

Liquid-phase hydrodechlorination of chlorobenzene by molecular hydrogen: The influence of reaction medium on process efficiency*

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Abstract: Catalytic hydrodechlorination (HDCI) of chlorobenzene was carried out in a two-phase aqueous–organic solvent system and a single-phase solvent composed of saturated KOH solution in a secondary alcohol over Pd-based catalysts at 50 °C and atmospheric pressure of H₂. It was shown that an aqueous–organic solvent system containing propan-2-ol and aqueous KOH increases catalyst activity by promoting mass transfer of the formed chloride ions to water phase that prevents catalyst deactivation. It is inferred that propan-2-ol favors hydrogen activation during the HDCI process. Use of the Pd catalysts based on hydrophobic carbon support enables chlorobenzene HDCI to proceed in a two-phase solvent at a satisfactory rate, even in the absence of phase-transfer catalysts.

Keywords: chlorinated organics; hydrodechlorination; isopropyl alcohol; solvent; Pd catalyst; propan-2-ol.

INTRODUCTION

Persistent chlorinated organic pollutants (POPs) have become serious environmental problems of global concern. Development of efficient methods for utilization of polychlorinated organics is an important task both for industry and environmental protection. Various methods have been proposed for reducing and controlling chlorinated pollutants such as polychlorinated biphenyls, chlorinated benzene, or chlorinated hydrocarbons [1–3]. The catalytic hydrodechlorination (HDCI) method over noble- and transition-metal catalysts has economic and environmental advantages and is a safer alternative to the traditional methods, allowing for reuse of reaction products. Other advantages of the liquid-phase HDCI are low operation temperatures and pressures, a high degree of conversion of different types of chlorinated substrates, the absence of harmful side products, a smaller sensitivity to pollutant concentrations, and the possibility of selective removal of chlorine [2,4,5]. Molecular hydrogen, formic acid, propan-2-ol, hydrazine, and hydrides are often used as hydrogen sources in liquid-phase HDCI. Generally organic solvents are applied as the reaction medium.

The choice of the reaction medium for liquid-phase catalytic processes of organic synthesis has a considerable effect on reaction rate and substrate conversion. This impact is caused by various factors,

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such as reagent solubility, substrate activation due to coordination interactions, and processes of adsorption–desorption of the reagents and products onto a catalyst surface.

When comparing the results of research on liquid-phase catalytic hydrodehalogenation (HDG) of different halogenated aromatic compounds by molecular hydrogen, a definite connection is observed between reaction rate and the solvent utilized [6,7]. A literature survey indicates that organic solvents applied in liquid-phase HDG are diverse, and include primary and secondary alcohols, aromatic compounds, hydrocarbons, etc. The use of alcohols has been shown to increase the reaction rate [8], supposedly because of their role as hydrogen donors as well as their solvent properties. Displacement of chlorine atoms in aromatic halides by hydrogen occurs selectively on the catalysts, and involves hydrogen transfer from alcohol to the chlorinated substrate. Secondary alcohols are considered to be the best hydrogen sources [5,8,9]. However, those under consideration are characterized by somewhat low boiling points (e.g., 82.4 °C for propan-2-ol) which leads to significant solvent evaporation during the HDG reaction in a temperature range of 50–70 °C. Moreover, heavy polychlorinated aromatic compounds are poorly soluble in alcohols.

The foregoing problems may be solved by adding aromatic solvents to the reaction system, but this leads to another problem, arising from competitive adsorption of reagents and solvent molecules on catalyst active sites and resultant decrease in catalyst activity [10]. In spite of this, mixtures of toluene and alcohols are employed for HDG processes [11,12]. However, the question of optimal proportions of propan-2-ol and toluene to ensure high substrate conversion rates is not discussed in the literature.

It is well known that hydrochloric acid is a by-product of HDCl of chlorinated aromatic compounds by molecular hydrogen. Its formation leads to catalyst deactivation. For HCl neutralization, alkali compounds are usually introduced in the reaction medium. Published data indicate that different methods are used to add alkali. The traditional approach entails introducing solid alkali powder directly into the organic solvent with its full or partial dissolution [6,13]. An interesting alternative is to add aqueous alkali to an organic solvent with formation of a two-phase solvent system [13–15]. Under these conditions, the reaction proceeds in the presence of phase-transfer catalysts. Most often, onium salts are applied as phase-transfer agents as they accelerate anion mass transfer.

The purpose of this work is to study the influence of reaction-medium composition and alkali addition methodology upon liquid-phase HDCl of chlorobenzene by molecular hydrogen on Pd/C catalysts. In addition, we report here on the influence of support of the Pd catalysts on the efficiency of HDCl of chlorobenzene.

EXPERIMENTAL

Catalyst preparation

Supported palladium catalyst (Pd/C) was prepared by impregnation from a hydrochloric acid solution of PdCl₂. Carbon material “Sibunit” [16] with a grain diameter of 0.1–0.125 mm was used as a support. The specific surface area of Sibunit determined by the Brunauer–Emmett–Teller (BET) method was 530 m²/g.

An amount of support material was wetted with water, then the solution of appropriate concentration was added, and the mixture was stirred at 80 °C to allow slow evaporation of water. The residue was then dried at 110–130 °C for 3 h. The calculated amount of Pd was equal to 1 wt % and was verified by X-ray fluorescence analysis using VRA-30 analyzer with a Cr anode. The reduction of the catalyst was performed at room temperature by adding aqueous sodium borohydride in the molar ratio of Pd:NaBH₄ = 1:3. After reduction, the catalyst was washed with water until no chloride ions could be detected in the filtrate, by testing with silver nitrate. The same procedures were used for preparation of Pd catalysts based on anatase modification of titanium dioxide (Pd/TiO₂) and zeolite with the structure of ZSM-5 (Pd/ZSM-5).

Hydrodechlorination of chlorobenzene by H_2

HDCI of chlorobenzene in two-phase aqueous–organic solvent system was carried out in a glass temperature-controlled reactor equipped with a magnetic stirrer and a condenser. Reduced catalyst (95.7 mg) was placed in the reactor, mixed with aqueous 50 % KOH (4 ml), and activated at 50 °C for 1 h with constant stirring, under atmospheric pressure of hydrogen. In one case, specially discussed in the text below, distilled water was used instead of aqueous alkali. The activation process was followed by introduction of chlorobenzene (0.91 ml) in an organic solvent (11 ml of propan-2-ol, toluene, or mixtures in various ratios) into the reaction medium to begin HDCI.

When a single-phase solvent, saturated KOH solution in propan-2-ol, was applied, the reduced Pd/C catalyst (95.7 mg) was placed in the reactor, mixed with a saturated solution of KOH in propan-2-ol (15 ml) and activated in the same way at 50 °C for 1 h under hydrogen at atmospheric pressure. The saturated KOH solution was prepared by dissolving an excess of finely pounded KOH in propan-2-ol at room temperature with constant stirring for 24 h. Chlorobenzene (0.91 ml) was then added and the HDCI process was started.

Liquid-phase HDCI of chlorobenzene by hydrogen was conducted under constant stirring (stirring speed 800 rpm), 50 °C and at atmospheric pressure of hydrogen. It has been shown earlier, that when a stirring rate above 800 rpm is maintained, the influence of external diffusion processes may be neglected [12]. The products of HDCI in the organic phase were analyzed by gas chromatograph “Crystall-2000” equipped with a flame-ionization detector. The instrument was operated under the conditions of Ar carrier gas, column temperature region 50–100 °C, column length 3 m, column diameter 2.5 mm, filling sorbent “Chromosorb” with stationary phases OW – 101 and SE – 52.

RESULTS AND DISCUSSION

The results of the Pd/C catalyst tests in liquid-phase chlorobenzene HDCI in different reaction media are shown in Table 1. The maximum catalytic activity was achieved in the two-phase water–organic medium consisting of a potassium hydroxide solution and propan-2-ol. Switch from the water–alkali solution to water led to a decline in catalytic activity. Nevertheless, the HDCI degree of 62 % attained in the case of water is substantially higher than that in the reaction medium containing saturated KOH solution in propan-2-ol (25 %). The low catalyst activity in the toluene-containing medium may be explained by the chlorobenzene and toluene competing for adsorption sites on the catalyst surface [10,17] and insufficient hydrogen solubility in toluene [18].

Table 1 Dechlorination degree (X) of chlorobenzene over Pd/C catalyst depending on reaction medium at 50 °C and atmospheric pressure of H_2 .

No.	Reaction media*	Chlorobenzene: KOH molar ratio	Reaction time, min	X, %
1	Propan-2-ol–aqueous KOH	1:6	150	99
2	Propan-2-ol–water	–	240	62
3	Toluene–aqueous KOH	1:6	240	11
4	Saturated KOH solution in propan-2-ol	1:2	240	25

*Initial chlorobenzene concentration was 0.00894 mol. Pd:chlorobenzene molar ratio was 1:1000.

The above-described results probably may be linked to different degrees of the Pd/C catalyst deactivation in different reaction media. It is known from the literature that the addition of a solid alkali to a single-phase organic solvent not only leads to HCl neutralization but also has some negative effects.

The solubility of alkali compounds and the corresponding alkali metals chlorides are rather low in many organics. This causes their deposition on the catalyst surface and an inhibition of the catalytic activity [7,11,19,20]. The addition of water that easily dissolves both the alkali agents and the forming salts may help to restore the activity. It was reported that in the case of an ethyl alcohol solvent the addition of water significantly improved the rate and efficiency of the HDCl process over a Pd/C catalyst [7,21]. This effect was linked by the authors to hydrochloric acid solubility in water. As a result, fewer chloride ions get adsorbed on the catalyst active sites.

Our results confirm this data. Analysis of the chloride ions content in the water phase after complete conversion of the substrate has shown that in the presence of water 26 rel. % of all the chloride ions formed in the reaction were contained in the water phase. When an aqueous solution of KOH was added, the water-phase chloride ion contents increased twofold to as high as 47 rel. %. Thus, it can be concluded that the presence of an alkali compound increases chloride ion transport efficiency in the water phase, preventing catalyst poisoning.

Figure 1a shows a reaction system consisting of catalyst, isopropyl alcohol, and a water–alkali phase modeled in a test-tube. It can be seen that most of the Pd/C catalyst is contained in the aqueous–organic interface and so is more accessible both for the reagents in the organic phase and the alkali–water phase. Such a distribution of the catalyst over the reaction medium serves to facilitate chloride ion transport to the water phase.

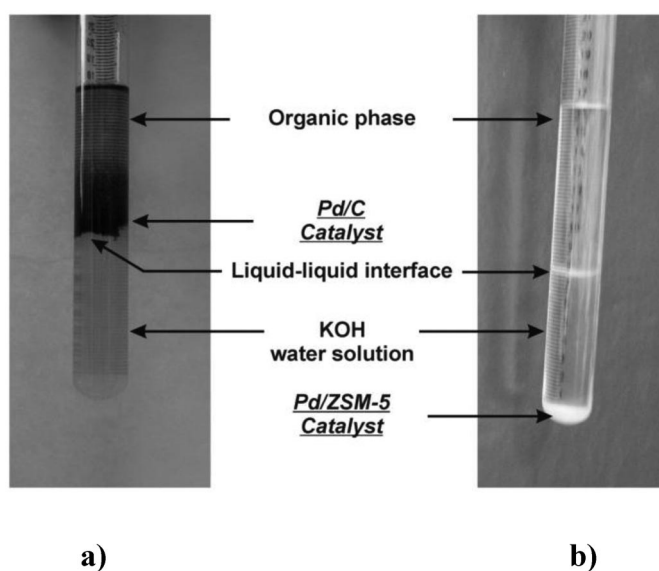


Fig. 1 Distribution of Pd/C (a) and Pd/ZSM-5 (b) catalysts in the system consisting of propan-2-ol and water–alkali solution.

The aqueous–organic solvent system was successfully applied in HDCl of polychlorinated benzenes, chlorinated alkylbenzenes, polychlorinated biphenyls and halogenated aryl ketones and benzyl alcohols [14,22–24] in the presence of phase-transfer catalysts. According to our evidence, with the use of Pd catalysts on a carbon support that ensures that the catalyst is mainly present at the aqueous–organic phase interface, HDCl proceeds at a rather high rate even in the absence of phase-transfer catalysts.

Pd catalysts based on hydrophilic supports (Pd/TiO₂, Pd/ZSM-5) are mostly found in the water phase (Fig. 1b). Their surface is not wetted by the organic phase, and the substrate does not contact with the catalyst active sites. As a result, these catalysts were not active in the described two-phase reaction

medium. When the aqueous–organic solvent system was replaced by a reaction medium containing a saturated KOH solution in alcohol, the initial activity of these catalysts was enhanced dramatically. However, after 30 min of the reaction, the chlorobenzene HDCl over Pd/ZSM-5 catalyst had ceased, most probably because of catalyst deactivation in strong basic medium ($pH > 13$). NMR ^{27}Al spectra confirmed the presence of a partial destruction of the zeolite ZSM-5 framework as a result of dealumination.

As shown above, the solvent ensuring the highest activity of Pd/C catalysts in liquid-phase chlorobenzene HDCl is propan-2-ol. However, for practical applications, toluene would be a more convenient solvent as it is capable of dissolving heavy chloroaromatic substrates and evaporates less during the reaction but is definitely inferior to propan-2-ol in terms of catalyst activity (Table 1). We have studied the possibility of using for chlorobenzene HDCl a two-phase solvent system consisting of a mixture of propan-2-ol, toluene, and water–alkali solution. Figure 2 shows variation in the degree of chlorobenzene conversion as toluene was gradually replaced by propan-2-ol. The catalyst activities were calculated from the conversion achieved after 60 min of the reaction (Table 2).

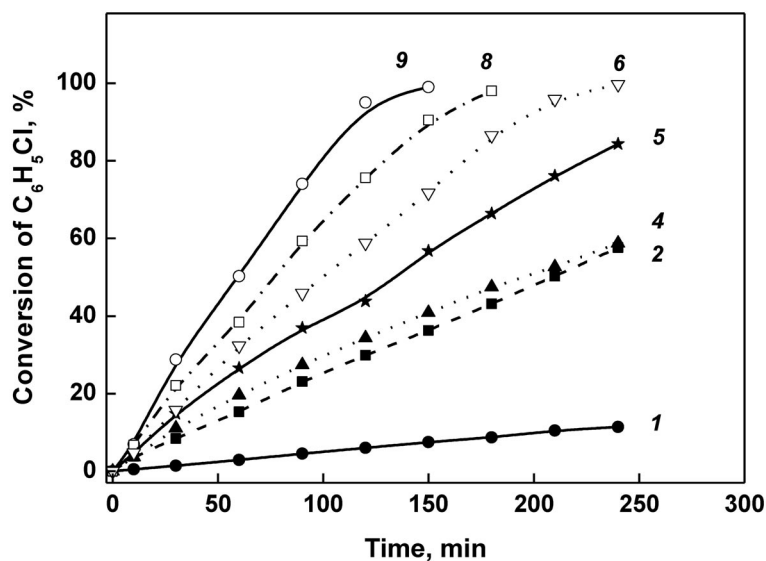


Fig. 2 Conversion of chlorobenzene over Pd/C catalyst vs. reaction time depending on propan-2-ol content in the reaction medium. The curve numbers correspond to experiment numbers in Table 2.

The results in Table 2 show that the replacement of 9 vol % of toluene by propan-2-ol leads to more than a five-fold increase in catalyst activity. This content of propan-2-ol corresponds to a chlorobenzene:propan-2-ol molar ratio of 1:1.5. On the whole, with the change from toluene to propan-2-ol there is increase in activity by a factor of 17.5.

Table 2 Pd/C catalyst activity after 60 min of HDCl reaction depending on propan-2-ol content in the reaction medium at 50 °C and atmospheric pressure of H₂.

No.	Organic phase composition*		Activity, mol _{chlorobenzene} mol ⁻¹ _{Pd} min ⁻¹
	Propan-2-ol:chlorobenzene molar ratio	Propan-2-ol:toluene, vol %:vol %	
1	0	0:100	0.48
2	1.5	9:91	2.6
3	2.9	18:82	2.7
4	4.4	27:73	3.3
5	5.8	36:64	4.4
6	7.3	45:55	5.4
7	8.7	55:45	5.0
8	10.2	64:36	6.4
9	16.0	100:0	8.4

*Initial chlorobenzene concentration was 0.00894 mol. Pd:chlorobenzene molar ratio was 1:1000. Chlorobenzene:KOH molar ratio was 1:6. Total organic phase (propan-2-ol+toluene) volume was 11 ml. The aqueous 50 % KOH solution volume was 4 ml.

This effect may be explained by two factors: the alcohols dissolve the molecular hydrogen better than toluene and this favors a rise of catalyst activity [18], and the alcohols do not compete with substrate for the catalyst active sites [7]. Since the high increase in activity was observed when propan-2-ol was added in amount stoichiometric toward chlorobenzene, the effect is hardly explainable by the properties of the alcohol as a solvent. Several publications have been discussing the possibility for propan-2-ol to be involved in the HDCl reaction as a source of hydrogen when the necessary hydrogen species form directly on the catalyst as a result of dehydrogenation of the secondary alcohol [8,9,25–27]. In this case, the HDCl process was accompanied by production of acetone [8,9,26].

To study propan-2-ol as an alternative source of hydrogen for liquid-phase chlorobenzene HDCl, an experiment was performed in a reaction medium consisting of a aqueous alkali solution and propan-2-ol under nitrogen at 50 °C using a Pd catalyst. The results are presented in Table 3.

Table 3 Dechlorination degree (X) of chlorobenzene over Pd/C catalyst in HDCl run under nitrogen atmosphere in the reaction medium consisting of propan-2-ol and aqueous 50 % KOH solution at 50 °C*.

No.	Reaction time, min	X, %
1	120	0
2**	120	0.2

*Initial chlorobenzene concentration was 0.00894 mol. Pd:chlorobenzene molar ratio was 1:1000. Chlorobenzene:KOH molar ratio was 1:6. The volumes of propan-2-ol and 50 % KOH solution were 11 and 4 ml, respectively.

**Prior catalyst activation under atmospheric pressure of hydrogen in water solution of KOH at 50 °C for 1 h was performed.

Table 3 shows that in the absence of molecular hydrogen no noticeable conversion of chlorobenzene could be achieved. The small conversion in the experiment with a preactivated catalyst in H₂ is attributable to Pd saturation by hydrogen, which further acted as a reagent. To verify that it was not the

catalyst deactivation that had led to the low activity, another experiment has conducted under the conditions where hydrogen was introduced into the reaction medium after 2 h of the reaction in nitrogen after which the reaction proceeded under hydrogen atmosphere. The results are presented in Fig. 3.

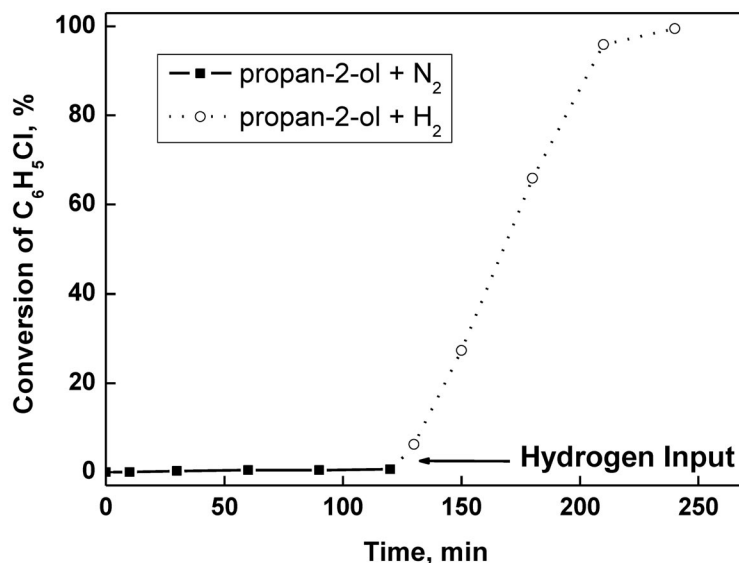


Fig. 3 Conversion of chlorobenzene over Pd/C catalyst vs. reaction time depending on gas-phase composition at 50 °C. Initial chlorobenzene concentration was 0.00894 mol. Pd:chlorobenzene molar ratio was 1:1000. Chlorobenzene:KOH molar ratio was 1:6. The volumes of propan-2-ol and 50 % KOH solution were 11 and 4 ml, respectively.

From the data of Fig. 3, it can be seen that the catalyst that was little active in the 2-h reaction under nitrogen had completely converted the same portion of chlorobenzene during 3 h following the addition of hydrogen gas. It may be concluded that it is the absence of a source of hydrogen rather than catalyst deactivation that was responsible for the low chlorobenzene conversion under a nitrogen atmosphere. These results are in agreement with the evidence [28], that propan-2-ol is not always capable of producing a sufficient amount of hydrogen for hydrogenolysis reactions.

The observed increase in activity with the addition of propan-2-ol may be associated with the fact that propan-2-ol is capable of facilitating the formation of active species of hydrogen and accelerating the process of chlorobenzene HDCl. A positive influence of propan-2-ol on isophorone hydrogenation over Au/MgO catalysts has been reported in [29], where it has been suggested that propan-2-ol donates hydrogen to a substrate molecule and then gaseous hydrogen reacts with the adsorbed dehydrogenated propan-2-ol species. In other words, propan-2-ol acts as a “shuttle agent” for the gaseous hydrogen. We will continue the study of the propan-2-ol effects on chlorobenzene HDCl by hydrogen using different physical–chemical methods of investigation.

CONCLUSIONS

The effect of the conditions of liquid-phase chlorobenzene HDCl by molecular hydrogen on the activity of Pd/C catalyst has been studied. It was shown that an aqueous–organic solvent system containing propan-2-ol (or a propan-2-ol–toluene mixture) and a water phase leads to increase in the catalyst activity by promoting the mass transfer of the forming chloride ions to the water phase that prevents catalyst deactivation. An aqueous solution of potassium hydroxide is twice as effective for the chloride ion

transfer than water. The use of a Pd catalyst based on a hydrophobic carbon support and an aqueous–organic solvent system allows the chlorobenzene HDCl process to proceed with a sufficiently high rate even in the absence of phase-transfer catalysts. Propan-2-ol was found to be a more efficient organic phase than toluene. The addition of small amounts of propan-2-ol to toluene results in considerable acceleration of the process. From the available evidence it can be suggested that propan-2-ol serves to favor hydrogen activation. At the same time, a toluene–alcohol solvent mixture may be an effective solvent in the case of HDCl of heavy polychlorinated aromatic compounds that are poorly soluble in 2-propanol.

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