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Liquid phase catalytic hydrodechlorination of chlorobenzene over supported nickel and palladium catalysts: an NMR insight into solvent function

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Abstract

The catalytic hydrodechlorination of chlorobenzene with Ni/C, Pd/C and $Ni_{98}Pd_2$/C in ethanol was studied with ^{2}D and ^{13}C{^{1}H} NMR. Two dechlorination routes of this reaction (ionic and free-radical) are suggested depending upon the nature of the active hydrogen species. At the same time two competitive sources of hydrogen for hydrogenolysis of the C−Cl bond – molecular hydrogen and solvent (ethanol) molecules – are readily apparent from experiments with molecular deuterium. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Chlorinated hydrocarbons are hazardous pollutants found in various waste organic liquids including oils. The methods of their disposal include direct incineration, catalytic incineration, pyrolysis, reaction with alkali metals or their compounds, catalytic hydrogenolysis, etc. [1,2]. However, for wastes such as polychlorobiphenyl compounds and halogenated petrochemical byproducts (chlorinated alkanes and benzenes), liquid and gas phase hydrodechlorination provide a more economical solution than other methods [3–5]. Liquid phase catalytic hydrodechlorination is simple, safe and effective simultaneously. The HCl can be easily separated and the refined hydrocarbons can be recycled. As a rule, liquid phase hydrodechlorination is catalyzed by transition metals of the VIIIth group in an aliphatic alcohol medium under mild conditions [6–8]. Recent studies [9,10] have shown that the solvent plays an important role in this process, influencing both its efficiency and selectivity. Besides their solvent function, alcohols frequently serve as hydrogen donors for hydrodechlorination. For instance, in Refs. [11,12], methanol and isopropanol were used to dechlorinate polychlorinated benzenes with Pd catalysts in an inert atmosphere. As demonstrated in these works, in the reaction course methanol oxidized to CO_3^{2-} [11], while isopropanol oxidized to acetone [12].

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Earlier [13], we have shown that nickel (Ni/C), palladium (Pd/C) and Pd-promoted nickel ($Ni_{98}Pd_2/C$) catalysts supported on the carbon material ''Sibunit'' [14] allowed successful hydrodechlorination of polychlorinated aromatic compounds in ethanol with dissolved NaOH under mild conditions (20–70°C, 1–20 atm H_2).

The present work discusses the possible role of the solvent medium (ethanol) in hydrodechlorination and the peculiarities of this reaction with the nickel and palladium catalysts.

2. Experimental

We used supported nickel (Ni/C) and Pd-promoted nickel ($Ni_{98}Pd_2/C$) catalysts containing 6.81×10^{-4} mole of transition metal per gram of catalyst, and Pd/C catalyst (3.4×10^{-4} mole Pd/g cat).

Mono- and bimetallic catalysts were prepared in the following manner: nickel chloride ($NiCl_2$) and palladium hydrochloric acid (H_2PdCl_4), the latter produced by dissolving of $PdCl_2$ in HCl ($HCl/PdCl_2 = 2/1$), were supported on Sibunit by impregnation with subsequent drying. Then the samples were reduced by $NaBH_4$ in ethanol and twice washed by a water–ethanol (1:1) mixture.

Hydrodechlorination was carried out in a thermostatted ($t = 50°C$) glass reactor equipped with a magnetic stirrer at a pressure of 1 atm. In regular experiments, a freshly-prepared catalyst containing 0.5 mmol of metal was added to 2.6 mmol of chlorobenzene dissolved in 10 ml of 95% ethanol. The ethanol contained an excess of NaOH relative to stoichiometric amount required to accept the evolving HCl. The mixture was vigorously stirred.

The reaction products were analyzed with NMR spectroscopy. The $^{13}C\{^1H\}$ NMR spectra were obtained with an AVANCE DPX-250 Bruker spectrometer at a frequency of 62.90 MHz. Inversely-gated proton decoupling was performed to avoid Nuclear Overhauser Enhancement (NOE). Integral line intensities in these spectra correspond to the relative number of carbon atoms of different types and should not be corrected for NOE effects.

The ^2D NMR spectra were obtained with an MSL-400 Bruker spectrometer at 61.4 MHz of resonance frequency with chemical shifts referenced to external d_6-benzene.

3. Results and discussion

In order to elucidate the function of solvent in hydrodechlorination, a set of experiments has been carried out on chlorobenzene conversion in ethanol at 50°C and 1 atm D_2. The reaction was performed for 3 h in the case of Ni/C, 1 h with $Ni_{98}Pd_2/C$ and 30 min with Pd/C; then the reaction mixture was filtered and the liquid phase was analyzed by ^2D and $^{13}C\{^1H\}$ NMR. Hydrodechlorination of chlorobenzene during the time periods mentioned attained 98%–100%. Molar concentrations of hydrodechlorination products are presented in Table 1.

Apart from h_6- and d_1-benzenes (PhH and PhD, respectively), biphenyl (PhPh) and sodium acetate (CH_3COO^-) were the reaction products (Table 1). This set of products leads to certain conclusions on the reaction mechanism.

It is suggested that in chlorinated aromatics, C−Cl bonds acquire a distinct double-bond character as the chlorine atom loses p-electrons due to resonance. Upon the adsorption of chloroaromatic compounds in ethanol on nickel and palladium catalysts, diadsorbed chloroaromatic species are produced [15–17]. Further, dechlorination is supposed to proceed by ionic mechanism when diadsorbed species is attacked by hydride ion. In the case of chlorobenzene, this will result in the formation of adsorbed phenyl anions, which can accept protons and thus convert to benzene.

However, this mechanism does not explain the formation of biphenyl observed in our experiments (Table 1). Indeed, the adsorbed phenyl anions cannot recombine owing to coulombic repulsion of negatively charged species.

Table 1

Molar concentrations (M) of products formed upon catalytic hydrodechlorination of chlorobenzene ([PhCl]$_o$ = 0.255 M) at 50°C and D$_2$ atmosphere in the ethanol solution (reaction time 3 h)

No.	Catalyst	[PhD]	[PhH]	[PhPh]	[CH$_3$COO$^-$]	[−CH$_2$D]	[−CHD−]	[−OD]	[PhCl]
1	(ethanol)	–	–	–	–	0.007	0.006	0.003	–
2	Ni/C	0.094	0.135	–	0.060	0.007	0.084	0.217	0.026
3	Ni$_{98}$Pd$_2$/C	0.113	0.118	0.012	0.054	0.007	0.028	0.243	–
4	Pd/C	0.049	0.182	0.013	0.187	0.007	0.014	0.522	–
5	Pd/C	0.0004[a]	0.255[b]	–	0.016	0.007	0.008	0.727	–
6	Ni/C(Ar)[c]	–	0.190	–	0.136	–	–	–	0.065
7	Pd/C (Ar)[c]	–	0.231	0.012	0.124	–	–	–	–

[a] Concentration comparable with natural content PhD (0.0002 M) in 0.255 M of benzene.

[b] Initial concentration of benzene in the test experiment C$_6$H$_6$ + D$_2$ + Pd/C (3 h).

[c] Dechlorination was carried out for 3 h under argon atmosphere.

On the other hand, it has been shown [11] that chlorobenzene dechlorination in an alcohol-basic medium in the presence of palladium catalysts may proceed by a radical mechanism through the formation of phenyl radicals. The radicals either interact with adsorbed hydrogen atoms producing benzene or recombine producing biphenyl.

Apart from the ionic mechanism, the presence of biphenyl in the reaction mixture in our experiments also proves a radical mechanism for chlorobenzene dechlorination with palladium catalysts. This suggests a mechanism combining both ionic and radical dechlorination routes (Scheme 1).

Note that biphenyl is found in the reaction mixture only if Pd-containing catalysts (Pd/C and Ni$_{98}$Pd$_2$/C) are used (Table 1).

This difference can be well correlated with the dominant type of active hydrogen inherent for each catalyst. On one hand, it is known that interaction of hydrogen with Ni-metal under
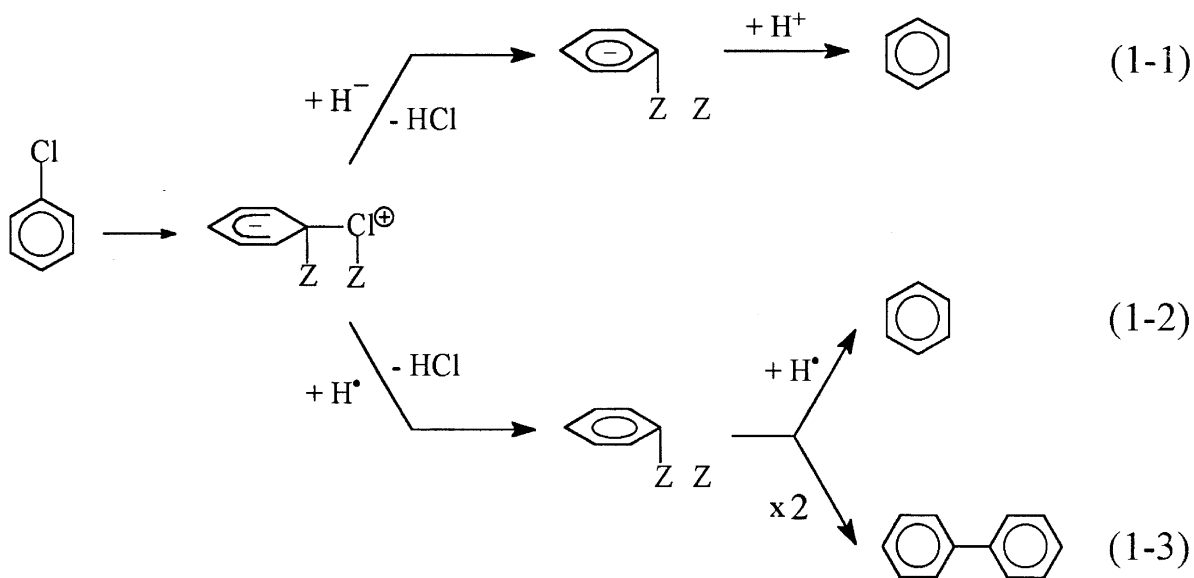
Scheme 1.

normal conditions leads mainly to ionic forms of hydrogen [18], which will obviously participate in the ionic route (1–1) of the hydrodechlorination process. On the other hand, in hydrogen occluded by metal palladium species two different forms of Pd hydrides are distinguished [19]: (i) α-PdH — supposed to contain ionic forms of hydrogen; (ii) β-PdH — presumably contains atomic hydrogen. Therefore, in contrast with Ni catalyst, Pd catalysts will activate both ionic (1–1) and radical (1–2,3) routes. The contribution of each route to the total conversion of chlorobenzene will depend upon the reaction conditions.

As Table 1 shows, the contribution of the biphenyl-producing route (1–3) in a basic medium remains constant regardless of the type of palladium catalyst. Under strong acidic conditions (pH = 1), no biphenyl was found in dechlorination products for either Pd catalysts or Ni catalysts. It seems likely that the excess of protons in the liquid phase and on the catalyst's surface is not favourable for the radical route of hydrodechlorination.

One more side product detected in the reaction mixture is acetate ion (Table 1). It appears in amounts comparable with the initial chloroben-zene content as a result of the oxidation of ethanol in the course of chlorobenzene hydrodechlorination process. Only traces of acetate were found during the stirring of ethanol with dissolved NaOH for 3 h at 50°C in an inert atmosphere in the presence of Ni/C ([CH_3COO^-] = 0.009 M) or Pd/C ([CH_3COO^-] = 0.017 M) when no dechlorination occurred. Therefore, it is obvious that ethanol in a basic medium participates in the hydrodechlorination reaction as the hydrogen source. Note that ethanol oxidizes to acetate, whether the experiment is performed in hydrogen or an inert (Ar) atmosphere. In the latter case, ethanol possesses sufficient dechlorination capacity both with Pd/C and Ni/C (Table 1, experiments 5 and 6).

For better understanding of the function of ethanol in hydrodechlorination, the products of

chlorobenzene conversion in the presence of D_2 were analyzed by ^2D NMR. Fig. 1 shows the ^2D NMR spectra of the liquid phase yielding chlorobenzene hydrodechlorination with Ni/C (spectrum 2), $Ni_{98}Pd_2$/C (spectrum 3), Pd/C (spectrum 4) vs. standard ethanol (spectrum 1).

Besides the line corresponding to deuterated d_1-benzene (7.4 ppm), the ^2D NMR spectra contain lines from ethanol deuterated at the methyl- ($-CH_2D$, 1.2 ppm), methylene- ($-CHD-$, 3.6 ppm) and hydroxyl ($-OD$, 5.7 ppm) positions. Intensity of the line corresponding to methyl group was almost the same for all samples studied and corresponded to the natural content of deuterium in pure ethanol (0.015% mol). Concentrations of other deuterated reaction products were referenced to this line (Table 1). To find out the possible contribution of isotopic exchange, which may occur on the catalyst's surface simultaneously with the dechlorination process, we have performed a test experiment on benzene conversion over Pd/C at 1 atm D_2 for 3 h. The ^2D NMR spectrum of the reaction products is given in Fig. 1 (spectra 1–5). The substitution of proton in h_6-benzene by deuterium in this experiment was negligible
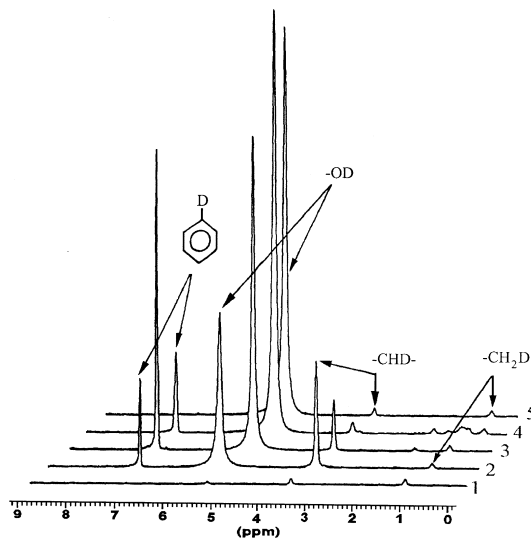

Fig. 1. ^2D NMR spectra of the liquid phase after chlorobenzene dechlorination with Ni/C (spectrum 2), $Ni_{98}Pd_2$/C (spectrum 3), Pd/C (spectrum 4) and after treatment of benzene with Pd/C at D_2 atmosphere (spectrum 5) vs. standard ethanol (spectrum 1).

(Table 1). Therefore, d_1-benzene forms only in the course of dechlorination.

Either molecular hydrogen [15–17] or aliphatic alcohol solvent [11,12] is considered in the literature as a hydrogen source for hydrodechlorination. However, in our experiments chlorobenzene hydrodechlorination in D_2 atmosphere yielded both deuterated and non-deuterated benzenes (Table 1). So, considering liquid phase hydrodechlorination of chlorinated aromatic compounds in a hydrogen atmosphere, it seems reasonable to recognize two competitive sources (molecular hydrogen and solvent) supplying hydrogen for C−Cl hydrogenolysis.

Since in the presence of Ni/C chlorobenzene hydrodechlorination in an inert or hydrogen atmosphere does not yield biphenyl as a side product, and since biphenyl forms in equal amounts over palladium catalysts (Pd/C and $Ni_{98}Pd_2/C$) in inert and hydrogen atmospheres, the hydrogen source (solvent or H_2) is of no importance for the reaction mechanism. It is the adsorbed hydrogen species that determine the main reaction route. The nature and properties of these hydrogen species in turn depend upon both the catalyst type and reaction conditions, as mentioned above.

Note that in the inert atmosphere, approximately two benzene molecules are formed per molecule of acetate (Table 1), while two hydrogen atoms are required for the hydrogenolysis of the C−Cl bond. Therefore, to explain the experimental benzene/acetate ratio, sodium acetate yielding the ethanol dehydrogenation

should generate four equivalents of adsorbed hydrogen atoms.

Scheme 2 shows a possible mechanism of the oxidation of ethanol to sodium acetate by which one ethanol molecule produces four adsorbed hydrogen atoms (HZ) via route (2–1).

This scheme does not consider the charge of adparticles, since the chemisorbing ethanol and D_2 may dissociate both heterolytically and homolytically [20,21], depending upon the type of catalyst.

So, it should be emphasized on the basis of ^2D NMR data that the mechanism of ethanol oxidation falls into several steps (Scheme 2). The first step includes multiple adsorption of ethanol on the surface of metal particle with formation of diadsorbed species (I). These intermediate complexes can be further dehydrogenated into mono-adsorbed species (II), or can interact with adsorbed hydrogen and release ethanol molecule. Indeed, in the case of an Ni catalyst further oxidation of species (II) via route (2–1) is rather slow and the first step is practically reversible. That is why, in the presence of Ni catalyst and D_2, a great amount of ethanol deuterated in the methylene position via route (2–2) can be detected with ^2D NMR (Table 1). More active Pd catalysts will readily oxidized ethanol into acetate, and for these systems no considerable excess of ethanol deuterated in methylene position was found.

In contrast to the methylene position, an isotopic exchange of hydroxyl groups of ethanol with adsorbed protons (deuterons) is not needed
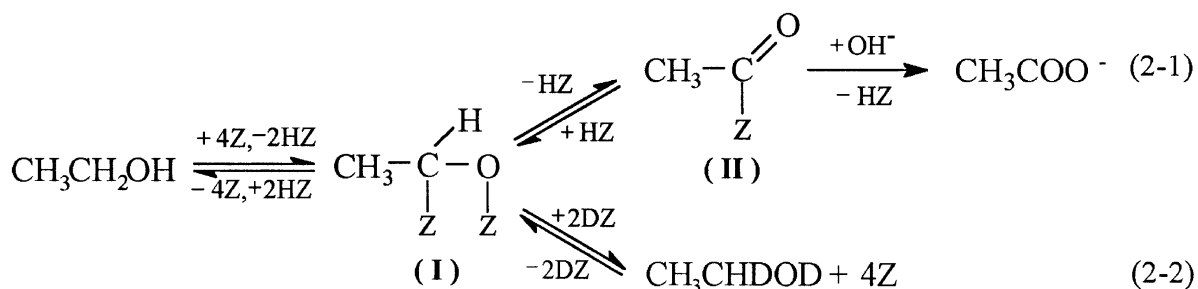
Scheme 2.

for an intermediate dehydrogenation step. This exchange is faster for a Pd catalyst than for an Ni-one, as follows from the data on the content of OD groups for each system (Table 1). For good reasons this results in a lower content of d_1-benzene obtained with a Pd catalyst as compared with an Ni-one both in the presence of D_2 (Table 1).

4. Conclusion

Considering the liquid phase catalytic chlorobenzene hydrodechlorination in a hydrogen atmosphere, it seems reasonable to consider two competitive sources of hydrogen for hydrogenolysis of the C—Cl bond. These are molecular hydrogen and solvent (ethanol), since they both may be the hydrogen donors. Delivering hydrogen in a basic medium, the ethanol oxidizes to sodium acetate. The proposed mechanism of ethanol oxidation explains not only the quantitative ratio of sodium acetate to benzene in an inert atmosphere, but also the presence of the ethanol deuterated at the methylene position in experiments with D_2.

The type of adsorbed hydrogen species determined by the nature of the catalyst plays the key role in hydrodechlorination mechanism. Two hydrodechlorination routes of chlorobenzene hydrodechlorination are considered: (1) an ionic mechanism in which hydride ion attacks adsorbed chlorobenzene molecule, and the phenyl anion produced accepts a proton; (2) a free-radical mechanism through the formation of adsorbed phenyl radical. The second route necessarily requires the presence of a palladium-containing catalyst.

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