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TEM and XRD investigation of Pd on ultradispersed diamond, correlation with catalytic activity

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The relationship between the catalytic activity and Pd particle size in Pd/ultradispersed diamond catalysts is established in the hydrodechlorination of 1,3,5-trichlorobenzene under multiphase conditions.

Chlorinated hydrocarbons are hazardous pollutants contained in various waste oils and other organic liquids.[1] The detoxification of halogenated aromatic wastes by catalytic hydrodechlorination is an environmentally friendly and cost saving alternative to traditional disposal.[2] In a reductive environment, no polychlorinated dibenzodioxins are formed, and the products of hydrodechlorination can be reused.

Carbon materials are suitable supports for hydrodechlorination processes because they possess a high surface area, allow an easy recovery of supported metal by the combustion of the support and show chemical inertness.[3] A unique type of carbon support such as ultradispersed diamond (UDD) could be successfully used in catalysts design. UDD possesses high specific surface area with several types of carbonyl functional groups predominant on the surface,[4] a highly defective structure, extremely large number of uncompensated surface bonds,[5–7] nanosize (particle size of 5–20 nm),[8,9] superhardness and chemical stability.

The aim of this work was to study the activity and stability of Pd/UDD with 0.5–5 wt% Pd loading in the multiphase hydrodechlorination of 1,3,5-trichlorobenzene (1,3,5-TCB).[†]

Table 1 Multiphase hydrodechlorination of 1,3,5-TCB in the presence of Pd/UDD catalysts.

Catalyst	Amount of TCB[a]/mmol	Total amount of converted TCB/mmol	Specific catalytic activity, [*n*(1,3,5-TCB)/*n*(Pd)][b]
0.5% Pd/UDD	1.98	1.77	1510
0.5% Pd/UDD	0.66/0.66/0.66	1.75	1492
1% Pd/UDD	1.98	0.95	405
1% Pd/UDD	0.66/0.66/0.66	0.94	401
2% Pd/UDD	1.98	1.95	416
2% Pd/UDD	0.66/0.66/0.66	1.94	413
5% Pd/UDD	2.64	2.35	200
5% Pd/UDD	0.88/0.88/0.88	2.29	195

[a] If substrate was added by portions, its amount in each next portion is divided by a slash. [b] Molar ratio of the total amount of converted TCB per Pd in catalyst.

A number of applications of multiphase catalytic systems to the hydrodechlorination of chlorobenzenes with hydrogen on Pd/C were reported previously.[11,12] It was considered to use Pd supported on UDD under multiphase conditions for the first time. The activity of catalysts with different Pd loadings prepared in this work was tested in the multiphase hydrodechlorination of 1,3,5-trichlorobenzene as the model substrate. Reaction passes through the consecutive formation of dichlorobenzene, chlorobenzene and benzene; no signs of benzene hydrogenation were observed.

The results of catalytic tests are shown in Table 1. Since the reaction system is periodic in type, the substrate amount in the reaction medium could influence the reaction performance. Thus, different methods of substrate introduction were used. In all cases, the total amount of substrate was 1.98 mmol (2.64 mmol in the case of 5% Pd/UDD), but it was inserted into the reaction system either all at once or in portions of 0.66 mmol (or 0.88 mmol in the case of 5% Pd/UDD).

As can be seen in Table 1, the amount of converted TCB does not depend on the method of substrate introduction into the reaction system. Thus, catalysts were compared by the amount of 1,3,5-TCB converted until complete catalyst deactivation. Since the Pd loading was different in each catalyst, the total amount of converted TCB was also different. It was surprising that the quantity of converted TCB had extreme dependence on Pd loading. The lowest amount of TCB was transformed in the presence of 1% Pd/UDD. To compare catalysts with different Pd loadings, specific catalytic activity was calculated as the amount (in moles) of transformed TCB per mole of Pd (Table 1).

[†] Commercial reagents and solvents were used without further purification. The catalysts were prepared according to a standard wet impregnation procedure. An acidic solution of $Pd(NO_3)_2$ (Reachem, $c_{Pd} = 464.6$ g dm^{-3}) in distilled water with pH 3 was added within 1 h to the support (0.5 g) at room temperature under stirring. Solvent was slowly evaporated at 80 °C. The impregnated catalyst was consequently dried at room temperature for 12 h in air, heated to 150 °C, calcined at 150 °C for 2 h to dispose nitrates, and then cooled to room temperature. Catalysts were reduced at 280 °C for 2 h by hydrogen (flow rate of 12 ml min^{-1}). Catalysts with 0.5; 1; 2 and 5 wt% Pd were prepared. The specific surface areas (BET) of all catalysts were about 260 m^2 g^{-1}.

The hydrodechlorination was performed under multiphase conditions as described elsewhere.[10] Reaction conditions were the following: 1,3,5-TCB (total amount of 1.98 or 2.64 mmol), 50 °C reaction temperature, 0.26 mmol of Aliquat 336 (tricaprylmethylammonium chloride, Aldrich), 5 mmol of KOH (5% aqueous solution), 25 mg of the catalyst, hydrogen flow of 5 ml min^{-1} and nonane (0.12 mmol) as the internal standard. Samples were taken from organic phase during the reaction at fixed intervals and analyzed by GC (Agilent 6890N, FID, column DB-Wax, 30 m).

X-ray diffraction patterns were recorded using Ni-filtered CuKα radiation (30 mA, 40 kV) in air at room temperature, with a step of 0.05° in a 2θ scattering angle. The intensities were collected in several runs at the preset time mode of 10 s per angular step. A Philips X'Pert system was used.

High-resolution transmission electron microscopy investigation was carried out with a JEOL JEM-3010 microscope operated at 300 kV. Bright field and selected area electron diffraction (SAED) revealed the morphology and the crystalline phase of the samples.

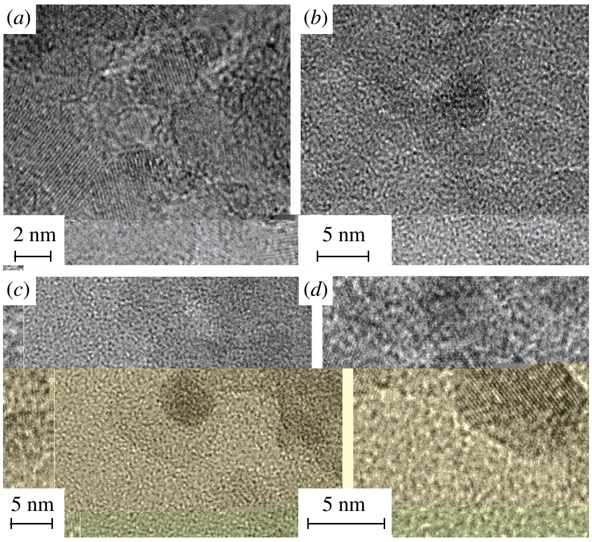

Figure 1 HR-TEM for (*a*) UDD, (*b*) 1% Pd/UDD, (*c*) 2% Pd/UDD and (*d*) 5% Pd/UDD.

For each catalyst, the calculated value of specific catalytic activity does not depend on the method of 1,3,5-TCB loading, at once or by portions. Specific catalytic activity depends on the Pd content of the catalyst. The highest of specific activity value was in 0.5% Pd/UDD (about 1500), 1% Pd/UDD and 2% Pd/UDD exhibits an equal specific activity (about 400 mol of converted 1,3,5-TCB per mole of Pd). Specific catalytic activity was the lowest for 5%/UDD. The same molar ratios of reacted TCB per mole of Pd in 1% and 2% Pd/UDD points out similar characteristics of these catalysts.

The Pd particle size was estimated from a number of TEM images and XRD data. In Figure 1, TEM micrographs for UDD and catalysts with 1, 2 and 5% Pd content are presented. It is clearly seen in Figure 1(*a*) that a particle of UDD consists of the cores with diamond structure, which are combined by amorphous carbon. Diamond particles were identified by interatomic spacing (2.06 Å for cubic diamond).[13]

According to TEM data, the size of diamond cores is about 4–10 nm, which is in agreement with literature data.[6] On the TEM micrograph of 5% Pd/UDD, a well crystalline Pd particle is seen. Metal particle is situated on the edge of diamond particle. Palladium particle size is about 8 nm. For 1 and 2% Pd/UDD catalysts, metal particles are close in size of about 5 nm [Figure 1(*b*),(*c*)]. For 0.5% Pd/UDD size of palladium particles is less than 2 nm (TEM is not shown). Thus, the structure of ultradispersed diamond support favors high metal dispersion.

Figure 2 shows the XRD patterns of UDD and Pd/UDD with different Pd loadings. For all samples, an intense reflection at $2\theta = 44°$ was observed. This peak is typical of the cubic diamond lattice.[6] The presence of this peak for all Pd/UDD catalysts confirms that the diamond structure is stable under the conditions of Pd impregnation and reduction.

Another peak at 2θ of about 40° was also observed in all samples. This peak can be attributed to Pd metal.[14] The peak widening points out very small Pd particle size. Only in XRD pattern for 5% Pd/UDD the peak at $2\theta = 40°$ has relatively high intensity. This fact is in agreement with TEM data indicating that Pd particle size is the highest (about 8–10 nm) in 5% Pd/UDD; *i.e.*, this catalyst has the lowest dispersion among catalysts under study.

The intensity of this peak ($2\theta = 40°$) decreases with decreasing Pd loading and becomes hardly noticeable for 0.5% Pd/UDD.

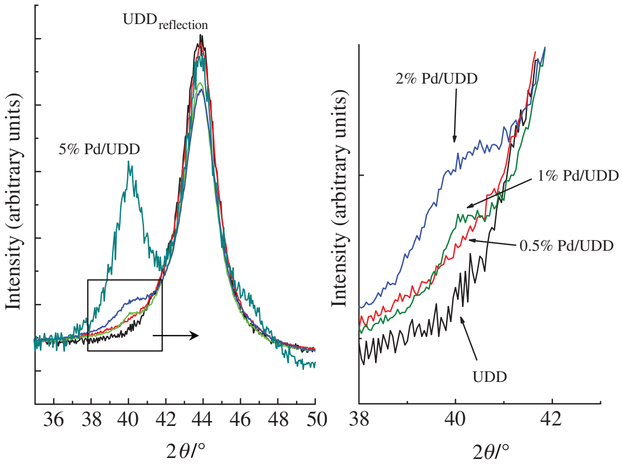

Figure 2 XRD of UDD and Pd/UDD samples with 0.5–5% Pd loading (right figure enlarges part from the Pd reflection region).

Pd crystallite size for catalysts was estimated from XRD and TEM data: for the 0.5%Pd/UDD system it is the smallest one (1.5–2 nm); mean Pd particle size for 1% and 2% Pd/UDD is 5–6 nm; 5% Pd/UDD was found to have the lowest dispersion (particle size is about 8–10 nm).

As mentioned above, the specific catalytic activity of Pd/UDD did not change in a row with Pd content in catalyst (see Table 1): it has the highest value for 0.5% Pd/UDD, lowest for 5% Pd/UDD, and it is about equal for 1 and 2% Pd/UDD. Possible reason of such a behaviour could be found by comparing catalytic results with TEM and XRD data. It is well known that catalytic activity in most cases strongly depends on the active surface of supported metal that is closely related with metal dispersion (particle size).

It is clear that the mean size of Pd particles affects the catalyst performance. The catalytic activity is influenced by many parameters, but working under the same conditions excludes influence of diffusion, support nature, temperature and other factors.

The dependence of the specific catalytic activity on metal particle size reflects a structure-sensitive character of the reaction. According to Boudart's classification,[15] higher catalytic activity of small metal particles is typical when they are strongly electronic influenced by support. Such close electronic influence is usual for oxide supported catalysts, but it is not typical of carbon supports.

The presence of both metallic and partially oxidized Pd in active site provides for effective hydrodechlorination catalyst.[16] Indeed, the facts that UDD has very defective structure and supported metal is small in size allow an optimal electronic structure of supported palladium to be achieved.

The relationship between the catalytic activity and Pd particle size in Pd/UDD catalysts is established in this work. The hydrodechlorination of 1,3,5-TCB under multiphase conditions was found to be structure-sensitive, and specific catalytic activity is the highest for small Pd particles. Use of such a unique carbon support as UDD allows us to stabilize nanosized Pd particles and most likely influence the electronic state of metal. From this point of view, ultradispersed diamond is promising support for the preparation of Pd-containing catalysts, effective in the dechlorination of polychlorinated aromatics.

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