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Hydrotreating processes for catalytic abatement of water pollutants

Yurii Matatov-Meytal, Moshe Sheintuch[*]

Department of Chemical Engineering, Technion Israel Institute of Technology, Haifa 32000, Israel

Abstract

Opportunities and problems in application of catalytic hydrotreating processes, which are presented a viable approach in the abatement of water pollutants, are discussed. Analysis of the hydrodechlorination (HDC) and hydrodenitrification (HDN) using Pd-based catalysts supported on various materials like granulated activated carbon (GAC), fibrous activated carbon cloths (ACCs) or glass fiber cloths (GFCs) studied recently in our laboratory suggests the following perspectives:

(1) Exhaustive regeneration of Pd/GAC saturated with *p*-chlorophenol can be achieved in a two-step approach, incorporating gas-phase HDC by hydrogen followed by oxidation by air.
(2) Pd/ACC catalysts are good candidates for the liquid-phase HDC showing activity higher than that of Pd/GAC or Pd/GFC; the high adsorption capacity of Pd/ACC lead suggesting its use in a technology with periodic adsorption and HDC, in similarity to adsorption with regeneration of GAC.
(3) Pd/GFC and Pd–Cu/GFC are promising catalyst for removal of nitrites and nitrates, showing activity and selectivity that compares favorably with those of powdered catalysts.

Keywords: Water treatment; Adsorption; Heterogeneous catalysis; Hydrodechlorination; Activated carbon; Granular; Fibrous cloth; Hydrodenitrification; Glass fiber cloth

1. Introduction

Most catalytic processes designed for purification of wastewater generally include a strong oxidation step [1]. Hydrotreating is an advantageous for converting halogenated organic compounds since oxidation can generate highly toxic products such as phosgene, dioxins and chlorine [2] which may also poison most catalysts or at least leads to their deactivation [3]. Obviously, oxidation cannot convert certain ions, like nitrates, which have become a major problem in drinking water treatment [4]. Moreover, during oxidative treatment of water, bromide ions may turn into toxic bromates.

In this paper, we assess the viability of catalytic hydrotreating processes like hydrodechlorination (HDC) and hydrodenitrification (HDN) using Pd-based catalysts supported on various materials like granulated activated carbon (GAC), fibrous activated carbon cloths (ACCs) or glass fiber cloths (GFCs). The comparative analysis here is based on previously published studies of ours that were devoted to individual processes. While catalytic hydroprocessing is well established, reductive catalytic steps for water purification are still in formative stages. It is known that Pd-based catalysts rapidly dehalogenate a variety of chlorinated organics both in the gas [5] and liquid [6] phases. Similarly Pd and Pd–Cu catalyze the reduction of nitrite and nitrate, respectively, to nitrogen

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[*] Corresponding author. Tel.: +972-4-829-2823;
fax: +972-4-8230-476.
E-mail address: cermsll@techunix.technion.ac.il (M. Sheintuch).

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[7]. The presence of dissolved oxygen does not stop the HDC and HDN reaction through competition for hydrogen (although reaction rates may be reduced).

We discuss here two main classes of processes:

(a) For low concentration of contaminants, we suggest to use adsorption and catalytic regeneration. Catalytic treatment of spent GAC, although not currently used for GAC regeneration, has been claimed to be promising as an alternative to thermal regeneration [8]. Catalyst(s) may be deposited on the adsorbents so that the adsorbent/catalyst would act both as an adsorbent for capturing the dissolved contaminants and as a catalyst for destroying the adsorbed compounds. This provides intimate contact in a single unit, reduces diffusion paths and accelerates desorption rate, but it may diminish the adsorption capacity and may lead to metal elution. Most importantly, the adsorption is conducted at room temperature while the regeneration is conducted at the gas phase at relatively low temperatures so that it can be conducted in situ within at hour. In the case of GAC saturated with chlorinated organics, catalytic regeneration can proceed in a step-wise manner using HDC to generate a dechlorinated product, followed by oxidation.

(b) In an attempt to overcome the diffusion limitations associated with liquid-phase operation, we used Pd-based catalysts supported on fibrous materials like ACC and GFC, for direct HDC of dissolved *p*-chlorophenol (4-CP) and for reduction of nitrate and nitrite. Due to their mechanical elasticity and geometric flexibility these cloths can be shaped to fit the particular use in a structured reactor that may be an attractive alternative in a three-phase operation to the conventional multiphase reactors [9].

1.1. Adsorption with catalytic regeneration

Exhaustive regeneration of Pd/GAC adsorbent saturated with a halorganics can be achieved in a two-step approach, incorporating HDC followed by oxidation by air (Fig. 1). After adsorption in the liquid phase, GAC adsorbent saturated with 4-CP is exposed to gas-phase hydrogen at 200 °C to convert it into phenol. The HDC conversions varied with temperature and the nature of catalyst, but were largely insensitive to Pd catalyst loading [3]. The second step is oxidation by air at 270 °C which eliminates the phenol and yields complete recovery of adsorption capacity in several subsequent cycles (up to three were tested, see Fig. 2). One-step oxidative regeneration was found not to be sufficient for eliminating 4-CP; such a step is sufficient for abating phenol and other simple hydrocarbons [10].

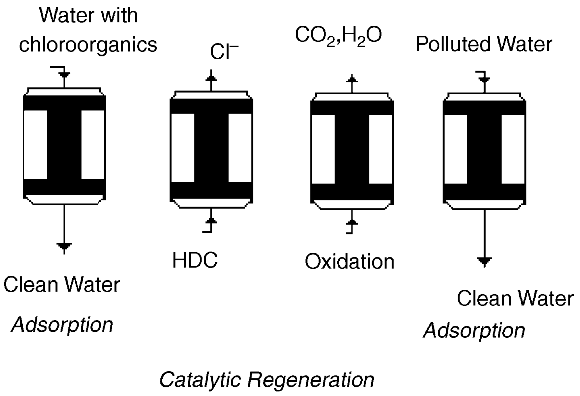

Fig. 1. Flow sheet of the adsorption-regeneration strategy concept (from [3]).

Pd/GAC saturated with 4-CP may also be regenerated with a solution of hydrazine sulfate but the exhaustive liquid-phase HDC requires a very long time: complete HDC of 2.1 mmol 4-CP/g GAC was achieved within 30 h with 0.6 mol/l hydrazine sulfate and equimolar ammonium hydroxide at 52 °C versus 9 h with hydrogen at 200 °C.

Catalytic regeneration should overcome several problems: (a) techniques for better bonding of catalyst to GAC should be developed to avoid metal leaching; (b) the window of operation temperatures between regeneration and carbon combustion should be sufficiently wide; (c) the catalyst(s) should be able to abate a wider range of pollutant molecules. Moreover, similar techniques may be suggested for removing other heteroatom-contained organic pollutants (e.g., hydrodesulfurization).

1.2. Wet HDC using cloth-supported Pd catalyst

While feasibility of liquid-phase HDC has been already demonstrated by several researchers, this

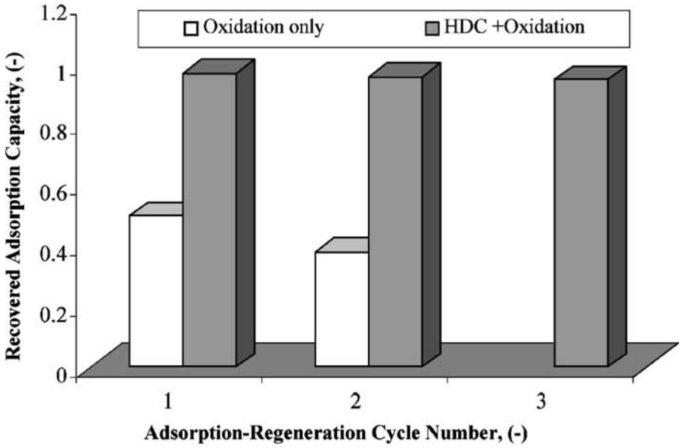

Fig. 2. The recovered adsorption capacity the GAC/catalyst versus regeneration cycle number (from [3]).

process does not appear to be widely practiced as a means of water pollution abatement.

We studied HDC using Pd supported on ACC (Kynol Gmbh, Germany) and GFC (Steklovolokno, Polotsk, Belarus) woven of fibers of 7–10 μm in diameter (as well as Pd/GAC for comparison). All tested catalysts exhibited complete selectivity to phenol irrespective of the surface area of the carrier and no products other than phenol were detected.

The HDC activity (per g catalyst) monotonically increased with increased palladium content (Fig. 3a) but the data suggest that Pd loading should probably be around 2 wt.%. The HDC activity (per g Pd) of Pd/ACC was found to be higher than that of Pd/GAC or Pd/GFC (Fig. 3 a and b) [11], probably, due to low hydrogen spillover on metal/glass surface [12]. It has been reported that the surface concentrations of hydrogen on Pd/SiO_2 and Pd/C are $\sim10^{12}$ and $\sim10^{16}$ atom cm^{-2}, respectively, and that the diffusion coefficient of the H atoms on the carbon surface is about 10^3 times higher than at the silica supports [13].

The experimental rates of HDC of 4-CP in a batch autoclave suggest a strong adsorption of reactant and product. A linear dependence of the specific rate calculated from experimental kinetic data while accounting for adsorption was found (at constant hydrogen pressure). The reaction rate is also linear as function of the hydrogen pressure. Simulations of adsorption, diffusion and reaction showing the effect of pellet size, of hydrogen pressure and of adsorbent loading shows

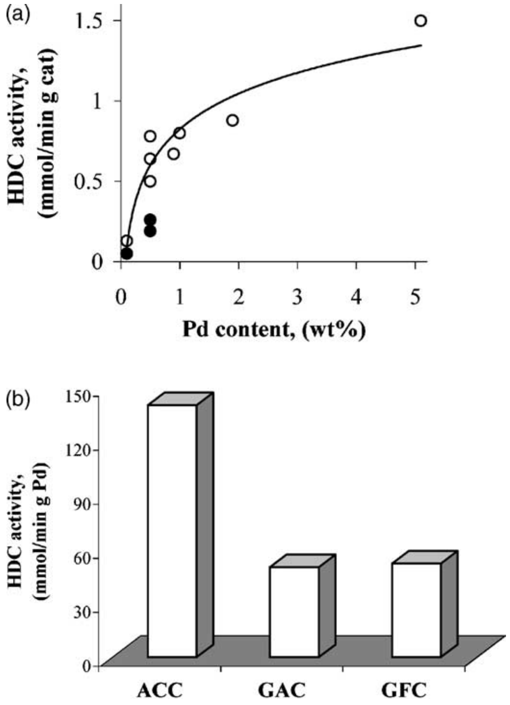

Fig. 3. (a) Effect of Pd content in ACC on HDC activity (the activity of Pd/GAC is denoted by bold symbols); (b) comparison of HDC activity of Pd catalyst supported on different supports; Pd 0.5 wt.%, 60 °C, hydrogen pressure 2.8 bar (from [11]).

that diffusion resistance will be significant in granules larger than 100 μm [11].

The high adsorption capacity of ACC suggested its use in a technology with periodic adsorption and HDC, in similarity to adsorption with regeneration of GAC. We are now attempting to assess Pd/ACC as a catalyst for hydroprocessing of polychlorinated phenols. Pd/ACC may also catalyze hydrodebromination processes, which received scant attention so far [16].

1.3. Nitrate removal using cloth-supported Pd-based catalysts

The catalytic systems most studied for reduction of dissolved nitrites and nitrates by hydrogen are Pd and Pd–Cu catalysts [7]. While the feasibility of these catalysts has already demonstrated, using various supporting materials of different shape and size, a drawback of the catalyzed hydrogenation of nitrates is represented by accumulation of dissolved ammonium and nitrite ions, which are formed during the reaction; the permitted level of these in drinking water is 0.5 and 0.1 mg/l, respectively, while the general requirement of nitrates is not to exceed 50 mg/l.

We have proposed the use of novel Pd [14] and Pd–Cu [15] catalysts supported on cloth woven of glass fibers (GFC), having the same diameter as powder (about 10 μm). The first screening of these catalysts indicated that Pd/GFC and Pd–Cu/GFC are good candidates for these reactions. A comparison of the catalytic activity and yields of ammonium ions for Pd catalysts during nitrite hydrogenation as well as for Pd–Cu catalysts (with Pd/Cu mass ratio of 4, that seems to be optimal) for nitrate hydrogenation is reported in Fig. 4a and b, respectively. Both figures indicate that the form and size of catalyst support definitely affect its activity (per g metal) and selectivity to N_2. HDN activity of cloth catalyst compares favorably with those of powdered catalysts while selectivity of cloth catalysts is higher than that for spheres.

There is a direct relationship between the maximal nitrite concentration and the final yield of ammonium ions: ammonia formation increases significantly even when nitrite concentrations are still significant for nitrite reduction. Increasing pH led to a decline in the nitrate removal activity, while the maximal nitrite and the final ammonia concentrations increased.

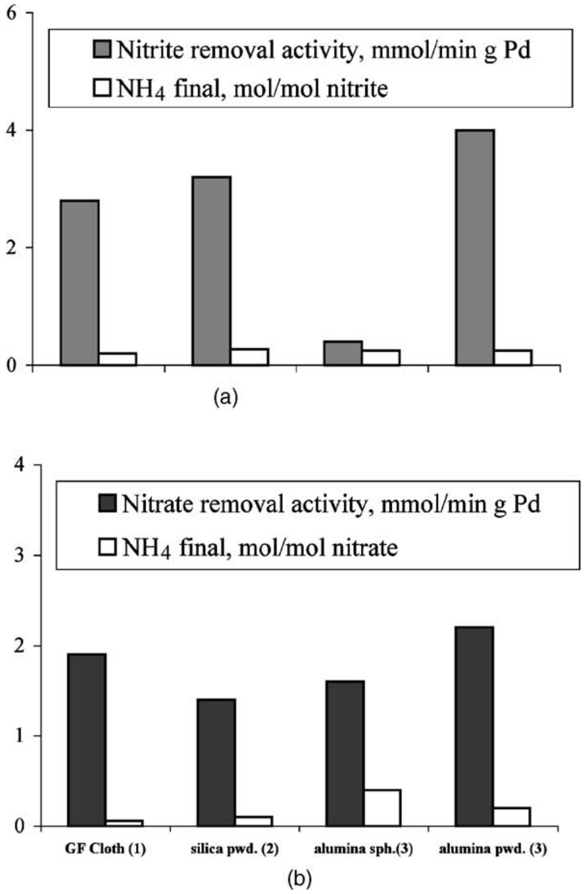

Fig. 4. (a) Comparison of performance of supported Pd catalysts for nitrite reduction, and (b) of Pd–Cu catalysts for nitrate reduction (data for (1) from [14,15], for (2) calculated from [7], and for (3) from [17]). Conditions: 100 mg/l of nitrate (nitrite), 25 °C, pH 5.5–6.0.

The nitrate consumption rate (r_1) curve, constructed by plotting the specific rates against nitrate concentration, shows a typical Langmuir–Hinshelwood behavior:

$$r_1 = -\frac{\mathrm{d}C_1}{\mathrm{d}t} = k_1 \frac{k_1 C_1}{1 + K_1 C_1} \tag{1}$$

Nitrate decomposition appears to occur via a multi-step mechanism going through NO_2^-, NO and atomic nitrogen. At each step, atomic oxygen (or OH^-) is produced that tends to be strongly adsorbed on the catalytic surface, blocking the active sites and reducing its activity. The rate-limiting step in nitrate reduction on Pd–Cu/GFC is the removal of hydroxyl groups from the copper surface. There is, however, a dynamic equilibrium between the adsorbed species and the species in solution, and the anions present in water, like Cl^-, $HCO_3{}^-$ and $SO_4{}^-$, could compete with OH^- and partially modify the coverage of the catalytic surface. Several other salts present in water may affect the hydrogenation processes, e.g.

$$HCO_3{}^- + H_2 \rightarrow HCO_2{}^- + H_2O$$

2. Summary

The processes for abatement of water pollutants can be conducted at conditions that are economically and environmentally more favorable than thermal or catalytic oxidation methods. The analysis of hydrotreating processes applied recently to water purification in our laboratory by using Pd-based catalysts suggests the following perspectives:

1. Exhaustive regeneration of GAC/Pd adsorbent saturated with a 4-CP can be achieved in a two-step approach, incorporating gas-phase HDC by hydrogen followed by oxidation by air. We expect that similar techniques may be suggested for removing other heteroatom-contained organic pollutants (e.g., hydrodesulfurization).
2. Pd/ACC catalysts are good candidates for the liquid-phase HDC showing activity (per g metal) higher than that Pd/GAC or Pd/GFC. The high adsorption capacity of ACC suggested its use in a technology with periodic adsorption and regenerative HDC, in similarity to process described for GAC.
3. Pd/GFC and Pd–Cu/GFC catalyst are promising catalysts for removal of nitrites and nitrates showing activity (per g metal) and selectivity comparable with those of powdered catalysts. However, they are limited by the amount of metal loaded on GFC.

Acknowledgements

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References

[1] Yu. Matatov-Meytal, M. Sheintuch, Ind. Chem. Eng. Res. 37 (1998) 309.
[2] A. Converti, M. Zilli, D.M. De Faveri, G. Ferraiolo, J. Hazard. Mater. 24 (1994) 127.
[3] Yu. Matatov-Meytal, M. Sheintuch, Ind. Eng. Chem. Res. 40 (2000) 609.
[4] A. Kapoor, T. Viraraghavan, J. Environ. Eng. 4 (1997) 371.
[5] P. Bodnariuk, B. Coq, G. Ferrat, F. Figueras, J. Catal. 116 (1989) 459.
[6] J.B. Hoke, G.A. Gramiccioni, E.N. Balko, Appl. Catal. B 1 (1992) 285.
[7] K.-D. Vorlop, M. Prusse, Catal. Sci. Ser. 1 (1999) 195.
[8] M. Sheintuch, Yu. Matatov-Meytal, Catal. Today 53 (1999) 73.
[9] L. Kiwi-Minsker, Y. Yuranov, V. Holler, A. Renken, Chem. Eng. Sci. 54 (1999) 4785.
[10] Yu. Matatov-Meytal, M. Sheintuch, Ind. Eng. Chem. Res. 36 (1997) 3567.
[11] Yu. Shindler, Yu. Matatov-Meytal, M. Sheintuch, Ind. Eng. Chem. Res. 40 (2001) 3301.
[12] A. Stanislaus, B.H. Cooper, Catal. Rev. Sci. Eng. 36 (1994) 75.
[13] S. Khoobiar, The spillover phenomenon of adsorbed species, in: A.B. Stiles (Ed.), Catalyst Supports and Supported Catalysts, Butterworths, London, 1987, p. 201.
[14] Yu. Matatov-Meytal, V. Barelko, I. Yuranov, M. Sheintuch, Appl. Catal. B 27 (2000) 127.
[15] Yu. Matatov-Meytal, V. Barelko, I. Yuranov, L. Kiwi-Minsker, A. Renken, M. Sheintuch, Appl. Catal. B 31 (2001) 233.
[16] Z. Yu, S. Liao, Y. Xu, React. Funct. Polym. 29 (1996) 151.
[17] G. Strukul, F. Pinna, M. Marella, L. Meregalli, M. Tomaselli, Catal. Today 27 (1996) 209.