

Palladium-Catalyzed Hydrodechlorination for Water Remediation: Catalyst Deactivation and Regeneration

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Abstract—Palladium-catalyzed hydrodechlorination is a promising alternative for the treatment of environmentally relevant water bodies, such as groundwater, contaminated with chlorinated organic compounds (COCs). In the aqueous phase hydrodechlorination of COCs, Pd-based catalysts were found to have a very high catalytic activity. However, the full utilization of the catalyst's potential is impeded by the sensitivity of the catalyst to poisoning and deactivation induced by reduced sulfur compounds (e.g. sulfides). Several regenerants have been tested before to recover the performance of sulfide-fouled Pd catalyst. But these only delivered partial success with respect to re-establishment of the catalyst activity. In this study, the deactivation behaviour of Pd/Al₂O₃ in the presence of sulfide was investigated. Subsequent to total deactivation the catalyst was regenerated in the aqueous phase using potassium permanganate. Under neutral pH condition, oxidative regeneration with permanganate delivered a slow recovery of catalyst activity. However, changing the pH of the bulk solution to acidic resulted in the complete recovery of catalyst activity within a regeneration time of about half an hour. These findings suggest the superiority of permanganate as regenerant in re-activating Pd/Al₂O₃ by oxidizing Pd-bound sulfide.

Keywords—Deactivation, hydrodechlorination, Pd catalyst, regeneration.

I. INTRODUCTION

CHLORINATED organic compounds are environmentally-related chemicals which are often found in water bodies, especially in groundwater. Conventional treatment method for COCs in water include air-stripping followed by adsorption leaving spent materials that need further disposal or treatment. A promising alternative treatment is hydrodechlorination in the water phase whereby chlorinated contaminants are catalytically reduced with an electron donor (e.g. H₂) to less toxic and more biodegradable compounds without leaving spent materials and toxic by-products. In clean deionized water, palladium-based catalysts (e.g. commercially available Pd/Al₂O₃) are found to have high catalytic activity for this reaction and they are able to dechlorinate a wide range of COCs under mild reaction conditions [1]-[2]. A significant

drawback of this method is the sensitivity of Pd catalyst to poisoning by reduced sulfur compounds (RSCs). The RSCs are known to have strong affinity for palladium and they can deactivate the catalyst completely. Since sulfides especially H₂S/HS⁻ are natural constituent in waters due to microbial sulfate reduction, they remain an ubiquitous poison for Pd catalyst during field application.

To maintain a stable and poison-resistant Pd catalyst system under real environmental condition is of high practical significance. A few authors have addressed this necessity by protecting the catalyst system via hydrophobic coating using polydimethylsiloxane material [3] or embedment of Pd clusters in a hydrophobic zeolite carrier [4]. This can then allow the target reactants to diffuse to the metal while repelling the unwanted inorganic salts and ionic poisons that deactivate the catalyst. Due to transport limitation, coatings can reduce the catalyst activity. A total prevention of sulfide-induced deactivation of Pd catalyst systems was achieved by preventing the contact between sulfide species and the Pd metal in waters. This was attained by conducting water pretreatment with potassium permanganate to oxidize RSCs to sulfate which in turn is harmless to the catalyst [5].

In catalytic processes, catalyst materials are usually composed of precious metals that are rare and of high-cost. Hence, in any event of catalyst deactivation it is very valuable to have a simple, cost-effective, and efficient regeneration procedure to recover catalyst performance. In the case of sulfide-deactivated Pd catalysts, they are regenerated by oxidizing the RSCs bound to the catalyst system. The only study which seemed to show success in recovering catalyst performance of sulfide-fouled Pd-based catalysts is via oxidative regeneration with hypochlorite [6]-[7]. But this mostly required longer regeneration time if not multiple regeneration cycles. Testing of other regenerants like heated air and H₂O₂ showed minimal success [6]-[7] while Fenton's reagent and Peroxone (H₂O₂ + O₃) showed no success in re-activating Pd/Al₂O₃ fouled by sulfide [unpublished own results].

In this paper, the deactivation behaviour of Pd/Al₂O₃ induced by sulfide was investigated. This sulfur compound can appear as H₂S, HS⁻, or S²⁻ depending on the pH of the water (pK_{A1} = 7.05, pK_{A2} = 14.0 at 20°C). The totally deactivated catalyst was regenerated in the aqueous phase

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using potassium permanganate. The pH value as the parameter which controls the efficiency of catalyst regeneration was evaluated. The catalyst activity was tested by following the dechlorination kinetics over Pd/Al₂O₃ using chlorobenzene as probe compound.

II. EXPERIMENTAL

A. Chemicals

A 99.8% purity monochlorobenzene (MCB) and a reagent grade Na₂S(9H₂O) were obtained from Sigma-Aldrich and were used as received. An extra pure crystalline potassium permanganate used in the regeneration experiment was supplied by Merck. For the catalyst, the commercially available egg-shell Pd on γ-Al₂O₃ with 0.5 wt% Pd (G-133 D purchased from Commercial, Germany, with a BET surface area of 160 m² g⁻¹) was crushed and sieved. The pre-reduced fraction 25 - 63 μm with a measured Pd content of 0.51 wt% (determined by EDXRF analysis) was used in all experiments.

B. Hydrodechlorination of MCB with Pd/Al₂O₃

The hydrodechlorination of MCB using Pd/Al₂O₃ was conducted as batch experiment using 250-mL amber screw-cap bottles equipped with a Mininert® valve. About 30 mg Pd/Al₂O₃ was added into the batch bottle containing 200 mL deionized water. This was then purged with He for 1 hr. Then, the headspace was filled with hydrogen gas. A defined volume of MCB stock solution was spiked into the batch bottle giving an initial concentration of 20 mg L⁻¹. The bottle was shaken (180 rpm in horizontal shaker) to start the dechlorination reaction. The kinetics of the dechlorination of MCB was followed either through educt disappearance or product formation via headspace analysis using a GC-MS QP2010 (Shimadzu).

C. Poisoning and Regeneration of the Pd/Al₂O₃ Catalyst

Similar to dechlorination experiments, catalyst poisoning and regeneration were conducted as batch experiments using the same 250-mL bottles. The catalyst suspension of 30 mg Pd/Al₂O₃ (0.5 wt% Pd) in 200 mL deionized water or HCl-amended deionized water (pH = 3) was purged with He for 1 hr. Afterwards, a defined volume of Na₂S(9H₂O) stock solution was spiked into the batch bottle to give the desired sulfide concentration of 1.77 μM (Pd : S is 1 : 0.25 mole per mole) and 14.2 μM (Pd : S is 1 : 2 mole per mole). The bottle was shaken overnight to induce catalyst deactivation by the added sulfides. The fouled catalyst was tested for its remaining activity by adding hydrogen and MCB into the batch bottle. For the totally deactivated catalyst (Pd : S = 1 : 2), oxidative regeneration was conducted by spiking an aqueous solution of potassium permanganate into the bottle giving an initial concentration of 0.18 mM. The bottle was shaken (180 rpm, horizontal shaker) for definite time periods. Afterwards, unconsumed permanganate in the bulk solution was quenched by adding hydrazine. Then hydrogen and MCB were added to test if the fouled Pd/Al₂O₃ was regenerated.

III. RESULTS AND DISCUSSION

The performance of Pd/Al₂O₃ for hydrodechlorination of a reactant *i* (e.g., MCB) can be expressed in terms of specific Pd catalyst activity $A_{Pd,i}$ as described in ref [8]. This is calculated according to $A_{Pd,i} = (c_{Pd} \cdot \tau_{1/2})^{-1}$ [L g⁻¹ min⁻¹] where c_{Pd} is the concentration of Pd metal and $\tau_{1/2}$ is the half-life of the probe compound as obtained from its disappearance kinetics. The numerical value for $A_{Pd,i}$ is equivalent to a second-order rate constant k_{obs} for the disappearance kinetics according to $k_{obs} = \ln 2 \cdot A_{Pd,i}$. In case of significant deviations of the observed kinetics from a first order with respect to the chlorinated reactants $A_{Pd,i}$ is still defined based on $\tau_{1/2}$, whereas k_{obs} is not.

The kinetics of the batch hydrodechlorination of MCB on Pd/Al₂O₃ in clean deionized water is shown in Fig. 1. It follows a first order reaction kinetics as can be seen from the semi-logarithmic plot of the MCB disappearance shown in Fig. 2. The specific Pd catalyst activity $A_{Pd,MCB} = 133$ L g⁻¹ min⁻¹ calculated from this experiment is taken as the baseline or reference activity for fresh Pd/Al₂O₃. This value has been approved in a set of independent data and can be regarded as the baseline activity of the catalyst under study.

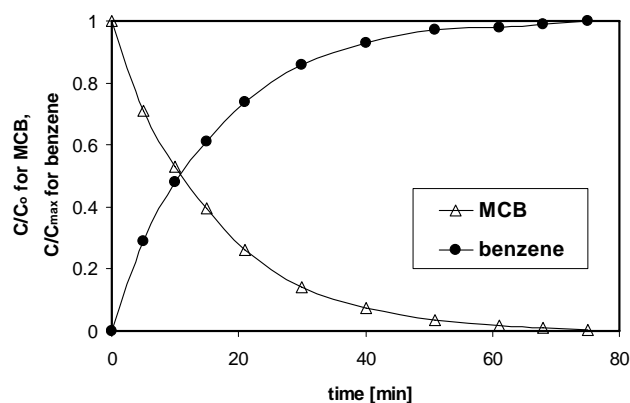


Fig. 1 Batch hydrodechlorination of MCB to benzene on Pd/Al₂O₃ in clean deionized water. Reaction conditions: $c_{0,MCB} = 20$ mg L⁻¹, $c_{Pd} = 0.75$ mg L⁻¹

The addition of sulfides to the water poisons the catalyst resulting in a significant decrease in the dechlorination performance of Pd/Al₂O₃ (Fig. 2). A low sulfide concentration such as 1.77 μM already reduced the catalyst activity by an order of magnitude from 133 to 10 L g⁻¹ min⁻¹. In the presence of 14.2 μM sulfide the catalyst was totally and permanently deactivated. In this state, there are no more reactive sites remaining free for the target dechlorination reaction. The mechanism of catalyst poisoning may include formation of strong Pd-S bonds and formation of adlayers of sulfide around the Pd clusters [9]-[10].

The regeneration of sulfide-deactivated Pd/Al₂O₃ is possible when sulfide bound to the catalyst system is oxidized to sulfate. Sulfate in return has a low affinity for Pd metal and when release to the aqueous phase does not affect the dechlorination reaction. In this study, the oxidant potassium permanganate was used to regenerate totally deactivated

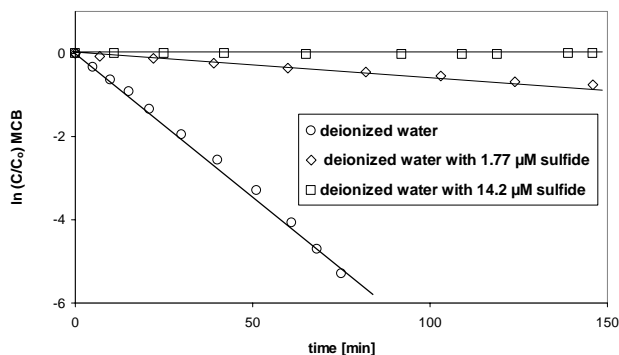


Fig. 2 Deactivation of Pd/Al₂O₃ catalyst in the presence of sulfide. Dechlorination of MCB in deionized water without sulfide is taken as catalyst baseline activity with $A_{Pd,MCB} = 133 \text{ L g}^{-1} \text{ min}^{-1}$. Reaction conditions: $c_{0,MCB} = 20 \text{ mg L}^{-1}$, $c_{Pd} = 0.75 \text{ mg L}^{-1}$

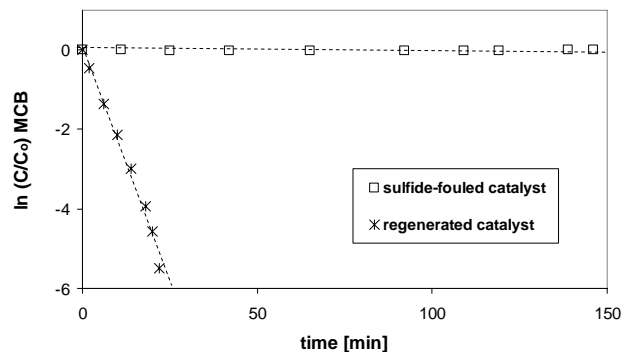


Fig. 3 Oxidative regeneration of sulfide-fouled Pd/Al₂O₃ catalyst (Pd : S is 1 : 2 mole per mole) under acidic conditions (pH = 3). Regeneration was conducted with 0.18 mM potassium permanganate for 30 min. Reaction conditions: $c_{0,MCB} = 20 \text{ mg L}^{-1}$, $c_{Pd} = 0.75 \text{ mg L}^{-1}$

catalyst induced by sulfide poisoning. It is important to note that after a given regeneration period, the unconsumed permanganate was quenched with hydrazine. This is due to the inhibitory effect of permanganate on the Pd-catalyzed hydrodechlorination when present at higher than a threshold concentration of about 0.08 mM as described in ref [5]. The Pd/Al₂O₃ poisoned by 14.2 μM sulfide (Pd : S is 1 : 2 mole per mole) was used in all regeneration experiments using 0.18 mM permanganate. In this Pd to sulfide molar ratio total and permanent deactivation of Pd/Al₂O₃ took place regardless of the pH conditions of the bulk solution. Interestingly, the efficiency of catalyst regeneration with permanganate showed strong pH dependence. The regeneration under neutral conditions (non-amended deionized water) is a slow process recovering a catalyst performance of around 20% after overnight regeneration. A complete regeneration is possible when regeneration is increased up to 48 hr. A totally different behavior can be observed when the sulfide-fouled catalyst is regenerated under acidic conditions (Fig. 3). A regeneration time of 30 min resulted in the complete recovery of catalyst performance. Furthermore, the calculated catalyst activity ($A_{Pd,MCB} \approx 450 \text{ L g}^{-1} \text{ min}^{-1}$) even was significantly higher under this condition than the baseline activity of fresh non-poisoned Pd/Al₂O₃ under neutral conditions shown in Figs. 1 and 2. It should be noted that baseline activity of fresh Pd/Al₂O₃ for the dechlorination of MCB under neutral or acidic condition falls in the same order of magnitude.

The phenomenon shown in Fig. 3 needs further elucidation. However, it should be considered that catalyst, sulfide, and permanganate are all pH sensitive components. Under acidic conditions, the oxidation half reaction is $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ with an oxidation potential of $E^\circ = 1.68 \text{ V}$. Under this condition, the reduction of permanganate proceeds to the formation of the Mn^{2+} cation which is soluble in water. On the other hand, colloidal manganese dioxide (MnO_2) is the end product of the reduction of permanganate under neutral to basic conditions. The oxidation potential according to the half reaction $\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$ is $E^\circ = 0.60 \text{ V}$. Therefore, the observed fast and highly efficient catalyst

regeneration at low pH can possibly be accounted to the higher redox potential of the oxidant under this condition. It should not be disregarded, however, that the surface charge of the catalyst Pd/Al₂O₃ is pH sensitive as well. At low pH condition, the catalyst has a positive surface charge such that the negatively charged oxidant MnO_4^- may have an easier access to the Pd-bound sulfide. This is the kinetic aspect of reaction, which may be more significant than the thermodynamic aspect considered above. Although H_2S speciation is also pH dependent we do not recognize a clear pH effect on the speciation of the catalyst-bound sulfur.

The catalyst activity after regeneration under acidic conditions was found to be higher by a factor of about 3 than the baseline activity of the fresh catalyst. This may be due to changed reaction conditions (pH ≈ 3 instead of 7, residual hydrazine from permanganate quenching present). Nevertheless, it is unexpected and needs further investigation.

IV. CONCLUSION

In this paper, the catalyst Pd/Al₂O₃ was deactivated completely and permanently by the addition of sulfide with a Pd : S molar ratio of 1 : 2 mole per mole. Oxidative regeneration of the totally deactivated catalyst with potassium permanganate (0.18 mM) under neutral conditions (pH = 6-8) showed a complete but slow recovery of catalyst activity. However, changing the pH of the bulk solution to acidic conditions (pH = 3) accelerated the regeneration significantly. 30 min of permanganate treatment are sufficient to completely recover the catalyst performance. This phenomenon of fast and complete recovery at low pH still needs further elucidation. The findings in this study suggest that permanganate is an efficient regenerant in re-activating sulfide-fouled Pd/Al₂O₃. This makes it possible to re-use the precious Pd catalyst in the event of sulfide-induced deactivation during environmental application.

REFERENCES

- [1] Lowry, G. V.; Reinhard, M. Hydrodehalogenation of 1- to 3-carbon halogenated organic compounds in water using a palladium catalyst and hydrogen gas. *Environ. Sci. Technol.* 1999, *33*, 1905-1910.
- [2] Schueth, C.; Reinhard, M. Hydrodechlorination and hydrogenation of aromatic compounds over palladium on alumina in hydrogen-saturated water. *Appl. Catal. B* 1998, *18*, 215-221.
- [3] Fritsch, D.; Kuhr, K.; Mackenzie, K.; Kopinke, F.-D. Hydrodechlorination of chloroorganic compounds in ground water by palladium catalysts: Part 1. Development of polymer-based catalysts and membrane reactor tests. *Catal. Today* 2003, *82*, 105-118.
- [4] Schueth, C.; Disser S.; Schueth F.; Reinhard M. Tailoring catalysts for hydrodechlorinating chlorinated hydrocarbon contaminants in groundwater. *Appl. Catal. B* 2000, *28*, 147-152.
- [5] Angeles-Wedler, D.; Mackenzie, K.; Kopinke, F.-D. Permanganate oxidation of sulfur compounds to prevent poisoning of Pd catalysts in water treatment processes. *Environ. Sci. Technol.* in press.
- [6] Chaplin, B. P.; Shapley J. R.; Werth C. J. Regeneration of sulfur-fouled bimetallic Pd-based catalysts. *Environ. Sci. Technol.* 2007, *41*, 5491-5497.
- [7] Lowry, G. V.; Reinhard M. Pd-Catalyzed TCE dechlorination in groundwater: Solute effects, biological control, and oxidative catalyst regeneration. *Environ. Sci. Technol.* 2000, *34*, 3217-3223.
- [8] Kopinke, F.-D.; Mackenzie K.; Koehler R. Catalytic hydrodechlorination of groundwater contaminants in water and in the gas phase using Pd/ γ -Al₂O₃. *Appl. Catal. B* 2003, *44*, 15-24.
- [9] Yu, T. C.; Shaw, H. The effect of sulfur poisoning on methane oxidation over palladium supported on γ -alumina catalysts. *Appl. Catal. B* 1998, *18*, 105-114.
- [10] Jones, J. M.; Dupont, V. A.; Brydson, R.; Fullerton, D. J.; Nasri, N. S.; Ross, A. B.; Westwood, A. V. K. Sulphur poisoning and regeneration of precious metal catalysed methane combustion. *Catal. Today* 2003, *81*, 589-601.