TRANSFORMATION OF CARBON TETRACHLORIDE ON MEMBRANE CATALYSTS

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The conversion of CCl_4 by the action of H_2 in the presence of metal catalysts has been the subject of only a few studies. According to Besprozvannyi et al. [1, 2], $CHCl_3$ and C_2Cl_6 are formed upon hydrogenation of CCl_4 in the liquid phase on a palladium catalyst with pH_2 = 0.4-2 MPa at 373°K. Chloroform and methane were obtained on a platinum catalyst under similar conditions, while C_2Cl_6 was not formed [3]. The reaction of CCl_4 with H_2 on Ni/zeolite is also accompanied by the formation of oligomerization product [4].

Catalysis on membranes opens new possibilities for studying catalytic reactions and the nature of the reaction steps [5]. In the present work, we studied the conversion of CCl_4 under conditions for the separate introduction of the reagent and H_2 to the reaction surface of a palladium membrane catalyst.

EXPERIMENTAL

Three membrane catalysts were prepared for this study from palladium alloys with modifying platinum, gallium, and aluminum additives (Cat 1-3) as well as a membrane catalyst using a palladium alloy with 6 mass % ruthenium (Cat 4).

The experiments were carried out in a flow system on 0.1 mm thick foils according to our previous procedure [6]. The hydrogen content in the gas and the composition of the reaction products were determined by chromatographic and mass spectrometric methods.

RESULTS AND DISCUSSION

The membrane catalysts studied displayed different activity and selectivity. Methane, ethane, chloromethane, and chloroform were the major products on Cat 4.

The major reaction products on Cat 1-3 were C_2Cl_4, C_2Cl_6, C_4Cl_6 (hexachloro-1,3-butadiene) and $CHCl_3$. The yield of the products relative to the reaction temperature is shown in Fig. 1. The yield of C_2Cl_4 on Cat 2 and 3 increases to 55-85% at 700°K, while the yield on Cat 1 passes through a maximum of 50%. The yield of C_2Cl_6 increases with the temperature only on Cat 1 and it passes through a maximum of 21% on Cat 3. At 620°K, the C_2Cl_6 yield of Cat 3 is only 3-5%. The yield of C_4Cl_6 also passes through a maximum (12%).

In contrast to previous results [1-4], the quantitative formation of C_2Cl_4 and C_4Cl_6 is observed. The previously proposed mechanism involving the formation of free radicals does not account for the formation of C_2Cl_4 and C_4Cl_6 in our case. A radical chain reaction would give saturated compounds as products of hydrogenation and oligomerization.

Membrane catalysts contain dissolved hydrogen in atomic form, which arrives at the reaction surface as a result of diffusion through the palladium alloy. The following reaction presumably occurs in the first step:

$$CCl_4 + H_dZ \rightarrow HCl + CCl_3Z \quad (1)$$

where H_d is dissolved hydrogen and Z is the active site of the catalyst.

The formation of adsorbed CCl_2Z, $CClZ$, and CZ is possible upon subsequent removal of chlorine atoms. These compounds react with dissolved or adsorbed hydrogen atoms to give $CHCl_3$, CH_2Cl_2, CH_3Cl, and, finally, CH_4. The formation of C_2Cl_6, C_2Cl_4, and C_4Cl_6 may be attributed to fusion of the adsorbed compounds with each other.

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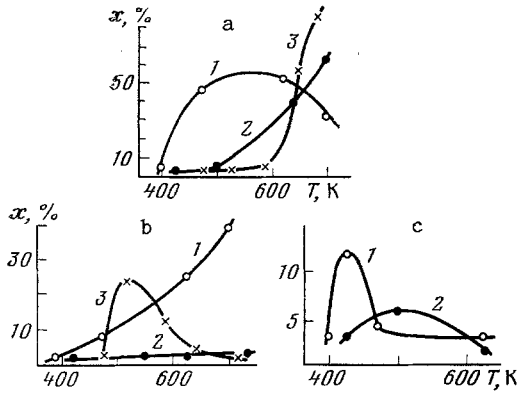

Fig. 1. Dependence of the yield (x) of tetrachloroethene (a), hexachloroethane (b) and hexachloro-1,3-butadiene (c) on temperature on Cat 1-3.

The following scheme leading to the products found appears most likely

$$CCl_4 + 2Z \rightarrow CCl_3Z + ClZ \quad (2)$$

$$CCl_3Z + H_d \rightarrow HCCl_3 + Z \quad (3)$$

$$CCl_3Z + CCl_3Z \rightarrow C_2Cl_6 + 2Z \quad (4)$$

$$CCl_3Z + Z \rightarrow CCl_2Z + ClZ\,. \quad (5)$$

Fusion of the CCl_3 and CCl_2 radicals adsorbed on the surface occurs on the surface of the membrane catalyst to form oligomeric structures

$$\begin{matrix} CCl_2 \\ | \\ Z \end{matrix} + \begin{matrix} CCl_2 \\ | \\ Z \end{matrix} \rightarrow \begin{matrix} Cl & Cl \\ | & | \\ ClC-CCl \\ | & | \\ Z & Z \end{matrix} \rightarrow C_2Cl_4 + 2Z \quad (6)$$

$$\begin{matrix} CCl_2CClCClCCl_2 \\ | \quad | \quad | \quad | \\ Z \quad Z \quad Z \quad Z \end{matrix} \rightarrow C_4Cl_6 + 4Z\,. \quad (7)$$

The addition of hydrogen to the adsorbed radicals leads to $CHCl_3$, CH_2Cl_2, CH_4, and C_2H_6. The metal chloride readily decomposes upon the action of dissolved hydrogen to form HCl as follows:

$$ClZ + H_d \rightarrow HCl + Z\,. \quad (8)$$

CONCLUSIONS

1. Tetrachloroethene and hexachloro-1,3-butadiene are formed upon the reaction of CCl_4 with H_2 on palladium membrane catalysts.

2. A mechanism was proposed for the conversion of CCl_4 upon its reaction with dissolved hydrogen.

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