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Eco-efficient catalytic hydrodechlorination of carbon tetrachloride in aqueous cyclodextrin solutions

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An eco-efficient process of catalytic hydrodechlorination of carbon tetrachloride into methane and chloride salts has been developed in aqueous basic medium at room temperature. The organic pollutants are trapped in water by cyclodextrins (CDs) *via* the formation of inclusion complexes and dechlorinated by a supported heterogeneous palladium catalyst. Catalytic investigations demonstrate that CDs act as efficient CCl_4 solubilizers and, much more interesting, as protective molecules against side reactions.

KEY WORDS: cyclodextrins; absorption; noble metal catalyst; chlorohydrocarbons; volatile organic compound.

1. Introduction

Volatile chlorinated hydrocarbons are toxic compounds and cause noxious effects on the environment, particularly a high ozone potential depletion. Their effective removal or destruction is an important task. Indeed, the rules regulating the emissions of the volatile chlorinated hydrocarbons are more and more severe and the industrial installations should be equipped of efficient treatment methods in order to respect the legislations [1]. Generally, the technologies of volatile chlorinated hydrocarbons abatement are divided into two categories: non-destructive or destructive.

The non-destructive methods are based on solid adsorption processes, membrane technologies or liquid phase absorption processes. Hence, vapor-phase carbon adsorption [2,3] removes pollutants from air by physical adsorption onto activated carbon grains. Unfortunately, the regeneration of the saturated activated carbon is not easily achieved and the replacement of adsorbents is periodically required. In the liquid phase absorption processes, the gas phase is brought into close contact with a liquid phase, in which the pollutant is soluble [4]. Water, aqueous solutions containing basic, acid or oxidative reagents can be used. Unfortunately, this method is generally restricted to water-soluble chlorinated hydrocarbons (CHCs).

The destructive methods such as thermal oxidations and catalytic processes transform the pollutants into harmless products. These methods are potentially preferable since no secondary waste streams are produced. Thermal combustion in gas phase is based on the total oxidation at high temperatures generally above 800 °C of the molecules in the ultimate products such as carbon dioxide, water, and hydrochloric gas [5]. Furthermore, the addition of an oxidation catalyst enables the reaction to occur at lower temperatures than those required by conventional thermal oxidation [6,7]. Nevertheless, oxidation processes (thermal or catalytic) remain energetically expensive and require the installation of special reactors that should be resistant against the corrosive gas emissions. There is also a significant risk of producing new and more toxic emissions, including chlorodioxins or volatile metal chlorides. In recent years, biotechnologies gain attention for waste gas treatments [8] but they require acclimated biological mixtures and become ineffective at high concentrations.

In this context, the development of new treatment methods for the volatile CHCs abatement remains a great challenge. Surprisingly, the possibility to combine an absorption process with a catalytic process has never been imagined for dechlorinating volatile CHCs. The bubbling of the gaseous effluent contaminated by volatile CHCs through an aqueous solution containing cyclodextrins (CDs) and a supported noble metal catalyst could be considered as such a process (figure 1).

So, when the gaseous effluents are put in contact with a solution containing CDs, the pollutants could be trapped in the hydrophobic cavity of the CDs and, consequently solubilized in water (absorption process). Indeed, CDs are water-soluble cyclic oligosaccharides composed of six, seven, or eight D-glucopyranose units that can include in their cavity a wide range of hydrophobic molecules (Scheme 1) [9]. The pollutant/CD complexes could be then transformed into harmless products by a heterogeneous catalyst *via* reductive dechlorination in water (catalytic process). After reaction, the "host–guest"

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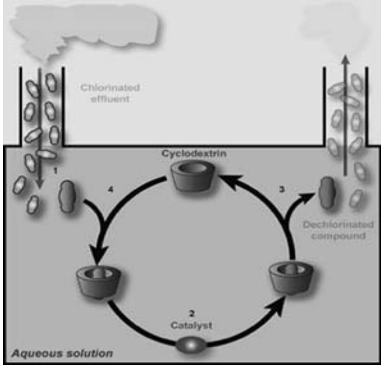


Figure 1. Illustration of the dechlorination process of gaseous effluent through an aqueous solution containing CD as a solubilizing agent and a catalyst.

complexes would dissociate to give the dechlorinated products that can be either used for chemical or energy valorization.

In order to examine the feasibility of such a process, we have investigated the hydrodechlorination of carbon tetrachloride (CCl_4) in a batch reactor in the presence of an aqueous CD solution and a supported heterogeneous palladium catalyst. Among the different catalysts generally reported in the literature for such applications, palladium catalysts on activated carbon (Pd/C) are particularly attractive for developing dechlorination reactions in water [10–14]. Indeed, palladium is known to be the most active metal towards hydrodehalogenation [15] while activated carbon appears to be a favored support to form a good interface in aqueous medium with hydrophobic reactants [10,16]. According to the equation (1), molecular hydrogen and sodium hydroxide (NaOH) were added to the reaction medium to (i) reduce the CCl_4 and (ii) neutralize the produced hydrochloric acid, respectively:

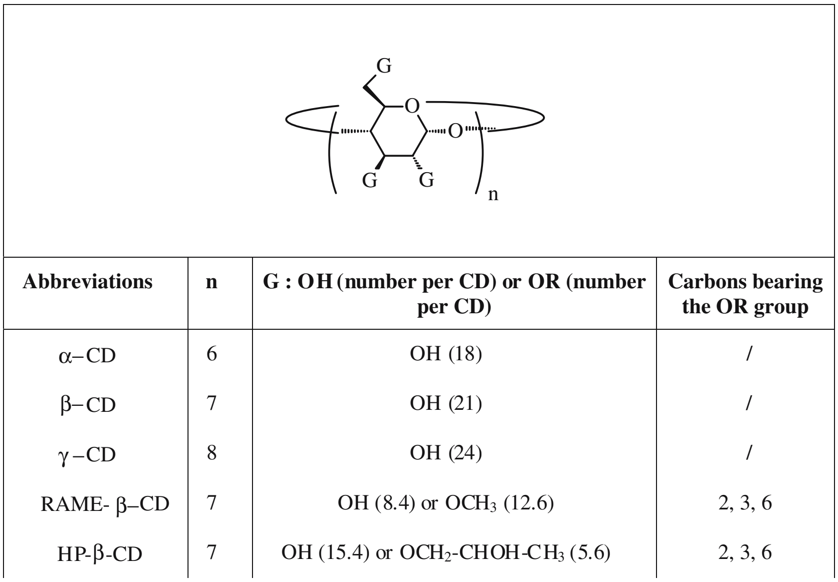
$$CCl_4 + 4OH^- + 4H_2 \xrightarrow{Pd/C} CH_4 + 4H_2O + 4Cl^-. \quad (1)$$

Much attention has been focused in this work on the optimization of OH^- and CD concentrations leading to the large amount of methane. The results of our batch experiments are described below.

2. Experimental

2.1. Chemicals

Carbon tetrachloride, chloroform and dichloromethane (Aldrich) were all of analytical reagent grade and were used as received. Distilled water was used throughout this work. Palladium on activated carbon denoted Pd/C (Specific surface area: 820 $m^2\ g^{-1}$, pore



Abbreviations	n	G : OH (number per CD) or OR (number per CD)	Carbons bearing the OR group
α–CD	6	OH (18)	/
β–CD	7	OH (21)	/
γ–CD	8	OH (24)	/
RAME- β–CD	7	OH (8.4) or OCH_3 (12.6)	2, 3, 6
HP-β-CD	7	OH (15.4) or OCH_2-CHOH-CH_3 (5.6)	2, 3, 6

Scheme 1. Chemical structures of the CDs.

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HP-β-CD	7	OH (15.4) or OCH_2–CHOH–CH_3 (5.6)	2, 3, 6

volume: 0.49 $cm^3\ g^{-1}$, mean pore diameter: 24 Å) was purchased from Acros and the palladium metal loading (9 wt%) has been checked by elemental analysis. Native CDs (α- and β-), RAME-β-CD and HP-β-CD were purchased from Aldrich. The RAME-β-CD was a native β-CD partially *O*-methylated with statistically 12.6 OH groups modified per CD. The HP-β-CD was a native β-CD partially *O*-2-hydroxypropylated with statistically 5.6 OH groups modified per CD.

2.2. Measurements of reduction of volatility

Volatility measurements were done with a *Varian Genesis static headspace*. Sample solutions of 10 mL containing 100 ppm of pollutant were introduced into 22 mL headspace vials. The vials were then thermostated at 30 ± 0.1 °C and shaken overnight prior to analysis. After the equilibrium was established, 1 mL of vapor from the above solution was drawn out from the vial using a gas-tight syringe and analyzed by gas chromatography (Perkin Elmer Autosystem XL) with a flame-ionization detector using a DB624 column. The volatility-changing effect of CDs was investigated by comparing the areas in the absence and presence of CD. The reduction of volatility, denoted *R*, is calculated according to the equation (2):

$$R = \left(\frac{A_0 - A_{CD}}{A_0}\right) \times 100, \qquad (2)$$

where A_0 and A_{CD} represent the areas of the chromatographic peak without and with CD, respectively.

2.3. Illustrative view of the 1:1 Inclusion complex between β-CD and carbon tetrachloride generated by computer

The steric complementarity between β-CD and carbon tetrachloride has been illustrated by means of computed tri-dimensional models. β-CD structure corresponds to a non-distorted conformation with C7 symmetry. Carbon tetrachloride has been docked into the cavity of β-CD *via* Monte-Carlo statistical mechanics simulations (100,000 deformations) associated to the OPLS all-atom force field. The absence of steric hindrance has been checked for each atom of the inclusion compound computed structure.

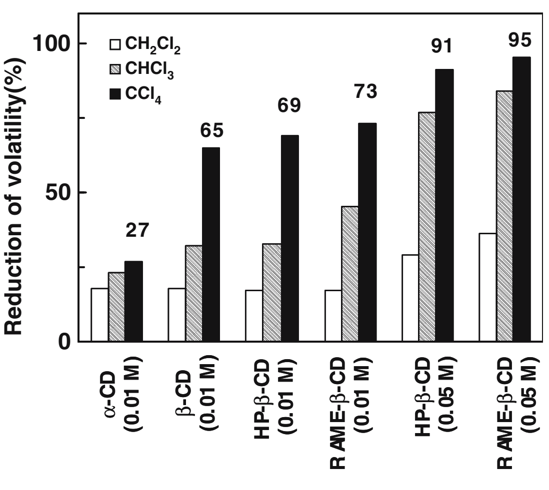

Figure 2. Reduction of volatility of CCl_4, $CHCl_3$, and CH_2Cl_2 in different aqueous solutions of CDs at 30°C (*in brackets: CD concentrations*).

2.4. Catalytic hydrodechlorination of CCl_4

The catalytic tests of CCl_4 hydrodechlorination were carried out at 30 °C in a magnetically stirred glass reactor (volume = 41 mL) by introducing CCl_4 (0.325 mmol, 51 mg) in 3 mL of an aqueous solution containing the Pd/C catalyst (4.4 μmol, 5.2 mg) and the required amounts of CD and NaOH. The pressure inside the reactor was fixed at 2×10^5 Pa by adding gaseous hydrogen. After 60 min, the reaction was stopped by immersing the flask in a bath at 0 °C. The gas phase above the solution is analyzed by gas chromatography (Perkin Elmer Clarus 500) equipped with a TCD detector, using Porapak Q and molecular sieve 5 Å columns. Then the solid catalyst was separated from the aqueous solution with a 0.22 μm filter and washed thoroughly. The total amount of chloride ions released during the test was quantified by ion chromatography (Dionex DX-120) equipped with a CS-12A column. The conversion is calculated from the chloride content on the basis that one mole of CCl_4 can release four moles of chloride ions and consequently expresses the percentage of C–Cl bonds that have been cleaved during the catalytic test. The catalytic tests were repeated three times to check the reproducibility.

3. Results and discussion

Before examining the capacity of Pd/C catalyst to hydrodechlorine CCl_4 in the presence of CDs, the ability of these supramolecular hosts to trap CCl_4 has been studied by static headspace-gas chromatography.

Figure 2 displays the reductions of volatility of $CH_{4-x}Cl_x$ (x = 2–4) in the presence of aqueous solutions of CDs. The reduction of volatility of chloroform and dichloromethane were also determined as they are potential intermediates in the dechlorination process.

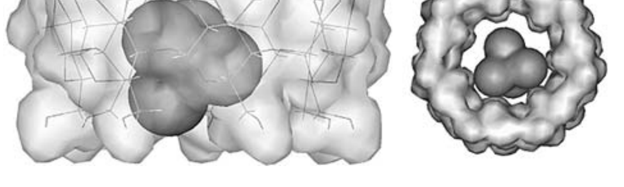

Figure 3. Illustrative views generated by computer of the 1:1 inclusion complex between CCl_4 and β-CD.

Table 1
Hydrodechlorination results at 30°C in the presence or absence of CDs[a]

Entry	catalyst	*t* (h)	Substrate	CD	CD/Substrate	Conversion (%)	CH_4:CO
1	no	1	CCl_4	no	0	0	/
2	yes	1	CCl_4	no	0	50.7	4.6
3	no	1	$CHCl_3$	no	0	10.8	0[b]
4	no	1	CH_2Cl_2	no	0	0	/
5	yes	1	CCl_4	β-CD	0.25	58.7	3.0
6	yes	1	CCl_4	HP-β-CD	0.25	88.5	11
7	yes	1	CCl_4	RAME-β-CD	0.25	80.9	32

[a] *Reaction conditions:* 5 mg of Pd/C catalyst (4.4 μmol Pd); 0.325 mmol of Substrate in 3 mL of water; initial H_2 pressure: 2 bar; Substrate: Pd = 75:1; NaOH:Substrate = 10:1.

[b] Gas phase analysis: 100% CO.

Our data demonstrate that the volatility of CCl_4 was greatly reduced in presence of CDs. However, the volatility reduction strongly depended on the nature of the CD. So, the diameter of the cavity appeared as a crucial point since the reduction of volatility in the presence of α-CD was very low and that no reduction in the presence of γ-CD was observed. The β-CDs that have intermediate diameters (i.e. 5.2, 6.6 and 8.4 Å for α-CD, β-CD and γ-CD, respectively [9]) was undoubtedly the best host since the volatility of CCl_4 was notably reduced whatever the β-CD studied. Consequently, the efficiency of β-CD derivatives relatives to others CD is directly linked to size of the β-CD cavity. This result is in line with the literature data [17,18] and our computer molecular modeling showing that CCl_4 fits tightly in the β-CD cavity as shown in the figure 3.

Interestingly, it was found that the reduction of volatility increased versus the concentration of β-CD and depended on the chemical modification of the β-CD. The best results were obtained with the randomly methylated β-CD (RAME-β-CD). For instance, the use of RAME-β-CD at a concentration of 0.05 M led to a reduction of volatility of 95%. Much more interesting is the fact that CCl_4 is better recognized by the β-CDs than the chlorinated intermediates, avoiding all inhibition by the reaction products during catalysis. Since the catalytic tests will be carried out in alkaline solutions, additional experiments of CCl_4 absorption have been performed in basic solutions of β-CDs (pH = 12). In these conditions, the reductions of volatility were similar to those measured at neutral pH, indicating that the ability of β-CDs to trap CCl_4 is not altered at high pH (results not presented).

Hence, these previous results have provided evidence of the successful contribution of the β-CD moieties for improving the water solubility of CCl_4. In the second part of this work, our objective was then to study the influence of the β-CD in the catalytic dechlorination process carried out in water.

The results of CCl_4 hydrodechlorination obtained at 30 °C in the absence or presence of β-CD derivatives are regrouped in table 1. As previously mentioned, the conversion expresses the percentage of C–Cl bonds that are cleaved during the catalytic run on the basis that one mole of CCl_4 can release four moles of chloride ions.

As expected, no activity was observed without catalyst in the presence of NaOH (entry 1). When adding the catalyst, the conversion reached up to 50% (entry 2) and the gas phase analysis has revealed the formation of chloroform and methane as the main reaction products, with traces of dichloromethane and chloromethane as

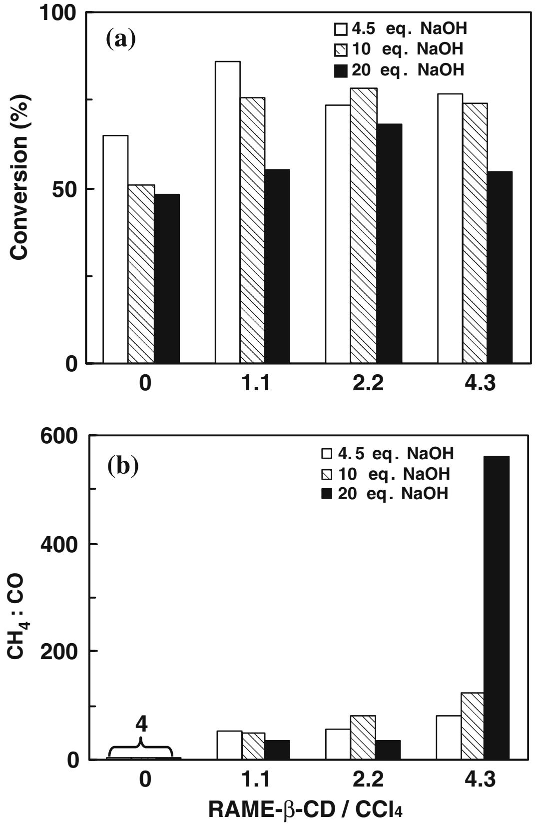

Figure 4. Influence of the RAME-β-CD and NaOH contents in the catalytic hydrodechlorination of CCl_4 carried out at 30 °C: (a) conversion and (b) CH_4:CO ratio. *Reaction conditions*: 1-hour test; Pd/C catalyst: 5 mg (4.4 μmol Pd); CCl_4: 51 mg (0.325 mmol) in 3 mL of water; initial H_2 pressure: 2 bar; CCl_4:Pd = 75; NaOH: CCl_4 = 4.5, 10 and 20 and RAME-β-CD:CCl_4 = 0, 1.1, 2.2 and 4.3.

by-products. This product distribution is in agreement with recent mechanistic studies [19,20] that proposed that CCl_4 transformation proceeds *via* parallel pathways on the Pd/C surface. Unfortunately, an appreciable amount of carbon monoxide (CO) was also detected in the gaseous phase. Additional test performed with $CHCl_3$ as substrate has clearly shown that the CO formation was unambiguously linked to the non-catalytic degradation of chloroform that is unstable in basic medium (entry 3) according to the equation 3).

$$CHCl_3 + 3OH^- \rightarrow CO + 2H_2O + 3Cl^-. \quad (3)$$

In the same conditions, no degradation of dichloromethane was detected (entry 4). So, in order to compare between the catalytic and non-catalytic pathways, the CH_4:CO ratio was then chosen to monitor the selectivity since the methane and CO are the only reaction products having no affinity with β-CDs.

Addition of native or chemically modified β-CDs into the reaction medium allowed to increase notably the conversion (entries 5–7). This dechlorination rate enhancement in the presence of β-CDs is directly linked to the formation of inclusion complexes that enable to increase the water solubility of the chlorinated substrate and consequently the catalytic turnover.

Interestingly when using chemically modified β-CDs, i.e. RAME- and HP (entries 6 and 7), an increase in the CH_4:CO ratio was also observed. RAME-β-CD was clearly the most efficient one, showing an enhancement by a factor six of the CH_4:CO ratio. These results and the fact that RAME-β-CD is the most efficient one to reduce the volatility of CCl_4 led us to focus our catalytic study on this particular CD.

The effect of the RAME-β-CD concentration has been investigated at different NaOH concentrations (figure 4). Indeed, the addition of NaOH is essential since it ensures the neutralization of the produced hydrochloric acid, the neutralization of the acid sites present on the carbon support [21] and avoids also the acidic hydrolysis of CDs. But, for a fast and complete reaction, the amount of NaOH needs optimizing since it depends on the type of activated carbon, the adsorption strength of the reactants and also the level conversion. Moreover, it should be reminded that the minimal amount of base needed to neutralize all the acid that could be formed during the dechlorination process of CCl_4 is four.

When the tests were performed without RAME-β-CD, the maximum conversion achieved was about 70% with 4.5 eq. of NaOH in the medium, with no change in selectivity. These results show that only a slight excess of NaOH is preferable to reach a high conversion efficiency. By adding RAME-β-CD, better dechlorination activities were observed, in agreement with the great ability of CD molecules to act as solubilizing agents. However the rate enhancement is less pronounced when the concentration of RAME-β-CD is above 2.2 eq. From the selectivity point of view, it appeared that the higher the CD concentration is, the lower the CO emissions are. Indeed, the formation of CO was almost totally eliminated at the highest content of RAME-β-CD (4.3 eq.) and NaOH (20 eq.), respectively (CH_4: CO = 530). This outstanding result is clearly in connection with fact that the RAME-β-CD plays a major role in the chloroform protection *via* the hydrophobic cavities, impeding the basic attack of the hydroxide anions and consequently the CO formation.

4. Conclusions

We have described an original example of catalysis in a multi-phase system, where enhancements of CCl_4 hydrodechlorination rate in water have been obtained under mild reaction conditions in presence of a noble metal catalyst with β-CD. The positive role played by the β-CD molecules can be decomposed into two main functions. First, they act as classical and efficient mass transfer agents. Indeed, β-CDs allow to increase the water solubility of the chlorinated substrate by forming inclusion complexes, and consequently improve the turnover frequencies on the surface of the Pd/C catalyst. Second, our study has brought out remarkable and unexpected abilities of certain β-CDs to protect the substrate against side reactions through the formation of inclusion compounds. The case of degradation of $CHCl_3$, which is the first reaction intermediate, issued from the degradation of CCl_4 is particularly interesting. Actually it appears that adding chemically modified β-CDs such as the RAME-β-CD in the reaction medium increase the stability of the chloroform in aqueous basic medium and thus promotes selectively the catalytic route in water, now allowing the development of continuous processes in water.

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