OXIDES PREPARED IN SUPERCRITICAL WATER AS SUPPORTS FOR CATALYSTS OF CHLOROBENZENES HYDRODECHLORINATION.

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Disposal of chlorinated compounds is an important problem at present. Chlorinated hydrocarbons are hazardous pollutants contained in various wastes. For destruction of such compounds thermal and catalytic burning or dehydrodechlorination and hydrodechlorination are usually used. The latter is more promising because it allows recovering useful products.

Palladium supported on TiO_2 and ZrO_2 catalysts were investigated in hydrodechlorination of 1,4-dichlorobenzene. Two types of oxides were used: commercial and prepared in supercritical water. TiO_2 and ZrO_2 were prepared from isopropoxyacetate of titanium and $ZrO(NO_3)_2$, correspondingly (TiO_2*, ZrO_2*).

Reaction was carried-out in vapour phase in flow-type reactor in H_2 at atmospheric pressure and temperatures 150-210°C. Hydrodechlorination led to formation of chlorobenzene and benzene. Products of hydrogenation, such as cyclohexane, were not observed. In the presence of Pd on both TiO_2* and ZrO_2* benzene was the main product (Table 1).

Table 1. Selectivity of 1,4-dichlorobenzene hydrodechlorination in the presence of Pd supported catalysts (150°C, 100 mg_{cat}, 0.07 $mmol_{(1,4\text{-dichlorobenzene})}$/min)

Catalyst	Selectivity, wt.%	
	Benzene	Chlorobenzene
1% Pd/TiO_2	23.2	76.8
1% Pd/TiO_2*	69.7	30.3
1% Pd/ZrO_2	95.3	4.7
1% Pd/ZrO_2*	72.3	27.7

In the case of Pd supported on commercial oxides selectivity dependence changes. In the presence of Pd/TiO_2 chlorobenzene was the main product (76.8%). At the same time 95% selectivity of benzene formation was achieved in the presence of Pd/ZrO_2.

In this way, the nature of TiO_2 plays an important role in the reaction selectivity. If chlorobenzene was the main product in the presence of Pd/TiO_2, benzene predominated in the case of Pd/TiO_2*. Changing in the reaction selectivity, most likely, points what titania prepared in supercritical water is more stable to poisoning by HCl. Contrary to titania, the nature of ZrO_2 didn't strongly influence on the selectivity of 1,4-dichlorobenzene hydrodechlorination. Decrease in benzene formation in the case of ZrO_2* may be caused by the presence of Zr^{3+} species on the surface.