Comparison of bimetallic and trimetallic catalyst in reductive dechlorination; influence of copper addition

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***Abstract*— Efficiency of reduction of PCBs in aqueous solution was examined with the help of bimetallic catalyst Fe-C/Pd consisting of palladized grey cast iron and with a newly designed trimetallic catalyst (Cu-Fe-C/Pd) consisting of a copper metal plate with embodied microparticles of palladized grey iron (bimetallic catalyst). PCB solutions were prepared using DELOR 103. The trimetallic catalyst was significantly more efficient than bimetallic one. Trimetallic catalyst reduced concentration of PCBs to approximately 1% of its initial value during 70 minutes and bimetallic one during 48 hours. Moreover, more than 20% of declined PCBs were found adsorbed on the surfaces of the bimetallic catalysts. Contrary, presence of metal copper accelerates formation of the oxidation products and their release from the catalyst surface as the individual flocks which recovers activity of the trimetallic catalyst. These facts can significantly change the previous belief, widely published for decades that the reductive dechlorination of PCBs is the only decisive control step in the reduction of their content in water by zero valence metals.**

***Keywords*— PCB, reductive dechlorination, cast iron containing graphite, bimetallic and trimetallic catalysts, palladium, copper**

I. INTRODUCTION

Iron in its oxidation state (so called zero valence iron Fe(0)) as a reducing agent with combination of various noble metals as carriers has been applied for reductive dechlorination of chlorinated hydrocarbons for last 20 years [1-8]. Such combinations of base and noble metals are known as bimetallic catalysts, where Ag, Ni, Pt, Pd, Cu, etc., on Fe, Mg, Zn, Al have been usually used [8-14], nevertheless, the most studied and proven variation is Pd on iron (Pd/Fe) owing to its highest effectiveness [15, 16]. The application of bimetallic catalysts has been focused on chlorinated aliphatic or aromatic hydrocarbons [e.g. 17-26], or PCBs [3, 5, 7, 10, 14, 27, 28].

Basically, the processes taking place in a bimetallic system can be viewed as processes taking place in an electrochemical cell, where the base and noble metals serve as electrodes. The proposed mechanism also holds for cast iron, in which the heterogeneous system of grains of graphite inside the ferrous matrix can be considered as a type of a special bimetallic catalyst. Cast iron undergoes an active corrosion and the cathodically protected surface of Pd then captures the protons by a specific process of chemisorption. The chlorinated substance is adsorbed on the surface of Pd and subsequently is hydrogenated [8, 22-24]. Moreover, a slightly acidic environment which causes corrosion of the base metal seems to be advantage. It provides additional protons to produce native hydrogen and slows the formation of insoluble oxides, hydrates or carbonates, which can be deposited on the surface of the metals and can adsorb the chlorinated compounds [29]. Another indisputable problem that hinders reductive dechlorination is the formation of oxidation films [30]. Thus, a barrier which prevents oxygen, water and the compounds residing in water to reach the surface of the metal is created [29]. Therefore, maintaining the pH at around 4 is recommended [10, 23, 31], nevertheless, such low pH in practice, for example when underground reactive barriers are used, is really problematic. Possible solution seems to be a joint combination of more, probably two, noble metals with iron in a catalyst. However, the use of so called trimetallic catalysts is not widespread, yet [13].

The aim of this work was to experimentally verify the efficiency of dechlorination of PCB water solutions using trimetallic Cu-Fe-C/Pd catalyst and comparison with the classic bimetallic catalysts Fe-C/Pd. The objective was to determine whether the combination of zero valent metals: iron / copper / palladium may exhibit acceptable efficiency of dechlorination even at low concentrations of Pd. Experiments were performed under conditions close to actual contamination of groundwater at near neutral pH. Additional aim was to verify whether the partial loss of chlorinated compounds might be due to previously often ignored phenomena, such as their adsorption on metal corrosion products (either immobilized on the surface of the metal, or disengaged from the metal and floating in clusters in the treated water).

II. EXPERIMENTAL

A. *Materials*

Fe–flake graphite cast iron, with ferrite-perlite structure manufactured by Armaturka Dysina s.r.o. (turnings, irregular shape, size 1-3 mm, composition: 3.8% C, 1.8% Si 0.5% Mn), Mg- turnings (99.95% trace metal basis, Sigma Aldrich) and Cu-strip (min.99.9%), thickness 0.4 mm, width 20 mm (Med Povrly, a.s., Czech Republic together with PCBs technical mixture DELOR 103 (Chemko Strazske, Slovakia) were used as chemicals.

Samples of the bimetallic Pd/Fe-C catalyst were prepared and subsequently treated by dissolving 0.06 g of K_2PdCl_4 in the solution that contained 9 mL of ethanol, 1 mL of water and 5 g of Fe-cast iron (turnings). A pH of 3 was maintained throughout the reaction to prevent sedimentation of any oxidation products on the surface of cast iron [32]. The ratio Fe-C:Pd, which represents a compromise between efficiency and cost of the catalyst, was selected with regard to results published by Stepanek [12]. Particles of bimetallic catalyst were dried in a nitrogen flow.

Trimetallic catalyst Cu-Fe-C/Pd was prepared by embedding of the bimetallic catalyst into a copper strip. Micro photo of obtained trimetallic catalyst is shown in Fig. 1. The PCB solution was prepared by adding approx. 5 g of technical mixture DELOR 103 into 5 L of distilled water. The solution was then stirred at an ambient temperature for 48 hours. The concentration of the six indicator congeners in the solution was determined at 1030 µg/L with pH of 6.82.

B. *Experiments*

During experiments all catalysts were placed into flasks containing 200 mL of the PCB solution describes above. Samples were then agitated on a shaker for the selected reaction times (0 - 240 hours). At the end of the reaction and before analysis, the catalyst was separated. The total amount of PCB congeners trapped on the catalysts and on the particles of the oxidation products was before analysis soluted in the mixture of hexane and absolute ethanol in the ratio 6:1. Analyses were performed on Gas chromatograph Hewlett-Packard 5890 with an electron capture detector.

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Fig.1 *SEM image of Cu-Fe-C/Pd catalyst surface*

X-ray analyses were performed on the Bruker D8 Discover powder diffractometer equipped with a primary focusing Johansson Ge (111) monochromator producing CuKα1 radiation, samples deposited on zero diffraction Si plate. The structure of the surface of bimetallic catalysts was analyzed using a Hitachi S450 scanning electron microscope. Texture analyses were performed on the ASAP2020M (Micromeritics, USA).

III. RESULTS AND DISCUSSION

A. *Bimetallic catalysts*

Firstly, behavior of bimetallic catalyst during reductive dechlorination of PCB water solutions was studied. Obtained results are shown in Fig. 2, where decrease of PCB concentration in water solution for a long-term experiment is demonstrated. It can be easily seen that a rate of PCB decomposition markedly decreases. This fact can be explained by description of changes on a catalyst surface. After insertion of the Fe-C/Pd catalyst into the reaction solution, its surface undergoes rapid oxidation, which causes its gradual covering together with decrease of a specific surface area. A fresh catalyst possessed a specific surface area of 111 m^2/g and after reaction (240 hours) it fell down to 3.2 m^2/g on an average.

During the first approximately 2 hours of the reaction the concentration decrease of PCBs (40 %) occurs probably due to reductive dechlorination even though the surface of the catalyst is already partially oxidized. Under these reaction conditions, the PCB congeners are able to penetrate the oxidation layer and the overall reaction rate is controlled by the rate of the chemical reaction. Using the customary assumption of the first order reaction, the decline of concentration of the indicative congeners with time (first two hours – see detail in Fig. 2 can be expressed as:

$$c(t)=c_0e^{-kt}, \text{ where } k=3.92.10^{-3}, \text{ the error for } k=\pm1.42\% \qquad (1)$$

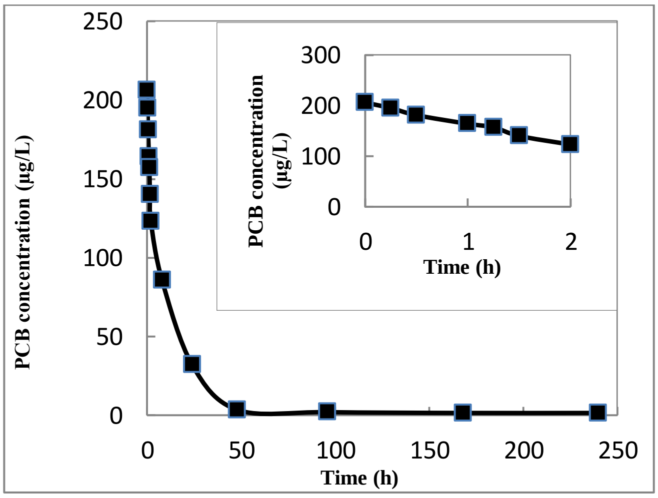

Fig.2: *Time dependence of PCB concentration for Fe-C/Pd catalyst (with detail of first two hours)*

Subsequently, a reaction rate significantly decreases and after 420 hours a residual concentration of PCBs in water solution stays on a same level, thus, a reaction is stopped. Nevertheless, concentration of the sum of indicator congeners decreased on 0.8 % of the original amount. It is necessary to mention that data represent an average of three measurements and the error of the measurement is less than ± 12%.

Simultaneously, a possible adsorption of PCB congeners on a catalyst surface was checked. It was determined that after first two hours 13.5 μg and at the experiment termination (600 hours) 41 μg were adsorbed at 5 g of catalyst which correspond to adsorption amounts of 2.7 and 8.2 μg per 1 g of the catalyst. It can be summarized that adsorption plays a significant role in the reduction of PCB concentration on the Fe-C/Pd catalyst owing to that 20% of the decrease in the amount of PCB in the water solution is due to the adsorption. Our results emphasized the groundbreaking role of adsorption in the process of reductive dechlorination published by Noutbactep [33] and Ghauck [34, 35].

In the heterogeneous cast iron, Fe plays the role of an anode, graphite particles act as a cathode on which the reduction reactions are accelerated; the reductive efficiency is therefore much higher compared to pure zero-valent metals. The presence of the third phase - the heterogeneous “islets” of palladium - on the graphitic cast iron further increases the reduction efficiency (apparently via activation of hydrogen). To some extent, system Fe-C/Pd may be considered as a ternary electrochemical catalyst, which will show higher efficiency for reductive dechlorination than the bimetallic system of pure palladized iron usually mentioned in the literature.

B. *Trimetallic catalyst*

In comparison with the efficiency of dechlorination using bimetallic catalyst, the rate of reductive dechlorination of PCBs with the help of trimetallic Cu-Fe-C/Pd catalyst is considerable faster, see Fig.3.

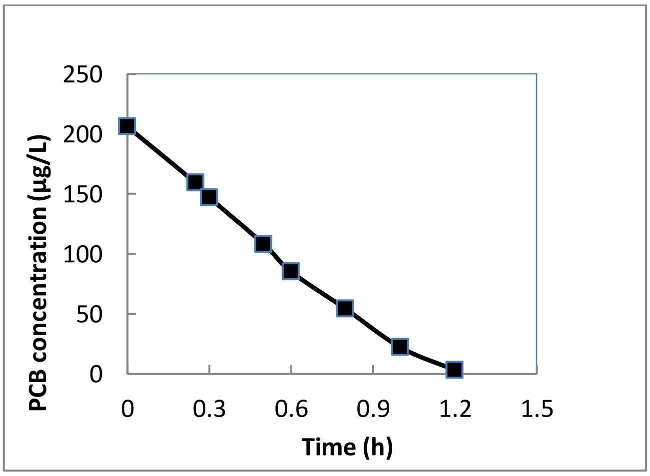

Fig.3: *Time dependence of PCB concentration decrease for Cu-Fe-C/Pd*

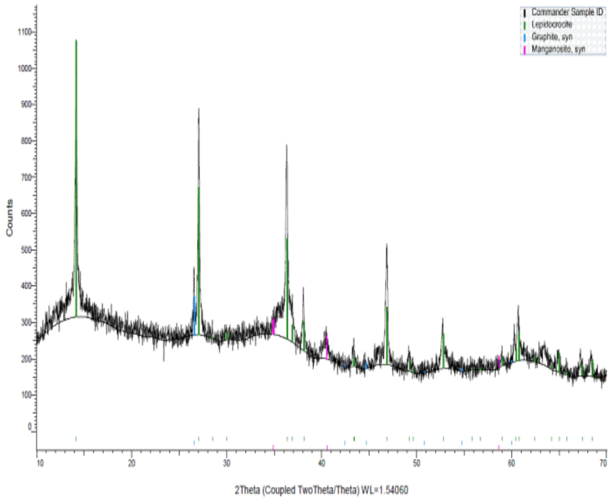

Fig.4: *XRD image of peeled oxidation product from Cu-Fe-C/Pd catalyst*

It is possible to speculate that there is synergy between the effects of Cu and Pd because even at the presence of minute amounts of Pd (<0.1% w/w) during the first phases of the reaction, the rate of the decline in the PCB content is much higher compared with a bimetallic catalyst; 70 minutes contrary to 48 hours.

Metal copper as a noble metal accelerates the formation of the oxidation products. During experiment a formation of the oxidation products as separate particles (flocks) was detected. Thus, the original catalyst activity is recovered by removal of oxidation products from the catalyst surface in the form of flocks. Probably, this effect caused by presence of copper significantly accelerates rate of reductive dechlorination on the trimetallic catalyst compared to the bimetallic catalysts. Fig. 4 brings identification of the peeled oxidation products. From roentgenogram it can be seen that the vast majority of oxidation products consist of γ-$Fe^{3+}O(OH)$ (gamma iron(III) oxide-hydroxide), mineralogical equivalent to lepidocrocite.

It can be summarized that the occurrence of copper in the trimetallic catalyst takes active part in the reaction of reductive dechlorination of PCBs, however, our experiments did not confirm whether copper could initiate or participate in any chemical reaction. The anchoring of metal catalysts on copper plates can be used, among other things, in a practical arrangement of geometrically oriented package in a continuous decontamination in reaction underground barriers.

IV. CONCLUSIONS

Experiments, which determined effectiveness of reductive catalytic dechlorination of PCB content in aqueous solutions, were performed at a laboratory batch arrangement. Bimetallic and trimetallic catalysts were based on a zero-valent iron (represented by grey graphitic cast iron) together with palladium and copper as noble metals. The highest efficiency of decontamination was exhibited by the catalyst containing particles of pallatized cast iron squeezed on copper strips. According to these experiments the idea that the controlling mechanism of decontamination is reductive dechlorination may be correct only in the initial stages of the process. It means, when the surface of the catalyst is still mostly free of the oxidation products that could hinder the access of PCB to the catalyst. This finding is contrary to a large number of previously published claims. Additionally, the effect of PCB adsorption on bimetallic catalyst surface (8.2 µg per 1 g of the catalyst) can simulate PCB decomposition.

Very effective in reducing the PCB content in water, compared with bimetallic iron-palladium catalyst, was the trimetallic catalyst. It was detected a relatively rapid oxidation of the metal surfaces with subsequent release of fractal particles of oxidation products. Thus, the original catalyst activity was recovered. This phenomenon can have a decisive influence on the views about the efficiency and the mechanism of dechlorination of PCB in aqueous solutions by metals and zero-valence metals.

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