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Kinetics study of the hydrodechlorination of chlorobenzene catalyzed by immobilized copper complexes

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The hydrodechlorination of chlorobenzene to benzene and biphenyl was studied using poly(4-vinylpyridine)-immobilized Cu catalysts under CO in basic (NaOH, $N(C_2H_5)_3$ or $Na(CH_3CO_2)$) aqueous 2-ethoxyethanol medium. This Cu system also catalyzed the water gas shift reaction. The catalytic activities for hydrodechlorination of chlorobenzene to benzene were studied as functions of the reaction parameters (nature of the base, reaction time, [Cu], P(CO), *T*, and S/C). Among the different base studied activity is maximum for NaOH. The rate of benzene formation displays a first-order dependence on [Cu] over the range 1.25–12.50 wt%. This observation was interpreted in terms of the presence of active species having the same nuclearity. The catalytic activity towards benzene formation proved to be first order dependence on P(CO) over the range 5–35 atm. The kinetics behavior with respect to P(CO) leads to the proposal that CO addition to the catalytic species precedes the rate-limiting step. The catalytic activity proved to be non-linear in chlorobenzene/Cu content, over the range 50–400 molar ratio. The results suggest that the rate-limiting step is preceded by reversible oxidative addition of chlorobenzene to Cu immobilized species.

KEY WORDS: hydrodechlorination; chlorobenzene; copper; carbon monoxide; poly(4-vinylpyridine).

1. Introduction

The chlorinated hydrocarbons are recognized as hazardous pollutants [1]. Disposal of them by techniques like degradation and incineration has the inconvenience of being high-energy intensive and producing toxic chemicals. For these reasons, the catalytic hydrodechlorination of chlorinated hydrocarbons is attractive and it has recently emerged as a viable non-destructive technology for the transformation of these compounds into safer and valuable chemicals in the reductive reaction conditions [2].

Metal compounds based on Rh [3,4], Pt [5,7], Pd [4,6–16] and Ni [7,14,17–22] have been used as catalysts for hydrodechlorination of halogenated organic compounds. However, and to the best of our knowledge, little work has been published regarding the use of copper compounds as a catalyst system for hydrodechlorination of chlorobenzene and organic halides. For instance, the reducing system composed of $CuCl_2 \cdot 2H_2O$, an excess of lithium sand and a catalytic amount of 4,4-di-tert-butylbiphenyl as electron carrier, was utilized in the hydrodehalogenations of alkyl and aryl fluorides, chlorides, bromides, and iodides [23]. On the other hand, molecular hydrogen is the most popular reducing agent employed in the catalytic hydrodechlorination of chlorobenzene. However, little is known about the alternative use of the couple CO/H_2O as reducing agent for the hydrodechlorination of chlorobenzene to benzene, even that few examples of a related reaction to the hydrodechlorination of chlorobenzene under the same reductive medium has been known, specifically, the catalytic hydrocarbonylation of chlorobenzene to benzoic acid by transition metal complexes under CO/H_2O [24–28].

In this work, the catalytic hydrodechlorination of chlorobenzene to benzene and biphenyl by copper immobilized complexes in contact with a basic medium using CO/H_2O as reducing agent is reported. In addition, the effect of the variation of reaction parameters (nature of the base, reaction time, copper content, carbon monoxide pressure, temperature, and chlorobenzene/Cu molar ratio) on the catalytic activity was examined.

2. Experimental

2.1. Materials

2-Ethoxyethanol (Aldrich) was distilled from anhydrous stannous chloride. Water was doubly distilled. Poly(4-vinylpyridine)/divinylbenzene(2%) (P(4-VP)) was used as provided by Reilly Industries. Chlorobenzene (Aldrich) was distilled prior to use. All gas mixtures He/H_2 (91.4%/8.6%, v/v), CO/CH_4 (95.8%/4.2%, v/v) and $CO/CH_4/CO_2/H_2$ (84.8%/5.1%/5.3%/4.8%, v/v) were purchased from BOC Gases and were used as received. Dichlorocopper(II) salt (Merck) was used as received. The copper-immobilized complex was prepared as reported in [29]. This material will be referred hereafter as Cu/P(4-VP).

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2.2. Instrumentation

Analyses of Cu in solution were performed on a GBC Avanta atomic absorption (AA) spectrometer operated in the flame mode and on a Perkin-Elmer Lambda 10 UV-Visible spectrophotometer. Gas samples analyses from catalytic runs were performed as described in detail previously [30] on a Hewlett-Packard 5890 Series II programmable (ChemStation) gas chromatograph fitted with a thermal conductivity detector. The column used was Carbosieve-B (80–100) mesh obtained from Hewlett-Packard using a He/H_2 mixture as the carrier gas. Analyses of liquid phase were done on a Chrompack CD9001 programmable gas chromatograph fitted with a methyl silicone, $30\ \mathrm{m} \times 0.323\ \mathrm{mm} \times 0.17\ \mu\mathrm{m}$ capillary column and flame ionization detector, and using He as the carrier gas. A Varian Chrompack 3800 programmable gas chromatograph fitted with a CP-Sil-8-CB (phenyldimethylpolysiloxane) ($30\ \mathrm{m} \times 0.250\ \mathrm{mm}$) column and a Varian Chrompack, Saturn 2000 mass selective detector were used to confirm the identity of the organic reaction products at the end of each run. Also the organic products were separated by column chromatography and analyzed by ^{13}C and ^{1}H-NMR in a Jeol Eclipse 270 NMR spectrometer.

2.3. Catalyst testing

The catalytic and kinetics runs were conducted in a 150 ml mechanically stirred stainless steel Parr reactor. In a typical run, 0.5 g of the catalyst, 10 ml of 80% aqueous 2-ethoxyethanol, 0.8 g of NaOH and 2 ml chlorobenzene (1.98×10^{-2} mol, S/C = 100) were added to the reaction vessel. The reactor was charged with the CO/CH_4 gas mixture at the required pressure (5–35 atm partial CO pressure at 150 °C) and placed in a stirred thermostated silicone oil bath at a given temperature (100–150 °C) for 4–120 h. These pressures and temperatures were chosen as an average from some previous reported systems [4]. After a given time, the reaction was stopped; the reactor was cooled to room temperature, excess pressure was vented and products analyzed by GC and GC–MS techniques. A response factor method for the GC analyses of the benzene and biphenyl was employed [31]. The GC–MS of the benzene (molecular ion peak at $m/e = 78$ and base peak at $m/e = 50$) and biphenyl (molecular ion peak at $m/e = 154$ and base peak at $m/e = 76$) products are similar to a pure sample of each. Also the organic products were separated by column chromatography and analyzed by ^{13}C and ^{1}H-NMR in a Jeol Eclipse 270 NMR spectrometer.

3. Results and discussion

3.1. General aspects

Dissolution of a solid sample of $CuCl_2 \cdot 2H_2O$ (typically, 0.0341 g, 2.0×10^{-4} mol) in 10 ml of 80% aqueous 2-ethoxyethanol at room temperature leads to the gradual formation of a green-blue solution. This solution in contact with 0.5 g of P(4-VP)/divinylbenzene(2%) under continuous stirring for 72 h in air at room temperature gradually leads to the formation of a blue solid material and a colorless supernatant solution.

The characterization studies of this solid material by UV-Vis/DR, FT-IR, EPR, SEM, and XPS techniques suggest the presence of two immobilized Cu(II), $[P(4\text{-}VP)_x\text{-}Cu(OH)(Cl)]$ ($x = 2$ or 3), complexes [29].

This Cu/P(4-VP) solid material in contact with 80% aqueous 2-ethoxyethanol basic medium (NaOH, $N(C_2H_5)_3$ or $Na(CH_3CO_2)$) catalyzes the reduction of chlorobenzene to benzene (equation (1)), the chlorobenzene coupling reaction to biphenyl (equation (2)), and the water gas shift reaction (WGSR) (equation (3)). The calculated catalytic activity defined as TF(product) = [(mol of product)/((mol of Cu) × (rt))] × 24 h) was reproducible to ca. 10 % for a series of experimental runs. The data obtained from these studies are summarized in Table 1.

Table 1
Base effects on WGSR and hydrodechlorination of chlorobenzene in aqueous 2-ethoxyethanol, catalyzed by Cu immobilized poly(4-vinylpyridine) complex[a]

Base[b](amount)	$[CO_2]$ mol × 10^{-5}	$TF(CO_2)$[c] total	$[H_2]$ *mol* × 10^{-5}	$TF(H_2)$[c]	[BZ][d] mol × 10^{-5} (Yield %)	TF(BZ)[c,d]	[BPH][e] mol × 10^{-5} (yield %)	TF[BPH][b,d]	pH initial	pH final
–	27	3.1	25	3.3	–	–	–	–	6.2	6.5
$Na(CH_3COO)$(1.65 g)	76	9.3	55	6.7	19(91)	2.3	2(9)	> 1	10.9	9.0
$N(C_2H_5)_3$(2.8 ml)	75	9.2	46	5.6	24(92)	2.9	4(8)	1	11.4	9.7
NaOH (0.8 g)	80	9.7	30	3.6	37(76)	4.5	12(24)	2	14.0	11.7

[a] [Cu] = 2.0×10^{-4} mol (2.5 wt%), 0.5 g P(4-VP), P(CO) = 20 atm at 150 °C for 8 h, 10 ml of 80% aqueous 2-ethoxyethanol, 2 ml of chlorobenzene (1.98×10^{-2} mol), chlorobenzene/Cu molar ratio = 100.

[b] 1.98×10^{-2} mol of base. Base/chlorobenzene molar ratio = 1.

[c] TF(product) = [(mol of product)/((mol of Cu) × (rt))] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%.

[d] [BZ] = Benzene.

[e] [BPH] = Biphenyl.

$$C_6H_5Cl + CO + H_2O \longrightarrow C_6H_6 + CO_2 + HCl \qquad (1)$$

$$2C_6H_5Cl + CO + H_2O \longrightarrow (C_6H_5)_2 + CO_2 + 2HCl \qquad (2)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (3)$$

GC analyses of the gas phase from the catalytic runs allowed the identification of H_2 and CO_2 as sole gaseous products. It is also important to stress here that we have considered three likely sources for CO_2 formation: reduction of chlorobenzene to benzene (equation (1)), the chlorobenzene coupling reaction to biphenyl (equation (2)), and the WGSR (equation (3)). For that reason the amount of CO_2 detected by GC analysis of the gas phase is greater then the amount of H_2, which comes from the WGSR. However the mass balance shows that formation of WGSR products, CO_2 and H_2, equaled stoichiometrically (1:1 CO_2/H_2, within experimental uncertainties) as required by equation (3), after subtracting from the observed CO_2 (total) the amounts of CO_2 corresponding to equations (1) and (2), which are based on the quantities of benzene and biphenyl determined by GC and keeping the molar ratios, C_6H_6/CO_2 and $(C_6H_5)_2/CO_2$ equal to 1.

The supernatant solution left after separation of the Cu/P(4-VP) solid exhibited no activity towards either WGSR or hydrodechlorination of chlorobenzene when tested in the absence of the immobilized copper catalytic precursor in the presence of chlorobenzene under conditions similar to describe in Table 1. Additionally, the supernatant solution remaining after a catalytic run was analyzed by UV-Vis and by AA spectrophotometry techniques and less than 0.1% of copper was detected in this solution indicating absence of leaching. Moreover, in the absence of the listed bases in Table 1, the Cu/P(4VP) system is not active for the chlorobenzene reduction to benzene or for the chlorobenzene coupling reaction to biphenyl. However, catalysis of the WGSR is observed. Because of the formation of HCl as by product, which could have a poisoning effect on the catalysts, the presence of the base as additive is desirable. On the other hand, the choice of base/chlorobenzene molar ratio = 1 stands on the amount of base required to neutralize the HCl produced assuming 100% of chlorobenzene conversion. Further, Table 1 shows the change in the pH of the supernatant solution during the catalytic process. The decrease of the pH indicates the consumption of the base by the formed HCl. Amongst the different Brønsted base studied activity for hydrodechlorination of chlorobenzene to benzene and biphenyl is maximum for NaOH followed by $N(C_2H_5)_3$ and $Na(CH_3CO_2)$. Noteworthy in Table 1 is the observed reverse tendency of the competitive WGSR as a function the nature of the base ($TF(H_2)$/24 h values are $Na[CH_3CO_2]$ (55) > $N(C_2H_5)_3$ (46) > NaOH (30)). These results indicate a base-dependent competition between the chlorobenzene conversion and WGSR. It is well known that the catalysis of the WGSR by transition metals complexes in basic medium [32,33].

3.2. Kinetics studies

For the most active hydrodechlorinating Cu/P(4-VP)/NaOH catalytic system the effects of varying reaction time, copper content, carbon monoxide pressure, temperature, and chlorobenzene/Cu molar ratio on catalysis were explored. The results reported in Tables 2–6 represent the average value of duplicate runs performed under identical experimental conditions. The calculated kinetics activity defined as TF(product) = ([(mol of product)/((mol of Cu) × (rt))] × 24 h) (rt = reaction time in h) was reproducible to within less than 10% for a series of experimental runs. In addition, the TF(product) for the kinetics runs were determined for short periods (4–8 h)

Table 2

Reaction time effects on WGSR and hydrodechlorination of chlorobenzene in aqueous 2-ethoxyethanol in basic medium, catalyzed by Cu immobilized poly(4-vinylpyridine) complex[a]

Reaction time (h)	$[CO_2]$ mol × 10^{-5}	$TF(CO_2)$[b] total	$[H_2]$ mol × 10^{-5}	$TF(H_2)$[b]	[BZ][c] mol × 10^{-5} (yield %)	TF(BZ)[b,c]	[BPH][d] mol × 10^{-5} (yield %)	TF[BPH][b,d]	pH[e] final
4	29	7.0	8	2.0	16 (84)	3.9	3 (16)	0.8	12.1
8	80	9.8	30	3.6	37 (76)	4.5	12 (24)	1.5	11.7
12	145	11.9	64	5.4	66 (79)	5.6	18 (21)	1.6	11.5
24	309	12.5	114	4.8	153 (77)	6.4	44 (23)	1.9	11.1
48	878	17.6	344	7.2	423 (79)	8.8	113 (21)	2.5	10.7
72	1864	25.3	714	9.6	825 (72)	11.1	322 (28)	4.3	10.4

[a] [Cu] = 2.0×10^{-4} mol (2.5 wt%), 0.5 g P(4-VP), P(CO) = 20 atm at 150 °C, 10 ml of 80 % aqueous 2-ethoxyethanol, 2 ml of chlorobenzene (1.98×10^{-2} mol), chlorobenzene/Cu molar ratio = 100, 0.8 g of NaOH, NaOH/chlorobenzene molar ratio = 1.

[b] TF(product) = [(mol of product)/((mol of Cu) × (rt))] × 24 h, where (rt) = *reaction* time in hours. Experimental uncertainty < 10%.

[c] [BZ] = Benzene.

[d] [BPH] = Biphenyl.

[e] pH (initial) = 14.0.

Table 3

Copper content effects on WGSR and hydrodechlorination of chlorobenzene in aqueous 2-ethoxyethanol in basic medium, catalyzed by Cu immobilized poly(4-vinylpyridine) complex[a]

[Cu] (wt%)	[CO$_2$] mol× 10^{-5}	TF(CO$_2$)[b] total	[H$_2$] mol × 10^{-5}	TF(H$_2$)[b]	[BZ][c] mol× 10^{-5} (Yield %)	TF(BZ)[b,c]	[BPH][d] mol × 10^{-5} (yield %)	TF[BPH][b,d]	pH[e] (final)
1.25	25	6.1	9	2.3	11 (73)	2.7	4 (27)	1.0	12.2
2.50	80	9.8	30	3.6	37 (76)	4.5	12 (24)	1.5	11.7
5.00	362	22.1	139	8.5	171 (81)	10.4	41 (19)	2.5	11.1
7.50	704	28.6	239	9.7	359 (80)	14.6	91 (20)	3.7	10.7
10.00	1099	33.5	374	11.4	553 (79)	16.8	146 (21)	4.4	10.5
12.50	1575	38.4	537	13.1	816 (80)	19.9	217 (20)	5.3	10.4

[a] 0.5 g P(4-VP), P(CO) = 20 atm at 150 °C for 8 h, 10 ml of 80% aqueous 2-ethoxyethanol, 2 ml of chlorobenzene (1.98 × 10^{-2} mol), 0.8 g of NaOH, NaOH/chlorobenzene molar ratio = 1.

[b] TF(product) = [(mol of product)/((mol of Cu) × (rt))] × 24 h, where (rt) = *reaction* time in hours. Experimental uncertainty < 10%.

[c] [BZ] = Benzene.

[d] [BPH] = Biphenyl.

[e] pH (initial) = 14.0

Table 4

Carbon monoxide effects on WGSR and hydrodechlorination of chlorobenzene in aqueous 2-ethoxyethanol in basic medium, catalyzed by Cu immobilized poly(4-vinylpyridine) complex[a]

P(CO) (atm)	[CO$_2$] mol × 10^{-5}	TF(CO$_2$)[b] total	[H$_2$] mol × 10^{-5}	TF(H$_2$)[b]	[BZ][c] mol × 10^{-5} (yield %)	TF(BZ)[b,c]	[BPH][d] mol × 10^{-5} (yield %)	TF[BPH][b,d]	pH[e] final
5	21	5.2	16	3.8	5 (100)	1.1	–	–	12.7
10	26	6.4	18	4.5	7 (100)	1.8	–	–	12.4
15	27	6.6	12	3.0	13 (87)	3.2	2 (13)	< 1	12.2
20	29	7.0	8	2.0	16 (84)	3.9	3 (16)	< 1	12.1
25	37	9.1	14	3.3	18 (82)	4.4	4 (18)	1.0	12.0
30	49	12.0	17	3.9	25 (81)	5.9	6 (19)	1.2	11.9
35	65	15.8	22	5.3	36 (84)	8.3	7 (16)	1.4	11.8

[a] [Cu] = 2.0 × 10^{-4} mol (2.5 wt%), 0.5 g P(4-VP), $T = 150$ °C for 4, 10 ml of 80% aqueous 2-ethoxyethanol, 2 mL of chlorobenzene (1.98 × 10^{-2} mol), chlorobenzene/Cu molar ratio = 100, 0.8 g of NaOH, NaOH/chlorobenzene molar ratio = 1.

[b] TF(product) = [(mol of product)/((mol of Cu) × (rt))] × 24 h, where (rt) = *reaction* time in hours. Experimental uncertainty < 10%.

[c] [BZ] = Benzene.

[d] [BPH] = Biphenyl.

[e] pH (initial) = 14.0.

Table 5

Temperature effects on WGSR and hydrodechlorination of chlorobenzene in aqueous 2-ethoxyethanol in basic medium, catalyzed by Cu immobilized poly(4-vinylpyridine) complex[a]

Temperature (°C)	[CO$_2$] mol × 10^{-5}	TF(CO$_2$)[b] total	[H$_2$] mol × 10^{-5}	TF(H$_2$)[b]	[BZ][c] mol × 10^{-5} (Yield %)	TF(BZ)[b,c]	[BPH][d] mol × 10^{-5} (yield %)	TF[BPH][b,d]	pH[e] final
100	20	5.0	15	3.7	6 (100)	1.4	–	–	12.6
110	22	5.3	16	3.8	7 (100)	1.6	–	–	12.5
120	23	5.5	12	2.9	8 (100)	2.0	–	–	12.4
130	25	6.1	11	2.8	12 (86)	2.9	2 (14)	1.0	12.2
140	28	6.8	11	2.8	13 (87)	3.1	2 (13)	1.0	12.2
150	29	7.0	8	2.0	16 (84)	3.9	3 (16)	1.1	12.1

[a] [Cu] = 2.0 × 10^{-4} mol (2.5 wt%), 0.5 g P(4-VP), P(CO) = 20 atm for 4 h, 10 ml of 80% aqueous 2-ethoxyethanol, 2 ml of chlorobenzene (1.98 × 10^{-2} mol), chlorobenzene/Cu molar ratio = 100, 0.8 g of NaOH, NaOH/chlorobenzene molar ratio = 1.

[b] TF(product) = [(mol of product)/((mol of Cu) × (rt))] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%.

[c] [BZ] = Benzene.

[d] [BPH] = Biphenyl.

[e] pH (initial) = 14.0.

Table 6
Chlorobenzene/Cu (S/C) molar ratio effects on WGSR and hydrodechlorination of chlorobenzene in aqueous 2-ethoxyethanol in basic medium, catalyzed by Cu immobilized poly(4-vinylpyridine) complex[a]

S/C (molar ratio)	$[CO_2]$ mol × 10^{-5}	$TF(CO_2)$[b] total	$[H_2]$ mol × 10^{-5}	$TF(H_2)$[b]	[BZ][c] mol × 10^{-5} (Yield %)	TF(BZ)[b,c]	[BPH][d] mol × 10^{-5} (yield %)	TF[BPH][b,d]	pH[e] final
50	52	6.3	33	4.0	16 (76)	1.9	5 (24)	< 1	12.1
100	80	9.8	30	3.6	37 (76)	4.5	12 (24)	1.5	11.7
150	110	13.4	25	3.0	64 (76)	7.8	20 (24)	2.4	11.5
200	120	14.6	20	2.4	80 (75)	9.8	26 (25)	3.2	11.4
250	121	14.7	17	2.1	80 (73)	9.8	29 (27)	3.5	11.5
300	121	14.8	16	2.0	82 (73)	10.0	30 (27)	3.6	11.5
350	120	14.6	15	1.8	84 (75)	10.2	28 (25)	3.4	11.6
400	120	14.6	16	1.9	82 (74)	10.0	29 (26)	3.5	11.6

[a] $[Cu] = 2.0 \times 10^{-4}$ mol (2.5 wt%), 0.5 g P(4-VP), P(CO) = 20 atm at 150 °C for 8 h, 10 ml of 80% aqueous 2-ethoxyethanol, 0.8 g of NaOH, NaOH/chlorobenzene molar ratio = 1.
[b] TF(product) = [(mol of product)/((mol of Cu) × (rt))] × 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%.
[c] [BZ] = Benzene.
[d] [BPH] = Biphenyl.
[e] pH (initial) = 14.0.

where (CO), $[H_2O]$ and [chlorobenzene] were essentially constant, diminishing by less than 20% overall. Hence, possible shifts in P(CO)-, $[H_2O]$-, and [chlorobenzene]-dependent equilibria among the catalyst component during a run were minimized owing to the near constancy of P(CO), $[H_2O]$ and [chlorobenzene] values.

3.3. Effect of reaction time variation

The results of the effect of reaction time variation on the catalytic activity are shown in Table 2. It can be observed that the reaction time variation has slight influence on the TF(product) and on the organic product distribution (yield %) values (Figure 1). The yields of benzene and biphenyl were calculated from GC data and by considering the total yields of the above two organic products equal to 100%. The observed changes can be associated with the slight shift to the acid zone on the pH final value of the catalytic mixture due to the increase of the amount of HCl byproduct and consumption of the base with the time.

3.4. Effect of copper content

The effect of varying the copper content (1.25 – 12.50 wt%) on the P(4-VP) is summarized in Table 3. As can be observed, an increase on [Cu] from 1.25 to 12.50 wt% enhances the TF(BZ) values from 2.7 to 19.9 $(24\ h)^{-1}$. This trend can be visualized in Figure 2, where the plot of TF(BZ)/24 h values versus [Cu] is linear. This behavior was also confirmed by plotting Ln TF(BZ)/24 h versus Ln [Cu] where a slope of 0.9 ± 0.1 ($R^2 = 0.988$) indicates that the reaction is first order on Cu concentration in the Cu (1.25–12.50) wt% range and suggesting the presence of copper species all of the same nuclearity.

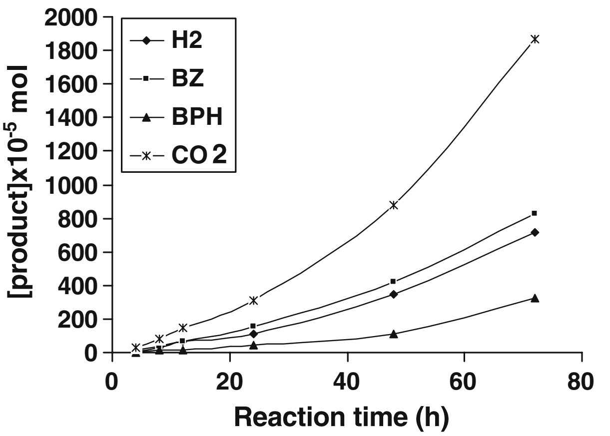


Figure 1. A plot of [product] vs. reaction time. The reaction conditions are given in Table 2. Lines drawn for illustrative purpose only.

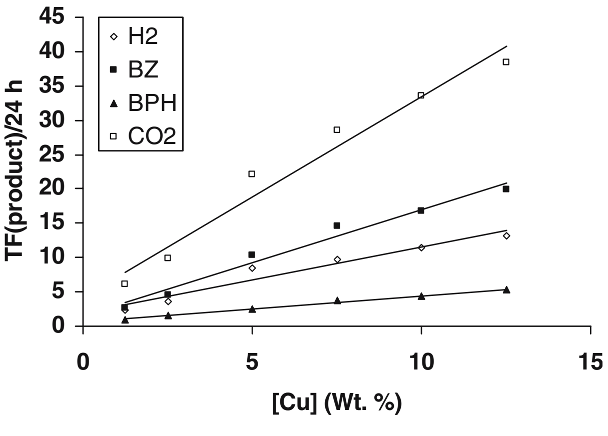


Figure 2. A plot of TF(product)/24 h vs. copper content on nitrobenzene reduction. The reaction conditions are given in Table 3. Lines drawn for illustrative purpose only.

Previous, IR, EPR, and XPS characterization studies led us to determine the presence of carbonylcopper(I) immobilized species [28]. Mononuclear Cu(I) species of the type [P(4-VP)$_x$-Cu(OH)(CO)] ($x = 2$ and 3) were proposed to be formed under CO/H_2O from the reduction of $CuCl_2$ salt dissolved in 80% aqueous 2-ethoxyethanol solution in contact with a solid sample of P(4-VP) for 72 h, Eq. (4). Reduction of transition metal salts by the CO/H_2O couple is known [34,35].

$$2CuCl_2 + 3H_2O + 3CO + 2xP(4-VP) \rightarrow 2[P(4-VP)_x - Cu(OH)(CO)] + CO_2 + 4HCl \tag{4}$$

Regarding WGSR and the chlorobenzene coupling reaction, the increase of copper content also enhances their catalytic activities. Plotting the Ln TF(product)/24 h versus Ln [Cu] (product = H_2 or biphenyl) we obtained slopes of 0.9 ± 0.1 ($R^2 = 0.974$) and 0.8 ± 0.1 ($R^2 = 0.977$), respectively. Accordingly, both reactions are also first order on [Cu] in the range studied.

3.5. *Effect of carbon monoxide pressure*

Figure 3 is a plot of TF(product)/24 h versus P(CO) (product = H_2, BZ or CO_2), for [Cu] = 2.50 wt% at 150 °C for 4 h. The TF(BPH)/24 values were omitted due to the low activity observed for this coupling reaction on the studied range (Table 4). As can be observed from Figure 3, increase in carbon monoxide pressure on the 5–35 atm range is not accompanied by a marked improvement in TF(H_2)/24 h values.

On the other hand, a linear dependence of TF(BZ)/24 h on P(CO) variation in 5–35 atm range is noted, indicating that coordination of CO to Cu(I) center is followed by a slower reaction to give benzene. In addition, the Ln–Ln plot of this curve has a slope of 1.0 ± 0.1 ($R^2 = 0.974$), which clearly establishes a first order dependence on [CO] for reduction of chlorobenzene to benzene in the range studied.

3.6. *Effect of temperature*

The hydrodechlorination and WGSR extend observed at various temperatures is summarized in Table 5. As can be seen from Table 5, increase in the reaction temperature from 100 to 150 °C is accompanied by just a slight improving in TF(BZ)/24 values. However, TF(H_2)/24 h values start decreasing on this temperature range and formation of biphenyl is observed only at temperatures higher than 130 °C.

Accordingly, the activation parameter was recorded only for hydrodechlorination of chlorobenzene to benzene. Figure 4 displays a plot of Ln TF(BZ) versus 1/T for [Cu] = 2.50 wt% at P(CO) = 20 atm. The resulting Arrhenius-type plot is linear on the 100–150 °C range and an activation energy ($E_a = 27.4$ kJ/mol·K) was calculated.

3.7. *Effect of chlorobenzene/Cu molar ratio*

The study of the effect chlorobenzene/Cu molar ratio variation, showed in Table 6, was made in order to complete the optimization of the experimental conditions toward the hydrodechlorination reaction under CO/H_2O. The TF(BZ)/24 h increases from 1.9 (24 h^{-1}) at chlorobenzene/Cu molar ratio = 50, reaching maximum values of 10.2 (24 h^{-1}) at chlorobenzene/Cu molar ratio = 350. The plot of TF(BZ)/24 h values versus chlorobenzene/Cu molar ratio shown in Figure 5 indicates a reversible oxidative addition of chlorobenzene to Cu(I) center on the S/C (50–400) molar ratio range, e.g.,

$$\text{P-[Cu]}^+ + \text{CO} \underset{-CO_2}{\overset{k_1,H_2O}{\longrightarrow}} \text{P-[CU}(H_2)]^+ \overset{+C_6H_5Cl,Keq}{\rightleftharpoons} \text{P-[Cu}(H_2)(C_6H_5)(Cl)]^+ \xrightarrow{k_3} \text{products} \tag{5}$$

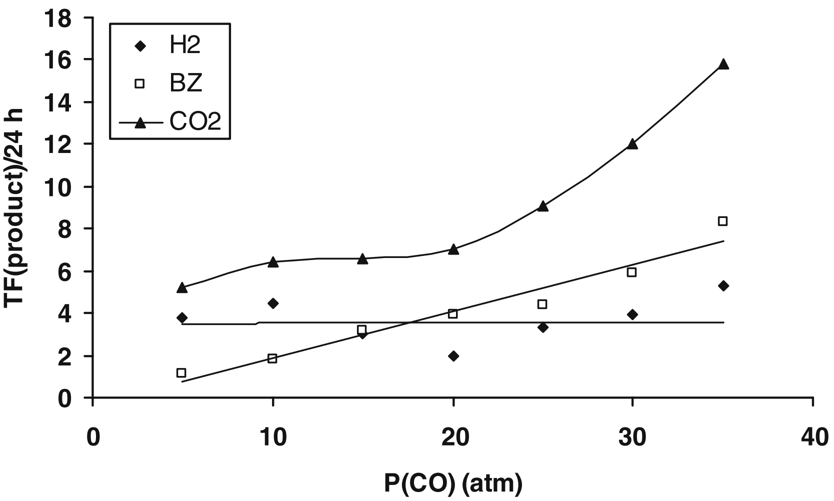


Figure 3. A plot of TF(product)/24 h vs. P(CO). The reaction conditions are given in Table 4. Lines drawn for illustrative purpose only.

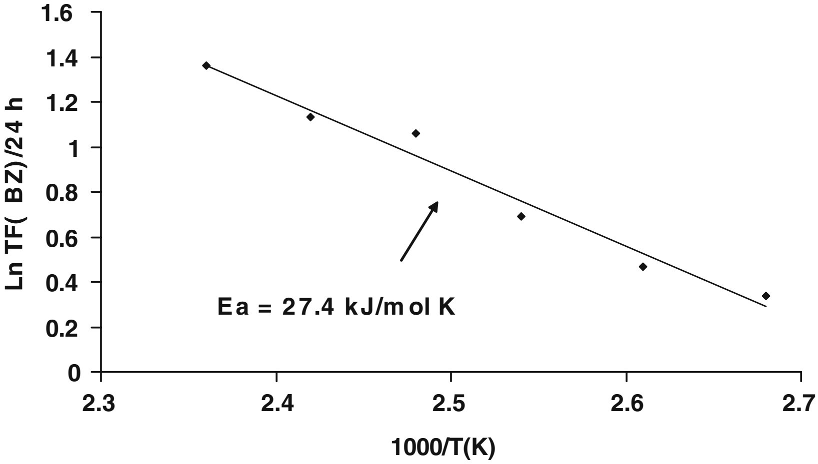


Figure 4. The Arrhenius plot for hydrodechlorination of chlorobenzene to benzene. The reaction conditions are given in Table 5.

P = P(4-VP) The rate law (r_{BZ}) for such behavior would be

$$r_{BZ}=(k_1k_3K_{eq}P(CO)[C_6H_5Cl][Cu]_{tot})(1+K_{eq}[C_6H_5Cl])^{-1} \quad (6)$$

where $[Cu]_{tot}$ = P-$[Cu]^+$ + P-$[Cu(H_2)]^+$ + P-$[Cu(H_2)(C_6H_5)(Cl)]^+$ and k_1 includes the solubility of CO in the medium. Equation (6) can be reduced to equation (7) (note that TF(BZ) would be the rate of benzene formation divided by $[Cu]_{tot}$):

$$TF(BZ)=(k_1k_3KeqP(CO)[C_6H_5Cl])(1+K_{eq}[C_6H_5Cl])^{-1} \quad (7)$$

At high $[C_6H_5Cl]$, $K_{eq}[C_6H_5Cl] > 1$, then equation (7) can be reduced to:

$$TF(BZ) = k_1k_3P(CO) \quad (8)$$

On the other hand, at low-chlorobenzene concentration $K_{eq}[C_6H_5Cl] > 1$, then equation (7) is reduced to:

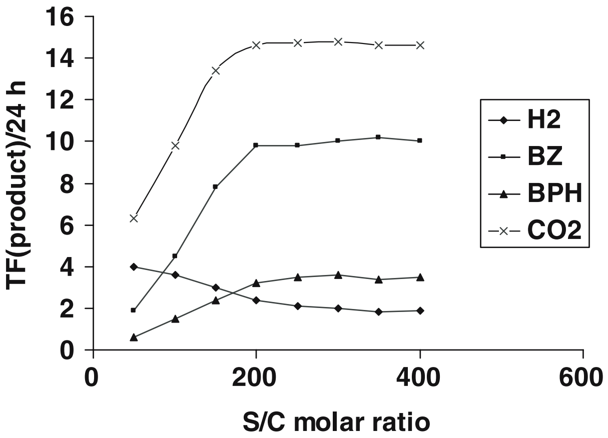


Figure 5. A plot of TF(product)/24 h vs. chlorobenzene/Cu molar ratio. The reaction conditions are given in Table 6. Lines drawn for illustrative purpose only.

$$TF(Bz) = k_1k_3K_{eq}P(CO)[C_6H_5Cl] \quad (9)$$

For this kinetics model, a plot of TF(BZ)/day versus $[C_6H_5Cl]$ at low-chlorobenzene concentration should be linear with slopes of $k_1k_3P(CO)$ and zero intercept. Indeed, the experimental plot is linear in the 50–200 molar range with nearly zero intercept value as predicted by equation (9).

Similar behavior was observed for biphenyl production as a function of the *S*/*C* variation. However, the WGSR activity diminishes at higher chlorobenzene contents as expected.

3.8. Recycling of the immobilized catalyst

The recycling efficiency of the $CuCl_2$/P(4-VP) catalyst was studied for the hydrodechlorination of chlorobenzene. The catalyst was filtered from the supernatant solution (in nitrogen atmosphere) and returned to the autoclave with fresh reactants. The results are presented in Table 7. A dramatic change of the catalytic activity was observed after a second use. A drop of ca. 71, 75, and 80% was observed for the catalytic activity toward hydrodechlorination, chlorobenzene coupling, and WGSR, respectively. Additionally, the supernatant solution left after a catalytic run was analyzed by AA spectrometry and less than 0.1% of copper was detected in the solution. The catalytic results show that the polymer-anchored catalyst is not highly stable due to air contamination on handling during the recycling process.

3.9. Mechanistic consideration

The evaluation of the mechanism for benzene, biphenyl, CO_2 and H_2, formation catalyzed by Cu/P(4-VP) in contact with 80% aqueous 2-ethoxyetanol and chlorobenzene in basic medium under CO shows some key features: First, IR and XPS spectroscopy studies of

Table 7

Recycling efficiency of WGSR and hydrodechlorination of chlorobenzene in aqueous 2-ethoxyethanol in basic medium, catalyzed by Cu immobilized poly(4-vinylpyridine) complex[a]

Used time	$[CO_2]$ mol × 10^{-3}	$TF(CO_2)$[b] total	$[H_2]$ mol × 10^{-3}	$TF(H_2)$[b]	[BZ][c] mol × 10^{-3} (Yield %)	TF(BZ)[b,c]	[BPH][d] mol × 10^{-3} (yield %)	TF[BPH][b,d]	pH[e] final
1st	82	67	39	31	31 (72)	24.9	11 28	8.6	9.7
2nd	21	17	8	6	9 (75)	7.4	3 (25)	2.1	10.6

[a] [Cu] = 2.0×10^{-4} mol (2.5 wt%), 0.5 g P(4-VP), P(CO) = 35 atm at 150 °C for 120 h, 10 ml of 80% aqueous 2-ethoxyethanol, 4 ml of chlorobenzene (3.96×10^{-2} mol), chlorobenzene/Cu molar ratio = 200, 0.8 g of NaOH, NaOH/chlorobenzene molar ratio = 1.

[b] TF(product) = [(mol of product)/((mol of Cu) × (rt))] × 24 h, where (rt) = reaction *time* in hours. Experimental uncertainty < 10%.

[c] [BZ] = Benzene.

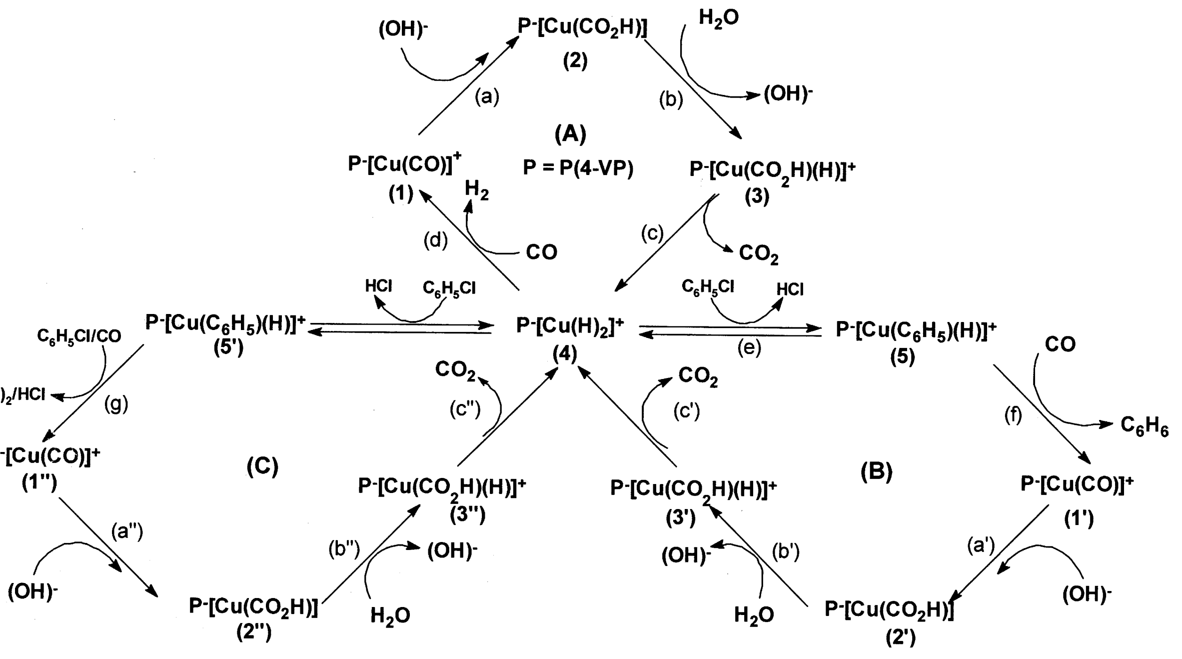
[d] [BPH] = Biphenyl.

[e] pH (initial) = 14.0.

the used catalysts [29] point to the presence of Cu(I)–CO species (equation (4)). Second, kinetics study of the hydrodechlorination reaction indicates that the reaction is first order in [CO] and [Cu]. Third, S/C studies suggest a mechanism in which the rate-limiting step is preceded by reversible coordination of chlorobenzene to active Cu(I) immobilized species. Fourth, a similar mechanism for the hydrodehalogenations of organic compound catalyzed by Rh and Pd complexes has been proposed [3,4]. Fifth, a blank experiment using H_2 as an alternative to CO/H_2O was carried out in order to examine the possibility that molecular H_2 (coming from the WGSR) in presence of chlorobenzene forms benzene and/or biphenyl under the catalytic conditions described in Tables 1–6. Therefore, a 0.5 sample of Cu/P(4-VP) ([Cu] = 2.50 wt%), 2 ml (1.98×10^{-2} mol) of chlorobenzene, 0.8 g of NaOH and 10 ml of 80% aqueous 2-ethoxyethanol were added to a 150 ml mechanically stirred stainless steel Parr reactor. The resulting mixture was degassed and charged with H_2 ($P(H_2)$ = 20 atm) and heated at 150 °C for 8 h. GC and GC-mass analyses of the liquid phase reveal absence of benzene or biphenyl in the reaction mixture. This result strong suggests that the H_2 formed under CO/H_2O (equation (3)) does not further react with chlorobenzene. Given the above, the reaction mechanism depicted in Scheme 1 is proposed for the WGSR, reduction of chlorobenzene to benzene and chlorobenzene coupling reaction to biphenyl catalyzed by the $[P(4\text{-VP})_x\text{–Cu(OH)(CO)}]$ immobilized species.

In Scheme 1, the Cu(I)–carbonyl complex, $[P(4\text{-VP})_x\text{–Cu(OH)(CO)}]$, will be referred as $P\text{-}[Cu(CO)]^+$ for clarity. Three cycles account for the observed products. In cycle (**A**), the formation of H_2 via WGSR implies a nucleophilic attack by OH^- on coordinated CO of complex (1), yielding a hydroxycarbonyl complex $P\text{-}[Cu(CO_2H)]$ (2) (step a). Protonation by a water molecule (step b) followed by elimination of CO_2 from the complex (3) gives the dihydride $P\text{-}[Cu(H_2)]^+$ complex (4) (step c). Reductive elimination of H_2 induced by CO coordination (step d), regenerates the starting $P\text{-}[Cu(CO)]^+$ complex (1) and closes the WGSR cycle [36].

Cycle (**B**) describes the reduction of chlorobenzene to benzene. Reversible oxidative addition of chlorobenzene to specie (4), $P\text{-}[Cu(H_2)]^+$, (formed under WGSR conditions (Cycle **A**)) followed by elimination of HCl gives complex (5), $P\text{-}[Cu(C_6H_5)H]^+$ (step e). Reductive elimination of the coordinated phenyl and H ligands from the complex (5) assisted by CO coordination (step f) gives benzene and complex (1′). Coordination of CO molecule prior to the reductive elimination (rate determining step) accounts for the first order dependence of benzene formation on P(CO). Further, the resulting complex (1′) goes through several transformations (steps a′ – c′), which leads to formation of the dihydride–Cu(I) complex (4) to get the catalytic cycle (**B**) closed.



Scheme 1. Proposed Mechanism.

Cycle (**C**) describes the formation of biphenyl, which comes from the chlorobenzene coupling reaction (step h). Coordination of a second molecule of chlorobenzene to complex (5′), P-[Cu(C_6H_5)H]$^+$, followed by HCl elimination (step g) gives the Cu(I)-biphenyl complex, P-[Cu(C_6H_5)$_2$]$^+$ (non-shown in Scheme 1). Phenyl–phenyl coupling perhaps assisted by coordination of CO gives the biphenyl product and the Cu(I)–carbonyl complex P-[Cu(CO)]$^+$ (1$''$) (step h). Formation of Cu(I)–diaryl complex, P-[Cu(C_6H_5)$_2$]$^+$, must not be an easy step due to steric hindered constraints associated to its formation and that could account for the observed low yields for biphenyl production. Further, the resulting complex (1$''$) undergoes several transformations (steps a$''$ – c$''$), which leads to formation of the dihydride–Cu(I) complex (4) to get the catalytic cycle (**C**) closed. The overall reaction formation is shown in equation (10):

$$\begin{aligned}3C_6H_5Cl + 3CO + 3H_2O &\longrightarrow (C_6H_5)_2 + C_6H_6 \\ &+ 3CO_2 + 3HCl + H_2\end{aligned} \tag{10}$$

Furthermore, the highest TF(BZ)/24 *h* = 37.2 (91% yield) and TF(BZ)/24 h = 3.9 (9% yield) values were achieved under optimal conditions, e.g., [Cu] = 12.5 wt%, P(CO) = 35 atm at 150 °C for 72 h, 10 ml of 80% aqueous 2-etoxyethanol, 4 ml of chlorobenzene ((3.96 × 10^{-2} mol)), chlorobenzene/Cu molar ratio = 200 and 0.8 g of NaOH, NaOH/chlorobenzene molar ratio = 1.

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