion (on fresh samples) depending on the Pd concentration in the catalyst at different temperatures. It can be seen that, with all of the catalysts examined, the rate of reaction increased by a factor of ~1.5 as the reaction temperature was increased from 150 to 230°C. The stability of catalysts reduced with sodium borohydride also increased with temperature (Fig. 5), and the selectivity remained almost unchanged. The catalyst activity per unit concentration of the active component increased with a decrease in the Pd concentration. The sample of 0.5% Pd/C exhibited the maximal initial activity at 230°C. A comparison of Figs. 1 and 5 demonstrates that the stability of the low-percentage catalyst in operation increased as the temperature increased from 150 to 230°C; however, the activity dramatically decreased after two hours of reaction. It is likely that a more finely dispersed state of the metal on the support surface is favorable for a more efficient use of the metal; however, these uniform active centers are also

**Table 2.** Rates of $CCl_4$ conversion on fresh catalysts with different Pd contents

| Catalyst | Reaction temperature, °C | $w_{CCl_4}$, mol (g of Pd)$^{-1}$ min$^{-1}$ |
|---|---|---|
| 0.5% Pd/C | 150 | 0.29 |
| ″ | 230 | 0.41 |
| 1.0% Pd/C | 150 | 0.14 |
| ″ | 230 | 0.21 |
| 2.0% Pd/C | 150 | 0.07 |
| ″ | 230 | 0.11 |

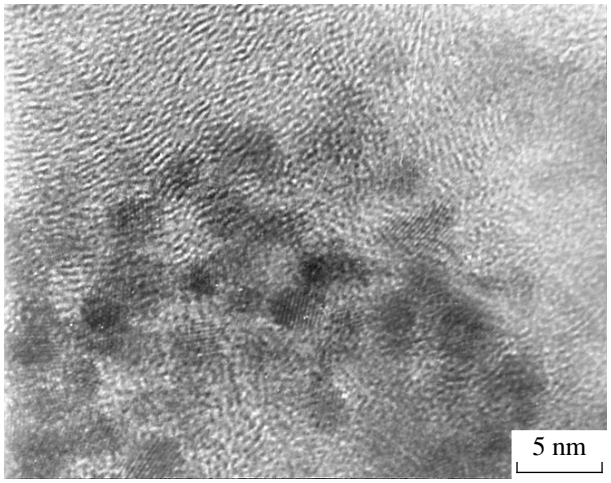
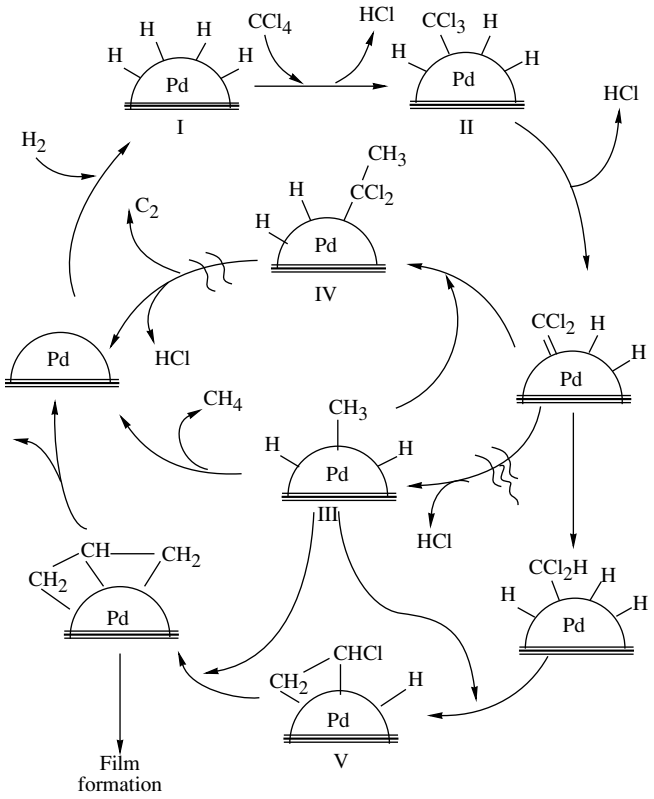



**Fig. 4.** Electron microscopic pattern of 5.0% Pd/C reduced with $NaBH_4$.

more sensitive to catalytic poisons. In contrast, the 5.0% Pd/C catalyst reduced with molecular hydrogen lost its stability with temperature.

In the second use of a catalyst without additional activation, the short-term restoration of its activity followed by a rapid drop was observed. It is likely that a polymer film is formed on the surface via carbon chain growth, and more severe conditions for catalyst recovering are required to remove this film.

The mechanism of formation of oligomer products in the hydrodechlorination of tetrachloromethane is poorly known. It was suggested that the reaction proceeds by the interaction between dissociatively adsorbed molecules with monoradicals [8]; otherwise, the reaction involves carbenes [5]. The presence of structural isomers in the products and the absence of chlorine derivatives of condensed hydrocarbons suggest that the methyl radical and surface carbene species participate in coupling occurs, for example, according to the following scheme:




At the first stage, the dissociative adsorption of hydrogen molecules on the catalyst surface (I) takes place. After carbon tetrachloride was supplied to the catalyst, $\dot{C}Cl_3$ radicals were formed on the surface (II). Then, this radical either undergoes complete dechlorination to form methane (III) or reacts with other products of partial dechlorination (carbenes, hydrocarbon radicals, etc.). In the latter case, carbene species can be

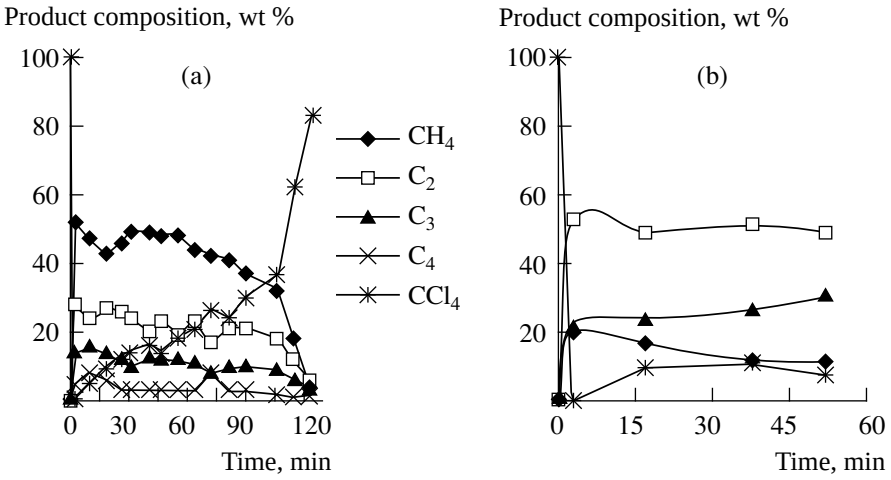



**Fig. 5.** Composition of the products of $CCl_4$ conversion in the presence of Pd/C catalysts with the (a) 0.5 and (b) 1.0% Pd content at 230°C.

inserted into the radical–surface bond (IV) to increase the length of the hydrocarbon chain. We detected desorbed $C_2$ and higher hydrocarbons in the gas phase. The interaction between radicals adsorbed on adjacent sites (V) can also take place, resulting in the formation of a hydrocarbon film on the surface.

Thus, the coupling of the hydrodechlorination reaction of tetrachloromethane with the oligomerization of hydrodechlorination products to hydrocarbons $C_2$–$C_4$ opens up new possibilities for the use of methane and its chlorine derivatives in organic synthesis and for the synthesis of valuable products on this basis.

## ACKNOWLEDGMENTS

We are grateful to Dr. N.S. Kulikov (Moscow State University) for his assistance in performing quadrupole mass spectrometric analysis and interpreting the data. This work was supported by the Russian Foundation for Basic Research (project no. 98-03-32159) and the Leading Scientific Schools of Russia Program (grant no. 96-15-97469).

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