

Liquid-phase Hydrodechlorination of CCl₄ with Co-production of Diethylcarbonate and Acetal

Jong Wook Bae, Jae Sung Lee, Kyung Hee Lee,* and Eun Joo Jang[†]

Department of Chemical Engineering and School of Environmental Engineering

Pohang University of Science and Technology (POSTECH), San 31, Hyoja-dong, Pohang, 790-784, Korea

[†]*Samsung Advanced Institute of Technology, P. O. box 111, Suwon, 440-600, Korea*

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Liquid-phase hydrodechlorination of CCl₄ over supported Pd or Pt catalysts in the presence of C₂H₅OH gave not only the selective synthesis of CHCl₃, but also conversion of C₂H₅OH to diethyl carbonate (DEC) and 1,1-diethoxyethane (acetal; DEE).

Catalytic hydrodechlorination (HDC)^{1–7} of CCl₄ is a useful method for disposal of this ozone-depleting compound. An obstacle in practicing hydrodechlorination of CCl₄ in gas phase is the difficulty in reaction temperature control due to the large exotherm of the reaction. (For example, the heat of reaction- ΔH° of CCl₄ + H₂ = CHCl₃ + HCl is -101.3 kJoule/mol). The local high temperature in the hydrodechlorination reactor leads to a reduced selectivity and an accelerated catalyst fouling due to carbon deposition.³ Liquid phase reactions would allow more facile control of reaction temperatures.^{6,7} In search for a reaction system for effective hydrodechlorination of CCl₄ in liquid phase, we found that the reaction over supported Pd or Pt in a medium of C₂H₅OH gave high reaction rates and high selectivity to CHCl₃. Interestingly, ethanol did not simply act as a solvent, but actively participated in the reaction to co-produce diethyl carbonate (DEC) and 1,1-diethoxyethane (acetal; abbreviated to DEE). New synthetic routes for environmentally benign production of dialkyl carbonates^{8,9} have been actively sought to replace commercialized hazardous phosgene processes. Acetal is produced from ethanol and acetaldehyde,¹⁰ and used for a solvent, fragrant material, protecting agent of carbonyl group and additive in diesel fuel. In this communications, we report a reaction system that gives not only the HDC of CCl₄ but also co-production of DEC and DEE.

Palladium or platinum catalysts grafted to montmorillonite (Pd/Mont or Pt/Mont) were prepared by ion exchange of H-montmorillonite with (CH₃CN)₂PdCl₂ or (CH₃CN)₂PtCl₂. Other supported catalysts were prepared from the conventional wet impregnation with aqueous solutions of PdCl₂ and H₂PtCl₆. Various supports were employed including montmorillonite, activated carbon (AC) and Al₂O₃ (specific surface area, Sg = 155 m²/g and pH of slurry = 7.0) purchased from Aldrich, Al₂O₃ (Sg = 105 m²/g) from Strem, and SiO₂-Al₂O₃ form JRC (Japan Reference Catalyst). The prepared catalysts were previously dried in an oven at ca. 380 K for over 12 h. All reactions were carried out in a 300 ml Parr hastelloy bomb reactor with an inner glass liner of 50 ml to avoid corrosion problem with HCl. Products were analyzed by HP GC 5890 series II equipped with a 60 m DB-5 capillary column and a flame ionization detector and HP GC-MSD (mass selective detector) 5973.

Some properties of catalysts used for liquid phase selective hydrodechlorination of CCl₄ are shown in Table 1. In particular, the surface acidity was characterized by temperature-programmed desorption (TPD) of NH₃ and represented by the

Table 1. Properties of catalysts used for liquid-phase hydrodechlorination of CCl₄

Catalysts	Metal loading ^a /wt%	Surface area of support /m ² /g ^b	Acidity (μ mol of NH ₃ /g) ^c	
			weak	strong
Pd/Mont	2.8	227	48.7	37.4
Pd/AC	3.0	864	32.7	0.1
Pd/Al ₂ O ₃	5.0	105	63.4	4.9
Pd/SiO ₂ -Al ₂ O ₃	3.0	511	107.9	5.8
Pt/Mont	2.5	227	62.3	44.7
Pt/AC	3.0	864	—	—
Pt/Al ₂ O ₃	1.0	155	52.3	19.7

^aMetal content was characterized by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy). ^bSurface area of support itself was determined by BET methods. ^cSurface acidity of catalysts was determined by TPD (temperature-programmed desorption) of NH₃.

amounts of desorbed NH₃ at temperatures of ca. 410 K (weak acidity) and ca. 750 K (strong acidity). Pd/Mont and Pt/Mont were characterized by relatively high concentrations of stronger acid sites compared to others. Table 2 shows the conversions of CCl₄ and C₂H₅OH, and product distributions obtained at 323 K after 12 h reaction with or without dioxygen. When H₂ was replaced with He, the conversion of CCl₄ over Pd/Mont was below 0.5 mol%. The hydrodechlorination of CCl₄ without C₂H₅OH showed high selectivity to undesired chlorinated C₂ compounds at the same reaction conditions as Run 1. The conversion of C₂H₅OH itself without CCl₄ under the same reaction conditions was trivial (below 0.1 mol%). But, addition of C₂H₅OH greatly enhanced not only the CCl₄ conversion but also the selectivity to desired CHCl₃.

All supported Pd and Pt catalysts showed high CCl₄ conversions and high selectivity to CHCl₃ although montmorillonite- and activated carbon-supported catalysts showed slightly better performance. Montmorillonite-supported catalysts showed higher C₂H₅OH conversions. The generation of chlorinated C₂ compounds (C₂Cl₄, C₂HCl₃ and C₂Cl₆ were the main by-products) from CCl₄ was much larger over the more acidic catalysts such as Mont, Al₂O₃ and SiO₂-Al₂O₃ (Run 1, 3, 4, 7 and 9) than over activated carbon (AC). Bulk Pd metal also produced a particularly large amount of C₂ compounds (Run 5). The selectivity to DEE was much higher on the acidic supports as mentioned by Capeletti, et al., who showed the effects of support acidity at the reaction of ethanol with acetaldehyde (see below).¹⁰ When the small amount of dioxygen was added at the beginning of the reaction (Run 10–13), the formation of diethyl carbonate was greatly enhanced without much effect on hydrodechlorination of CCl₄. It appears that C₂H₅OH donates proton to remove chlorine from CCl₄ to form acetaldehyde (AA) and HCl on the supported Pd or Pt sites. It was confirmed by a complementary

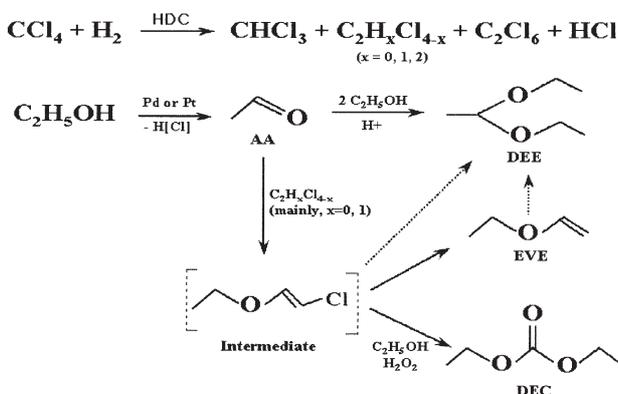
Table 2. Conversion and product distribution in liquid-phase hydrodechlorination of CCl₄

Run #	Catalysts	Conversion of CCl ₄	Product distribution (mole %)			Conversion of C ₂ H ₅ OH	Product distribution (mole %)			
			CHCl ₃	C ₂ H _x Cl _{4-x}	C ₂ Cl ₆		DEE	AA	EVE	DEC
1	Pd/Mont	43.5	93.3	1.3	5.4	17.3	77.4	12.1	8.8	1.7
2	Pd/AC	47.8	97.2	1.2	1.6	9.9	30.7	36.7	32.2	0.4
3	Pd/Al ₂ O ₃	40.3	91.0	2.9	6.1	12.2	43.7	49.0	7.1	0.2
4	Pd/SiO ₂ -Al ₂ O ₃	32.9	90.4	4.7	4.9	17.6	68.4	25.8	5.3	0.5
5	Pd metal	22.8	72.8	5.1	22.1	7.4	55.4	25.5	8.6	10.5
6	PdCl ₂	24.1	90.2	4.7	5.1	9.4	36.7	56.3	3.7	3.3
7	Pt/Mont	48.4	95.6	0.9	3.5	19.7	71.0	7.6	18.9	2.5
8	Pt/AC	30.5	98.9	0.6	0.5	5.2	61.6	12.3	22.4	3.7
9	Pt/Al ₂ O ₃	12.3	75.5	5.3	19.2	5.3	44.0	51.2	3.9	0.9
10	Pd/Mont	36.7	91.9	2.5	5.6	20.0	67.4	14.0	7.4	11.2
11	Pd/AC	55.0	96.1	1.9	2.0	14.3	53.1	19.7	17.8	9.4
12	Pt/Mont	31.4	95.3	1.5	3.2	18.5	68.8	12.4	8.1	10.7
13	Pt/AC	24.3	95.3	2.7	2.0	11.2	57.0	18.3	12.1	12.6

Reaction condition of Run 1 to 9: T = 323 K; P(H₂) = 3.0 MPa; CCl₄ = 64.5 mmol; C₂H₅OH = 217.4 mmol; internal standard (n-undecane) = 1.3 mmol; catalyst = 0.1 g; reaction for 12 h. Reaction condition of Run 10 to 13: Same as Run 1 except for the P(H₂) = 1.5 MPa and P(O₂) = 0.1 MPa. Run 5 and 6: Amount of palladium loading was equivalent to the supported 5.0 wt% palladium catalyst of 0.1 g. ^aC₂Cl₄ and C₂HCl₃ were the main products in C₂H_xCl_{4-x} (x = 0, 1, 2). Abbreviation: DEE=1,1-diethoxyethane; AA=acetaldehyde; EVE=ethyl vinyl ether; DEC=diethyl carbonate.

isotope experiment with C₂H₅OD and CCl₄. A large amount of DCl with HCl was produced, but chloroform in the form of CDCl₃ was not detected. Thus, C₂H₅OH is not directly involved in the formation of CHCl₃, but could exert the positive effects in activity and selectivity by rapidly scavenging chlorine. This would also increase the catalyst life because catalyst deactivation in HDC of CCl₄ is generally induced from the strongly adsorbed chlorine or carbonaceous species.³⁻⁵

A possible reaction pathway to form DEC, EVE and DEE during the hydrodechlorination of CCl₄ in the presence of C₂H₅OH is shown in Figure 1. Catalytic hydrodechlorination of CCl₄ proceeds according to the known pathway over Pt or Pd to produce mainly CHCl₃ with gaseous hydrogen as the hydrogen source. As a protic solvent, C₂H₅OH could donate the proton to chlorine produced in the main reaction, and turned itself to acetaldehyde (AA) on Pd or Pt sites. The reaction of acetaldehyde with ethanol produces DEE by acid-catalyzed aldol condensation. Ethyl vinyl ether (EVE) could be formed from the reaction of AA with C₂H_xCl_{4-x} (mainly, x = 0 or 1). Furthermore, chlorine-containing C=C group in EVE precursors could be easily dechlorinated to DEE by hydrogen mainly from the proton in C₂H₅OH adsorbed on the catalyst surfaces. Diethyl carbonate is produced by the addition of oxygen to carbon-carbon double bonds¹¹ in an intermediate of chlorine-containing C=C group in

**Figure 1.** A proposed reaction pathway.

EVE precursors. The oxidizing agent may be hydrogen peroxide generated in-situ on the transition metal by the reaction of dihydrogen and dioxygen.^{12,13} When hydrogen peroxide was added ex-situ at the beginning of reaction, the formation of DEC was greatly enhanced. The oxidative cleavage of EVE intermediates to produce DEC is only possible in acidic media, but no reaction occurred only with C₂H₅OH itself even on the acidic support. To enhance the generation of DEC in our phosgene-free reaction conditions, the amount of reaction intermediates, chlorine-containing EVE precursors with the terminal vinyl group, should be an important variable. The larger are the amounts of C₂H_xCl_{4-x} (mainly, x = 0 or 1) and in-situ generated hydrogen peroxide, the higher selectivity to DEC is expected.

In summary, catalytic hydrodechlorination of CCl₄ over supported Pd or Pt in the presence of ethanol gives not only the selective synthesis of CHCl₃, but also co-production of valuable diethyl carbonate and 1,1-diethoxyethane.

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