Liquid-phase Hydrodechlorination of CCl_4 with Co-production of Diethylcarbonate and Acetal

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(Received June 5, 2002; CL-020483)

Liquid-phase hydrodechlorination of CCl_4 over supported Pd or Pt catalysts in the presence of C_2H_5OH gave not only the selective synthesis of $CHCl_3$, but also conversion of C_2H_5OH to diethyl carbonate (DEC) and 1,1-diethoxyethane (acetal; DEE).

Catalytic hydrodechlorination (HDC)[1–7] of CCl_4 is a useful method for disposal of this ozone-depleting compound. An obstacle in practicing hydrodechlorination of CCl_4 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^o of $CCl_4 + H_2 = CHCl_3 + HCl$ 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 CCl_4 in liquid phase, we found that the reaction over supported Pd or Pt in a medium of C_2H_5OH gave high reaction rates and high selectivity to $CHCl_3$. 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 CCl_4 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 $(CH_3CN)_2PdCl_2$ or $(CH_3CN)_2PtCl_2$. Other supported catalysts were prepared from the conventional wet impregnation with aqueous solutions of $PdCl_2$ and H_2PtCl_6. Various supports were employed including montmorillonite, activated carbon (AC) and Al_2O_3 (specific surface area, $Sg = 155\,m^2/g$ and pH of slurry = 7.0) purchased from Aldrich, Al_2O_3 ($Sg = 105\,m^2/g$) from Strem, and SiO_2-Al_2O_3 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 CCl_4 are shown in Table 1. In particular, the surface acidity was characterized by temperature-programmed desorption (TPD) of NH_3 and represented by the amounts of desorbed NH_3 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 CCl_4 and C_2H_5OH, and product distributions obtained at 323 K after 12 h reaction with or without dioxygen. When H_2 was replaced with He, the conversion of CCl_4 over Pd/Mont was below 0.5 mol%. The hydrodechlorination of CCl_4 without C_2H_5OH showed high selectivity to undesired chlorinated C_2 compounds at the same reaction conditions as Run 1. The conversion of C_2H_5OH itself without CCl_4 under the same reaction conditions was trivial (below 0.1 mol%). But, addition of C_2H_5OH greatly enhanced not only the CCl_4 conversion but also the selectivity to desired $CHCl_3$.

Table 1. Properties of catalysts used for liquid-phase hydrodechlorination of CCl_4

Catalysts	Metal loading[a] /wt%	Suface area of support /m^2/g^b	Acidity (μmol 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_2O_3	5.0	105	63.4	4.9
Pd/SiO_2-Al_2O_3	3.0	511	107.9	5.8
Pt/Mont	2.5	227	62.3	44.7
Pt/AC	3.0	864	—	—
Pt/Al_2O_3	1.0	155	52.3	19.7

[a]Metal content was characterized by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy). [b]Surface area of support itself was edtermined by BET methods. [c]Surface acidity of catalysts was determined by TPD (temperature-programmed desorption) of NH_3.

All supported Pd and Pt catalysts showed high CCl_4 conversions and high selectivity to $CHCl_3$ although montmorillonite- and activated carbon-supported catalysts showed slightly better performance. Montmorillonite-supported catalysts showed higher C_2H_5OH conversions. The generation of chlorinated C_2 compounds (C_2Cl_4, C_2HCl_3 and C_2Cl_6 were the main by-products) from CCl_4 was much larger over the more acidic catalysts such as Mont, Al_2O_3 and SiO_2-Al_2O_3 (Run 1, 3, 4, 7 and 9) than over activated carbon (AC). Bulk Pd metal also produced a particularly large amount of C_2 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 CCl_4. It appears that C_2H_5OH donates proton to remove chlorine from CCl_4 to form acetaldehyde (AA) and HCl on the supported Pd or Pt sites. It was confirmed by a complementary

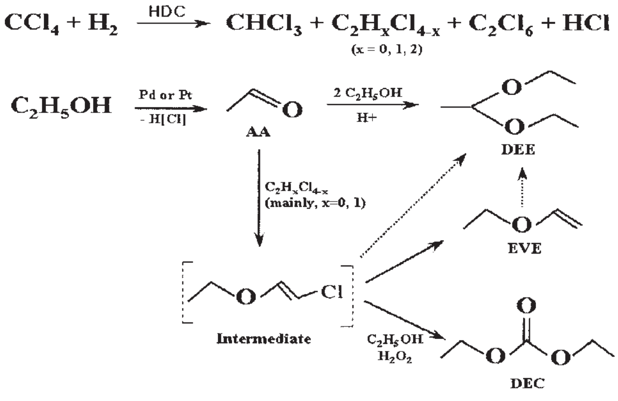
Table 2. Conversion and product distribution in liquid-phase hydrodechlorination of CCl_4

Run #	Catalysts	Conversion of CCl_4	Product distribution (mole %)			Conversion of C_2H_5OH	Product distribution (mole %)			
			$CHCl_3$	$C_2H_xCl^a_{4-x}$	C_2Cl_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_2O_3	40.3	91.0	2.9	6.1	12.2	43.7	49.0	7.1	0.2
4	Pd/SiO_2-Al_2O_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_2O_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; $P(H_2) = 3.0$ MPa; $CCl_4 = 64.5$ mmol; $C_2H_5OH = 217.4$ 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 $P(H_2) = 1.5$ MPa and $P(O_2) = 0.1$ MPa. Run 5 and 6: Amount of palladium loading was equivalent to the surpported 5.0 wt% palladium catalyst of 0.1 g. [a]C_2Cl_4 and C_2HCl_3 were the main products in $C_2H_xCl_{4-x}$ ($x = 0, 1, 2$). Abbreviation: DEE=1,1-diethoxyethane; AA=acetaldehyde; EVE=ethyl vinyl ether; DEC=diethyl carbonate.

isotope experiment with C_2H_5OD and CCl_4. A large amount of DCl with HCl was produced, but chloroform in the form of $CDCl_3$ was not detected. Thus, C_2H_5OH is not directly involved in the formation of $CHCl_3$, 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 CCl_4 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 CCl_4 in the presence of C_2H_5OH is shown in Figure 1. Catalytic hydrodechlorination of CCl_4 proceeds according to the known pathway over Pt or Pd to produce mainly $CHCl_3$ with gaseous hydrogen as the hydrogen source. As a protic solvent, C_2H_5OH 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 $C_2H_xCl_{4-x}$ (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 C_2H_5OH adsorbed on the catalyst surfaces. Diethyl carbonate is produced by the addition of oxygen to carbon-carbon double bonds[11] in an intermediate of chlorine-containing C=C group in 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 C_2H_5OH 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 $C_2H_xCl_{4-x}$ (mainly, $x = 0$ or 1) and in-situ generated hydrogen peroxide, the higher selectivity to DEC is expected.



$$CCl_4 + H_2 \xrightarrow{HDC} CHCl_3 + C_2H_xCl_{4-x} + C_2Cl_6 + HCl$$

Figure 1. A proposed reaction pathway.

In summary, catalytic hydrodechlorination of CCl_4 over supported Pd or Pt in the presence of ethanol gives not only the selective synthesis of $CHCl_3$, but also co-production of valuable diethyl carbonate and 1,1-diethoxyethane.

We are grateful for the financial support provided by the Brain Korea 21 project of Ministry of Education in 2002, Korea.

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