

NEW ENVIRONMENTALLY SAFE AND EFFICIENT WAY FOR DESTRUCTION OF TOXIC CHEMICALS

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Abstract. Reductive hydrodechlorination was used as a base reaction for the destruction of toxic chlorinated compounds including chlorobenzenes and polychlorinated biphenyls. Very effective catalytic systems for this process have been developed. They include new Pd and Ni containing catalysts supported on carbon and oxide supports prepared by unusual method of laser electrodispersion. Metal content in these catalysts is extremely low, but activity of each metal atom is extremely high due to inter-cluster interaction in comparison with the catalysts prepared by impregnation or deposition-precipitation. The effect of inter-cluster interaction is discussed. Another prospective system includes metals supported on ultradispersed diamond. Scheme of the process of multi-phase hydrodechlorination of high-boiling wastes is presented. New approaches could be valuable for the development of prospective catalytic systems for different catalytic processes.

Keywords: chlorobenzenes, polychlorinated biphenyls, PCB, hydrodechlorination, Pd catalysts, Ni catalysts, laser electrodispersion.

1. Introduction

The problem of utilization of chlorinated compounds is of great concern from ecological point of view. Nowadays, the production of many chlorinated organic compounds is limited, but due to their unique properties they are still widely used in the industry as plastics, insecticides, solvents for resins and adhesives, disinfectors for leather, etc. The production of chlorinated chemicals is very dirty. A rich variety of persistent toxic wastes are formed during their production and utilization. Risks

from the use polychlorinated substances arise from their wide spreading and high stability to biodegradation, their bioaccumulation in food chains and high toxicity resulting in cancer, decrease of immunity, gene mutation, disruption of reproductive function, etc. Every year, two to three thousand tons of such wastes are produced only in Russia, and more than hundred thousand tons of early accumulated polychlorinated wastes have to be processed.

There are two main ways for the destruction of chlorinated wastes based on oxidation or reduction. At present, mainly the oxidative methods are used in industry. Weak points of oxidative methods are high technological expenditures, control difficulties, environmental risks due to formation of highly toxic dioxins during oxidation under uncontrolled conditions.

The second way, based on catalytic reduction is environmentally more safe. The formation of toxic by-products such as dioxins is totally excluded. Reductive methods are energy saving because hydrodechlorination proceeds under mild conditions. However, catalysts for this process include noble metals, so they are expensive and often unstable versus chlorination under reaction conditions [1–4].

The aim of this work was to develop new catalysts for reductive dechlorination, which are stable under the reaction conditions, and to improve the economics of the catalysts by the reduction of noble metal content and substitution of noble metals by not-noble ones. New catalysts were prepared by laser electrodispersion (LED) technique and compared with the catalysts prepared by conventional methods, for example, impregnation of carbon support by metal salt.

Recently, new catalysts supported on ultra dispersed diamond (UDD) have been developed. Crystallinity of the support, the absence of small pores, and possibly the presence of various defects on the surface make it possible to stabilize small metal particles on this support. In comparison with commercially available 5% Pd/Fluka 0.5–5% Pd/UDD demonstrated much better catalytic activities in hydrodechlorination (HDC) of 1,3,5-trichlorobenzene and hexachlorobenzene under multiphase conditions [5]. The HDC activity of UDD supported catalysts improves as the particle size decreases. This effect is the most evident in the case of chlorobenzene (CB) transformations.

2. Experimental

2.1. Catalysts preparation

LED technique has been described in [6]. This method is based on a cascade fission of liquid metal drops in a laser torch plasma. The process stops sharply when all drops become uniformly small. These small charged drops are further deposited on a support under the electric field. Different types of flat and granulated, dielectric and conducting materials can be used as supports. Special modification of LED technique that includes oscillating plate was used to prepare Pd and Ni

catalyst on granulated carbon support Sibunit [7, 8] (0.6–3 mm in diameter). Si (chemically polished silicon (100) wafers covered by thin natural oxide) and SiO₂/Si (thermally oxidized silicon wafers covered by thick layer of thermal oxide) supports were also used for Pd loading. The scheme of catalyst preparation is shown in Fig. 2.1.1. This method results in the formation of amorphous spherical metal nanoparticles of well-defined size on the support surface. The amounts of deposited metals and particle surface density were controlled by deposition time.

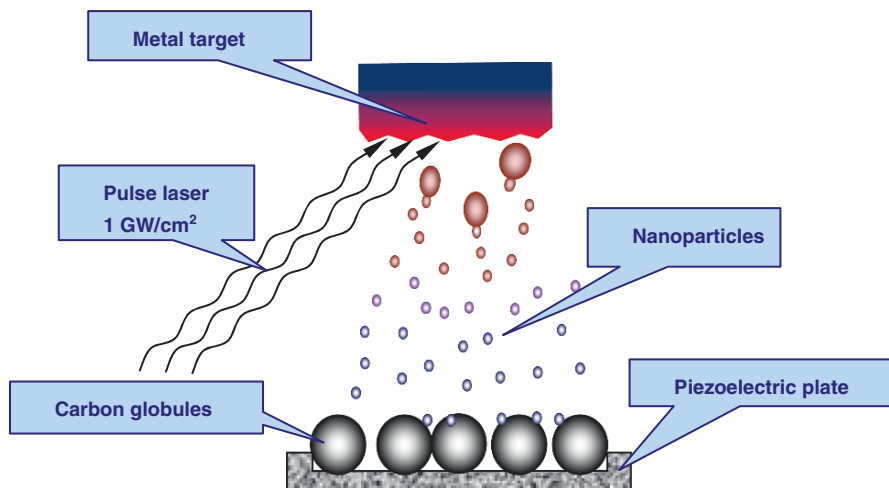


Fig. 2.1.1. Scheme for laser electrodispersion method for the preparation of Pd and Ni catalysts on granulated carbon support Sibunit.

Control catalysts Pd/UDD and Ni/UDD were prepared by wet impregnation of UDD powder using nitrates of corresponding metal solutions followed by calcination and reduction. Also commercially available 5% Pd/C by Fluka was used for comparison purposes. The metal content in catalysts varied over a wide range between 10⁻⁴ and 5% mass.

2.2. Catalytic experiments

Chlorobenzene HDC was performed by different methods. First, a fixed-bed flow reactor with 0,05 g of the catalyst at 150–250°C at atmospheric pressure was used. Flow rates were 3 h⁻¹ (chlorobenzene) and 3.5 h⁻¹ (hydrogen).

Multi-phase system for hydrodechlorination includes hydrocarbon solvent (e.g., heptane or *i*-octane), aqueous solution of KOH (0.89 M/l), H₂ and solid catalyst, and optionally some surfactant, which serves as phase-transfer catalyst (e.g., ammonium salts having long chain hydrocarbon moieties – so called quats).

Another system on the base of trickle-bed reactor was used for catalytic transformation of tetrachlorobiphenyl. The solution of NaOH (0.29 M/l) in methanol - water mixture (9:1) was used as reaction media. Tetrachlorobiphenyl's initial concentration was 0.063 M/l, reaction temperature 86°C, and reaction pressure 10 bar, reaction mixture flow rate 3.2 h⁻¹, H₂ flow rate 10.7 h⁻¹, catalyst loading 40 g.

The products were analyzed by gas chromatography (DBWAX column, 30 m, FID, carrier gas N₂, 35–200°C). Quantitative composition of reaction mixture was determined using internal standard technique. For this reason, calibration was made for each component by plotting the ratios of component/standard GC peak areas versus the ratios of known concentrations. Catalytic activities were calculated as moles of CB converted per mole of metal per hour. To estimate the activity of catalysts in PCB hydrodechlorination the conversion of PCB into less chlorinated products was compared as the function on time-on-stream.

2.3. Catalysts characterization

The amount of deposited metals was estimated by means of atom-absorption spectrometry using atom-absorption spectrometer Perkin Elmer 3030Z. Transmission electron spectroscopy (TEM) was used to investigate structure, particle size distribution, and arrangement in the deposited films. TEM images were obtained using Philips EM-42 (resolution of ~0.34 nm) and JEM 2100F (ultrahigh resolution of ~0.1 nm) transmission electron microscopes. Samples for TEM examinations were prepared by deposition of Pd nanoparticles onto standard grids using the laser electrodeposition method. The electron beam current was minimized to avoid the transformation (annealing) of the structure during imaging. The results obtained by both methods are in good agreement.

3. Results and discussion

Recently, it was found that catalytic activity of nano-structured catalysts depends not only on the particle size but also on an average intercluster distance or surface particle density [9, 10]. New approaches to catalyst design based on this phenomenon and associated with effect of intercluster interactions give us the instrument for multiple augmentation of catalytic activity of nano-structured catalysts [11–13]. Based on this effect the amount of noble metal in catalyst can be reduced in two to three orders in comparison with known supported catalysts.

Effects associated with electron exchange between nearby clusters are most pronounced with aggregates or ensembles of small clusters deposited on dielectric support and isolated from each other or with self-assembled catalysts [9, 10]. As a result of thermally activated electron tunneling between closely located clusters

within a neutral ensemble nearly half of all clusters become charging at temperature above 400 K and dielectric permittivity $\epsilon \geq 10$. The calculated lifetime of charge distribution is at least two orders longer compared to the typical time of catalytic reaction. The participation of these charged particles in the electron exchange with reagent may essentially reduce the activation energy of chloro-hydrocarbon reactions, and this may be a reason for the high catalytic activity of self-assembled catalysts. In another case, when catalyst consists of separated clusters, only electron exchange between supported cluster and conducting support is possible. An average cluster charge resulting from the contact potential difference between supported particle and support should strongly depend on support type and metal loading [14]. There are no such effects in highly loaded metal films. By this means, when catalytic reactions are sensitive to the charge state of a catalyst, one can expect that the catalytic activity will depend on the surface particle density or intercluster distance.

Some theoretical and experimental results providing support for this idea have been viewed previously [9–14]. They were obtained for monodispersed nanostructured catalysts prepared by the unconventional method of laser electrodispersion [6]. Coulomb interaction of charged particles on the support under certain deposition time or surface particle density leads to the formation of self-assembling films which are conductive due to electron tunneling. TEM images of typical supported metal catalysts prepared by this method are shown in Fig. 3.1. All metal clusters are uniform in shape and size (about 2.0 nm for Pd and 2.5 nm for Ni) at the very narrow size dispersion less than 10%. The nanoparticles deposited on dielectric SiO_2/Si are uniformly distributed on a support surface as separated granules or small aggregates of granules depending on deposition time. Absolutely different picture was observed when metal clusters were deposited on conducting support Au/C. In this case nickel clusters form very long chains on support steps.

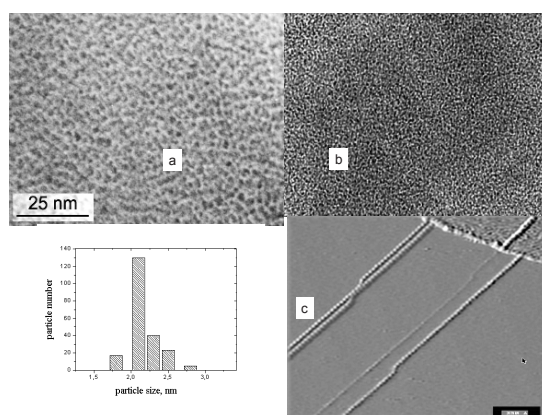


Fig. 3.1. TEM images for Pd/SiO₂/Si (a), Ni/SiO₂/Si (b) and Ni/Au/C (c) catalysts prepared by means of LED; particle size distribution for Pd/SiO₂/Si.

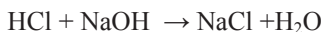
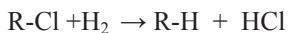
Metal clusters prepared by this means are amorphous, because during deposition they are cooled down extremely quickly, and they are unusually stable to oxidation. These specific features provided a possibility to study the role of inter-cluster interactions in catalysis and to produce unusually effective catalysts based on these effects.

Experimental evidences of the impact of cluster interaction on the charge state and catalytic properties of small supported clusters were obtained taking model reactions of chlorinated hydrocarbons and hydrogenation as examples. The following unusual experimental facts observed for a number of different reactions [5, 6, 9–12] provided support for the idea of the role of charged particles in catalysis:

- The unusually high catalytic activity of self-assembled catalysts based on Cu, Ni and Pd nanoparticles with size 5, 2.5 and 2 nm, respectively. For all reactions studied the activity of novel catalysts produced by means of laser electrodispersion technique with extremely low metal content was two to three orders of magnitude higher than that of known supported catalysts prepared by traditional methods.
- The sensitivity of self-assembled catalysts to solvent polarity in contrast to catalyst which includes separated clusters or highly loaded metal films.
- The correlation between catalytic properties and catalyst conductivity. For all reactions the catalytic activity increased when catalyst became conducting due to electron tunneling.
- Strong dependencies of catalytic activity of nano-structured catalysts on the surface particle density and the conductivity type of a support.

When two types of silicon with dielectric (SiO_2/Si) or semiconductor (Si) properties were used as supports for the deposition of absolutely similar clusters of Cu or Ni the strong extreme dependence of catalytic activity on the surface particle density was observed only for catalysts prepared on dielectric support [9, 10]. The highest activity in all cases corresponded to the catalysts consisting of ensembles of clusters. For the semiconductor support the catalytic activity only slightly increased with the decrease of metal loading. In this case, inter-cluster interactions become less important as a consequence of electron exchange between supported cluster and support [14].

These results were applied to design novel, highly effective and stable catalysts for the HDC of chlorinated organic compounds:



This process serves as a basis for the environmentally save destruction of polychlorinated wastes. It proceeds in vapor or liquid phase without formation of toxic by-products. In the latter case, the presence of alkali is necessary. Carbon supports are the most appropriate for the catalyst preparation due to their chemical stability. In the vapor-phase HDC catalysts on oxide supports that are stable to HCl can be used, too.

Figure 3.2 demonstrates that the catalytic activity of new Pd and Ni catalysts with extremely low metal content, prepared by means of laser electrodispersion technique in vapor phase, chlorobenzene HDC is many times higher than that of usual supported catalysts. Different types of surface particle density dependencies of the catalytic activity were also observed in this process for catalyst prepared on dielectric and conducting supports (Fig. 3.3). The highest catalytic activity corresponds to the films consisting of ensembles of clusters. Results of comparison studies of the catalytic activity of catalysts prepared by different methods are summarized in Table 3.1. One can see from these data that catalysts produced by usual methods also become more active with the decrease of metal content in the catalyst. Therefore, it can be proposed that effect associated with inter-cluster interactions is not a specific feature of catalysts prepared by means of laser electrodispersion. But it should be pointed out that in the case of usual supported catalysts the particle size as a rule increases with the growth of metal loading, and this fact may also cause the catalytic activity to change. It is also clearly seen that Pd catalysts are much more active than Ni ones, but Ni catalysts prepared by LED technique are better than Pd catalysts, prepared both by impregnation and deposition-precipitation, as well as commercially available catalyst by Fluka.

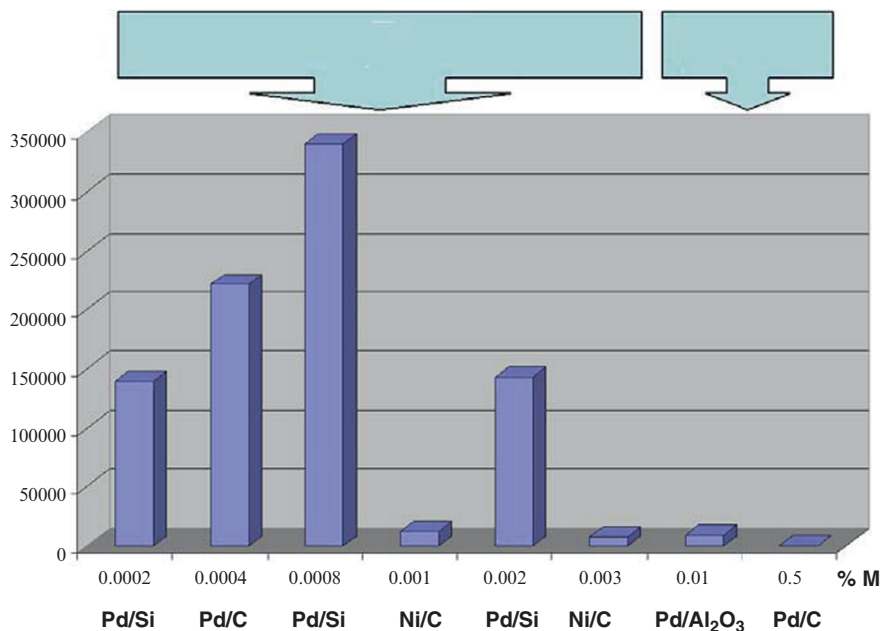


Fig. 3.2. A comparison of the catalytic activity of Pd and Ni catalysts prepared by LED and traditional methods in vapor phase hydrodechlorination of chlorobenzene at 150°C.

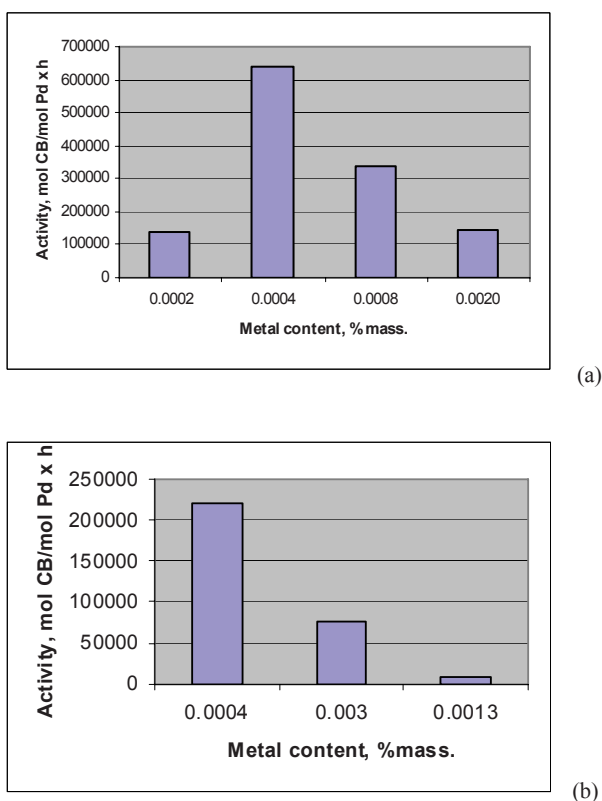


Fig. 3.3. Catalytic activity dependencies on Pd loading for catalysts on different supports in vapor phase chlorobenzene (CB) hydrodechlorination at 150°C: (a) Pd/SiO₂/Si; (b) Pd/C.

Liquid phase process is only suited for the HDC of real industrial wastes including high-boiling and solid compounds. As one can see from Fig. 3.4, novel Pd catalysts prepared by means of laser electrodispersion technique are also extremely active in multi-phase transformation of *o*-dichlorobenzene. These catalysts were also active in HDC of real technological wastes containing C₂Cl₆, C₄Cl₆, C₆Cl₆ and polychlorinated biphenyl which are the main components of electro-technical liquids.

Another important advantage of new catalysts is their unusual stability against chlorination. They keep the high activity for at least 7 h time-on-stream (Table 3.1). In accordance with X-ray photoelectron spectroscopy (XPS) data catalysts include Pd only in the metallic state even after long-term HDC [13]. The unusual fact of such high stability to chlorination is very important for this process.

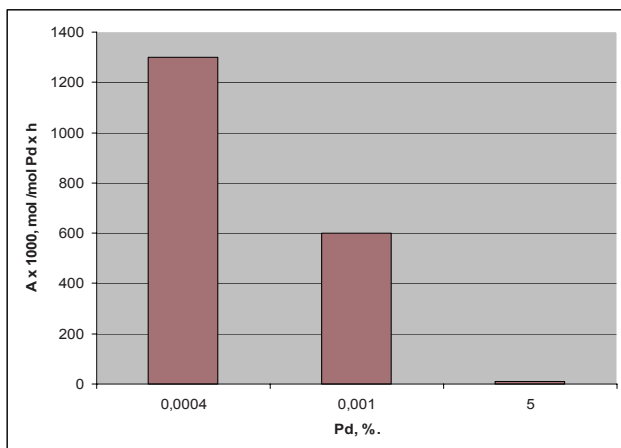


Fig. 3.4. A comparison of the catalytic activity of Pd catalysts prepared by LED with metal content $\leq 0.001\%$ and known 5% Pd/C (Nippon) in multi-phase hydrodechlorination of o-dichlorobenzene.

Table 3.1. Comparison of the catalysts in chlorobenzene hydrodechlorination.

Catalyst	Production method	Pd (% mass.)	T (°C)	Time-on-stream ^a (min)	CB conversion (%)	Activity ^a (mol/mol Pd h)
Pd/C	LED, granule size 2.5–3.0 mm	0.0004	150	120	33	230,000
			200	410	86	610,000
Pd/C	LED, granule size 1.6–2.0 mm	0.0004	200	240	53	620,000
				360	84	
				440	88	
Pd/C	LED, granule size 0.63–1.25 mm	0.001	150	120	35	97,000
				200	290	65
			200	350	85	
				420	89	
Pd/SiO ₂ /Si	LED	0.0002	200	228	29	410,000
				370	92	650,000
		0.0004	150	60	96	680,000
				200	288	92
		0.0008	150	60	100	350,000
				420	100	140,000
Pd/UDD	Impregnation	0.5	200	180	100	554
Pd/C	Fluka	5	100	60	90	50
			150	60	100	55
			200	60	100	55
Pd/Al ₂ O ₃	Deposition – precipitation	0.01	200	70	60	15,000
Ni/C	LED	0.001	200	220	37	42,000
				140	14	9,500
Ni/Al ₂ O ₃	Impregnation	0.03	200	100	28	1,460
Ni/UDD	Impregnation	5.0	200	90	22	18

^a If the conversion is constant during some period, the duration of such period is given in the column; if the conversion changes, there are some values of conversion at the moments of time.

In flow type HDC of tetrachlorobiphenyl under increased pressure (Fig. 3.5) high stability of the Pd/C in combination with high conversion was observed. One of the reasons of such a good performance was the use of reaction medium that includes methanol. There are some evidences that alcohols can participate in HDC

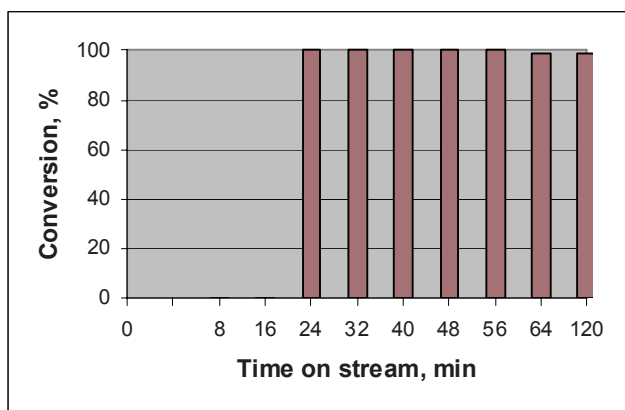


Fig. 3.5. Tetrachlorobiphenyl transformation on Pd/C in water-methanol mixture in flow-type system.

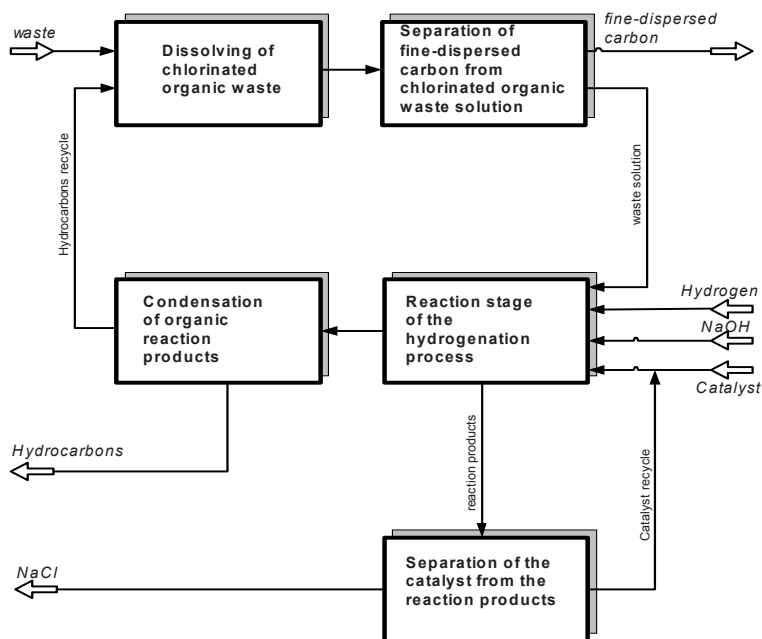


Fig. 3.6. Scheme of the process of multi-phase hydrodechlorination of high-boiling wastes.

process as hydrogen donors [15]. Also very efficient was Pd/UDD catalysts in hydrodechlorination of hexachlorobenzene in multi-phase system [5]. Full conversion of hexachlorobenzene to benzene was performed just within 60 min at 50°C.

Advantages of new catalysts associated with low metal content and high stability were used to work out the scheme of real technological process of multi-phase hydrodechlorination of high-boiling polychlorinated shown in Fig. 3.6. This scheme includes the following stages: dissolving of chlorinated organic compounds, removal of fine dispersed carbon from solution, catalytic reaction, condensation of hydrocarbons produced in the process, catalyst separation and recycling.

4. Conclusions

The use of effect of inter-cluster interactions resulting in cluster charging let design highly efficient catalysts based on ensembles of clusters for ecologically safe destruction of polychlorinated compounds. Extremely low metal content in these catalysts reduces significantly the cost of catalysts based on Pd. Even Ni catalysts prepared by this means surpass known supported Pd catalyst in activity. Economic and environmentally effective process for polychlorinated wastes destruction is developed based on this approach.

It can be expected that such effects associated with electron exchange between nearby clusters on dielectric support or between supported cluster and conducting support should be important in all cases when catalysts contain small clusters with an optimum particle sizes between 1 and 5 nm at low metal loading or low surface particle density. The use of such effects may be of advantage to reduce metal content in different types of catalysts for other chemical processes.

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