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Application of Heterogeneous Catalysts in Dechlorination of Chlorophenols

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Abstract

Chlorophenols (CPs) is a very important kind of basic organic chemical intermediates such as sanitizers, germicides, insecticides and so on; but CPs also constitutes a particular group of priority pollutants that widely distribute in wastewater and the polluted groundwater. Because of their acute toxicity, persistence and low biodegradability, their emissions have been progressively restricted by strong legal regulations. In this chapter, we focused on methods for degrading of CPs recent years, especially by using new heterogeneous catalytic hydrogenation methods to the dechlorination of CPs. The purpose is to introduce scientific research workers and companies to waste water treatments in order to inspire and further better protect the environment.

Keywords: heterogeneous catalysts, dechlorination, chlorophenol, core-shell, environment

1. Introduction

The global water storage is up to 1.45 billion cubic kilometers (**Figure 1**), but the number of water storage can be produced and used directly by people is very less. Water is widely used in industries, agriculture, homes and so on, but keeping water quality becomes a major challenge for the coming decades. There are many factors that cause water damage. Industrial wastewater, agricultural wastewater, and domestic wastewater may be the main pollution sources (**Figure 2**).



Figure 1. Beautiful earth.



Figure 2. Chemical pollution is the largest source of pollution.

The development of chemical technology growing changed our lives. More and more food, medicine, cars, and appliance made by industries come to our lives. However, pollution problems were generating while we are enjoying our lives. Not only polluting the water and the air, but also seriously polluting the people's physical and health. Solving and treating the toxic organic compounds in wastewater are becoming an important project and research in recent years. It is becoming an important things for the government, companies, and academic research [1].

Chlorophenols (CPs) constitute a series of common organic compounds and intermediate involved in industrial processes such as fungicides, insecticides and dye precursors [2]. Chlorophenols (CPs) are also used in preservatives, papermaking and cosmetics industries. But because of acute toxicity, persistence and low biodegradability, chlorophenols especially such as chlorophenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and 5-chlorophenol are highly toxic substances [3]. Their emissions have been progressively restricted by strong legal regulations. (Most chlorophenol compounds can interfere with endocrine, may cause cancer, cell mutations or teratogenesis, are almost non-biodegradable and difficult to remove from the environment. Therefore, they are a list of priority control pollutants by the US Environmental Protection Agency (EPA) and China Environmental Monitoring Center.)

In fact, chlorophenols and their derivatives may be produced by the chlorination of phenols. The phenol reacts with chlorination in the presence of high concentrations of chlorine and the toxicity of chlorophenols increases with its degree of chlorination and usually are difficult to

degrade. These chlorophenols released into the natural environment can cause serious pollution, especially causing water pollution.

Conventional wastewater treatment based primarily on biological processes are not very efficient for the treatment of toxic or non-biodegradable and high-concentration wastewaters. Therefore, in order to protect our environment, it is necessary to develop efficient technologies for treating organic wastewater containing chlorine.

2. Application of heterogeneous catalysts in dechlorination

Recent years, the scientific community and the engineering technical community have begun to pay more attention to the CPs degradation or removal. In order to achieve this goal, large numbers of methods have been employed, such as oxidation (Fenton, O_3 and so on), aerobic/anaerobic biodegradation [4, 5], photocatalytic degradation [6], thermal combustion, catalytic reaction based on polymer membrane [7] and reduction dechlorination. In the chapter of this book, we classified these methods into two major categories: oxidation and reduction reactions in **Table 1**. In order to give the readers a clear understanding of the processing methods of the entire CPs treatments, we generally explain each method briefly. Because of heterogeneous catalysis is a cost-effective method for CPs treatments. We will give a detailed explanation and summary.

2.1. Photo-catalytic oxidation

Photocatalytic method [8, 9] is an advanced oxidation process (AOP). In common, semiconductor photocatalysts were needed to the oxidation reaction. Using higher than the semiconductor energy band gap light. For example, anatase which band gap is about 3.2 eV. Thus only ultraviolet light (wavelength <388 nm) can be effectively applied for electricity to be inspired to the conduction band from electronic valence band to generating a pair of holes and electrons in **Figure 3**. The hole–electron pair may be not stable enough. If they are not to combine together immediately, the two species (hole–electron pair) respectively may react with oxygen or water to generate oxidizing species, such as hydroxyl radicals, hydrogen oxygen free radical, superoxide free radicals and so on, hydroxyl radicals directly attack the phenol. The

Oxidation method				Reduction method
Photo-catalytic oxidation [8, 9]	Ultrasonic reaction	Fenton	O_3 /CWAO Oxidation	Hydrodechlorination
Under light conditions, catalyst surface generate hole and electronics, then water reacts with oxygen free radicals.	Ultrasonic wave can greatly promote the AOP.	Fe^{2+} and H_2O_2 for generating hydroxyl radical ($\bullet OH$).	$\bullet OH$ to degradation of organochlorine.	Via halogen atoms elimination with hydrogen.

Table 1. The classification of dechlorination reaction.

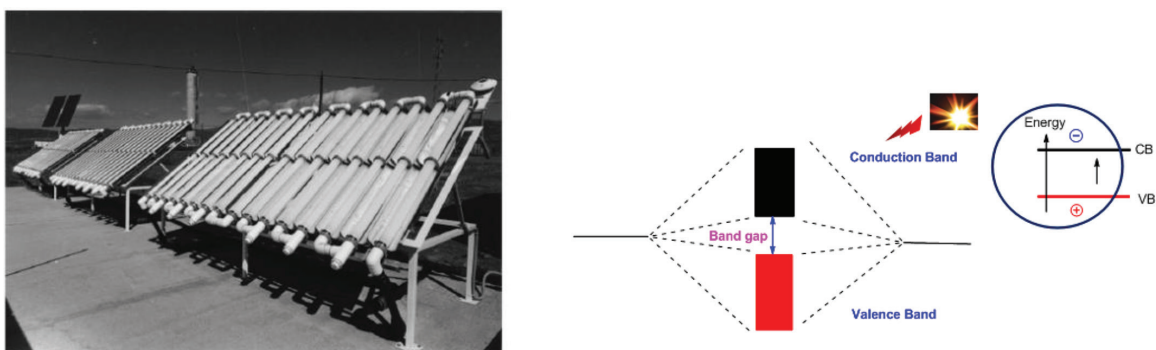


Figure 3. Theory of photocatalytic method.

proposed mechanism for the photocatalytic degradation of 4-chlorophenol by photocatalysts (GR-Eu₂O₃/TiO₂) was described by Mallanaicker Myilsamy in Figure 4 [10]:

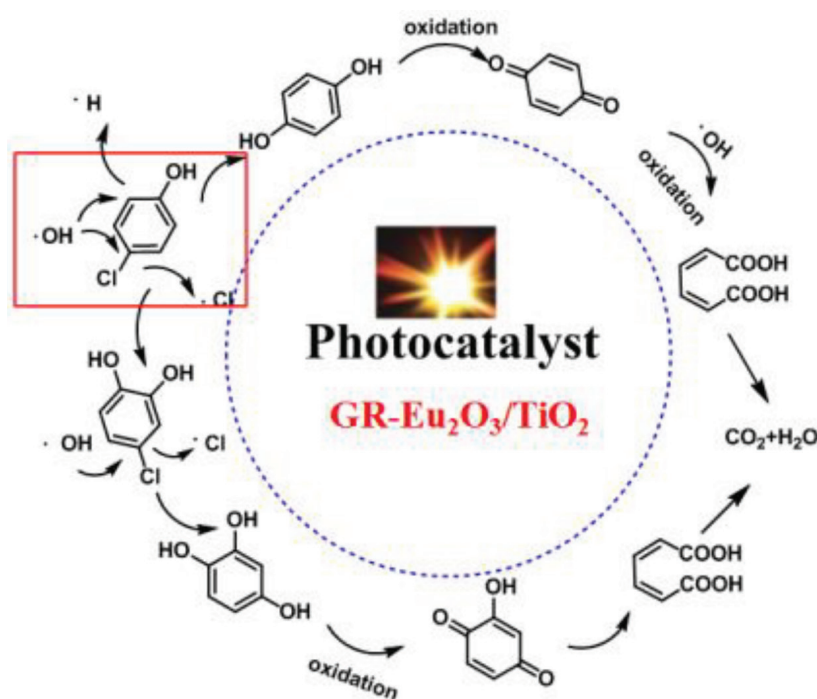


Figure 4. Proposed mechanism for the photocatalytic degradation of 4-chlorophenol [10].

There are several influence factors of this AOP.

The first: Photocatalysis: catalyst which determines the type of the light and speed of the reaction is a key factor we need to consider. Due to its high catalytic activity, low cost, chemical stability, non-toxicity, TiO₂ was usually applied as the most efficient photocatalyst in this AOP [11, 12]. Based on the photocatalytic mechanism of electron-hole, some metal nanoparticles were also used to prevent the combination of hole and electron pair [13, 14].

Other factors such as the amount of catalyst added, illumination angle, solvent, reaction temperature and so on will also affect the whole reaction efficiency [9].

Recent research directions focused on the development and synthesis of improved photocatalytic materials (such as core-shell nanoparticles, bimetal catalyst and so on), with two major lines aiming at (i) better charge separation and better charge migration (ii) visible-light driven photocatalysis. Claude Descorme has summed up most of the catalyst types in his review [9].

2.2. Sonocatalysis (ultrasonic reaction method)

Ultrasonic reaction (sonocatalysis) is also considered as an advanced oxidation process (AOP). It is well known that ultrasonic wave can greatly promote heat movement of molecules in the reaction, accelerating the reaction process, thus lots of scientists like to choose ultrasonic reaction method to the low reaction activities reagents, the entire process reaction temperature is not too high. The chemical processes of the sonocatalysis may involve two parts (I) free radical process and (II) pyrolysis process under ultrasonic wave. Recent research directions focused on the development of the more efficient reactor, for example (**Figure 5**), and catalyst which can be applied to decrease the frequencies [15, 16].

2.3. Fenton method

Fenton method [17] is also a AOP method which uses ferrous or cuprous salts ($\text{Fe}^{2+} + \text{Cu}^{2+}$) and hydrogen peroxide (H_2O_2) for generating powerful oxidant, i.e., hydroxyl radicals produced in situ **Figure 6**.

For the Fenton method to the dechlorination of Chlorophenols, the important parameter is probably the operating pH, In the presence of a homogeneous catalyst, an optimum is generally observed around pH 3. In fact, when $\text{pH} < 2.5$, the $\text{Fe(II)} (\text{H}_2\text{O})_2^+$ will generate while the pH higher than 4, free iron and reduced concentration of hydroxyl precipitation of iron oxide. The pH can also affect the stability of the heterogeneous catalyst, now most research has focused on the development of more stable and regeneration or be used in a wide pH range catalyst [18].

2.4. O_3 oxidation

Ozone oxidation is also a kind of VOP, both ozone oxidation and Fenton oxidation also produce free radicals such as $\bullet\text{OH}$ to degradation of organochlorine, especially for the organochlorine

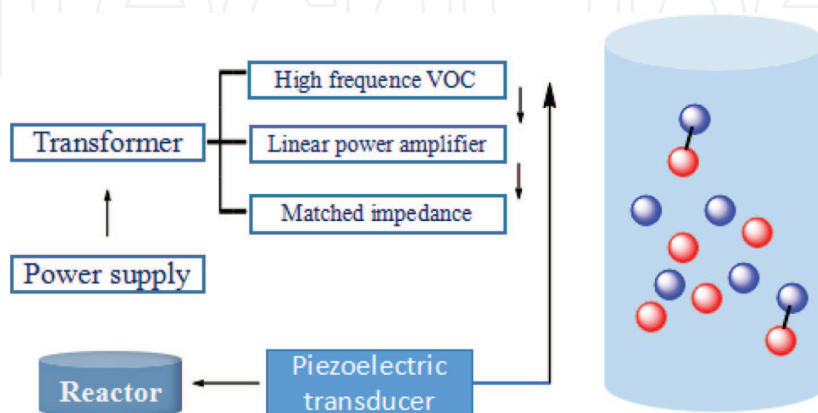


Figure 5. Scheme of the self-excited ultrasonic irradiation device.

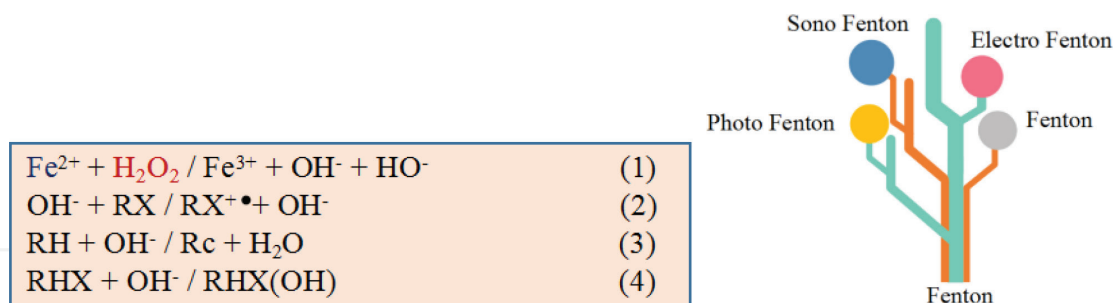


Figure 6. The mechanism of Fenton method.

pollution which contain multiple bonds such as $\text{C}=\text{N}$, $\text{C}=\text{C}$ has a better effect; while some limitations still exist in terms of the O_3 oxidation, chlorophenol concentrations, catalyst costs and its recovery and so on.

2.5. Hydrodechlorination

Heterogeneous catalyst replaced the homogeneous catalyst because of solving the catalyst recycling problem, especially for the precious metal catalysts, the catalyst costs were reduced. Heterogeneous catalyst have some advantages (Figure 7) compared with homogeneous catalyst, e.g., (I) Large surface area, especially for the porous heterogeneous catalyst, it may increase the reactant transmission rate in the catalyst. For gas phase reaction, surface adsorption effect will greatly increase the rate of the reaction. (II) The activity site will be discrete well in order to prevent its aggregation. (III) Diversified structure monomers to build diversified structure, morphology and functional catalyst. Wang Wei et al. [19], detailed introduced the nanocatalyst materials development which can be divided into three categories: inorganic materials, organic materials, and hybrid materials (Figure 8) and depicts some representative examples ranging from 0D discrete materials to 3D extended structures, from inorganic to pure organic components, from disordered to regular arrangements, and from non-porous to porous nature. In recent years, covalent organic frameworks attract more and more people's attention because of its large surface area and regular structure [20–22].

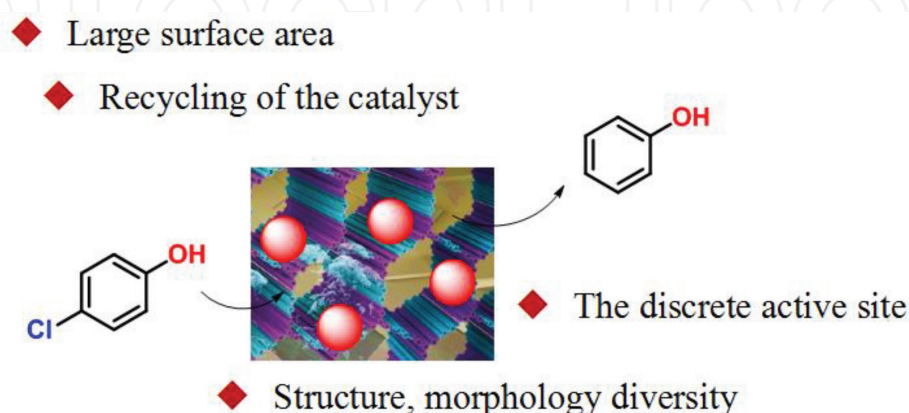


Figure 7. Heterogeneous catalysts applied in HDC.

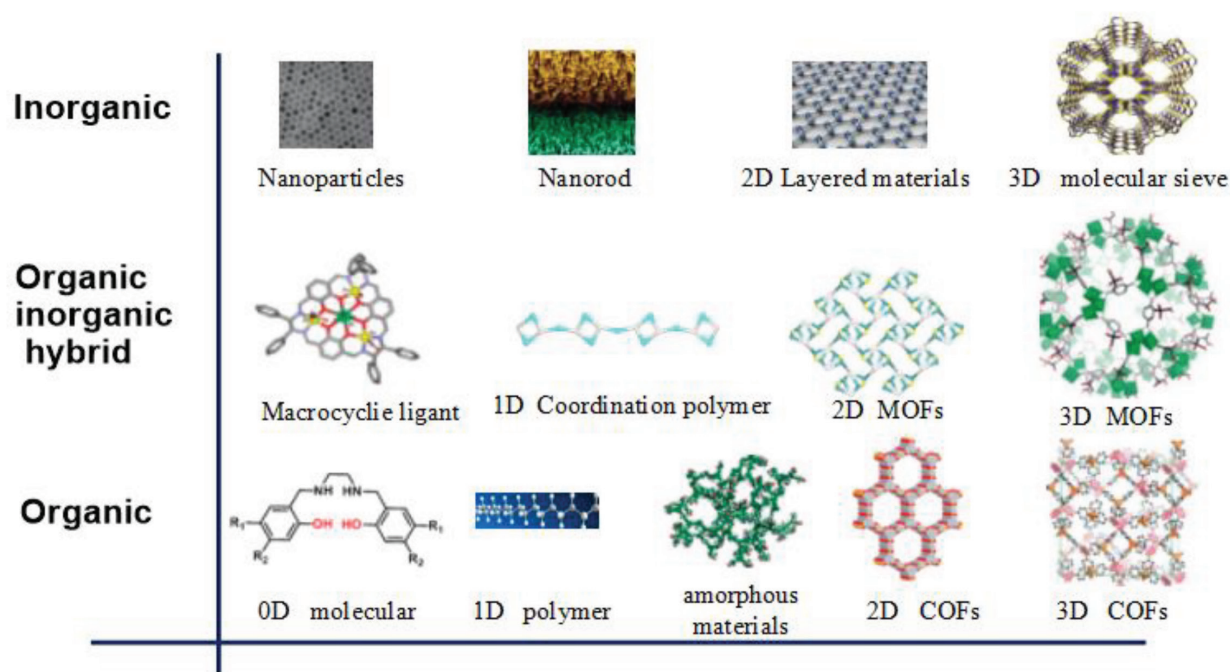


Figure 8. The classification of heterogeneous catalyst carrier and its development [19].

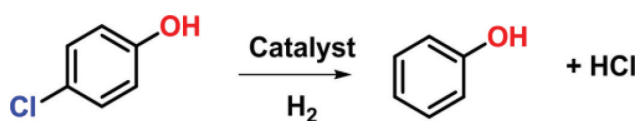


Figure 9. Hydrogenated dechlorination (HDC).

From 0D to 3D nanomaterials, all of them may be likely to be good candidates as the heterogeneous catalyst. Organic chlorides, especially of 4-chloride-phenol is a kind of highly toxic compound. Hydrogenated dechlorination (HDC) is an efficient method for toxic compound treating. Although this method does not lead to complete degradation of the organic chlorides pollutant but generates a less toxic (biodegradable) compound or a chemical of possible commercial important product via halogen atoms elimination with hydrogen (**Figure 9**) hydrochloric acid was produced in HDC reaction process in stoichiometric amount and the catalyst deactivation in this acid conditions is an important issue.

Recently most research focused on the development of more stable and efficient catalyst designed. According to the type and number of the metal, catalyst can be divided into single and bimetal center catalyst activity. Hence, a rapid, efficient, and green approach to the fabrication of effective catalyst Al_2O_3 shows a highly mechanical resistance with high catalytic activity and the potential applications the HDC of 4-CP has significant meaning for environmental protection. Pd^0 as the most effective metal active center for the HDC reaction usually applied with other metal cooperate to improve the catalytic efficiency and stability, like Pd-Bi [23, 24], Pd-Tl [25], Pd-Fe [26], and Ni@Pd [27] also have been extensively researched, in addition, the catalyst carrier has become the important role in improving the activity and stability of catalytic, such as Pd/ Al_2O_3 , Pd/zeolites, Pd/activated carbon (AC), SiO_2 supported Pd nanocatalysts.

As we know, for organic chloride, with chlorine content is higher, the toxicity become stronger at the same time, to be more difficult to removal chlorine from the organic chloride compound. Bimetal catalyst was reported to solve this issue by Anwar [28]. The pentachlorophenol (PCP, $10\text{--}20\text{ mg min}^{-1}$) through the bimetal catalyst Ag^0/Fe^0 loaded on the heating column ($25 \times 1\text{ cm}$) in scCO_2 (supercritical carbon dioxide) was removed. After the reaction was operated for 1 h at 450°C , organically-bound chlorine was liberated, virtually quantitatively, from a 20% (w/v) feedstock stream (0.1 ml min^{-1} merged with $4\text{ ml min}^{-1}\text{ scCO}_2$). In extended operations, about 70°C , the reactor to 14 h of continuous running, no obvious activity loss if the chloride ion was washed every 3 h. In fact, catalytic activity was also related with the reaction temperature, pressure, solvent, and so on. The production of the pentachlorophenol (PCP) was a series of methylated phenols or methylated benzenes (**Figure 10**).

Jovanovic studied the dechlorination of p-chlorophenol in a microreactor with bimetallic Pd/Fe catalysts [29]. The bimetallic catalyst Pd/Fe was prepared by electroless deposition of Pd on the reactor plate surfaces. The chemistry of the dechlorination of p-chlorophenol on Pd/Fe catalysts involves three sets of chemical reactions (**Figure 11**) namely surface reactions, solution reactions, and actual dechlorination reactions. These reactions are found to be dependent on several parameters, including the pH, the Pd/Fe interface area, the extent of palladization, the ratio of the Pd/Fe interfacial area to the amount of chlorine to be removed, and the amount of dissolved oxygen.

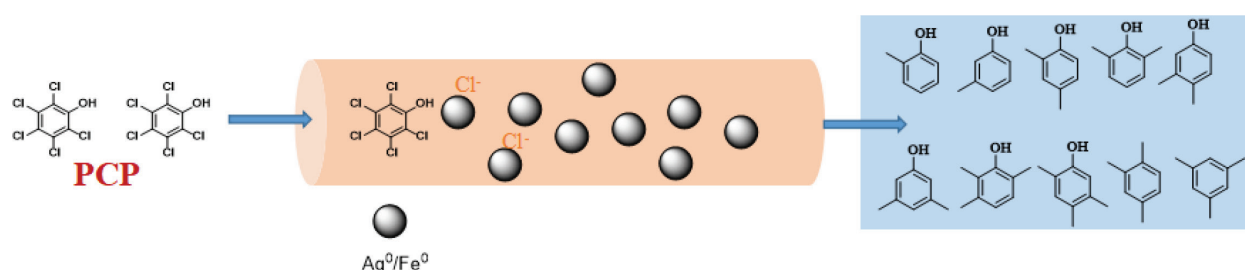


Figure 10. Pentachlorophenol treated by Ag^0/Fe^0 catalyst [28].

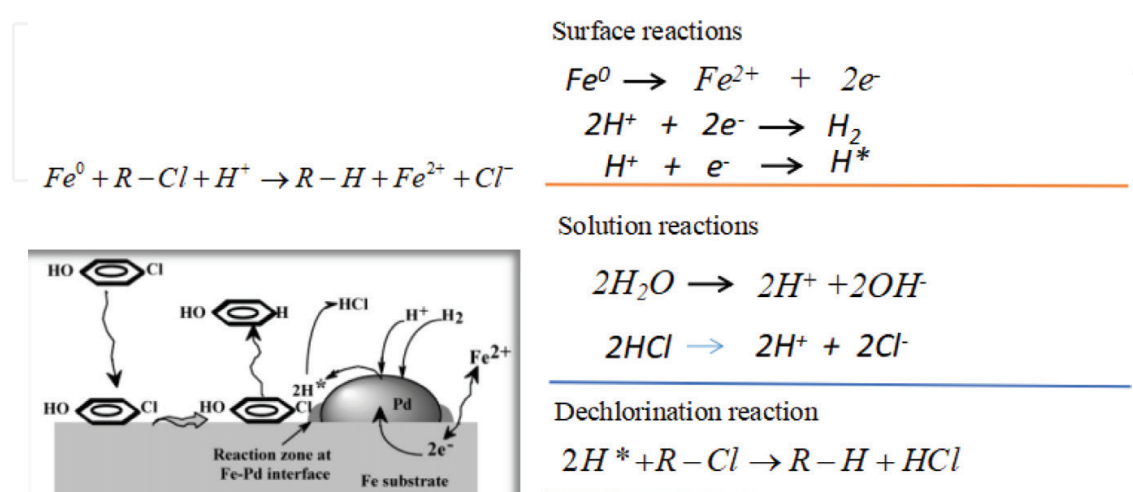


Figure 11. Dechlorination of p-chlorophenol on Pd/Fe catalysts.

2.5.1. How to design and synthesize catalyst of the HDC

- Catalyst carrier with large surface area to increase the adsorption quantity of H_2 in order to increase the speed of the reaction rate while could reduce the pressure.
- Improve the recovery efficiency of nanocatalyst.
- Prevent the by-products hydrochloric acid damage to the catalyst.

2.5.2. Core-shell catalyst

Nanometer catalysts because of their nanosize effect may be an efficient heterogeneous catalyst model which are widely used in many different catalytic reaction, such as, catalysis, biological

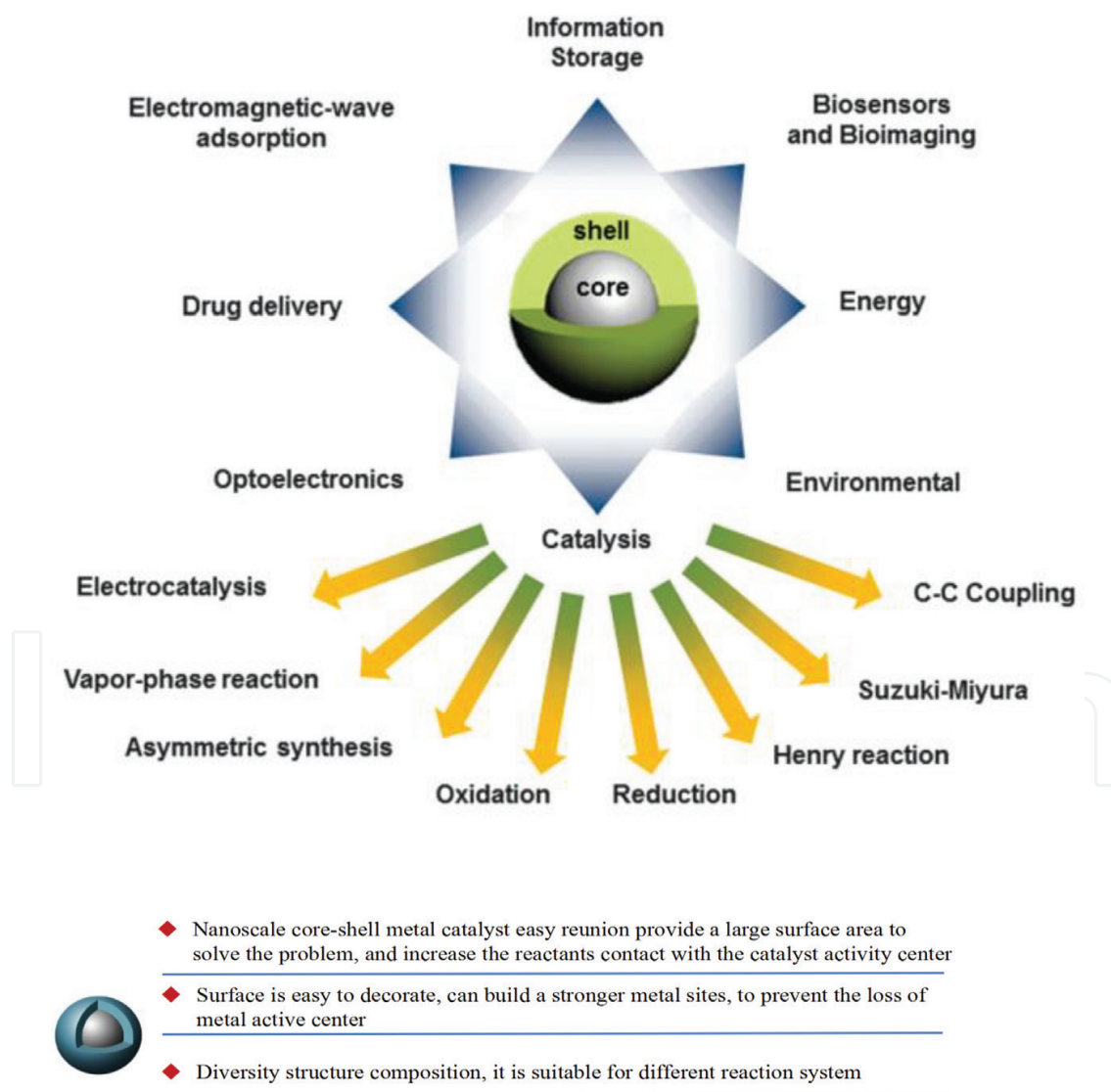


Figure 12. The advantages of core-shell nanoparticles.

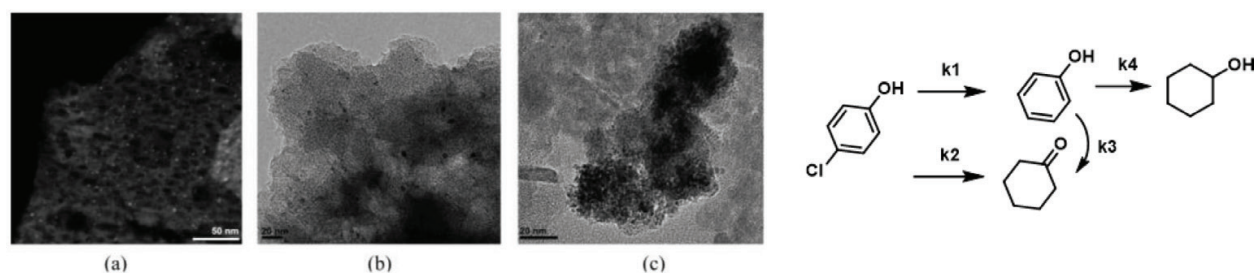


Figure 13. STEM micrograph of Pd/Al₂O₃ catalyst (a) and TEM micrographs of Pd/AC (b) and Rh/AC catalysts(c).

T (°C)	Kinetic constant (L/kg _{cat} h)	Pd/Al ₂ O ₃		Pd/AC		Rh/AC	
		k	r ²	k	r ²	k	r ²
20	k ₁	146 ± 5	0.995	179 ± 36	0.991	44 ± 5	0.992
	k ₂	10 ± 5		0		18 ± 5	
	k ₃	9 ± 3		10 ± 4		7 ± 5	
30	k ₁	201 ± 11	0.976	460 ± 37	0.976	96 ± 8	0.986
	k ₂	29 ± 10		0		41 ± 8	
	k ₃	20 ± 5		22 ± 7		13 ± 8	
	k ₄	—		—		8 ± 4	
40	k ₁	478 ± 16	0.994	713 ± 36	0.992	172 ± 13	0.982
	k ₂	66 ± 12		113 ± 19		65 ± 12	
	k ₃	45 ± 4		10 ± 3		11 ± 6	
	k ₄	—		—		10 ± 4	

Table 2. The kinetics of hydrodechlorination of 4-chlorophenol on Pd/Al₂O₃, Pd/AC, Rh/AC.

medicine, material chemistry, sensors and so on [30]. As a nanomaterials, core-shell structure catalyst materials can be synthesized through the grafting reaction method step by step.

Because of the advantages that core-shell nanomaterials own (**Figure 12**) precious metals (Pd, Rh, Au...) can be loaded on core-shell nanoparticles by stronger chemical bonds, such as coordination bond or covalent bonds.

Elena Diaz et al. [31] studied the kinetics of hydrodechlorination of 4-chlorophenol on alumina and activated carbon supported Pd and Rh catalysts. The hydrodechlorination of 4-chlorophenols based on Pd and Rh on γ -alumina and activated carbon was investigated in continuously stirred basket reactors (20–40°C and 1 bar). For 4-chlorophenol, the reaction rate shows a first-order dependence. All catalysts are effective in removing 4-chlorophenol. Phenol, cyclohexanone and cyclohexanol were identified as reaction products (**Figure 13**). The hydrogenation of 4-chlorophenol to phenol was in the range of 146–478 L/kgcat h for Pd/Al₂O₃, 179–713 L/kgcat h for Pd/AC, and 44–172 L/kgcat h for Rh/AC. In all cases, the k₁

constant shows a much larger value than k_2 , indicating that the formation of phenol is superior to cyclohexanone as the first reaction step (**Table 2**).

Wu et al. [32] designed and synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Pd-Au}$ catalyst (**Figure 14**). $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Pd-Au}$ was synthesized with the reduction of Pd^{2+} and Au^{3+} . The amine-modified silica is coated on the outer layer of magnetic Fe_3O_4 nanoparticles to be a carrier for Pd-Au nanoparticles, where in the amine acts as a bridge connecting the Pd-Au nanoparticles to the support, making it highly dispersible, the magnetic properties of Fe_3O_4 allows the catalyst to be recycled. The performance of the catalyst was evaluated by hydrodechlorination of 4-chlorophenol (25°C, atmospheric pressure, a certain amount of 4-CP, 0.05 g NaOH, 0.5 g catalyst). The results showed that Pd nanoparticles have higher activity in HDC of 4-CP then the Au

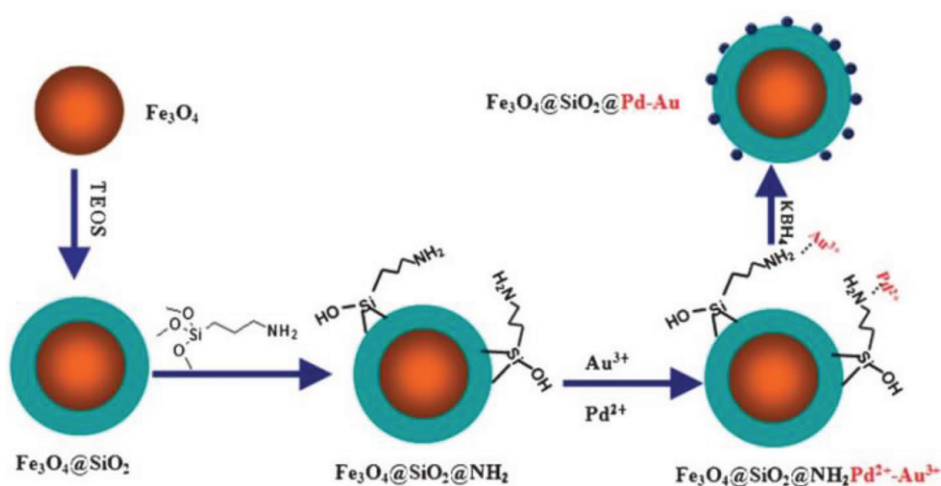


Figure 14. Synthesis procedure of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Pd-Au}$ catalyst.

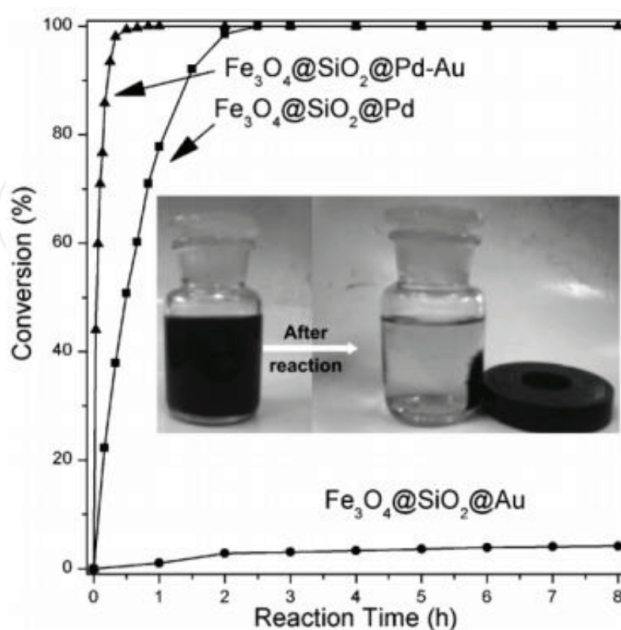


Figure 15. 4-CP HDC conversions on different catalysts.

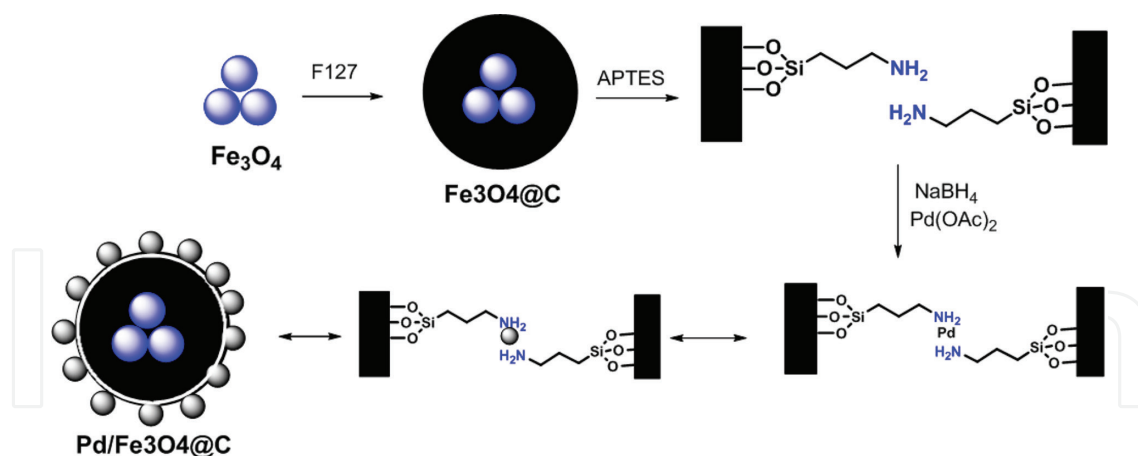


Figure 16. Design and synthesize the Pd/Fe₃O₄@C catalyst.

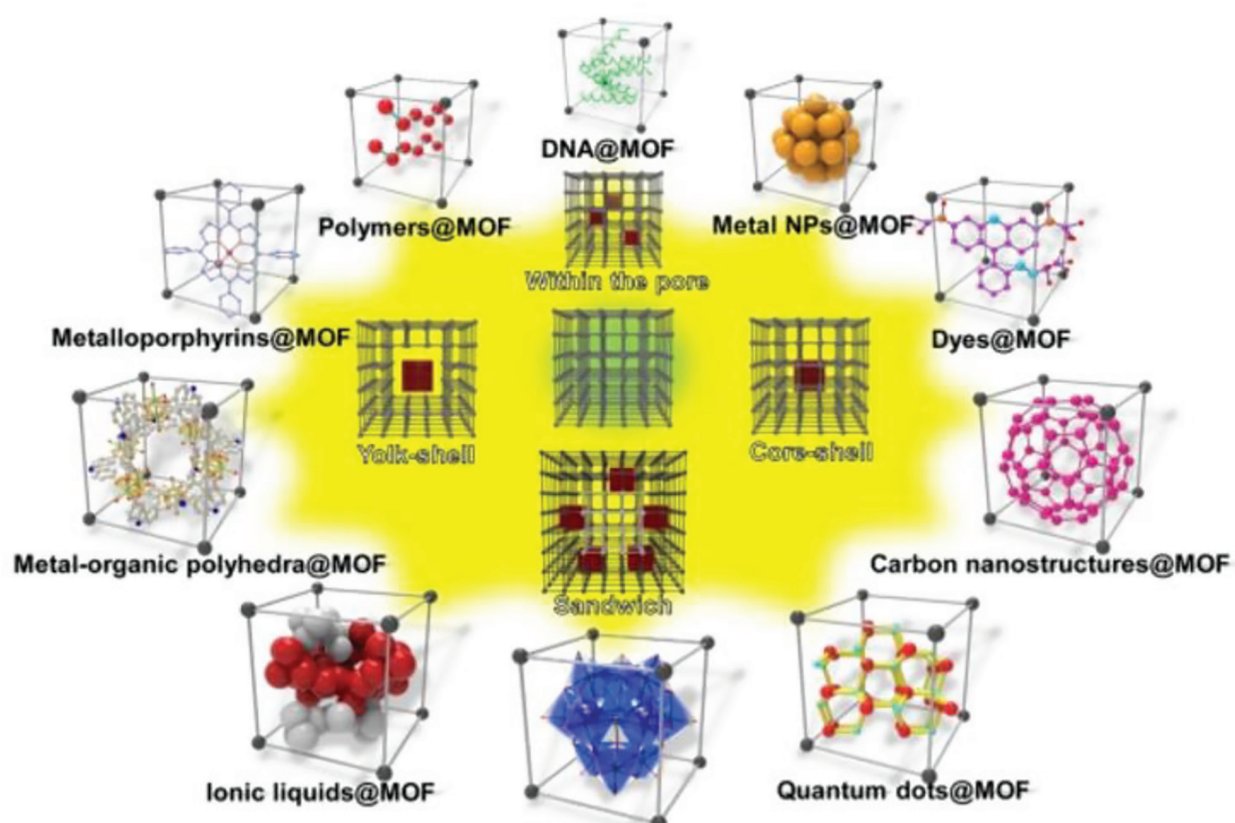


Figure 17. Controllable design of tunable nanostructures inside metal-organic frameworks.

nanoparticle, the Pd-Au alloy increases the conversion significantly and achieves a complete conversion of HDC within 20 min, much faster than the Pd metal catalyst (Figure 15).

Li et al. [33], studies a high efficient Pd nanocatalysts (Pd/Fe₃O₄@C) applied in HDC. Pd nanoparticles in magnetic carbon shell can effectively improve the catalytic activity, separation and reusable. Catalyst was synthesized by Fe₃O₄ nanoparticles as a core, and then a layer of carbon layer on the outside package, finally by APTES modified carbon layer improving Pd

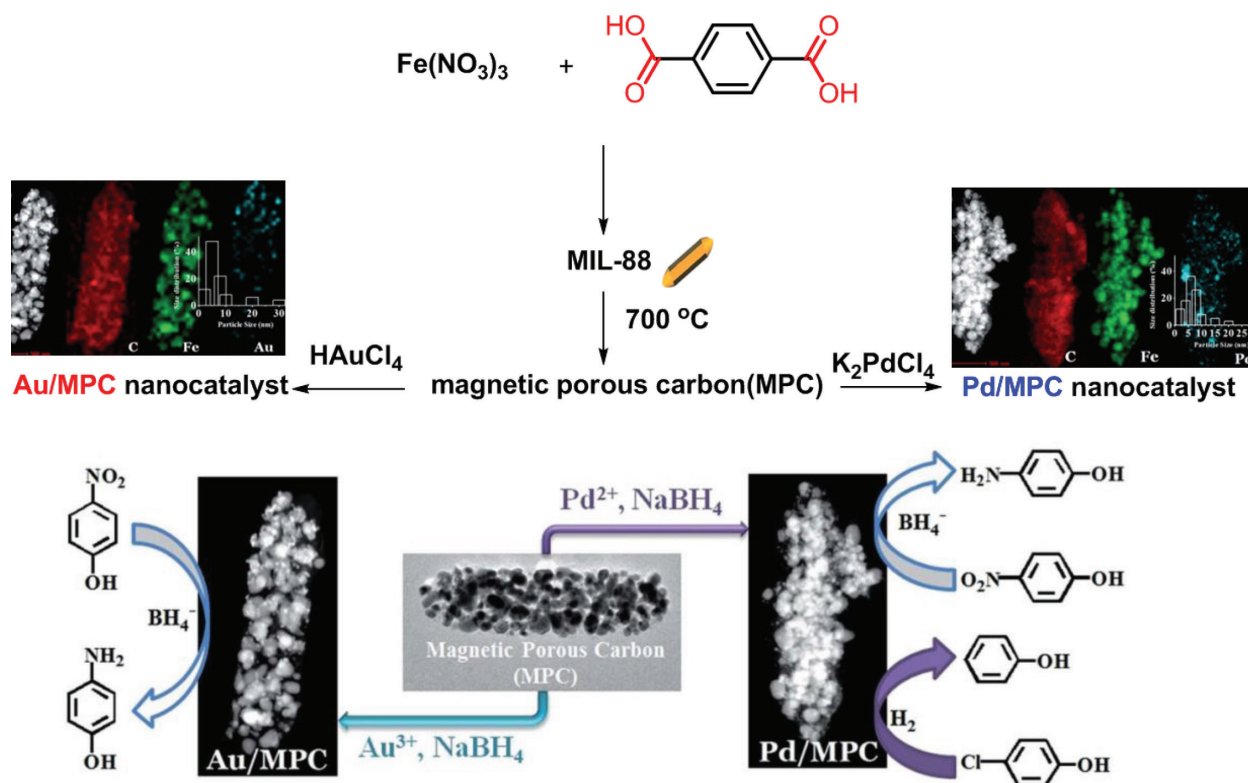


Figure 18. MPC utilized as a catalyst support to fabricate Au and Pd NP-based nanocatalysts.

loaded (Figure 16). $\text{Pd}/\text{Fe}_3\text{O}_4@\text{C}$ can be recycled at least five times without obvious loss activity. $\text{Pd}/\text{Fe}_3\text{O}_4@\text{C}$ is not only used in the aqueous solution of 4-chlorophenol hydrogenation dechlorination but also be used for reduction of 4-nitrophenol.

Porous materials are widely used in catalysis, gas adsorption, separation and other fields because of their large surface area and structure controllable. Metal organic frameworks (MOFs) materials are a kind of regular porous material formed by DCC chemistry by metal and organic ligand [34]. Controllable design of adjustable nanostructures in metal-organic frameworks is in Figure 17.

Noble metal nanoparticles (NMNPs) have attracted attention as the activity center. But NMNPs were easy blocking pores of active carbon, and leaching from carbon nanotubes, and graphene faces in the process of catalytic. In order to solve these problems, Dong used metal organic framework (MOF) to synthesize the porous carbon (MPC) which can provides a large surface area and pore (Figure 18) not only can make the active center (Pd NPs) scattered on it well, but also has paramagnetic behavior that the catalyst can be easily recycled [35].

3. Conclusion and outlook

Hydrogenated dechlorination degradation is an important method for the organochlorine degradation. Catalyst activity and its lifetime are two key points for the HCP, especially for the noble metal catalyst. In order to solve the recycling or reunion problems of noble metal catalyst,

designing a suitable catalyst support becomes more important, core-shell type, organic porous materials, especially organic crystal type of porous materials, which is developing rapidly in recent years, such as MOF (metal organic frameworks) and COFs (covalent organic frameworks) materials because of the rules of uniform structure and large specific surface area that can bring some advantages to metal catalyst loading, design and synthesis coordination bond or other stronger bond to combine the metal and carrier is one of the important measure to prevent the catalyst loss.

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