

## HEXACHLOROBENZENE HYDRODECHLORINATION IN THE PRESENCE OF BIMETALLIC CATALYSTS

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### Introduction

Polychlorinated organic compounds (PCOC) are environmentally persistent chemicals which bioaccumulate in fatty tissue and show carcinogenic and mutagenic activity. Catalytic hydrodechlorination is one of the ways of detoxification of the PCOC, which excludes the formation of more toxic substances as polychlorinated dibenzodioxins and dibenzofurans. This process is also a well-known method in synthetic organic chemistry [1-3].

Hydrodechlorination is known to be promoted by noble metals of group VIII. Literature data have shown that successful dechlorination of polychlorinated aromatic compounds by using Ni catalysts requires severe reaction conditions, high temperature and high hydrogen pressure. Pd, Ru catalysts permitting successful dechlorination of polychlorinated aromatic compounds under mild conditions are not adapted to large-scale applications because of their high cost [4]. Moreover designing a selective catalyst to convert environmentally problematic compounds into useful products is very important.

The goal of this study is the preparation and investigation of effective and inexpensive catalysts, permitting to carry out liquid-phase hydrodechlorination under mild conditions. It was decided to prepare bimetallic catalysts consisting of nickel or copper associated with palladium, supported on a high surface area carbon named "Sibunit".

As it is also known that the method of preparation of the catalyst has a marked effect on its selectivity, we have compared the reactivity of catalysts obtained either from organometallic compounds or from metal chlorides.

Finally to increase the reaction rate of hexachlorobenzene hydrodechlorination carried out in a two-phase system (aqueous KOH and organic solvent) onium salts were used as phase-transfer agents.

### Materials and methods

#### *NiPd/C catalysts reduced by H<sub>2</sub> from metalloorganic compounds*

A Sibunit carbon described in Ref [5] was used as support. It had the following characteristics: composition – carbon 99.4 wt.%, sulfur 0.03%, ashes 0.2%; surface area 370 m<sup>2</sup>/g (BET), average pore size of 40 Å, pore volume of 0.4 ml/g, and particle size 0.5 mm.

To obtain the catalyst by organometallic way, a carbon supported monometallic Pd catalyst was first prepared by exchange of Pd(NH<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub> in an ammonia solution. The catalyst was dried at 370 K, calcined at 740 K, and reduced in flowing hydrogen at 510 K. A solution of bis-cyclopentadienyl-nickel (nickelocene) in amylacetate was then added to this Pd catalyst. A

drafting reaction by exchange between the  $C_5H_5$  ligands and H atoms adsorbed at the surface of the Pd particles was then carried out. It was easily achieved by flowing hydrogen at 390 K during 4 h in suspension. It was also shown by X-ray diffraction that homogeneous alloys are obtained by heating these bimetallic samples at 720 K in flowing hydrogen [6].

### *NiPd/C catalyst reduced by $NaBH_4$ from metal chlorides*

The chloride salts used as catalyst precursor are palladium (II) chloride ( $PdCl_2$ ), and nickel (II) chloride hydrate ( $NiCl_2 \cdot 6H_2O$ ).

The catalyst was prepared by a method of impregnation. The transition metal chlorides, in appropriate amounts, were dissolved in water. To dissolve palladium chloride in water a few drops of concentrated HCl were added. Carbon support was added to the aqueous solution of both metal salts Ni and Pd for impregnation. Solvent excess was removed by heating at constant stirring. The samples were then dried at 150 °C for 3 hours and reduced by an ethanol solution of  $NaBH_4$  (ethanol :  $NaBH_4$  = 1:5) in hydrogen flow. Finally, the catalysts were washed with a water-ethanol mixture (ethanol: water = 1:1), and dried in argon flow at 80° C for 3 hours.

### *CuPd/C catalysts reduced by $H_2$ from metalloorganic compounds*

The first step consists in the deposition of organometallic precursors – bis(acetylacetonato)palladium(II) and copper(II) from Strem Chemicals – on Sibunit. The desired amounts of  $Pd(C_5H_7O_2)_2$  and  $Cu(C_5H_7O_2)_2$  are dissolved in 300 ml of toluene. Five grams of a carbon are added with stirring for 24 h at room temperature. The mixture is filtered under vacuum and dried at 350 K for 15 h [7-8].

### *Hydrodechlorination of hexachlorobenzene*

The standard experiments were carried out in a glass flask into which the reactive mixture was introduced. It is composed of KOH(aq) 50%, 4 ml, 11 ml organic solution (7 ml toluene and 4 ml i-propanol) of hexachlorobenzene ( $0.56 \times 10^{-3}$  mol, 0.036 mol), catalyst (metal  $3.4 \times 10^{-4}$  mol) and tetramethylammonium chloride ( $0.36 \times 10^{-3}$  mol in C-Cl fragment). The amount of KOH required to neutralize the HCl produced in the reaction was added to the solution. The flask was kept at 50° C and connected with a system for the inlet of hydrogen. During the reaction, sampling of the mixture were sent to GLC analysis. Undecane was used as an internal standard. Qualitative and quantitative analyses of the reaction products were carried out using a “Cvet-500” chromatograph (steel column 2m x 3mm filled with 5 % 8E 30 over chromatone N-AW-DMCS, fire-ionization detector, argon as gas-carrier, 60 ml/min).

### **Results and discussion**

The results of hexachlorobenzene hydrodechlorination over bimetallic  $Ni_{95}Pd_5/C$  catalyst prepared with organo-metallic compounds reduced by  $H_2$  at 500° C are presented in Fig. 1. It is observed that consecutive chlorine removal takes place in the presence of this catalyst. After two hours almost complete conversion of hexachlorobenzene into penta- and tetrachlorobenzene is achieved. During the next five hours the conversion of tetrachlorobenzene into tri- and dichlorobenzene proceeds.

Hexachlorobenzene hydrodechlorination results obtained with the bimetallic  $Ni_{95}Pd_5/C$  catalyst reduced by  $NaBH_4$  at 20-50° C from metal chlorides are shown in Fig. 2. The data suggest a multiple chlorine removal in one stage. From the very beginning of the reaction the whole

spectrum of chlorine substituted benzenes is present. Dechlorination in this case proceeds through a rapid (120 minutes) and progressive displacement of the chlorine atoms to benzene.

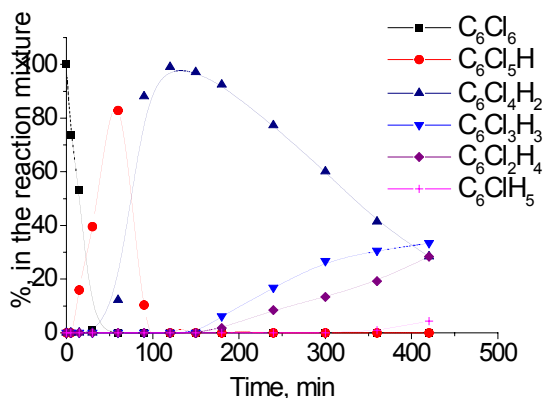
Probably the presence of Lewis acid centers produced by the presence of chlorine fixed on the support can explain the increase of activity and the more complete dechlorination observed with the catalyst obtained from metal chlorides.

These results have shown that using such bimetallic systems ( $\text{Ni}_{95}\text{Pd}_5/\text{C}$ ) one is able to carry out liquid phase hydrodechlorination under mild conditions ( $P_{\text{H}_2}$  1 atm;  $T = 50^\circ\text{C}$ ). This can be rather surprising since nickel is totally inactive in this reaction. However in Ref. 6, it was shown that  $\text{Pd-Ni/SiO}_2$  catalysts has an activity in the butadiene hydrogenation which is mainly governed by the surface palladium concentration. Actually, using modern surface science techniques, this high activity was explained by the segregation of palladium on the surface of the bimetallic particles. This is the reason why the addition of only five atomic percent of Pd to Ni leads to a rather high catalytic activity.

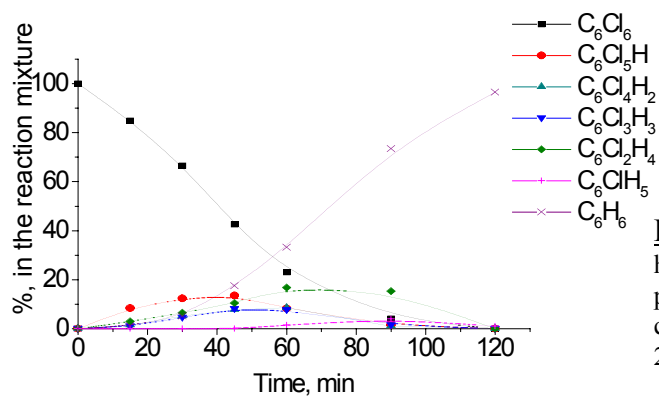
These results also demonstrate that catalyst preparation method have a marked effect on selectivity. In the case of the catalyst reduced by  $\text{H}_2$  at  $500^\circ\text{C}$  from organo-metallic compounds, we can isolate different intermediate chlorine substituted benzenes of economical interest such as tri- and dichlorobenzene, used as solvents.

We can also vary the dechlorination activity and selectivity by diluting an active site of the supported catalyst. For this purpose, hexachlorobenzene hydrodechlorination was investigated in the presence of bimetallic  $\text{Cu}_{80}\text{Pd}_{20}/\text{C}$  catalyst reduced by  $\text{H}_2$  at  $500^\circ\text{C}$  from organo-metallic precursors. The results are presented in Fig. 3. Apparently, a consecutive chlorine removal takes place as well as in the first case. But the reaction stops at the tetrachlorobenzene stage, which can be produced as a single product with 100% yield within 150 min of reaction. According to [7] this result may be explained by the preferential migration of Cu atoms on the catalyst surface.

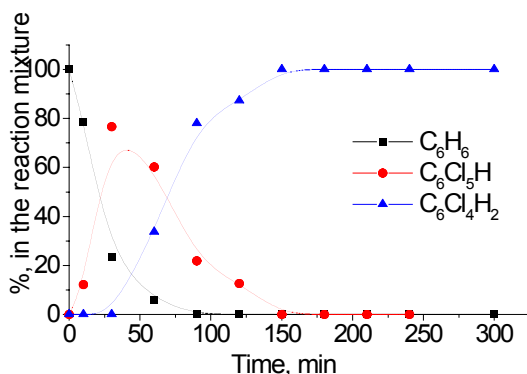
Thus these results have shown that such bimetallic systems permits to carry out liquid phase hydrodechlorination of hexachlorobenzene under mild conditions, but also that the methods of catalysts preparation has a strong effect on their selectivity.



**Figure 1.** Hexachlorobenzene hydrodechlorination in the presence of  $3\%\text{Ni}_{95}\text{Pd}_5/\text{C}$  catalyst reduced by  $\text{H}_2$  at  $500^\circ\text{C}$  from metalloorganic compounds



**Figure 2.** Hexachlorobenzene hydrodechlorination in the presence of 4%Ni<sub>95</sub>Pd<sub>5</sub>/C catalyst reduced by NaBH<sub>4</sub> at 20°C from metal chlorides



**Figure 3.** Hexachlorobenzene hydrodechlorination in the presence of 3%Cu<sub>80</sub>Pd<sub>20</sub>/C catalyst reduced by H<sub>2</sub> at 500°C from metalloorganic compounds

## References

1. Kalnes T. N., James R.B., *Environ. Prog.*, **1988**, 7, 185.
2. Kovenklioglu S., Cao Z., Shan D., Farrauto R.J., Balko E.N., *AIChE Journal*, **1992**, 38, 1003.
3. Pinder A.R., *Synthesis*, **1980**, 425.
4. Hagh B.F., Allen D.T., *Chem. Engineer. Science*, **1990**, 45, 2695.
5. Yermakov Yi.I., Surovikin V.F., Plaksin G.V. and Likholobov V.A., *React. Kinet. Catal. Lett.*, **1986**, 23, 435.
6. Renouprez A., Faudon J. F., Massardier J., Rousset J. R., Delichere P., Bergeret G., *J. Catal.*, **1997**, 170, 181.
7. Renouprez A., Lebas K., Bergeret G., Rousset J. R., Delichere P., in "Proc. 11th International Congress on Catalysis", Studies in Surface Science and Catalysis, **1996**, Vol. 101, 1105.
8. A. Renouprez, K. Lebas, G. Bergeret, *J. Mol. Catal.* **1997**, 120, 217.