

Catalytic reduction for water treatment

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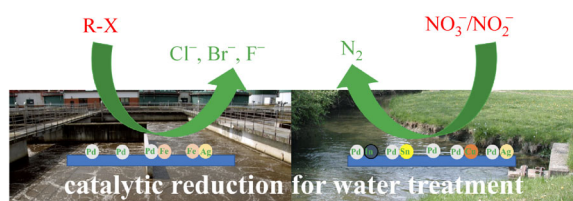
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HIGHLIGHTS

- Catalytic reduction technology for water treatment was reviewed.
- Hydrodehalogenation for wastewater treatment was covered.
- Hydrogenation of nitrate for groundwater remediation was introduced.
- Combination of water splitting with catalytic reduction was illustrated.

GRAPHIC ABSTRACT



ARTICLE INFO

Article history:

Received 9 March 2017

Revised 25 May 2017

Accepted 25 May 2017

Available online 2 July 2017

Keywords:

Halogenated compounds
Nitrate/nitrite contaminants
Hydrodechlorination
Hydrogenation
Wastewater treatment
Groundwater remediation

ABSTRACT

Treating water contaminants via heterogeneously catalyzed reduction reaction is a subject of growing interest due to its good activity and superior selectivity compared to conventional technology, yielding products that are non-toxic or substantially less toxic. This article reviews the application of catalytic reduction as a progressive approach to treat different types of contaminants in water, which covers hydrodehalogenation for wastewater treatment and hydrogenation of nitrate/nitrite for groundwater remediation. For hydrodehalogenation, an overview of the existing treatment technologies is provided with an assessment of the advantages of catalytic reduction over the conventional methodologies. Catalyst design for feasible catalytic reactions is considered with a critical analysis of the pertinent literature. For hydrogenation, hydrogenation of nitrate/nitrite contaminants in water is mainly focused. Several important nitrate reduction catalysts are discussed relating to their preparation method and catalytic performance. In addition, novel approach of catalytic reduction using in situ synthesized H_2 evolved from water splitting reaction is illustrated. Finally, the challenges and perspective for the extensive application of catalytic reduction technology in water treatment are discussed. This review provides key information to our community to apply catalytic reduction approach for water treatment.

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1 Introduction

As a by-product of industrialization and urbanization, water pollution with different contaminants has caused severe environmental issues all over the world [1–4]. The emerging challenge led to the development of various physical, chemical, and biological technologies for water

treatment, such as adsorption, air stripping, ion exchange resins, membrane technology, crystallization, and oxidative and photolytic transformation [1,5,6]. However, challenges are still remaining in the above techniques. For example, further treatments are usually required for the contaminants transferred from water in physical process such as adsorption and air stripping, while possible toxic byproducts may form during chemical process (e.g. catalytic oxidation reactions) due to the poor selectivity for targeted contaminants [7–9]. Biological water treatment was widely adopted in different facilities while potentially long startup times (e.g., weeks) and challenges associated with maintaining activity during intermittent

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Special Issue—Advanced Treatment Technology for Industrial Wastewaters (Responsible Editors: Junfeng Niu & Hongbin Cao)

operations are regarded as the two main disadvantages of biological systems [10,11]. Furthermore, in some cases, the inherent toxicity of industrial waste streams inhibits the application of biological processes [12,13]. The drawbacks of conventional systems, as well as the tightening regulations in treatment of aqueous waste [14,15], stimulate researchers to develop novel technologies to treat water pollutants in an effective and green way.

Catalytic reduction is an emerging and promising water treatment strategy, which has been extensively studied at the bench-scale while its applications in field-scale also demonstrated exciting results on both industrial wastewater and groundwater [10,16,17]. It exhibits good activity and superior selectivity compared to conventional technology, and yields products that are non-toxic or substantially less toxic and more readily biodegradable substances [18,19]. Here, “catalytic reduction” refers to heterogeneously catalyzed reduction, which involves the use of a solid material as the catalyst [20]. Homogeneous catalysis, which involves the use of a liquid-phase catalyst, is not well developed for water treatment, and is not included in this review. Because the separation of catalysts in homogeneous catalytic treatment of water is technically and/or economically unachievable and in many cases the dissolved catalysts would bring potential environmental problems. With adaptable solid catalyst (usually metal or metal on support), a small amount of metal catalyst can speed up the chemical reaction and treat water contaminants efficiently while the separation of catalyst is likely to be easy [21]. It's different from the zero-valent iron (ZVI)-based reduction technologies where the metal (iron) was consumed and the reactivity decreased with time due to the precipitation of metal hydroxides and metal carbonates [22].

There are several excellent reviews published on catalytic reduction of water contaminants, while some of which focused only on Pd-based catalysts, applications in groundwater remediation or limited type of contaminants (only on organohalogen, nitrate, or chlorinated contaminants), or was summarized in 20 years ago [10,23–25]. This review covers two main types of heterogeneously catalytic reduction approaches (i.e. hydrodehalogenation and hydrogenation) for treating industrial wastewater and groundwater with different compositions using various metal catalysts, which provides timely information to our community to apply this approach in practical applications (Fig. 1).

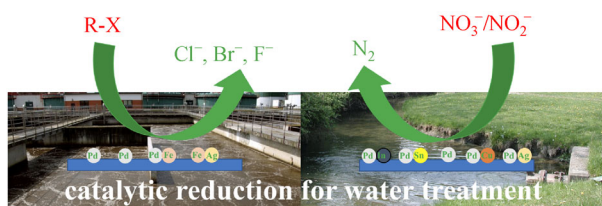


Fig. 1 Illustration of the coverage of this review

2 Catalytic hydrodehalogenation for wastewater treatment

2.1 Halogenated contaminants

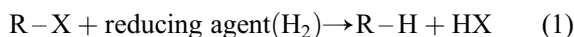
Halogenated compounds are one of the most important chemical products, which are widely used as the end products or intermediates in chemical and agrochemicals. As the byproducts of the rapid development of the halogenated raw materials industry, the release of organohalogen compounds into the natural environment becomes an increasing issue since the late 1960s [26]. Comparing to chlorinated compounds, the organo-fluorides get very limited attention initially. As more and more fluorinated compounds (i.e. organo-fluorides) have been extensively utilized as surfactants, refrigerants, stain-resistant agents and fluoroplastic monomers in our lives, its prevalence in the environment has raised growing ecological and human health concerns. For instance, the US Environment Protection Agency (EPA) started the investigation of perfluorooctylsulfonate (PFOS) in the 1990s. The perfluorooctylsulfonate has been found in the blood of the general population and the health effects which could be linked to such organofluorides include cancer, developmental toxicity, and bioaccumulation, particularly in humans. Although the EPA has not set MCLs for organofluorides, they have established provisional health advisory (PHA) values of $0.2 \mu\text{g} \cdot \text{L}^{-1}$ for PFOS in drinking water [10,25]. Many researches have proved that halogenated compounds showed negative effect on public health, ecological effects, and adverse stratospheric ozone [27]. Unfortunately, no natural means can ameliorate the negative impact caused by their emissions, which makes the development of artificial means for their degradation become critical and urgent.

Currently, there are various methods for halogenated compounds containing wastewater treatment. Among them, the standard treatment strategies include adsorption, incineration, and catalytic/chemical oxidation. The former two methods are usually combined together in practical applications. The contaminants are first stored in adsorbent (e.g. active carbon) and followed by incineration under high temperatures. The second combustion treatment aimed to complete remove such compounds, while some products due to in-complete combustion are far more toxic. Zero valent iron (ZVI) is used in dehalogenation technologies (i.e. the process to detoxify halogenated compounds by removing halogen atom from contaminants via chemical reaction with ZVI) [28]. The redox reaction would result into irreversible corrosion of raw material (ZVI) leading to cost increase. Moreover, the high concentration of produced Fe²⁺ ion in the water may create potential environmental problem. Another common used approach for wastewater treatment is the advanced oxidation technologies (AOT), where UV photolysis was combined with supercritical oxidation or ozonation [29].

However, the limitations of UV/oxidation are obvious: 1) good transmission (which is rare for industrial waste water) to UV light is required because high turbidity may cause interference; 2) required pre-treatment to remove solid contaminants for minimizing cleaning and maintenance of UV reactor, which may increase the investment and cost of the system; 3) selectivity is hard to control due to the intrinsic feature of the oxidation reaction, which lead to the formation of byproducts or even more toxic products; 4) extra process is required in the downstream to remove the residual oxidizers; 5) higher energy consumption than competing technologies, which results into the cost issue.

2.2 General mechanisms of catalytic hydrodehalogenation

The reaction of catalytic hydrodehalogenation can be illustrated by Eq. (1), involving hydrogenolysis of one or more C-X (X = F, Cl, Br) bonds. The halogen atom would be removed from halogenated compounds by forming a halogen acid (HX) after reaction which is non-toxic or substantially less toxic.



Compared with conventional methodologies such as separation or oxidation, following advantages from catalytic hydrodehalogenation are highlighted: 1) low temperature reaction which would save energy and cost; 2) high selectivity leading to the formation of non-toxic or less toxic product; 3) absence of post-treatment due to no induced free-radical generation; 4) applicable in both batch and continuous operation; 5) possible use as a pretreatment step to detoxify concentrated waste streams prior to other technology such as biodegradation.

Although it is not clear how exactly hydrodehalogenation proceeds on a catalyst surface due to the difficulty of identifying reaction intermediates during the reaction in liquid environment, it's widely accepted that the catalytic reaction follows the classical Langmuir-Hinshelwood mechanism. It involves several steps. First, the halogenated compounds adsorb at active sites on catalyst surface while H_2 dissociatively adsorbs on the active sites successively generating surface H atoms. Then, these surface adsorbed species react with one another via hydrogenolysis to form various surface intermediates. Finally, the products of dehalogenated compounds and halogen acid desorb from surface and go back into the aqueous phase (Fig. 2).

2.3 Catalysts in catalytic hydrodehalogenation for wastewater treatment

Many metal-based catalysts have been tested in catalytic hydrodehalogenation for wastewater treatment, which can be categorized roughly into Pd and non-Pd based catalysts. A summary of both types of catalysts reported in literature

since 2012 (few work before 2012 is added to make the review fruitful) is given in Table 1, which cover following contents: 1) the nature of the catalysts used for hydrodehalogenation; 2) the reaction conditions (temperature and pressure) employed in the catalytic hydrodehalogenation; 3) the removal efficiency and selectivity to major dehalogenated products.

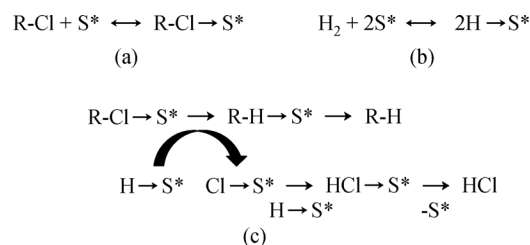


Fig. 2 General reaction mechanism for hydrodehalogenation (chlorinated compounds as example): (a) Chlorinated compounds adsorption; (b) H_2 dissociative adsorption; (c) Catalytic reaction on the surface

2.3.1 Pd based catalysts

Organic synthesis work indicated that Group VIII B metals (e.g. Pd) are good catalysts for the hydrodehalogenation of halogenated organic compounds. Actually, supported Pd is the most used catalyst in catalytic hydrodehalogenation of contaminants in water owing to its property to dissociate H_2 and promote the hydrogenolytic scission of C-X bond. The activity of the Pd can be attributed to the dual nature [Pd^{n+} - Pd^0] of palladium species on the catalyst surface, where Pd^0 is the active site for hydrogen dissociative adsorption while Pd^{n+} site serves the adsorption site for halogenated compounds [42].

The type of supports showed great effect on the catalytic performance of the Pd catalysts. Active carbon (AC), Al_2O_3 , TiO_2 , CeO_2 , and SiO_2 are the common supports for Pd in catalytic hydrodehalogenation [43–45]. For example, Díaz et al. used 0.5% (w/w) palladium supported on different supports including, AC, Al_2O_3 , carbon nanofiber (CNF), high surface area graphite (HSAG), and ZSM-5 zeolite, for hydrodechlorination of trichloroethylene (TCE) in water. The reaction proceeded in a batch reactor at mild conditions (27°C – 67°C) with a TCE concentration close to 1000 ppm [30]. To address the issue of the low hydrogen solubility in water, the authors used formic acid (FA) as hydrogen source due to its intrinsic liquid feature at room temperature and its high solubility in water. The effect of the different FA/TCE ratios (from 10 to 450) was investigated to obtain the optimal operation conditions. The activity of the five catalysts was found to follow the order: 0.5%Pd/CNF > 0.5%Pd/HSAG > 0.5%Pd/ Al_2O_3 > 0.5%Pd/ZSM-5 > 0.5%Pd/AC, which was attributed to the different strength of the interaction (determined

Table 1 Summary of catalytic hydrodehalogenation for wastewater treatment

target compound ^{a)}	catalyst ^{a)}	condition ^{b)}	removal efficiency	main products/activity	Ref.
TCE	Pd/CNF	80°C	~100%	10 ⁵ L·mol ⁻¹ Pd·min	[30]
MCPA	Pd-Pt/AC	RT	60%	NA	[31]
4-CP	Pd/resin	RT	91.8%	1608 mmol·g _{Pd} ⁻¹ ·h ⁻¹	[32]
Bromate	Pd/ CNF/SMF	RT	~45%	NA	[33]
TCE/MCB	Pd/ Magnetite	RT	≥90%	22500/3700 L·g ⁻¹ ·min ⁻¹	[34]
2,5-DBA	Pd ²⁺ /FHC	RT	100%	Aniline/0.0412 min ⁻¹	[35]
TBBPA	Pd/NG	RT	100%	0.166 mmol·L ⁻¹ ·min ⁻¹	[36]
2,4-DCP	Pd-Fe/SiO ₂	RT	97%	Phenol	[37]
p-CP	B/Fe/Pd	RT	98.7%	Phenol	[38]
TCE	Pd-Fe/BNPs	RT	NA ^{c)}	NA ^{c)}	[39]
1,2,3,4-TCDD	Ag/Fe	RT	>90%	0.0421 L·h ⁻¹ ·m ⁻²	[40]
4-CP	Ni-Fe	RT	100%	0.00214 L·min ⁻¹ ·m ⁻²	[41]
MCA	Ni-Fe	45°C	>88%	2.18 L·g ⁻¹ ·h ⁻¹	[17]

Notes: a) Full name of the target compounds and catalysts refer to **Nomenclature**; b) All in atmosphere pressure, RT: room temperature; c) Deactivation mechanism study only

by the enthalpy of adsorption) between TCE and supports. Strong interaction prevented the chemical reaction with hydrogen formed. Furthermore, the alternative hydrogen source from FA decomposition was believed to be technically feasible for TCE, and the optimum FA/TCE ratio was determined to be 35. High FA concentrations led to competitive adsorption of both reactants and would inhibit the desired reaction between hydrogen and TCE.

Activated carbon fibers (ACF) and sintered metal fibers coated by carbon nanofibers (CNF/SMF) were employed as support for Pd for the catalytic removal of bromates in wastewater with hydrogen as the reductant [33]. It was observed that Pd supported on CNF/SMF showed better performance than on ACF, which was attributed to that CNF/SMF minimized the mass-transfer limitation, leading to an efficient catalyst use. Moreover, the authors demonstrated that it was possible to reduce bromates in both batch and fixed-bed reactors, while hydrogen partial pressure played a key role on the bromate reduction rate. However, Pd/CNF/SMF showed low stability in the continuous system for real industrial wastewater, which was attributed to two factors: competitive adsorption and precipitation formation. The presence of other ions in the wastewater would competitively adsorb on active sites and accordingly inhibit the bromate reduction. More importantly, high calcium content of the wastewater (1000 mg·L⁻¹) with basic pH would lead to calcium salts precipitation inside of the reactor as well as on the catalyst surface, which finally caused system plugging. The authors proposed to add an acid solution to avoid precipitation of calcium salts for an adequate performance (Fig. 3).

Polymer materials were also used as supports for Pd in catalytic hydrodehalogenation. Jadbabaei et al. prepared Pd catalysts supported on three neutral resins (MN200, MN100, and XAD4) and two anion exchanged resins

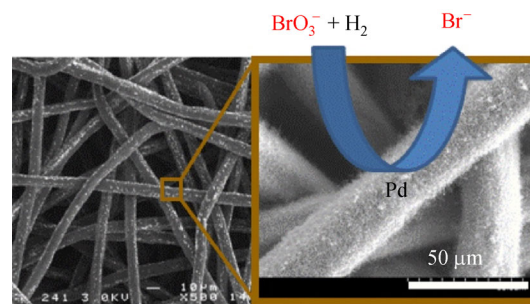


Fig. 3 Catalytic removal of bromates in wastewater over Pd supported CNF/SMF [33]

(IRA910 and IRA96) for hydrodechlorination of 4-chlorophenol (4-CP) [32]. The resins were selected as the supports to promote the target compound (4-CP) adsorption. The two types of resins showed different pH favoring values, adsorption and reduction were both faster at acidic pHs for the neutral resins but faster at basic pHs for the anionic resins. Moreover, neutral resins were observed to be more resistant to the poisoning effect of Cl⁻ than ionic resins. The authors proposed that the anion exchange nature of ionic resins facilitated adsorption of Cl⁻ and led to the formation of more PdCl₃⁻ and PdCl₄²⁻ species, and finally caused partial deactivation. Although the activity loss existed after multiple reaction cycles due to the accumulation of phenol on the catalyst surface, the catalysts can be easily regenerated while the activity can be largely restored. In addition, the surface reaction was determined to be the rate limiting step based on the well-fitting results from kinetic modeling using a Langmuir-Hinshelwood model, which confirmed the enhancing effect of adsorption on the catalytic reactivity. Furthermore, they presented a novel strategy to significantly reduce the

volume of secondary waste from resin regeneration by the integration of adsorption and catalytic treatment. The authors proposed to examine the potential benefits by running adsorption and catalytic reduction in sequence as the future work, which aimed to decrease the need for H_2 consumption while increase treatment efficiency simultaneously.

Emerging materials such as carbon nanotubes and graphene gained increasing interest in many applications including catalysis due to their unique properties [46–48], which were also employed for catalytic hydrodehalogenation. For example, Li et al. used palladium decorated nitrogen-doped graphene (Pd/NG) as catalyst to remove halogenated contaminants (i.e. tetrabromobisphenol A, TBBPA and triclosan, TCS) from water and further investigated the removal mechanism by combining experimental investigation with theoretical analysis [36]. Pd/NG catalyst demonstrated better performance for the removal of TBBPA from water compared to the Pd/graphene (Pd/G) and Pd/carbon (Pd/C). It can be attributed to the more favorable adsorption and activation of TBBPA molecular on the Pd/NG surface, leading to a higher TBBPA removal rate by Pd/NG, which was illustrated by combining Langmuir-Hinshelwood kinetic modeling and Density Functional Theory (DFT) calculations. The kinetic modeling determined the surface rate constant k_r and the equilibrium adsorption constant K of Pd/NG and Pd/G catalysts to be $0.166 \text{ mmol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$ and $0.553 \text{ L}\cdot\text{mmol}^{-1}$, and $0.155 \text{ mmol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$ and $0.458 \text{ L}\cdot\text{mmol}^{-1}$, respectively, which indicated that Pd/NG had better adsorption and surface catalytic abilities than those on Pd/G. With DFT, the authors further estimated the reaction energy barrier (E_a) for TBBPA activation and the energetically favorable adsorption energy (ΔE_{ads}) over the different simulated catalysts (i.e. Pd adsorption on NG or G). And it was found that Pd/NG had a lower reaction energy barrier as well as a more energetically favorable adsorption energy. The authors also studied the influence of various operational parameters including temperature, pH and catalyst dosage on the dehalogenation of TBBPA, and found that the higher temperature, pH and catalyst dosage facilitated the reaction while environmental factor, dissolved humic acid, displayed negative effect. The study suggested the promising potentials of graphene-based materials as supports for Pd in the reductive removal of halogenated pollutants from water.

The separation of solid catalyst (especially small size particles) from liquid environment (water) was considered as one of the main drawbacks for catalytic reduction of contaminants in wastewater. Hildebrand et al. developed palladium catalysts on the basis of colloidal magnetic carriers to address this issue [34]. The Pd supported on magnetite catalyst was tested in batch reactor for hydrodechlorination (HDC) of chloro-hydrocarbons, such as trichloroethene (TCE) and monochlorobenzene (MCB). The catalyst exhibited extreme high activities which had

never been described before for Pd-containing catalysts (e.g., Pd NPs, Pd/Au NPs or Pd/ Al_2O_3) in aqueous phase HDC reactions. More importantly, compared with other nano-catalyst, the ferri-magnetism of the carrier enabled an easy separation of this nano-catalyst from the treated water by magnetic separation. In addition, the catalyst stability and long-term performance results showed that the catalyst remained at a high activity level after many reaction cycles. All these results demonstrate that Pd/magnetite catalysts have the potential for recycling and repeated use at a high activity level.

An interesting work done by Wu et al. [35] examined the catalytic effects of Cu^{2+} , Ag^+ , and Pd^{2+} on the reducing ability of the ferrous hydroxy complex (FHC) suspensions for the reduction of 2,5-dibromoaniline (2,5-DBA), where the metal ions were used as the catalysts which was completely different with the above metal (Pd) catalytic system with Pd^0 as active species. It was observed that the target compound (2,5-DBA, $50 \text{ mg}\cdot\text{L}^{-1}$) could hardly be debrominated by FHC alone while Cu^{2+} , Ag^+ , and Pd^{2+} significantly promoted the catalytic reactivity of FHC on 2,5-DBA reduction. Moreover, the authors proposed varying degradation mechanisms and pathways of 2,5-DBA behind for different metal ions based on their different influence on the reduction capacity of FHC as well as the products distribution. Furthermore, two different types of mechanisms were proposed for Cu^{2+}/Ag^+ and Pd^{2+} , respectively. For Cu/Ag, the formation of galvanic cells was considered to be responsible for the promoted performance where FHC served as the anode and was oxidized, while 2,5-DBA would be reduced at the cathode (Ag, Cu) leading to the production of partially reduced products, 2-bromoaniline and 3-bromoaniline. For Pd, the limited steps were believed to be the generation of activated hydrogen species (H^*) from Pd-water interface and the resulting intermediates, which would finally react with 2,5-DBA and lead to complete reduction. Moreover, the authors considered that hydrogenolysis was a significant pathway for the reaction due to different levels of by-products during 2,5-DBA transformation. Accordingly, they proposed a two-step pathway for the 2,5-DBA debromination consisting of losing one bromine atom to form 2-BA or 3-BA and then the formation of aniline.

The other common approach to enhance the performance of Pd-based catalysts for catalytic hydrodehalogenation is by decorating Pd directly to form bimetallic catalysts [49,50]. Witońska et al. investigated the reaction performance of a group of bimetallic Pd-Fe/ SiO_2 and Pd-Fe/ Al_2O_3 catalysts containing 5 wt.% of Pd and 1wt.%–20 wt.% of Fe for catalytic hydrodechlorination of 2,4-dichlorophenol (2,4-DCP) [37]. Compared to monometallic Pd or Fe catalyst, both types of catalysts demonstrated high activity and high selectivity to phenol, which was very attractive. However, Pd-Fe/ Al_2O_3 catalysts with a higher dispersion of active phase had lower activity than Pd-Fe/ SiO_2 systems, while the selectivity to phenol was

comparable for both types of bimetallic catalysts. The promotion effect of selectivity to phenol over the bimetallic catalysts was believed to be the addition of iron into supported Pd systems, which prevented further reduction of phenol into cyclohexanone, a common side reaction on the surface of monometallic palladium catalysts. Furthermore, the interactions between Pd and Fe on the surface of bimetallic catalysts were regarded as the reason for this behavior based on the further characterization results (XPS and TPR-H₂). However, the interactions were proved to be not from the intermetallic Pd_xFe_y phases revealed by XRD and time-of-flight secondary mass spectrometry (ToF-SIMS) studies. The intrinsic mechanism of the improved activity and selectivity of Pd-Fe was still unclear due to the overlapping effects of active phase dispersion, surface structure, and chemical composition. Bentonite-supported bimetallic Fe/Pd nanoparticles (B/Fe/Pd) were adopted by Zhou et al. for catalytic hydrodechlorination of p-chlorophenol (p-CP) in wastewater. The experiment in a batch reactor was carried out using 5 g·L⁻¹ of B/Fe/Pd in 120 min and 98.7% of p-CP was removed while the selectivity to phenol reached 92.3% [38].

Catalyst stability is one of the key factors affecting potential practical applications of catalytic reduction on water treatment. Supported Pd-based catalysts showed high hydrodehalogenation activities while the rapid deactivation was also observed. Halogen poisoning, metal sintering, leaching of the active phase, and surface fouling were believed to be the four main reasons [31]. Many efforts were made to overcome this drawback. Diaz et al. analyzed the deactivation mechanism of monometallic Pd and bimetallic Pd-Pt or Pd-Rh on activated carbon catalysts in the hydrodechlorination (HDC) of the 4-chloro-2-methylphenoxyacetic acid (MCPA) herbicide [31]. The significant and progressive deactivation with a fairly low residual activity was observed on Pd/AC catalyst. With regeneration by NaOH washing, the activity was recovered partially, but a fairly rapid deactivation happened in the next test. The authors attributed the loss of activity to the accumulation of organochlorinated on the catalyst surface. The bimetallic Pd-Rh/AC and Pd-Pt/AC catalysts suffered from the same deactivation pattern with Pd/AC but with a higher stability. The authors used a simple method to modify the activated carbon support by HNO₃-oxidation. The improved stability of the Pd catalyst was achieved with a significantly higher value of residual activity although a similarly rapid deactivation was observed. The surface oxygen groups generated during the oxidation procedure in the Pd/AC_{OX} catalyst was considered to improve the metal dispersion, leading to the reduction of adsorption of MCPA, which is the main cause responsible for the deactivation. Although none of the three catalysts exhibited a really satisfactory stability, introducing surface oxygen groups over activated carbon via oxidation was a promising way to reduce the

adsorption of reaction species as well as the deactivation, which further provided new insight to promote the stability of Pd based catalysts.

Another work done by Han et al. proposed a solute-induced catalyst deactivation mechanism with analysis by carbon isotope fractionation over Pd-Fe bimetallic nanoparticles during trichloroethene (TCE) hydrodechlorination [39]. Four types of deactivation and the corresponding possible reasons were summarized based on the different water media (Fig. 4): 1) Surface deposition, buildup of mineral or organic carbon deposits due to the aging of bimetallic nanoparticles (BNPs) in deionized water and humic acid; 2) Catalyst poisoning, specific interactions between SO₃²⁻/Cl⁻ ions and Pd sites disable the catalyst functions; 3) Anodic passivation, iron corrosion inhibition by NO₃⁻ and HCO₃⁻ limits the production of H₂, and 4) Selective deactivation, ethene hydrogenation over BNPs aged in SO₄²⁻ and HPO₄²⁻ solutions leading to surface sites fouling. The findings suggest the great challenge of current technology.

2.3.2 Non-Pd based catalysts

Non-Pd based catalysts were also developed for catalytic hydrodehalogenation [51,52]. Wang et al. investigated the hydrodechlorination of 1,2,3,4-tetrachloro dibenzo-p-dioxin (1,2,3,4-TCDD) in the presence of bimetallic Ag/Fe catalysts [40]. Kinetic study showed that Ag/Fe catalyst could rapidly transform 1,2,3,4-TCDD to less chlorinated polychlorinated dibenzo-p-dioxins (PCDDs) while the reaction showed a pseudo-first-order with respect to the reactant concentration. The surface-area-normalized rate constant (k_{SA}) was used to evaluate the activity with different silver loading in Ag/Fe. The k_{SA} corresponding to the silver bulk loading of 0.0060 mol%, 0.0125 mol% and 0.0228 mol% was determined to be 0.0155, 0.0399 and 0.0421 L·h⁻¹·m⁻², respectively. The authors compared the results of this study to their prior work with bimetallic Pd/Fe as the catalyst for 1,2,3,4-TCDD hydrodechlorination, and observed a faster reaction with TCDD as well as much slower rate for the intermediates of trichlorodibenzo-p-dioxins (TrCDDs), dichlorodibenzo-p-dioxins (DCDDs) and monochlorodibenzo-p-dioxin (MCDD). Thus, they considered that bimetallic Ag/Fe would be a suitable candidate for rapid hydrodechlorination of PCDDs to less or non-chlorinated products. Moreover, based on the intermediate and final products identified and quantified, the author concluded that the process of hydrodechlorination of TCDD by bimetallic Ag/Fe was of stereoselectivity and stepwise, which is a chlorine atom being replaced by a hydrogen atom in a single reduction step. Accordingly, a possible mechanism and dechlorination pathway for this Ag/Fe system was proposed, which is a typical stepwise route with the pathway of 1,2,3,4-TCDD to dibenzo-p-dioxin (DD) via 1,2,4-trichlorodibenzo-p-dioxin (1,2,4-TrCDD), 1,2-dichlorodibenzo-p-dioxin (1,2-DCDD) and

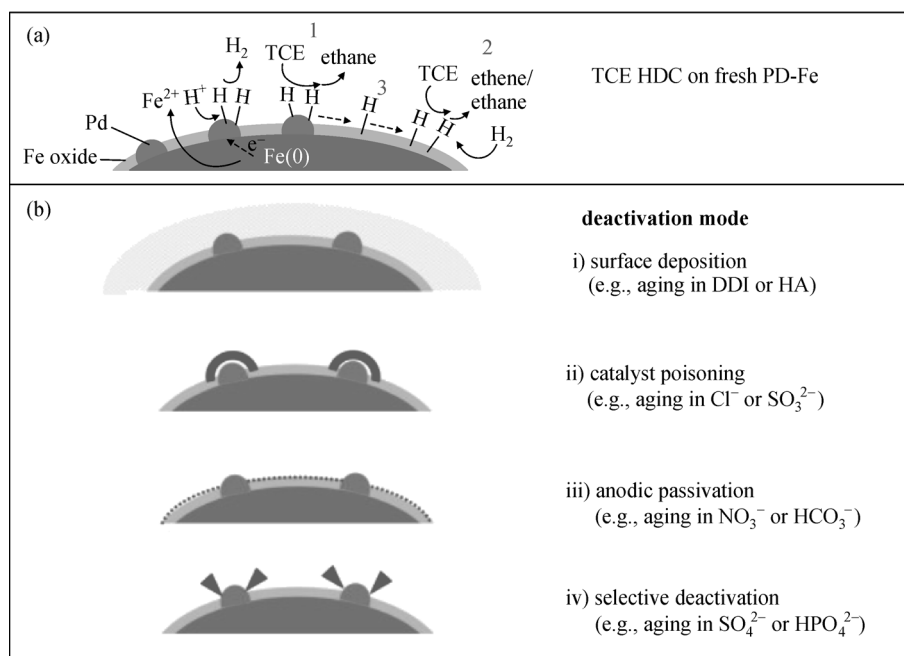


Fig. 4 Deactivation mechanisms of Pd-Fe bimetallic nanoparticles in different media [39]: (a) Mechanism of TCE HDC over fresh Pd-Fe catalyst; (b) Four deactivation modes of Pd-Fe catalyst

monochlorodibenzo-p-dioxin (MCDD) as the major one.

Ni-Fe bimetallic catalyst was also employed for catalytic dechlorination [41]. The catalyst was prepared by ball milling (BM) and showed high dechlorination activity for 4-chlorophenol (4-CP). It was found that the dechlorination activity of the Ni-Fe catalyst can be greatly enhanced by increasing Ni content and milling time, which was mainly ascribed to the homogeneous distribution of Ni nanoparticles (50–100 nm) in bulk Fe. Scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS) with image mapping provided visualized evidence for this assumption. The authors considered that the reason for the increased activity with the addition of Ni can be attributed to the mechanism of catalytic hydrogenation, where the adsorbed atomic hydrogen is responsible for the enhanced reactivity. Moreover, both the activity and stability of the Ni-Fe catalyst prepared by BM was observed higher than that via a chemical solution deposition (CSD) process. Kinetic study suggested that pH of the solution had a significant effect on the dechlorination of 4-CP, the dechlorination rates of 4-CP decreasing with increasing pH. The authors proposed that the formation of passivation film on the bimetallic surface, which was significantly accelerated due to enhanced pH, was responsible for the rate decrease.

Field-scale wastewater treatment with Ni-Fe bimetal was also performed [17]. The experiments were carried out for catalytic hydrodechlorination of monochloroacetic acid (MCA), which is cytotoxic and known to damage DNA and act as a carcinogen [53]. Furthermore, the intrinsic toxicity of MCA inhibits its biodegradation while only low

concentrations of MCA can be successfully biodegraded. However, degradation of MCA in industrial wastewater treatment was believed to be challenge, leading to an urgency to develop effective ways to treat MCA [54]. One to two tons of real industrial wastewater containing MCA (1.7 g·L⁻¹) from an enterprise in China was degraded in batch reactor in three different periods with 4–10 successive cycles per period. The initial pH and temperature were measured as 1.0–2.0 and 42°C–45°C, respectively, while continuous stirring was required to thoroughly mix the added bimetal and wastewater. During each period, the bimetal that had been added during the first cycle was used successively for the next several cycles. The Ni-Fe bimetal powder prepared by mechanical milling showed exciting performance for degrading high concentrations of MCA in wastewater. It was observed that the removal efficiency of chloride over MCA could reach more than 88%, which made the subsequent biological treatment possible because the biological toxicity of MCA wastewater was reduced significantly while the pH was adjusted to ~4–6 simultaneously.

Fluorinated compounds are very unique as they are generally more stable than other halogenated counterparts [55]. As a result, the initial attempts showed that the conventional Pd supported catalyst displayed low activity toward organofluoride. In organic chemistry, Rh based organometallics are generally considered among the most effective catalysts for C-F activation. Rh based catalysts have found use in several reported fluorochemical degradation studies although such harsh chemical defluorination condition (e.g. high temperature, pressure, organic

solvent involvement) could not be directly applied for water treatment process.

Baumgartner and McNeil [56] first successfully found a supported Rh heterogeneous catalyst (5% Rh/Al₂O₃) works for degradation of an aromatic organofluoride in environmentally relevant conditions (aqueous, 1 atm of H₂ gas). Fluorobenzene underwent a rapid tandem hydrodefluorination and hydrogenation reaction ($t_{1/2} \sim 0.2$ h) to form fluoride (F⁻) and cyclohexane as stable final products. With the success, McNeill and coworkers systematically investigated the hydrodehalogenation of polyhalogenated benzenes. The catalyst has a special preference toward fluorine removal. Hexafluorobenzene is degraded more than 10 times faster than hexachlorobenzene which could be caused by the steric hindrance [57,58].

In the meantime, Yu and Chiu [59] used vinyl fluoride (VF) as a model compound for reductive transformation of fluorine based alkanes under different reaction media. The authors found that a fast hydrogenation reaction is the leading route for gas phase VF, which forms saturated fluoro-ethane as the major final product. To the contrary, hydrogenation of VF is significantly suppressed in the liquid water. The limited H₂ concentration in the liquid water as well as the significant adsorbed water molecules on the catalyst surface created a major mass transfer limitation for VF being hydrogenated. Experiment and kinetic calculations exhibit the reaction was first order to both VF and rhodium catalyst and proceeded predominantly through hydrodefluorination route instead.

2.3.3 General summary on catalytic hydrodehalogenation reactivity

Generally, the target compounds in the hydrodehalogenation reaction fall into two categories: aliphatic and aromatic halogenated compounds. The major aliphatics are the short chain halogenated-hydrocarbons with a carbon number less than 4 e.g. trichloroethylene, trichloromethane while the aromatics are chlorobenzene, chlorophenol and their derivatives. In most cases, halogen removal from aromatic compounds has been found to be less facile than dehalogenation of aliphatics. This is because the C-X bond in an aromatic halogenated compound (Ar-X) possesses some double bond character (i.e., X is attached to carbon by little more than single pair of electrons) while the halogen atom is attached to carbon by a pure single bond in an aliphatic halogenated compound (R-X). Moreover, Ar-X is also stabilized by resonance effect caused by benzyl ring structure. All these factors make Ar-X much less reactive than R-X toward nucleophilic substitution reactions (De-halogenation mechanism).

In addition, the hydrodehalogenation activity tendency is also structure sensitive in each group. For aliphatics, it has been reported that the catalytic hydrodehalogenation of

halogenated ethene becomes progressively easier to react when it loses its halogens. For example, Based on experimental results, the activity order followed dichloroethylene>trichloroethylene>tetra chloroethylene [60]. However, the catalytic hydrodehalogenation of the chlorinated methane (e.g. carbon tetrachloride, chloroform and dichloromethane) becomes more and more difficult when it loses its chlorines. It was reported that the carbon tetrachloride reacted 15 times faster than chloroform over Pd/Al₂O₃ catalyst [61]. Also, there are some specific inorganic chlorinated compounds which are very difficult to remove due to their stable structures. A typical example is the perchlorinated compounds.

2.3.4 General considerations on hydrodehalogenation catalyst design and preparation

The activity and selectivity of hydrodehalogenation catalyst can be affected by many variables, which commonly involves the catalysts synthesis and composition. The following parameters have to be paid particular attentions: 1) catalyst precursor, 2) support, 3) additives, and 4) structure sensitivity [62–64].

2.3.4.1 Catalyst precursor

Metal catalysts' precursor influences the properties of final catalysts. It's well known that the interaction of metallic precursor with catalytic support exhibited crucial effect on the final catalyst metal dispersion. Thus, choosing suitable metallic precursor is critical for preparing highly dispersed catalyst. In addition, the self-poisoning effect, which commonly originates from ions in the precursor, has also to be considered. Many ions may poison the catalysts before their applications in the reaction. One of the best practices for a metallic precursor choice is to pick those free of chloride ions.

2.3.4.2 Support

In addition to the catalyst metal, the type of support also illustrated great effect on the catalytic performance for dehalogenation in water including selectivity, catalytic activity and catalyst stability, which has been reported by a number of works. Changing of support nature could influence on a formation of Pd-containing active site which modifies the electronic properties of palladium as well as the adsorption property. Inorganic supports including alumina, silica, zeolites, and other metal oxides such as MgO aren't suitable for catalytic hydrodehalogenation in water since the HX acids formed in the reaction would readily attacked the supports, which results into the degradation and deactivation of the catalyst. Another typical support is carbon materials (activated carbon, carbon nanotubes, or graphene), which are inert to the acid

and have been extensively studied for the reaction. For example, it has been found that activated carbon could facilitate the adsorption of hydrophobic organic halogenated compounds, which accordingly resulted into enhanced performance for catalytic hydrodehalogenation in the water. It's worthy to note that several variables including surface oxygen groups, pore-size distribution, and even the amount of impurities would affect the performance of activated carbon in the reactions. Therefore, it is still hard to build a relationship between only one of these properties and the performance of the catalysts, while the comprehensive understandings are required [62].

2.3.4.3 Additives

Obtaining highly stable and active catalysts is still one of the most important challenging tasks for catalytic hydrodehalogenation of contaminants in water. One practical approach to improve the selectivity, stability, and activity of the catalysts is by using bimetallic catalysts while the alloy of Pd and an inactive metal is the most widely adopted formulation. Metals such as iron, rhenium, silver, gold, cobalt, or potassium have been attempted in this system. The addition of the second metal leads to geometric effect such as the dilution of active Pd species which may alter the reaction rates of different reaction steps and finally optimize product distributions, or serves as the electric factors which may affect the adsorption intensity between Pd and targeted molecules and finally the selectivity of the catalysts. Degree of the interaction between Pd and the added metal and distribution of the two metals on the supports are the two major aspects that need to be considered when designing and preparing such catalysts.

2.3.4.4 Structure sensitivity

Though there is no general consensus about the mechanism of structure sensitivity on the hydrodehalogenation reaction, the existed great effect already make the investigation over it valuable [65]. However, due to the complex reaction system in water treatment, the detailed study is very challengeable. The reaction conditions, including catalyst supports, gas or liquid-phase reaction, reactants for hydrodehalogenation, etc., varied from one study to another, making it difficult to obtain a unified picture of the chemistry involved. Moreover, the inhibitory effect of HX formed during the reaction also makes it difficult to compare the results. Therefore, the consideration of structure sensitivity on the catalyst design and preparation required much more work.

During the last few years, although there is still some research on developing new catalyst, many of the research on catalytic hydrodehalogenation focuses on investigating the kinetics, mechanism and influence of the solvent (i.e.

pH) in order to better understand the theoretical aspects of reaction. Nanoscale catalysts have already been proved to potentially replace conventional heterogeneous catalysts due to their unique properties. The application of nano-sized catalyst in catalytic reactions may make it much more competitive in wastewater treatment. Thus, a feasible research approach is to develop new nano-catalysts and/or optimize current available nano-sized catalysts for reductive reaction (hydrogenation, hydro-dehalogenation and hydrogenolysis). This effort will lead to an engineered treatment system that can be studied for long-term operational stability and efficiency to treat industrial wastewater.

3 Application of catalytic hydrogenation for nitrate/nitrite reduction

Nitrate/nitrite are contaminants in water due to their threat to human health. Drinking water in high concentrations of nitrate can lead to methemoglobinemia caused by a lack of oxygen in blood. In addition, long-term exposure of nitrates can also lead to cancer [66]. Nitrate is highly soluble and is a natural constituent of plants. Varying levels in vegetables were found depending on the amounts of fertilizers. Nitrates in groundwater come from natural sources such as rainfall and excess irrigation, where the nitrates in soil may eventually reach groundwater or point sources, such as municipal sewage treatment systems and septic tanks [2].

3.1 Nitrate/nitrite treatment methods

Nitrates are commercially treated based on four different methods, ion exchange, reverse osmosis, electrodialysis, and biological denitrification [67,68]. Ion exchange, reverse osmosis and electrodialysis are physical methods to separate nitrates from water and lead to a concentrated waste stream of nitrate. Biological denitrification transforms nitrates to nitrogen through reduction reaction, but it's a slow reaction process. In all these commercial methods, the common concern is the waste management cost [69]. Hence, other alternative approach which could efficiently reduce the nitrates to non-toxic compounds attracts more and more interests recently.

Nitrate reduction via chemical reaction using a catalyst (catalytic reduction method) was first introduced in the late 1980s. In a catalytic reaction, nitrate is reduced with a catalyst and hydrogen. The advantage of catalytic denitrification technique compared to other commercial techniques is the reduced waste management cost. In addition, the process is generally run at room temperature and atmospheric pressure, thus is an energy efficient process [70]. The technical and economic feasibility of catalytic hydrogenation of nitrate/nitrite in water was

demonstrated at groundwater sites in field-scale [10,71]. The treatment was conducted in a three packed-bed reactor system with a water flow rate of $7 \text{ m}^3 \cdot \text{h}^{-1}$, while two of them were design for catalytically reducing NO_3^- (with 200 kg of 1.0 wt% Pd-0.25 wt% Cu/ γ -alumina as catalyst) and NO_2^- (with 150 kg of 1.0 wt % Pd/ γ -alumina as catalyst).

Clearly, nitrate reduction for groundwater treatment demands very active catalysts since the reaction has to be performed at the temperature of the groundwater. Moreover, a high selectivity is necessary to avoid the production of ammonium ions by over reduction of the intermediates of stepwise nitrate hydrogenation. Ammonium formation is the main concern of the process because it is also a contaminant in water (limits on several nitrogen-containing compounds in potable water set by World Health Organization are: $50 \text{ mg} \cdot \text{L}^{-1} \text{ NO}_3^-$, $0.5 \text{ mg} \cdot \text{L}^{-1} \text{ NO}_2^-$, $0.5 \text{ mg} \cdot \text{L}^{-1} \text{ NH}_4^+$) [72]. In this section, several main nitrate/nitrite reduction catalysts from recent literatures are covered to help better understand and accelerate practical application of catalytic hydrogenation for nitrate/nitrite reduction in groundwater.

3.2 Catalysts for nitrate/nitrite reduction

3.2.1 Bimetallic catalyst

It has been demonstrated that a bimetallic system is the priority option for nitrates reduction [24]. Commonly, the bimetallic catalysts consist of a precious metal (Pt or Pd) and an additive (Cu, Ni, Fe, Sn, In, Ag) which can catalyze nitrates/nitrites to final products such as nitrogen and ammonium. Main task with the bimetallic catalysts is to find an optimal formulation that compromises between nitrate removal and nitrogen selectivity. So far, many multiple combinations have been tested [73,74]. In general, Pd showed better performance than Pt for nitrate reduction in both conversion and selectivity [75,76], while Sn was determined to be the best promoter especially for selectivity [77,78]. The metal ratios were believed to be the key role in promoting performance of nitrates/nitrites reduction [79]. The metal ratios changed metal dispersion and exposed active phases. Moreover, metal interaction was also found to be closed related to the catalytic performance.

The formation of ammonium, one undesired reaction during nitrates/nitrites reduction, was observed to be related to the rise of the pH of water [24]. Impact of OH^- can be minimized by the neutralization with acid addition or adopting acidic support. Thus, the acidic support was suggested to be the promising option compared to basic one, which contributes on controlling OH^- concentration around active metal as well as constructs favorable environment for nitrogen formation. In respect to supports, bimetallic catalyst supported on activated carbon (AC)

exhibited higher selectivity to nitrogen compared to other supports such as SiO_2 , TiO_2 , ZrO_2 or Al_2O_3 . The higher metal dispersion and unique surface chemistry of the activated carbon contributed to the superior performance. Therefore, good adsorption ability to nitrates/nitrites, high metal dispersion, and slightly acidity are considered as the three criteria for a superior bimetallic catalyst for nitrates/nitrites reduction. Typical bimetallic catalysts are introduced below.

3.2.1.1 Pd-Cu bimetallic catalyst

Copper has been first reported as a suitable second metal in Pd catalyst. A bi-functional mechanism for nitrate hydrogenation with Pd-Cu catalyst was proposed by Epron et al. [80] that nitrate hydrogenation occurred first on copper sites through a direct redox mechanism and copper was maintained in metallic state by chemisorbed hydrogen from palladium. Trawczyński et al. reported a Pd-Cu/active carbon catalyst for nitrate reduction [81]. The reaction runs at room temperature (25°C) and atmospheric pressure giving a conversion of about 87% in the first 30 min with a Cu/Pd atomic ratio of 0.8. The nitrates are reduced to nitrogen (47.5%), ammonium (52%) and small amounts of nitrites (0.5%). The authors compared the activity of catalyst prepared by catalytic reduction method and incipient wetness impregnation method. They found that catalytic reduction is superior to impregnation attributing to the deposition of copper on the outer surface of the palladium. However, the catalyst preparation methods did not affect selectivities. The activities of catalysts increased with the addition of Cu and maximum value was obtained with a Cu/Pd atomic ratio of 0.8. Further increase of Cu restricted the access of H_2 to Pd. The increase of Cu favored the formation of ammonium.

Durkin et al. [82] used natural fiber welding (NFW) method to fabricate lignocellulose yarn support Pd and Pd-Cu catalysts for catalytic reduction of nitrate with hydrogen. The authors first optimized the catalyst formulation (Pd/Cu ratio) with conventional incipient wetness (IW) followed by a gentle reduction method in hydrogen gas. Then they selected the most reactive powder catalyst (5Pd3.3Cu) as the active component in the NFW “ink” to develop the fiber-welded catalyst. The untreated linen yarn was transformed into the desired shape to form a rigid, macroporous support for the catalyst scaffold. Then a batch of 5Pd3.3Cu powder was solubilized with ionic liquid into a catalyst “ink”, and further welded onto the surface of the linen scaffold through NFW. The fiber-welded catalyst had significantly stronger mechanic structure than the native linen yarns benefiting from the NFW process. SEM and EDS mapping results confirmed that the catalyst was welded on the surface of the linen scaffold. This fiber-welded catalyst showed effective catalytic reduction ability for nitrate, as well as long

stability even with five consecutive cycles of nitrate reduction tests. Moreover, the declined activity due to oxidation in air (left in air for several months) could easily be regenerated by thermal treatment.

Like the case in hydrodehalogenation, emerging materials such as graphene was also employed in catalytic hydrogenation for nitrate reduction. Yun et al. [83] used graphene-supported palladium-copper catalyst (Pd-Cu/graphene) with Fe^0 reductant in the advanced treatment of nitrate. After optimizing the operational conditions (such as mass ratio of Pd:Cu, catalyst amounts, reaction time, and pH of solution) with artificial solution, they used the selected optimal conditions for nitrate elimination of real effluent from a wastewater treatment plant in Beijing, China. The proposed catalysts showed superior performance 82% of nitrate removal and 66% of N_2 selectivity under the optimum condition: $5 \text{ g} \cdot \text{L}^{-1} \text{ Fe}^0$, 3:1 mass ratio (Pd:Cu), $4 \text{ g} \cdot \text{L}^{-1}$ catalyst, 2 h reaction time, and pH 5.1. The authors also proposed a catalytic reduction mechanism based on several characterization results.

3.2.1.2 Pd-Sn bimetallic catalyst

Prüsse et al. developed Pd-Sn bimetallic catalysts supported on alumina. Compared to the Pd-Cu catalysts [84], Pd-Sn on alumina catalysts are more efficient than Pd-Cu catalysts regarding nitrogen formation activity, selectivity and long-term stability. Garron et al. studied the effects of different supports on the activity of Pd-Sn catalysts [85]. The silica and alumina supported bimetallic Pd-Sn catalysts were synthesized by a controlled surface reaction, which aimed to favor metal-metal interactions. Although the same preparation procedure was used for Pd-Sn/SiO₂ and Pd-Sn/Al₂O₃ synthesis, the properties of the both catalysts were found to be different. The Pd-Sn/SiO₂ was observed to be more stable and selective than the alumina one while Pd-Sn/Al₂O₃ showed superior activity. The authors concluded that the difference of the interaction between the two metals as well as the affinity of tin with the support over the two supports was the main reason. In the following work, Garron et al. synthesized Pd-Sn-Au trimetallic catalyst on silica [86]. TEM and Mössbauer spectroscopy confirmed palladium/tin/gold phase alloy formation on silica. The catalytic test showed that this type of catalyst was very active in nitrate and nitrite reduction while the selectivity to N_2 was significantly promoted to 93.2% with the optimal tin and gold loadings. The authors attributed the superior performance to the stable trimetallic phase existing in the catalyst.

Costa et al. proposed a reaction mechanism for the catalytic reduction of nitrate by hydrogen in water on Pd-Sn/Al₂O₃ catalyst with a microkinetic model [87]. The model was developed based on the dual-site Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism where bimetallic Pd-Sn (S1) served as adsorption sites

for nitrate while monometallic Pd sites (S2) played the role as active sites for hydrogen dissociative adsorption. Moreover, the authors didn't make an a priori assumption of chemical equilibrium, pseudo steady-state nor rate determinant step. Kinetics data were collected with experiments in a semi-batch reactor with a temperature range of 5°C–45°C. The statistical analysis showed good fitting relation between the microkinetic modeling and the experimental practice, confirmed by the satisfactory statistical variance. Based on the modeling results, the authors proposed that the initially covered bimetallic (S1) sites (by nitrate ions) were emptied during reaction time. Nevertheless, initially covered palladium (S2) sites (by hydrogen) would be covered by the intermediates at low values during the reaction, indicating the validity of the steady-state approximation for these species. Furthermore, the coverage of NH_3 precursor species increased with higher reaction times, which suggested that the nitrogen selectivity could be maximized by optimizing the reaction time. In the following work [88], they presented a modified model for the same reaction taking into account the inherent transport phenomena as well as the pH effect. The complex system led to a considerably large (and stiff) system of ordinary differential equations while a set of empirical parameters was set for the data fitting. Accordingly, the model provided much more and detailed information about the catalytic reduction of nitrates and improved the understanding of the reaction. For example, the adsorbed species could be completely described. And the gradient of the pH within the pores can be illustrated, which allowed the prediction of NH_4^+ profiles be possible.

3.2.1.3 Pd-In bimetallic catalyst

Another type of second metal in the Pd bimetallic catalyst which improves the catalyst activity and selectivity is Indium (In). Krawczyk et al. investigated the effects of supports (i.e. SiO₂, TiO₂ and Al₂O₃) on the bimetallic Pd-In catalyst for catalytic reduction of nitrate [72]. The bimetallic catalyst 5%Pd-2%In/support was prepared by co-impregnation methods with Pd(NO₃)₂ and In(NO₃)₃ as precursors. The nitrate reduction was performed at room temperature and atmospheric pressure with pH 5.5 and hydrogen flow rate of $0.2 \text{ dm}^3 \cdot \text{min}^{-1}$. The main final products obtained from the hydrogenation of nitrate were ammonium and nitrogen. Formation of ammonia during the reaction led to the increase of pH. Hence, the pH was neutralized by addition of HCl. The authors revealed that the catalyst Pd (5%)-In (2%) with TiO₂ as support displayed best performance with the conversion of 99% and selectivity of nitrogen at 88%. The interactions between Pd and In as well as the porosity of the supports was believed to contribute on the different performance.

Mesoporous metal oxide is one of the major research directions for support optimization. Due to the complex

surface chemistry and porous structures, preparation of uniformly dispersed Pd-In nanoparticles over mesoporous metal oxides still remains challenge. Gao et al. [89] prepared Pd-In/mesoporous alumina with highly uniform distribution by a sol-gel process under strongly acidic conditions. The TEM results showed that the Pd and In nanoparticles efficiently dispersed into the mesopores of the alumina. With the similar Pd loading, the synthesized catalyst with a Pd-In ratio of 4 exhibited the highest activity with a first-order rate constant ($k_{\text{obs}} = 0.241 \text{ L} \cdot \text{min}^{-1} \cdot \text{gcata}^{-1}$), which was 1.3 times higher than that of conventional Pd-In/ Al_2O_3 . The authors attributed the superior activity to the larger surface area, and more highly dispersed and accessible metal nanoparticles.

3.2.1.4 Pd-Ag bimetallic catalyst

Most recently, Ding et al. developed a novel PdAg nanoparticles supported amine-functionalized SiO_2 (PdAg/ $\text{SiO}_2\text{-NH}_2$) catalyst to reduce nitrate in water while formic acid was employed as the in situ hydrogen source [73]. The PdAg/ $\text{SiO}_2\text{-NH}_2$ catalyst was synthesized via a three-step approach. First, SiO_2 support was modified by amine groups (-NH_2). The loading Pd on- NH_2 surface-modified SiO_2 was realized by a typical impregnation and subsequent reduction process. Finally, a controlled surface reaction was introduced to load Ag and further create PdAg alloy nanoparticles on $\text{SiO}_2\text{-NH}_2$ catalyst support. With this novel system, HCOOH would decomposed into H_2 and CO_2 on the catalyst surface due to the facilitated rupture of O-H bond in HCOOH by- NH_2 , which could generate in situ H_2 and enhance H_2 utilization efficiency in the reaction. Moreover, the excellent electron transfer efficiency from Ag to Pd due to their larger difference of work function was also beneficial for the catalytic HCOOH decomposition to provide in situ H_2 and buffer of CO_2 for the catalytic reduction of nitrate process (Fig. 5). The authors also optimized Ag content to achieve the best nitrate reduction performance over the PdAg/ $\text{SiO}_2\text{-NH}_2$ catalyst and found that the Pd:Ag molar ratio of 1:0.5 was the most efficient catalyst for the desired reaction.

3.2.2 Monometallic catalyst

Nitrates/nitrites reduction over monometallic catalyst was also investigated by many researchers while the extent is much less than those over the bimetallic systems. The thoroughly studied monometallic catalysts are palladium systems supported on Al_2O_3 , C, SnO_2 , CeO_2 , TiO_2 , and pumice. One of the reasons that limit the extensive study of monometallic palladium catalyst for nitrates/nitrites reduction is its intrinsic low activity in the reduction of nitrate. However, it shows high activity for nitrites reduction. Thus, the monometallic palladium catalyst is usually used in the second reactor of series reactor system to completely convert nitrites to nitrogen [10,71].

Although in general the bimetallic Pd based catalysts showed better performance for catalytic reduction of nitrate in water with hydrogen, the Pd monometallic catalysts were also developed by using different support to promote their chemisorption ability for H_2 , which is one of the key factors affecting the efficiency of the reaction. For example, Ye et al. [90] prepared Pd supported on multiwall carbon nanotubes (MWCNTs) modified carbon nanofiber (CNF) catalysts via a facile one-pot electrospinning approach, with a mixture of Pd acetylacetonate ($\text{Pd}(\text{acac})_2$), polyacrylonitrile (PAN), and nonfunctionalized MWCNTs as the electrospinning dope. The results of CO chemisorption confirmed that the addition of MWCNTs resulted into the decrease of the carbon nanofiber diameter as well as the increase of Pd exposure, which enhanced the hydrogen adsorption and reaction kinetics. The synthesized catalysts showed high performance for nitrate hydrogenation in water. Moreover, the one-pot electrospinning method allowed the development of sustainable and scalable catalyst possible due to its simplicity in catalyst preparation and highly tunable properties.

3.3 Nitrate/nitrite reduction perspective

The limited progress was made on catalytic nitrate/nitrite reduction process in the last decades due to the lack of novelty in the catalytic system development. The main

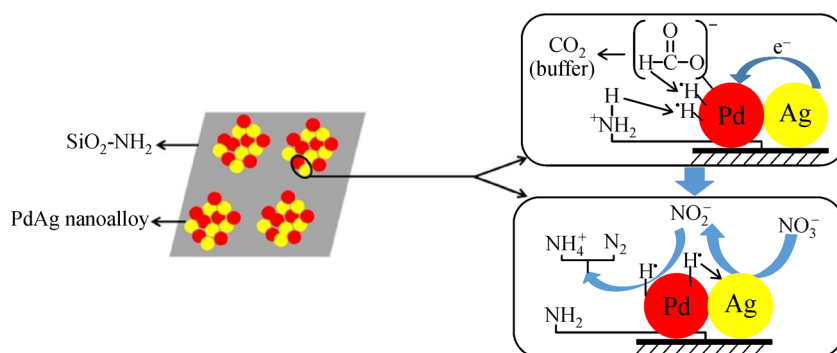


Fig. 5 PdAg alloy nanoparticles supported on amine-functionalized SiO_2 for catalytic reduction of nitrate in water [73]

formulation is still Pd based mono- or bimetallic catalysts, where cost is the one of most important issues. Developing high performance non-Pd catalysts especially with superior selectivity (with final product of desired N_2 or byproduct ammonium) is the most crucial factor in the future catalyst design.

For the reactor design, two reactors in series with the first one for selective reduction of nitrates to nitrites while the second one for conversion of nitrite to nitrogen was proposed to be one of the most promising choice [24]. The second part (nitrite to nitrogen) is less challenging while the manipulation of the pH of water is required in the first one (nitrate to nitrite) due to the possible formation of ammonium. Design involving the adoption of the complex chemical process to adjust the pH simultaneously should be performed to allow such approach for real applications.

In addition, the special attention should be paid to the catalyst deactivation. For example, Pintar et al. [91] found that an increase of hardness or salinity (e.g. Ca^{2+}) resulted into a decrease in catalytic performance. Therefore, the test of the catalysts in real waters, where hardness or salinity is varying depending on the test sites, would be a practical issue for the envisaged applications. In this area, Werth and coworkers systematically studied the bimetallic catalyst for the purpose of drinking water treatment [92–94]. The evaluation of the catalyst performance was conducted in two aspects: catalyst deactivation and catalyst regeneration. The presence of inhibitors such as sulfite, sulfide and high level of chloride could significantly reduce the catalyst activity for NO_3^- reduction. For example, fouling of 5Pd-1In catalyst with $0.42 \text{ mmol S} \cdot \text{g}^{-1}$ catalyst could completely terminate the NO_3^- reduction. Regeneration was attempted on the fouled catalyst. Different oxidation reagents such as dissolved oxygen, hydrogen peroxide, sodium hypochlorite and heated air were selected for oxidative removal. Only sodium hypochlorite and heated air were effective regenerants. The author found that Pd-In catalyst could restore its activity from 20% to between 39%–60% of original levels whereas sodium hypochlorite dissolves Cu metal from the Pd-Cu catalyst, causing a permanent deactivation of the catalyst.

4 Catalytic reduction with in situ hydrogen evolution from water splitting

4.1 Hydrogen mass transfer in catalytic reduction for water treatment

Catalytic reduction for water treatment is a typical three-phase system involving gaseous H_2 , dissolved contaminants in water, and solid catalyst. The overall reaction rate is controlled by a series of reactions, diffusion, and mass-transfer steps that proceed simultaneously (Fig. 6). The solubility of H_2 in water is sparing. Thus, the overall reaction rate of the reaction would be greatly affected by

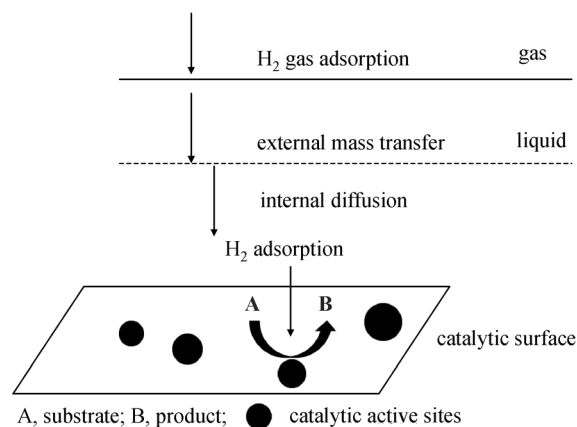


Fig. 6 Illustration of sequential transport of H_2 in a three-phase catalytic reaction

the diffusion of H_2 from gaseous phase to catalyst surface, leading to the reduction reaction with a diffusion or mass transfer limiting process.

Although molecular hydrogen (H_2) was employed as the major source for catalytic reductions in laboratory-scale experimental, other hydrogen sources being more compatible with water are more practical in real applications. This idea has attracted increasing attentions. One of the attempts is by using hydrogen transfer reagents (including inorganic salts e.g. phosphinates, or organics e.g. formates, formic acid, and alcohols) as hydrogen source. However, the addition of hydrogen transfer reagents may bring extra potential environmental issues as well as runs counter to the progressive low waste concept.

As water is formed with hydrogen and oxygen, producing hydrogen in situ from water is another attractive way to address the diffusion and mass transfer issue. The in situ evolved H_2 would avert mass transfer limitations resulting in substantial kinetic enhancement. The hydrogen evolution from water splitting reaction has been tested in many experiments [95]. With these catalysts under UV irradiation, H_2 could be in situ produced from water. More important, there is no waste residual or generated with this process. Therefore, pioneering work has been done with this concept.

4.2 Pioneering work

O'Keefe et al. testified the technical feasibility of the catalytic hydrodechlorination of carbon tetrachloride (CCl_4) utilizing H_2 produced in situ from photocatalytic water splitting [96]. The authors compared two types of catalysts in the study, multifunctional Pd – NiO/NaTaO₃:La catalyst and O/NaTaO₃:La + Pd-Au/IX (ion-exchange resin) mixture-of-catalyst (Fig. 7). The former one combined all reaction on the single multifunctional catalyst surface. By contrast, the latter one separated the hydrogen evolution procedure (from water splitting) with the

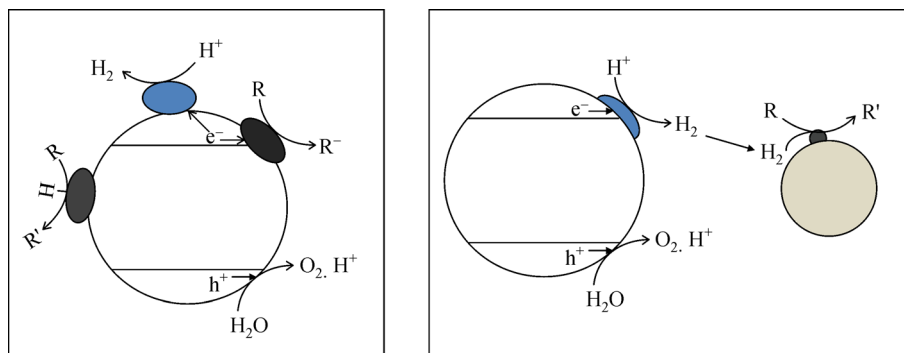


Fig. 7 Comparison of multifunctional catalyst approach (left) with mixture-of-catalysts method (right) for catalytic reduction (white: photocatalyst, blue: NiO nanoparticles, dark gray: metal catalyst, light gray: hydrogenation catalyst support) [96]

catalytic hydrodechlorination step by using two kinds of catalysts. The authors first illustrated the results from the latter catalyst and found it showed high activity for CCl_4 removal. The satisfying results confirmed the concept that catalytic reduction with in situ hydrogen evolution from water splitting is a promising approach to remove contaminants in water [96]. Moreover, with the observed intermediate species, the authors suggested a gradual chloride loss pathway going through chloroform and dichloromethane. Pd introduction over NiO/NaTaO₃:La aggravated the recombination effects of photo-generated holes with electrons, which led to a loss of three orders of magnitude of the H_2 evolution activity over the Pd/NiO/NaTaO₃:La multifunctional catalyst. However, the catalytic activity of the multifunctional catalyst for the hydrodechlorination of CCl_4 was enhanced significantly. Moreover, it also showed much higher efficiency on utilizing the H_2 than the mixture approach. For example, CCl_4 can be rapidly removed with conversions of higher than 95% in 10 min over multifunctional catalyst. Furthermore, the authors proposed a structure-sensitive reaction mechanism based on the facts that Pd loading and catalyst reduction temperature exhibited significant effect on the turnover frequency which is dependent on the Pd crystallite size and dispersion. The results obtained in this work successfully demonstrated the possibility of combining water splitting with catalytic reduction for water treatment.

5 Summary and perspective

This article covers two main types of heterogeneously catalytic reduction approaches: hydrodehalogenation for industrial wastewater treatment and hydrogenation of nitrate/nitrite for groundwater water remediation. The existing treatment technologies are overviewed with an assessment of the advantages of catalytic reduction over the conventional methodologies. Catalyst design for feasible catalytic reactions is considered in turn with a

critical analysis of the pertinent literature. In addition, novel approach of catalytic reduction using in situ synthesized H_2 evolved from water splitting reaction is illustrated. All of these are beneficial to our community and allow us to design and develop novel system with extraordinary performance for practical processes.

In spite of the remarkable progress made in catalytic reduction of contaminants, several general issues still exist in both hydrodehalogenation and hydrogenation of nitrate/nitrite, including: 1) unclear mechanism or fundamental understanding on the catalytic transformation processes in water, 2) difficulty in scale up of the technology, and 3) lack of comprehensive consideration of economic and environmental effect. Therefore, it's still a long road ahead before their extensive applications. In our opinion, the following directions may be helpful and should be paid more attention in the future research. First, advanced characterization approaches may be used for further understanding the mechanism in micro-scale even in atomic level. Although heterogeneous gas-solid catalysis has been extensively studied, the understanding of the gas-liquid-solid catalysis (the case of catalytic reduction for water treatment) is only at its very early stage. Some techniques such as spectroscopic techniques especially in situ or operando experiments (IR or Raman), detailed kinetic modeling consideration of the complex transport phenomena in the three-phase system, and theoretical simulations (DFT) on the interface system are the potential choices. In situ or operando experiments can provide "on-site" information on the catalyst surface which help to identify the adsorption pattern, intermediates, and fundamental information about the molecular structures of catalysts, leading to revealing the underlying mechanism [89]. Detailed kinetic modeling allowed the description of adsorbed species possible, which is critical for the pathway determination [97]. Theoretical simulations (DFT), in most case, is the only available approach to illustrate the complex system due to the difficulty existing in the former two methods and has been used more and more in the last several years in catalytic reduction for water treatment

[98]. Theoretical calculations could provide a conceptual framework to help understand how support and loaded catalytic species interact, how much the activation energies are as well as how the elementary reaction pathways process. Moreover, combining the theoretical computations (DFT) with the experimental observations is a useful and practical approach to fully understand catalytic transformation processes in water. Secondly, one huge obstacle that preventing the extensive application of catalytic reduction of contaminants in water is catalyst fouling. Though the applications in field-scale demonstrated exciting results with both industrial wastewater and groundwater [10,17], more efforts are still required to completely understand the technology barriers. Moreover, the combination of catalytic reduction with other technology may be an alternative way to address this issue. For example, with suitable pre-chemical treatment, the concentration of some ions (like Ca^{2+}), which may form precipitation and deposit on catalyst surface resulting into its fouling, can be controlled under an acceptable level. Thirdly, economic and environmental implications should be carefully evaluated, which would help the technology in practice. The high selectivity and activity allows catalytic reduction to be an effective, safe, and green technology for water treatment. Though its construction or maintenance cost may not be comparable with conventional approach, both the economic and environmental implications should be considered when going through these comparisons. Economic feasibility and environment impacts of Pd-based catalytic hydrogenation are critical for the practical application of the catalytic hydrogenation. While catalyst fouling is one of the main cost for this technology, the regeneration of these expensive Pd-based catalysts is very important. The oxidative regeneration is a novel idea to deal with this issue [92]. Developing integrated model for a hybrid ion exchange-catalytic treatment system can also contribute to lower the cost of the technology [99]. Both should be paid more attention specially in consideration of the potential application of the catalytic hydrogenation technology in water treatment.

Nomenclature

TCE	trichloroethylene
CNF	carbon nanofibers
Pt	platinum
4-CP	4-chlorophenol
MCB	monochlorobenzene
FHC	ferrous hydroxy complex
NG	nitrogen doped graphene
Fe	iron
B	bentonite
Ag	silver

Ni	nickle
Pd	palladium
MCPA	4-chloro-2-methylphenoxyacetic acid
AC	activated carbon
SMF	sintered metal fibers
2,5-DBA	2,5-dibromoaniline
TBBPA	tetrabromobisphenol A
2,4-DCP	2,4-dichlorophenol
p-CP	p-chlorophenol
BNPs	bimetallic nanoparticles
1,2,3,4-TCDD	1,2,3,4-tetrachloro dibenzo-p-dioxin
MCA	monochloroacetic acid

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