

Hydrodechlorination of polychlorinated benzenes in the presence of a bimetallic catalyst in combination with a phase-transfer catalyst

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Bimetallic supported catalysts (Pd–Ni/C and Ni–Cu/C) in combination with a phase-transfer catalyst were found efficient and selective in the liquid-phase hydrodechlorination of polychlorinated benzenes under mild conditions.

Polychlorinated aromatic compounds are carcinogenic and mutagenic chemicals, which are environmentally stable and can undergo bioaccumulation in fatty tissues.¹ Presently, catalytic hydrodechlorination is a viable alternative for halogenated waste handling because hazardous materials are transformed into recyclable products in a closed system with no toxic emissions.²

Hydrodechlorination is known to be promoted by Group VIII noble metals. Polychlorinated aromatic compounds can be successfully dechlorinated using nickel catalysts under severe reaction conditions (high temperature and high hydrogen pressure). Palladium and ruthenium catalysts make it possible to perform the dechlorination of polychlorinated aromatic compounds under mild conditions; however, they are expensive and hence cannot be used on industrial scale.³

It was found^{4,5} that the complete dechlorination of 1,2,4,5-tetrachlorobenzene in the presence of a Pd/C catalyst and Aliquat 336 (tricaprylmethylammonium chloride) as a phase-transfer agent with hydrogen can be performed at atmospheric pressure. However, only isomeric *o*-, *m*- and *p*-dichlorobenzenes (and dibromobenzenes) can be rapidly reduced with hydrogen under mild conditions using Raney nickel.

In this work, we found that efficient and inexpensive catalytic systems for the hydrodechlorination of hexachlorobenzene under mild conditions can be designed using a bimetallic (Ni–Pd/C or Cu–Ni/C) catalyst in combination with a phase-transfer agent.

Mono- and bimetallic catalysts were prepared by the impregnation of a support with aqueous solutions of transition metal chlorides followed by reduction with NaBH₄. The catalysts of choice are transition metals (Pd, Ni and bimetallic Pd–Ni and Ni–Cu catalysts) supported on a Sibunit carbon (C) support.⁶ Catalysts with the total metal (Ni, Pd, Ni + Pd or Ni + Cu) content 1.7×10^{-4} mol per gram of the catalyst were used. The catalysts were designated as Pd₂Ni₉₈/C and Ni₉₂Cu₈/C, where the subscripts indicate the mole ratios between the corresponding metals in the catalysts.

The hydrodechlorination reactions of chlorobenzene and hexachlorobenzene were studied in a two-phase system (an aqueous 50% KOH solution and an organic isopropanol–toluene phase) at 50 °C. The hydrodechlorination was performed in a thermostatically controlled glass reactor with a magnetic stirrer (700 rpm) under a constant (atmospheric) pressure of hydrogen. Hydrogen was supplied at a flow rate of about 4 cm³ min^{−1}. In the course

Table 1 Degree of dechlorination (*X*) of hexachlorobenzene in the presence of mono- and bimetallic catalysts; Me₄N⁺Cl[−] (phase-transfer catalyst), *T* = 50 °C, 50% KOH, *P*_{H₂} = 1 atm, isopropanol–toluene (4:7) solvent (15 ml).

Catalyst (Cat)	S(C–Cl):Cat ratio ^a	Time/h	<i>X</i> (%)
Pd/C ^b	50:1	0.5	98
Pd/C ^c	50:1	0.5	18
Pd ₂ Ni ₉₈ /C	10:1	1.5	98
Pd/C + Ni/C	10:1	1.5	54
Ni ₉₂ Cu ₈ /C	10:1	5.5	50
Ni/C	10:1	6	43

^aThe substrate (S):metal (Cat) ratio was determined as the substrate amount on a basis of the C–Cl unit. ^bThe ratio Pd (Cat):phase-transfer catalyst is 1:200. ^cThe reaction was carried out without phase-transfer agents.

Table 2 Degree of dechlorination (*X*) of hexachlorobenzene in the presence of alkylammonium salts; catalyst, Pd₂Ni₉₈/C; S(C–Cl):Cat ratio, 10:1; *T* = 50 °C; 50% KOH; *P*_{H₂} = 1 atm; solvent, isopropanol–toluene, 4:7 (15 ml).

Phase-transfer catalyst	Time/h	<i>X</i> (%)
Me ₄ N ⁺ Cl [−]	1.5	98
Et ₄ N ⁺ Cl [−]	1.5	85
Et ₄ N ⁺ OH [−]	4.0	94
(C ₈ H ₁₇) ₃ MeN ⁺ Cl [−]	1.5	90

of the reaction, samples of the reaction mixture were analysed by GLC on an LKhM-80 chromatograph using a 2 m×3 mm stainless-steel column packed with 5% SE 30 on Chromaton N AW-DMCS, a flame-ionisation detector, and argon as a carrier gas at a flow rate of 60 cm³ min^{−1}. Undecane was used as an internal standard.

The degree of dechlorination (*X*) was calculated as follows:

$$X = (1 - \sum_{i=0}^6 iC_i/6C^0) \times 100\%$$

where *C_i* is the molar concentration of a substance containing *i* chlorine atoms in the molecule and *C⁰* is the initial concentration of hexachlorobenzene.

Table 1 indicates that the reaction rate was very high in the presence of a phase-transfer agent. The Pd/C catalyst is most active among the studied catalysts. The Pd₂Ni₉₈/C bimetallic catalyst exhibits a higher activity in the hydrodechlorination than the nickel catalyst and a mixture of the monometallic catalysts with the same transition metal content as in the bimetallic catalyst. It is well known^{7,8} that the activity of bimetallic catalysts is a nonadditive function of the composition. Thus, the activity of a Pd–Ni/SiO₂ catalyst for butadiene hydrogenation increases with the content; however, this increase is not proportional to the concentration because palladium demonstrates a strong tendency to migrate to the surface.

Table 2 shows that the hydrodechlorination of hexachlorobenzene with Pd₂Ni₉₈ supported on Sibunit is effective in the

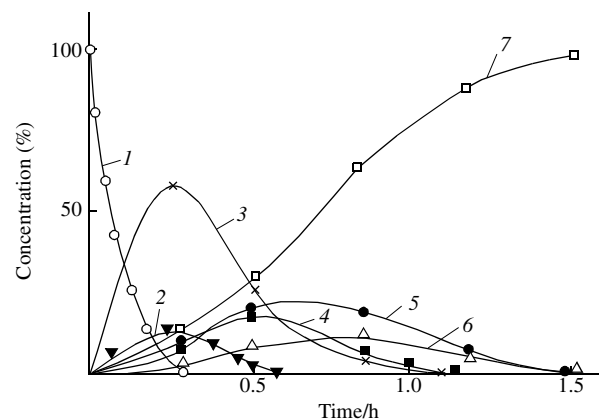


Figure 1 Hydrodechlorination of hexachlorobenzene with Ni₉₈Pd₂/C and Me₄N⁺Cl[−] as a phase-transfer catalyst: (1) hexachlorobenzene; (2) pentachlorobenzene; (3) tetrachlorobenzene isomers; (4) trichlorobenzene isomers; (5) dichlorobenzene isomers; (6) chlorobenzene; and (7) benzene.

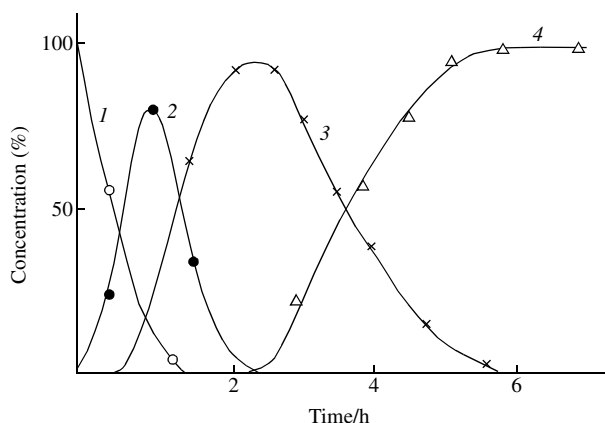


Figure 2 Hydrodechlorination of hexachlorobenzene with $\text{Ni}_{92}\text{Cu}_8/\text{C}$ and $\text{Me}_4\text{N}^+\text{Cl}^-$ as a phase-transfer catalyst: (1) hexachlorobenzene; (2) pentachlorobenzene; (3) 1,2,4,5-tetrachlorobenzene; and (4) trichlorobenzene isomers.

presence of alkylammonium chlorides as phase-transfer catalysts.

Different selectivity patterns were obtained with the use of various metal catalysts. The reaction of hexachlorobenzene with hydrogen catalysed by $\text{Pd}_2\text{Ni}_{98}/\text{C}$ at atmospheric pressure resulted in dehalogenation *via* the rapid replacement of chlorine atoms in polychlorinated benzenes to form benzene (Figure 1).

Figure 2 shows that dehalogenation with hydrogen at atmospheric pressure in the presence of a $\text{Ni}_{92}\text{Cu}_8/\text{C}$ catalyst proceeds only to the formation of trichlorobenzene isomers. Thus, a proper combination of metal catalysts can affect selectivity of halogen removal.

In conclusion, note that these results show the possibility of designing active bimetallic catalysts and catalytic processes for the hydrodechlorination of environmentally problematic compounds. Such reactions are also a very promising means for the selective removal of halogens from aromatic compounds in organic synthesis.

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