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Use of galvanic displacement in the synthesis of a Pd(Cu) hydrodechlorination catalyst

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The high prospects of galvanic displacement for the preparation of high-reactivity mixed catalysts with a small content of platinum metal have been shown for a Pd(Cu)/support system.

Due to the high cost and deficiency of platinum metals, decreasing the content of such metals in a catalyst remains one of the most important problems in catalysis. In order to solve this problem, it was suggested to use the galvanic displacement method in the creation of nanostructured catalysts (electrocatalysts) for fuel elements.[1–3] Displacement of a non-noble metal with a noble metal may result in the formation of both a 'core-shell' catalyst[1,2] and 3D nanoparticles of the noble (catalytically active) metal on an inert support.[1,3] In this work, the galvanic displacement method has been used to dope the Cu/support system with micro-quantities of palladium, since the latter is an active hydrodechlorination (HDC) catalyst.[4–6]

Nanoparticles of copper deposited on quartz or Aerosil particles 0.5–1.0 mm in size served as the precursor for the palladium-copper catalyst with a very small content of palladium. This copper catalyst was prepared by thermal decomposition of copper oxalate pre-deposited onto particles of the support. Decomposition was carried out under conditions of dynamic vacuum (~2 Pa) at 330 °C. Samples with 10 wt% copper were used.

X-ray diffraction analysis of the oxalate decomposition product under these conditions showed that small amounts of copper(I) oxide and copper(II) oxide were present in addition to metallic copper, and that the elementary sizes of crystallites in copper particles were 20–40 nm.

In order to dope micro-quantities of palladium by galvanic displacement, the copper catalyst was contacted for 1 h at 19±1 °C with a deaerated aqueous 2×10^{-3} M solution of $PdCl_2$. The volume of the $PdCl_2$ solution was varied depending on the amount of the copper catalyst to be treated, in such a way that the Pd:Cu ratio was 1:30, assuming the complete deposition of Pd^{2+}.

Pd(Cu)/quartz catalysts were studied on a JSM-6390LA JEOL scanning electron microscope allowing the elementary composition to be derived from characteristic X-ray spectra.

The reactivity of the resulting palladium catalyst was studied in the hydrodechlorination of chlorobenzene by the pulse microcatalytic method,[7] which allowed us to observe the substrate (chlorobenzene) conversion during a single pulse containing 1.1 μmol of chlorobenzene. Hydrogen simultaneously plays the roles of the carrier gas and the hydrogenating agent. The catalytic conversion products were determined on a Chrom-5 chromatograph with a Porapak-N column.

The original copper catalyst that served as the precursor for synthesising the palladium catalyst showed the complete absence of reactivity in HDC in the temperature range of 200–350 °C. Figure 1 demonstrates a plot of the reaction mixture composition as a function of temperature for the HDC of chlorobenzene on the Pd(Cu)/quartz catalyst. It is evident that a 100% conversion of chlorobenzene in a single pulse, where the substrate contacts the surface for less than 1 s, is observed at 350 °C; furthermore, the reaction selectivity with respect to benzene is 100% in the entire temperature range. The yield of benzene at 350 °C was 1.37 μmol mg^{-1} Pd (Figure 2, curve *1*). The amount of Pd in the catalyst portion did not exceed 0.8 mg.

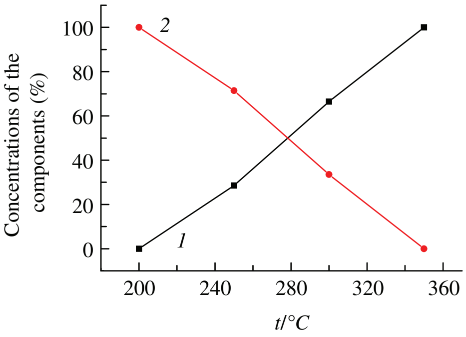

Figure 1 Plot of the reaction mixture composition *vs.* temperature in the hydrodechlorination of chlorobenzene on a Pd(Cu)/quartz catalyst: (*1*) benzene, (*2*) chlorobenzene.

An even higher reactivity of the catalyst was observed for the Pd(Cu) catalyst on Aerosil support (Figure 2, curve *2*), where the yield of benzene (*W*) at 350 °C amounted to 2.14 μmol mg^{-1} Pd, at a Pd content in the sample equal to 0.2 mg. The difference in the reactivities of the Pd(Cu)/quartz and Pd(Cu)/Aerosil catalysts is likely due to the high difference in the porosity of

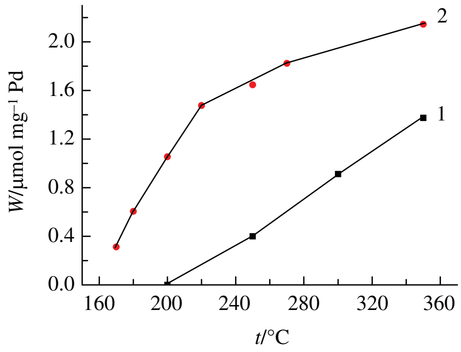

Figure 2 Effect of temperature on the yield of benzene (*W*): (*1*) Pd(Cu)/quartz, (*2*) Pd(Cu)/Aerosil.

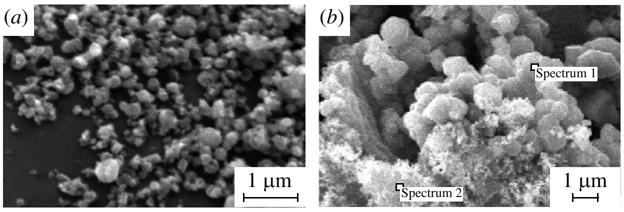

Figure 3 Electron micrographs: (*a*) original Cu/quartz catalyst; (*b*) Pd(Cu)/quartz ('spectrum 1' and 'spectrum 2' are areas where probing for elementary composition was performed).

the supports. The relatively small change in the yield of benzene with an increase in the temperature from ~230 °C can be explained by diffusion limitations.

Thus, galvanic displacement makes it possible to obtain a mixed Pd(Cu) catalyst that manifests high activity in HDC reactions at very small Pd concentrations. It was important to determine the structure of the catalysts obtained in order to reveal the nature of their activity. Figure 3(*a*) shows an electron micrograph of the original copper catalyst. One can see the presence of Cu and/or mixed Cu + Cu_2O, CuO particles, 100 to 400 nm in size. It can be concluded from Figure 3(*b*) that treatment of the copper catalyst with a $PdCl_2$ solution produces a surface containing both areas virtually free of Pd [the upper part of Figure 3(*b*)] and areas [the lower part of Figure 3(*b*)] coated with a 'mesh' of finely dispersed palladium (Pd nanoparticles contacting each other).

The non-uniform distribution of Pd is additionally supported by the results of microprobe elementary analysis. Palladium was not found in metal particles shown in the upper part of the mixed catalyst micrograph [Figure 3(*b*), 'spectrum 1' area], whereas the Pd:Cu atomic ratio in the particles shown in the lower part [Figure 3(*b*), 'spectrum 2' area] amounted to ~1:10. Hence, palladium is almost not deposited on some of the copper particles, whereas on other particles, obviously, replacement of copper atoms (Cu_s) on certain 'active' sites of the surface by palladium atoms initially occurs: $Cu_s + Pd^{2+} \rightarrow Cu^{2+} + Pd_s$. Further, nano-sized Pd particles are formed due to electrodeposition of palladium on palladium, *i.e.*, the structure of the mixed Pd(Cu) catalyst is mostly formed due to 'operation' of the galvanic couple:

$$Pd^{2+} + 2e \rightarrow Pd^0,$$

$$Cu^0 - 2e \rightarrow Cu^{2+}$$

under conditions where copper ionisation and discharge of palladium ions are spatially separated. This suggests that different areas of copper particles differ in activity. Apparently, this is mostly due to the presence of copper oxides (Cu_2O and CuO) in the original catalyst Cu/support (Figure 4), as noted above. The oxidized areas on the surface of copper particles are not involved in the exchange with Pd^{2+} ions ($E^0_{CuO/Cu_2O} = 0.67$ V).[8]

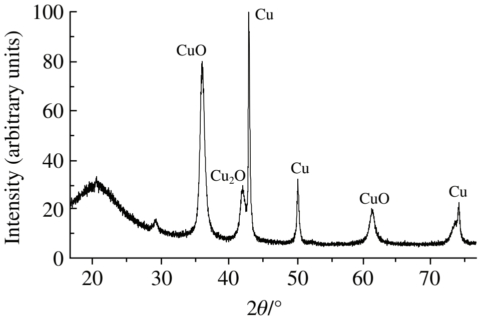

Figure 4 X-ray diffraction pattern of the original copper catalyst.

Apparently, the formation of copper oxides occurs both during the synthesis of the copper catalyst and during its treatment with an aqueous $PdCl_2$ solution.

Thus, it is believed that the high catalytic activity of the Pd(Cu)/support catalysts (with very low Pd content) synthesised in this study by galvanic displacement is mainly due to the high extent of Pd dispersion. From the practical point of view, an advantage of the method for synthesising a Pd(Cu) catalyst suggested here is that it is technologically simple to introduce the second component.

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