



Liquid-phase hydrodechlorination of CCl_4 in a medium of ethanol with co-production of acetal and diethyl carbonate

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Abstract

During the liquid-phase hydrodechlorination (HDC) of CCl_4 over supported Pd or Pt catalysts in the presence of $\text{C}_2\text{H}_5\text{OH}$ and molecular oxygen, the selective catalytic synthesis of CHCl_3 as well as the conversion of $\text{C}_2\text{H}_5\text{OH}$ to diethyl carbonate (DEC) and 1,1-diethoxyethane (DEE) was observed. The protic solvent, $\text{C}_2\text{H}_5\text{OH}$, could easily donate proton that reacts with the adsorbed chlorine on the catalyst surface to form HCl. This facile removal of chlorine from the catalyst surface could be the main reason for the enhancement of the catalytic stability and conversion of $\text{C}_2\text{H}_5\text{OH}$. The rate of DEC formation was accelerated with the increase in the partial pressure of molecular oxygen, and the selectivity to DEE was enhanced by the increased surface acidity of catalysts. Compared to the reactions of the hydrodechlorination of CCl_4 without $\text{C}_2\text{H}_5\text{OH}$, the conversion of CCl_4 and the selectivity to CHCl_3 was greatly enhanced in the presence of $\text{C}_2\text{H}_5\text{OH}$.

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1. Introduction

Carbon tetrachloride has been classified as a group IV compound at the London Conference and known as one of the substantial ozone-depleting materials at the stratosphere. Since a large amount of carbon tetrachloride has been produced in industrial chlorination processes, efficient disposal technologies have been intensively explored to satisfy economical feasibility without significant generation of secondary pollutants. Although catalytic hydrodechlorination (HDC)

of CCl_4 in the gas phase seemed to be useful for the disposal of this ozone-depleting compound [1–8], an obstacle in practicing hydrodechlorination of CCl_4 is the difficulty in reaction temperature control due to the large exotherm of the reaction (for example, the heat of reaction $-\Delta H^\circ$ of $\text{CCl}_4 + \text{H}_2 = \text{CHCl}_3 + \text{HCl}$ is -93.1 kJ/mol). The local high temperature in the gas-phase hydrodechlorination reactor leads to a reduced selectivity and an accelerated catalyst fouling due to carbon deposition [6].

In principle, liquid-phase reactions have the advantages of more facile control of reaction temperatures, and then problems of local hot-spots and catalyst fouling are less significant. Gomez-Sainero et al. [8] showed the reactivity of CCl_4 (without solvent) in

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the liquid-phase hydrodechlorination over supported metal catalysts such as Pd/C, Pd/SiO₂, Pd/Al₂O₃, and some other transition metals supported on activated carbon (AC). They have recommended palladium supported on carbon as the best catalyst showing high conversion of CCl₄ and selectivity to CHCl₃ owing to the high surface area of carbon supports and the uniform distribution of the active metal on them. Furthermore, it is claimed that the high density of the unoccupied d-orbital of palladium compared to the other transition metals could efficiently promote the facile dissociation of CCl₄ due to the strong electron-donor character of the chloride ions. It has been also reported that catalytic activities in the hydrodechlorination of chlorinated hydrocarbons are greatly affected by the solvents in both heterogeneous and homogeneous reactions [9,10] and by the morphology of supported metals (structure-sensitive reaction) as well [11–13]. Different solvents could have different solvation power depending on dielectric constants and then influence catalyst stabilization [9]. In addition to these intrinsic solvent effects, solvents (especially alcohols) could also donate proton to react with chlorinated hydrocarbons [10] during the hydrodechlorination reactions. Furthermore, when the metal particles were larger, the catalyst deactivation induced by the generated HCl was largely inhibited to result in enhancing catalyst stability [5,11,12].

In search of a reaction system for effective hydrodechlorination of CCl₄ in the liquid phase, we found that the reaction over supported Pd or Pt in 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 acetal (1,1-diethoxyethane, DEE). New synthetic routes for environmentally benign production of dialkyl carbonates [14–21], known as a useful alkylating agent for aromatic compounds, an intermediate for synthesizing polycarbonates and isocyanates and an additive in fuel to enhance octane number, have been actively sought to replace commercialized hazardous phosgene processes. Oxidative carbonylation of CH₃OH with carbon monoxide and molecular dioxygen over copper-based catalysts [15–17] was already commercialized and an attempt for dimethyl carbonate (DMC) synthesis with carbon dioxide as a raw material instead of toxic carbon monoxide has been

underway [18–20]. The synthetic routes of DEC were also reported [15,21] by the oxidative carbonylation of C₂H₅OH. Acetal is produced from ethanol and acetaldehyde (AA) over acidic catalysts [22], and used for a solvent, fragrant material, protecting agent of carbonyl group and additive in diesel fuel.

In this paper, we report a reaction system that gives not only the hydrodechlorination of CCl₄ but also co-production of DEC and DEE. Effects of reaction variables on catalytic activity have been investigated together with the following characterization experiments: X-ray photoelectron spectroscopy (XPS) analysis, Fourier-transformed infrared spectra (FT-IR) of adsorbed CO, temperature-programmed surface reaction (TPSR), temperature-programmed desorption (TPD) of NH₃ for surface acidity, and deuterium-exchange (C₂H₅OD) experiments. A possible reaction pathway is proposed based on these results.

2. Experimental

2.1. Catalyst preparation and activity measurement

Various supports were employed for catalysts preparation including montmorillonite, activated carbon and Al₂O₃ (specific surface area, S_g = 155 m²/g and pH of slurry = 7.0) purchased from Aldrich, Al₂O₃ (S_g = 105 m²/g) from Strem, and SiO₂–Al₂O₃ from Japan Reference Catalyst (JRC). The 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. The more detailed preparation methods of grafted montmorillonite catalysts were described elsewhere [23]. Other supported catalysts were prepared from the conventional wet impregnation with the excess aqueous solutions of PdCl₂ and H₂PtCl₆ purchased from Aldrich. The prepared catalysts were dried in an oven at ca. 380 K for over 12 h. All reactions were carried out in a 300 ml Parr stainless steel bomb reactor with an inner glass liner of 50 ml to avoid corrosion with HCl at an agitation speed of 100 rpm. The catalyst of 0.1 g was loaded in the desired amount of liquid reactants mixture (CCl₄ and C₂H₅OH) with the internal standard of *n*-undecane, and then molecular hydrogen with (or without) air

was charged to the reactor up to the desired reaction pressures. The reaction was carried out at the desired reaction temperature for the adequate duration. After quenching the reactor at ice-water temperature to minimize the loss of the lightweight materials followed by filtering of catalysts, liquid 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 as well.

2.2. Catalyst characterizations

The metal loading for most catalysts was targeted around 3 wt.% and the results of actual analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) are shown in Table 1. To determine the surface acidity of the selected catalysts, temperature-programmed desorption of NH₃ was carried out for the catalysts pretreated with a He flow of 41 μmol/s at 573 K for 2 h. The catalyst (0.5 g) pretreated in a U-type quartz reactor was heated at a linear ramping rate of 10 K/min from 323 K to a desired temperature. The total amount of desorbed NH₃ was analyzed continuously with a mass selective detector and was quantified in the unit of μmol of NH₃/g catalyst. In order to investigate the nature of carbonaceous species formed on the catalyst, temperature-programmed surface reaction was performed for the fresh (just dried) and used for hydrodechlorination catalysts (2.8 wt.% Pd/Mont) of 0.04 g under the following reaction conditions: $T = 323\text{ K}$; $P(\text{H}_2) = 3\text{ MPa}$; $\text{CCl}_4 = 64.5\text{ mmol}$; $\text{C}_2\text{H}_5\text{OH} = 217.4\text{ mmol}$; internal stan-

dard (*n*-undecane) = 1.3 mmol for 12 h reaction. The temperature ramping rate for TPSR was 10 K/min and the flow rate of H₂ was 20.5 μmol/s. The main products formed from the hydrogenation of surface carbonaceous species were methane ($m/z = 16$) and ethane ($m/z = 28$), and they were continuously analyzed by a mass selective detector (HP GC-MSD 5973). To measure the binding energy of palladium (3d_{5/2}) for fresh and used catalysts, X-ray photoelectron spectroscopy experiments were carried out on a Perkin-Elmer PHI 5400 ESCA spectrometer using a Mg Kα source. To acquire the Fourier-transformed infrared spectra, the fresh catalyst (12 ± 1.0 mg) were pressed into a thin pellet and loaded in an infrared cell equipped with CaF₂ windows. After the IR sample was dried in situ under a He flow (20.5 μmol/s) at 373 K for 1 h to remove physisorbed water, the pellet was evacuated at 10⁻⁶ Torr for 1 h at room temperature. Then, CO molecules were adsorbed at room temperature and atmospheric pressure of CO for 0.5 h and then re-evacuated at that temperature for 1 h to remove physisorbed CO molecules. The transmission infrared spectra were collected on a Perkin-Elmer 1000 FT-IR spectrometer.

3. Results and discussion

3.1. Physicochemical properties of the supported catalysts

Physicochemical properties of catalysts, which were employed in the liquid-phase selective hydrodechloro-

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

Catalyst	Metal loading ^a (wt.%)	Surface area of support (m ² /g) ^b	Acidity (μmol of NH ₃ /g) ^c	
			Weak	Strong
Pd/Mont	2.8	227	48.2	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

^a Metal content was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

^b Surface area of support itself was determined by the BET method.

^c Surface acidity of catalysts was determined by temperature-programmed desorption (TPD) of NH₃.

mination of CCl_4 , are shown in Table 1. The metal content and BET specific surface area of characteristic catalysts were determined by ICP–AES and nitrogen adsorption method at 77 K, respectively. Although BET surface areas of all the tested catalysts were different ranging from 105 to 864 m^2/g , metal loading was fixed at around 3 wt.% except 5 wt.% Pd/ Al_2O_3 and 1 wt.% Pt/ Al_2O_3 . In particular, the surface acidity was characterized by temperature-programmed desorption of NH_3 and represented by the concentrations 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 strong acidic sites compared to others. The palladium supported on activated carbons showed very low total acidic sites in spite of high surface area. Pd/ SiO_2 – Al_2O_3 showed a high concentration of weak acidic sites. The surface acidity, especially total amount of acidic sites or the high ratio of the strong acidic sites to the weak acidic ones, could be one of the important variables that affect the dehydrogenation of $\text{C}_2\text{H}_5\text{OH}$ and dimerization of CCl_4 [2,22].

3.2. Effects of the solvents

The hydrodechlorination of CCl_4 over Pd/activated carbon in different solvents of tetrahydrofuran, acetonitrile, 1,4-dioxane and ethanol was performed at 323 K for 12 h (Runs 1–4) as shown in Table 2. All the solvents were miscible homogeneously with CCl_4 under the reaction conditions except for acetonitrile. The above first three solvents are classified as aprotic solvents and the last one as protic solvent [24]. Their dielectric constants were also presented. As the

dielectric constant of aprotic solvents increases, conversion of CCl_4 and selectivity to C_2 compounds increased but selectivity to CHCl_3 decreased. The higher the polarity of solvents, the solubility of molecular hydrogen could be proportionally diminished. The stabilization effects of chloride ion by solvation, however, could be enhanced inversely. The chloride ion generated during the hydrodechlorination could generally induce the catalyst deactivation by strong adsorption on active metal sites [5,7,11]. Therefore, among aprotic solvents, acetonitrile showing higher polarity could keep away the catalyst from chloride ions and show high conversion of CCl_4 , but low selectivity to CHCl_3 is probably due to the lower solubility of molecular hydrogen. In spite of the high polarity of ethanol, however, the conversion of CCl_4 and selectivity to CHCl_3 was greatly enhanced because ethanol, a protic solvent, can donate protons and scavenge the chloride ion to form HCl. Therefore, aliphatic alcohols among the tested solvents could be the best solvent for hydrodechlorination of CCl_4 despite their high polarity.

Table 3 shows the effects of $\text{C}_2\text{H}_5\text{OH}/\text{CCl}_4$ mole ratio on hydrodechlorination of CCl_4 over Pd/Mont catalyst at 323 K for 12 h reaction. When H_2 was replaced with He, the conversion of CCl_4 over Pd/Mont was below 0.5 mol% (not shown here). Furthermore, the conversion of $\text{C}_2\text{H}_5\text{OH}$ without CCl_4 under the same reaction conditions (Run 5) was negligible (below 0.1 mol%). Although the hydrodechlorination of CCl_4 in the absence of $\text{C}_2\text{H}_5\text{OH}$ showed high selectivity to undesired chlorinated C_2 compounds (Run 5), addition of $\text{C}_2\text{H}_5\text{OH}$ greatly enhanced not only the CCl_4 conversion but also the selectivity to desired CHCl_3 (Runs 6–8). With the increase in the

Table 2

Conversion and product distribution in liquid-phase hydrodechlorination of CCl_4 on Pd/activated carbon: effects of solvents

Run #	Solvents	Conversion of CCl_4	Product distribution (mol%)			Dielectric constant/polarity ^b
			CHCl_3	$\text{C}_2\text{H}_x\text{Cl}_{4-x}$ ^a	C_2Cl_6	
1	1,4-Dioxane	1.5	96.1	0.3	3.6	Aprotic (2.2/–)
2	Tetrahydrofuran	8.0	94.3	1.2	4.5	Aprotic (7.6/37.4)
3	Acetonitrile	12.3	73.9	3.3	22.8	Aprotic (38.0/46.7)
4	Ethyl alcohol	47.8	97.2	1.2	1.6	Protic (24.5/51.9)

Reaction conditions: $T = 323$ K; $P(\text{H}_2) = 3$ MPa; $\text{CCl}_4 = 64.5$ mmol; $\text{CCl}_4/\text{solvent}$ weight ratio of 1.0; internal standard (*n*-undecane) = 1.3 mmol; catalyst = 0.1 g of 3.0 wt.% Pd/activated carbon; reaction for 12 h.

^a C_2Cl_4 and C_2HCl_3 were the main products in $\text{C}_2\text{H}_x\text{Cl}_{4-x}$ ($x = 0$ –2).

^b From [24].

Table 3

Conversion and product distribution on Pd/Mont: effects of the C₂H₅OH/CCl₄ mole ratio

Run #	Mole ratio of C ₂ H ₅ OH/CCl ₄	Conversion of CCl ₄	Product distribution (mol%)			Conversion of C ₂ H ₅ OH	Product distribution (mol%)			
			CHCl ₃	C ₂ H _x Cl _{4-x} ^a	C ₂ Cl ₆		DEE	AA	EVE	DEC
5	0.00	18.0	10.9	3.8	85.3	–	–	–	–	
6	1.68	19.5	91.2	1.2	7.6	5.6	82.1	8.4	6.9	2.6
7	3.35	43.5	93.3	1.3	5.4	17.3	77.4	12.1	8.8	1.7
8	6.70	61.6	94.6	1.9	3.5	23.3	49.9	8.1	41.8	0.2

Reaction conditions: 2.8 wt.% Pd/Mont; *T* = 323 K; *P*(H₂) = 3 MPa; CCl₄ = 64.5 mmol; internal standard (*n*-undecane) = 1.3 mmol; catalyst = 0.1 g; reaction for 12 h. Abbreviations: DEE, 1,1-diethoxyethane; AA, acetaldehyde; EVE, ethyl vinyl ether; DEC, diethyl carbonate.

^a C₂Cl₄ and C₂HCl₃ were the main products in C₂H_xCl_{4-x} (*x* = 0–2).

C₂H₅OH/CCl₄ mole ratio, the conversion of CCl₄ and C₂H₅OH as well as the selectivity to CHCl₃ was greatly enhanced (from 10.9 to 94.6 mol%). The products from the reaction of C₂H₅OH include mainly DEE, ethyl vinyl ether (EVE), AA, DEC and small quantities of undefined compounds. Interestingly, the amount of the formed DEE was inversely proportional to the conversion of ethanol owing to the possible reverse reaction of DEE to form EVE and C₂H₅OH (see Run 37 in Table 4). Overall, the higher conversions of CCl₄ and C₂H₅OH were obtained with the higher mole ratios of C₂H₅OH/CCl₄. Since the proton generated from ethanol could easily scavenge the adsorbed chlorine to form HCl, the catalysts deactivation was greatly suppressed at the higher mole ratios of C₂H₅OH/CCl₄.

3.3. Effects of supports

Table 5 shows the conversions of CCl₄ as well as C₂H₅OH, and product distributions obtained over various supported catalysts under the following reaction conditions: *T* = 323 K; *P*(H₂) = 3 MPa; CCl₄ = 64.5 mmol; C₂H₅OH = 217.4 mmol; internal standard (*n*-undecane) = 1.3 mmol; catalyst = 0.1 g; for 12 h reaction. 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. The generation of chlorinated C₂ compounds (C₂Cl₄, C₂HCl₃ and C₂Cl₆ were the main by-products) from the possible dimerization of adsorbed CCl₄ (CCl₃ radicals) was much larger over the more acidic catalysts such as Mont, Al₂O₃

and SiO₂–Al₂O₃ (Runs 7, 9, 10, 14 and 16) than over activated carbon (Runs 4 and 15) as shown in Table 1 and reported by Kim et al. [2], although their amounts were not necessarily proportional to the surface acidity of supports. Bulk Pd metal also produced a particularly large amount of C₂ compounds (Run 11). However, PdCl₂ showed somewhat higher selectivity to CHCl₃ and slightly higher conversion of CCl₄ and C₂H₅OH compared to Pd metal and PdO (Runs 11–13). Interestingly, the dehydrogenation activity of C₂H₅OH to AA showed a good correlation with the oxidation state of Pd following the order of PdO ≥ PdCl₂ > Pd metal [25,26]. This is the trend in oxidation states of platinum characterized by XANES analyses and its binding energies in X-ray photoelectron spectra [13,26]. Therefore, the conversion of C₂H₅OH to AA could be largely induced on the Pd sites. The formation of DEE could take place on Pd sites as well as acidic sites of supports. The selectivity to DEE was much higher on the acidic supports as mentioned by Capeletti et al. [22], who showed the effects of support acidity on the reaction of ethanol with acetaldehyde. Compared to other catalysts, montmorillonite-supported catalysts showed higher C₂H₅OH conversions to DEE and the smaller co-production of AA, EVE and DEC.

It appears that C₂H₅OH donates proton to remove the strongly adsorbed chlorine on the catalyst surface that originates from the dissociation of CCl₄ to form acetaldehyde and HCl. It was confirmed by a complementary isotope experiment using C₂H₅OD and CCl₄, which was carried out on Pd/Mont under the same reaction conditions as Run 7 except for the employment of C₂H₅OD isotope instead of C₂H₅OH.

Table 4
Conversion and product distribution: reactivity of intermediates

Run #	Added reactants (mmol)	Conversion (mol%)	Product distribution (mol%)				Conversion (mol%)	Product distribution (mol%)				
			CCl ₄ (6 h)	CHCl ₃	C ₂ H _x Cl _{4-x} ^b	C ₂ Cl ₆		DEE	C ₂ H ₅ OH	AA	EVE	DEC
35	C ₂ H ₅ OH (217.4), AA (109.0)	Conversion (12 h) ^a of AA (~100%)					C ₂ H ₅ OH (37.3)	AA + C ₂ H ₅ OH = DEE (main reaction)				
36	C ₂ H ₅ OH (217.4), EVE (69.3)	Conversion (12 h) ^a of EVE (82.1%)					C ₂ H ₅ OH (27.8)	EVE + C ₂ H ₅ OH = DEE (main reaction)				
37	DEE (84.6), CCl ₄ (64.5)		15.0 ^a	94.4	1.1	4.5		36.1	57.2	31.1	11.7	–
38	C ₂ Cl ₄ (30.2), C ₂ H ₅ OH (217.4)	Conversion (6 h) ^a of C ₂ Cl ₄ (18.6%)						46.1	12.3	9.6	13.7	30.6

Reaction conditions: $T = 323$ K; $P(\text{H}_2) = 1.5$ MPa; $P(\text{O}_2) = 0.1$ MPa; internal standard (*n*-undecane) = 1.3 mmol; catalyst = 2.5 wt.% Pt/Mont of 0.1 g.

^a Reaction duration for hydrodechlorination reaction.

^b C₂Cl₄ and C₂HCl₃ were the main products in C₂H_xCl_{4-x} ($x = 0-2$).

Table 5

Conversion and product distribution in liquid-phase hydrodechlorination of CCl₄: effects of supports

Run #	Catalyst	Conversion of CCl ₄	Product distribution (mol%)			Conversion of C ₂ H ₅ OH	Product distribution (mol%)				Leaching (wt.%) ^b
			CHCl ₃	C ₂ H _x Cl _{4-x} ^a	C ₂ Cl ₆		DEE	AA	EVE	DEC	
7	Pd/Mont	43.5	93.3	1.3	5.4	17.3	77.4	12.1	8.8	1.7	0.61
4	Pd/AC	47.8	97.2	1.2	1.6	9.9	30.7	36.7	32.2	0.4	0.55
9	Pd/Al ₂ O ₃	40.3	91.0	2.9	6.1	12.2	43.7	49.0	7.1	0.2	–
10	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	–
11	Pd metal	22.8	72.8	5.1	22.1	7.4	55.4	25.5	8.6	10.5	–
12	PdCl ₂	24.1	90.2	4.7	5.1	9.4	36.7	56.3	3.7	3.3	–
13	PdO	25.3	88.9	7.0	4.1	6.2	25.4	73.5	0.5	0.6	–
14	Pt/Mont	48.4	95.6	0.9	3.5	19.7	71.0	7.6	18.9	2.5	7.56
15	Pt/AC	30.5	98.9	0.6	0.5	5.2	61.6	12.3	22.4	3.7	32.5
16	Pt/Al ₂ O ₃	12.3	75.5	5.3	19.2	5.3	44.0	51.2	3.9	0.9	–

Reaction conditions: $T = 323$ K; $P(\text{H}_2) = 3$ Pa; $\text{CCl}_4 = 64.5$ mmol; $\text{C}_2\text{H}_5\text{OH} = 217.4$ mmol; internal standard (*n*-undecane) = 1.3 mmol; catalyst = 0.1 g; reaction for 12 h. Runs 11–13: Amount of palladium loading was equivalent to that of the supported 5.0 wt.% palladium catalyst of 0.1 g.

^a C₂Cl₄ and C₂HCl₃ were the main products in C₂H_xCl_{4-x} ($x = 0-2$).

^b The leached amount of metal (wt.%) was based on the total loaded amount of metallic composition in the fresh catalysts with 0.1 g.

A large amount of DCl with HCl was produced, but chloroform in the form of CDCl₃ was not detected in GC-MS. Thus, C₂H₅OH is not directly involved in the formation of CHCl₃ but could exert positive effects in activity and selectivity by rapidly scavenging chlorine. These phenomena would also affect the increase in the catalyst lifetime because catalyst deactivation in hydrodechlorination of CCl₄ is generally induced from the strongly adsorbed chlorine or carbonaceous species [5–7,11,13]. Among the tested catalysts, the best catalysts are Pd or Pt supported on Mont with respect to the conversion of CCl₄ and C₂H₅OH as well as selectivity to CHCl₃ and DEE. The catalyst stability in liquid-phase reactions was also correlated with the leached amount of active metals measured by ICP–AES methods after hydrodechlorination reaction. As shown in Table 5, the leached amount of palladium metal is around 0.6 wt.% of the total loaded Pd in the fresh catalyst for the palladium supported on AC and Mont. Compared to the palladium-based catalysts, however, supported platinum catalysts in our reaction systems are less stable showing larger amounts of metal leaching, i.e. as large as 32.5 wt.% Pt leaching for Pt/AC.

3.4. Characterization of Pd/Mont catalyst

The conversion of CCl₄ and C₂H₅OH as well as product distribution over Pd/Mont with time on stream

are shown in Fig. 1. The selectivity to CHCl₃ in the reaction of CCl₄ continuously increased and vice versa for C₂ compounds, but the conversion of CCl₄ was constant during around 12 h of the reaction. This could be mainly caused by the catalyst deactivation due to the strong adsorption of the generated chloride ions on active sites. Furthermore, the generated water could inhibit the further conversion of CCl₄ (see Table 6; Runs 32 and 33). The selectivity to DEE from C₂H₅OH also increased with reaction time until around 12 h with the concomitant reduction in selectivities of AA and EVE. Interestingly, the formation of DEC was not much changed with the reaction time. Furthermore, conversion of C₂H₅OH approached a limiting value after 15 h probably because of reverse reactions of products back to C₂H₅OH (see Table 4). To correlate changes in catalytic activity with the states of supported metals, characterizations were carried out for the Pd/Mont catalyst. X-ray photoelectron spectra of the fresh Pd or Pt/Mont (just dried at around 380 K) and the used ones are shown in Fig. 2. Two peaks in the Pd core level (3d_{5/2}) at the binding energy of ca. 336.4 eV (Pd(L)) and 338.0 eV (Pd(H); almost the same as Pd²⁺) were observed for Pd/Mont catalyst (Fig. 2(a)). Compared to the reference peak of Pd metal (335.2 eV for 3d_{5/2} core level) and PdCl₂ (337.8 eV), the peak of higher binding energy (Pd(H)) represents a higher oxidation state of supported palladium and its intensity is reduced after hydrodechlori-

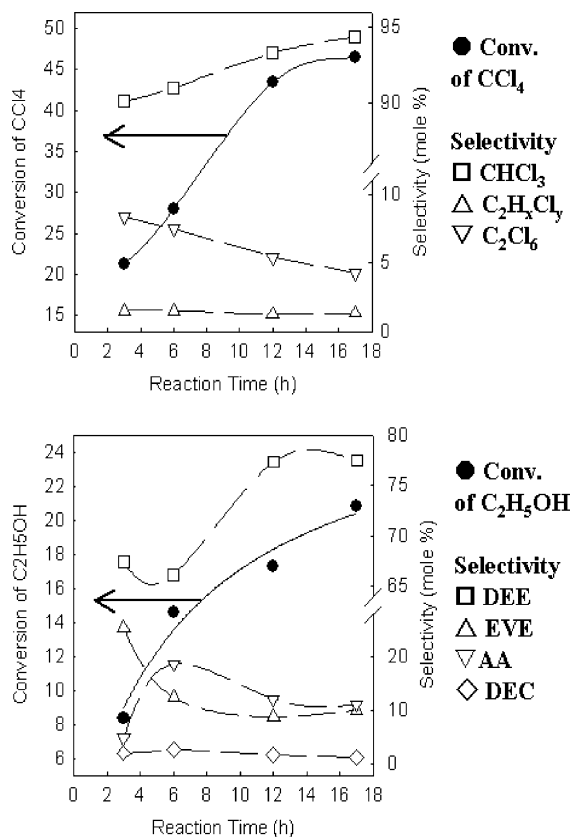


Fig. 1. Conversion of CCl₄ as well as C₂H₅OH and product distribution over Pd/Mont with reaction time. Pd/Mont: 2.8 wt.%; $T = 323$ K; $P(\text{H}_2) = 3$ MPa; CCl₄ = 64.5 mmol; C₂H₅OH = 217.4 mmol; internal standard (*n*-undecane) = 1.3 mmol; catalyst = 0.1 g.

nation of CCl₄, and vice versa for the lower binding energy peak (Pd(L)). Therefore, during hydrodechlorination reaction, the oxidation states of grafted palladium could be altered possibly due to the loss of chlorine from the palladium precursor. However, a large amount of palladium is still grafted on the montmorillonite support as confirmed by ICP–AES experiments (a low amount of leached Pd in Table 5) and only a small change in the intensity of XPS peak. The changes in oxidation states of supported palladium could be the main reason for the variation of selectivity to CHCl₃ and C₂ compounds with time on stream (Fig. 1). The higher oxidation states of palladium could possibly be the one of the reasons for deep dechlorination of CCl₄ to form C₂H_xCl_y or CH₂Cl₂

[4,6,13]. Furthermore, they could affect the formation rate of C₂Cl₆ due to the low conversion of C₂H₅OH (low concentration of protons) at the beginning of the reaction. The activity changes in HDC of CCl₄ were correlated with the oxidation states of supported (or grafted) palladium particles in our liquid-phase system. This is in line with the previous observations [8,13,27]. Thus, the lower the oxidation states of platinum were (i.e. lower white line area in XANES), the selectivity to CHCl₃ was enhanced in gas-phase hydrodechlorination. Furthermore, Gomez-Sainero et al. have observed the highest conversion of CCl₄ (TOF) in liquid-phase hydrodechlorination at the mole ratio of Pdⁿ⁺/Pd⁰ ~ 1, while the reduced Pd/AC catalysts having the electron-deficient palladium particles or the metal-like palladium particles show a lower catalytic activity. In addition, the selectivity to CHCl₃ increased with the increase in palladium particle size and vice versa for the selectivity of C₂ compounds at some high CCl₄ conversion levels above 35% [8,27]. The changes in catalytic activity with reaction time could be well correlated with the mole ratio of Pd(H)/Pd(L) characterized by XPS before and after the reaction as shown in Fig. 2(a). In the case of the Pt/Mont catalyst shown in Fig. 2(b), the oxidation states of Pt were not much altered after the reaction. However, the peak intensity for the core level 4d_{5/2} at the binding energy of 316 eV (this peak was compared instead of the largest 4f_{7/2} core level peak due to its overlapping with the Al 2p peak) was significantly reduced. This was in line with the large amount of leached platinum confirmed by ICP–AES. The catalytic activity of Pt/Mont, especially selectivity to CHCl₃, did not change greatly with time on stream (95.2 mol% of CHCl₃ at 6 h reaction and 95.6 mol% at 12 h reaction) compared to Pd/Mont. Although the peak intensity of adsorbed Cl was much larger in the used catalyst than in the fresh one (Cl atomic ratio of used/fresh catalysts was ca. 2.5), Cl/Pd ratio could not be determined because Cl could be adsorbed on the support itself as well as on transition metals.

The FT-IR spectra of adsorbed CO on H-Mont, Pd- and Pt/Mont catalysts are shown in Fig. 3. The characteristic FT-IR peaks of H-Mont around 1630, 1400–1500 and 1986 cm⁻¹ (shown in Fig. 3(a)) were assigned to the intrinsic peaks of silane-grafted montmorillonite during the preparation of catalyst (or carbonyl adsorbed by surface hydroxyl groups for the

Table 6
Conversion and product distribution: effects of additives

Run #	Catalysts	Additives	Conversion of CCl ₄	Product distribution (mol%)			Conversion of C ₂ H ₅ OH	Product distribution (mol%)			
				CHCl ₃	C ₂ H _x Cl _{4-x} ^a	C ₂ Cl ₆		DEE	AA	EVE	DEC
26	Pd/Mont	<i>P</i> (O ₂) = 0.1 MPa	36.7	91.9	2.5	5.6	20.0	67.4	14.0	7.4	11.2
27	Pd/AC	<i>P</i> (O ₂) = 0.1 MPa	55.0	96.1	1.9	2.0	14.3	53.1	19.7	17.8	9.4
28	Pt/Mont	<i>P</i> (O ₂) = 0.1 MPa	31.4	95.3	1.5	3.2	18.5	68.8	12.4	8.1	10.7
29	Pt/AC	<i>P</i> (O ₂) = 0.1 MPa	24.3	95.3	2.7	2.0	11.2	57.0	18.3	12.1	12.6
30	Pd/Mont	<i>P</i> (O ₂) = 1 MPa	44.1	73.2	17.0	9.8	15.1	13.4	10.0	24.5	52.1
31	5% Pd/AC	<i>P</i> (O ₂) = 1 MPa	46.5	81.6	9.3	9.1	11.7	6.4	13.0	32.3	48.3
32	Pd/Mont	H ₂ O/C ₂ H ₅ OH = 0.2	36.3	88.5	1.9	9.6	4.6	55.0	26.4	16.8	1.8
33	Pd/Mont	H ₂ O/C ₂ H ₅ OH = 1.0	17.9	62.8	2.1	35.1	4.3	28.2	44.0	27.0	0.8
34	Pt/Mont	H ₂ O ₂ /C ₂ H ₅ OH = 0.15	21.1	79.7	2.6	17.7	6.4	42.0	41.1	7.1	9.8

Effects of oxygen (I): Runs 26–29: same reaction conditions as Run 4 except for *P*(H₂) = 1.5 MPa and *P*(O₂) = 0.1 MPa. Effects of oxygen (II): Runs 30 and 31: same reaction conditions as Run 4 except for *P*(H₂) = 3 MPa and *P*(O₂) = 1 MPa. Effects of water: Runs 32 and 33: same reaction conditions as Run 4 except for mole ratio of H₂O/C₂H₅OH = 0.2–1.0. Effects of 30 wt.% H₂O₂: Run 34: same reaction conditions as Run 4 on Pt/Mont except for the addition of 110 mmol H₂O₂ solution.

^a C₂Cl₄ and C₂HCl₃ were the main products in C₂H_xCl_{4-x} (*x* = 0–2).

bands of 1660 cm⁻¹) [28]. In the case of Pd/Mont (Fig. 3(b)), the bridged CO band at 1930 cm⁻¹ as well as the linear-bonded (on-top sites) CO at 2160 cm⁻¹ was observed. In contrast, only linear-bonded CO band at 2114 cm⁻¹ with a shoulder at a somewhat lower frequency was observed for Pt/Mont (Fig. 3(c)). In the literature [29–31], bridged CO or shoulder peaks around main peaks are usually observed for the different morphologies (Miller indices) or larger metal clusters. Therefore, the grafted Pt- or Pd/Mont catalysts could contain differently grafted metal precursors or impregnated metal clusters on the montmorillonite surfaces. Furthermore, it could not be overlooked that grafted metal precursors might have the different electronic states. These different metallic states evolving during the reaction could alter the catalytic activity and the amount of leached metals with reaction time.

Fig. 4 shows the TPSR profiles of fresh Pd/Mont and the used one. The major reason for catalyst deactivation in our system could be the strongly adsorbed chlorine because much higher intensity of chlorine (*m/z* = 36) was observed in TPSR experiment for all used catalysts. In addition, the deposited carbonaceous species could also have contributed to the catalyst deactivation [6,13] as shown in Fig. 4. The peak intensities of generated CH₄ (*m/z* = 16) and C₂H₆ (*m/z* = 28) from used Pd/Mont were much larger than that for the fresh catalyst. The presence of carbon peaks

in the fresh catalyst could be from the silane ligand ((C₂H₅O)₃Si(CH₂)₂NH₂) and the palladium precursor ((CH₃CN)₂PdCl₂) during the functionalized montmorillonites preparation [23].

3.5. Effects of reaction variables

The effects of molecular hydrogen pressures are shown in Table 7 (Runs 17–19) on Pd/Mont. Although the selectivity to CHCl₃ was found to be affected by the amount of adsorbed hydrogen on active sites in gas-phase hydrodechlorination in our previous studies [6], the hydrogen pressures did not significantly affect the product distribution from CCl₄ in liquid-phase hydrodechlorination. However, conversion of CCl₄ and selectivity to DEE from C₂H₅OH increased significantly with the increase in hydrogen pressure. The enhancement in CCl₄ conversion could result from the slight increase in hydrogen solubility to induce the more acidic environments of reaction medium; then the reaction between AA and EVE intermediates to form DEE could be accelerated. Reaction temperatures were also one of the main reaction variables to affect conversion and product distribution (Runs 17, 20 and 21). As reaction temperatures increased from 323 to 353 K, the conversion of CCl₄ was abruptly enhanced from 27.9 to 62.8 mol%, but product distribution from CCl₄ did not change greatly. The selectivity

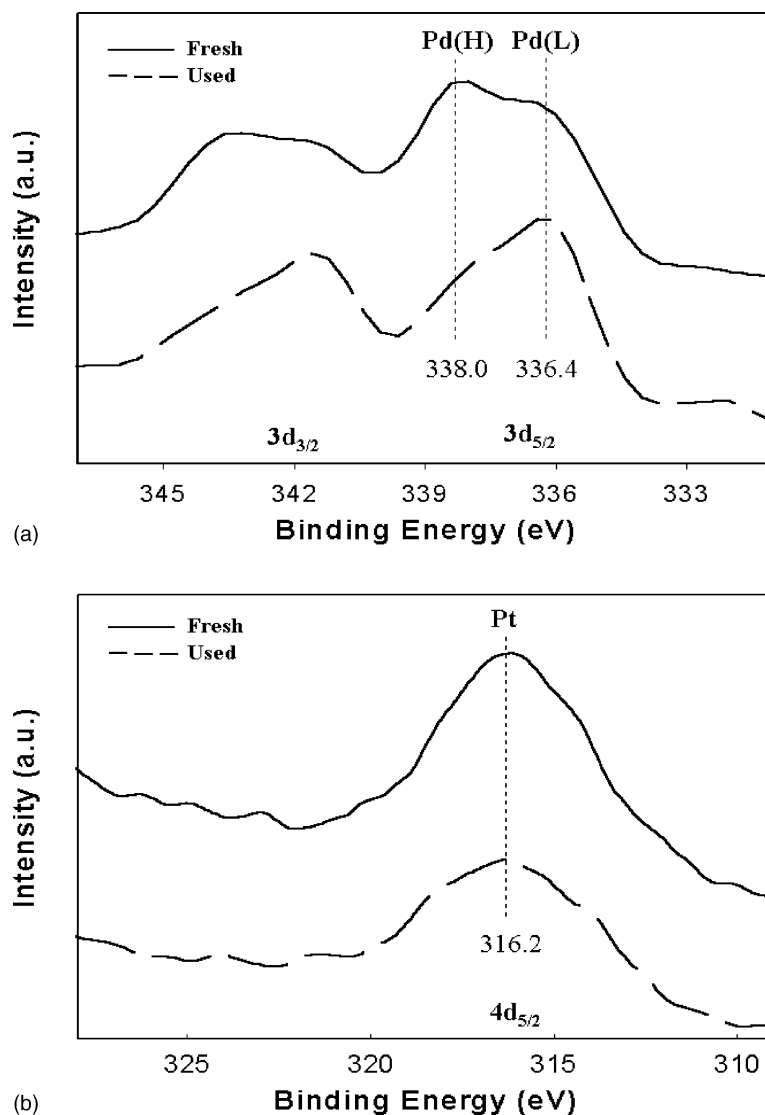


Fig. 2. X-ray photoelectron spectra of fresh and used (a) Pd/Mont and (b) Pt/Mont catalysts. Fresh one: just dried at 380 K for 12 h. Used one: after reaction for 12 h at the following conditions: $T = 323$ K; $P(\text{H}_2) = 3$ MPa; $\text{CCl}_4 = 64.5$ mmol; $\text{C}_2\text{H}_5\text{OH} = 434.8$ mmol; internal standard (*n*-undecane) = 1.3 mmol; catalyst = 0.1 g.

to DEE declined at 353 K possibly due to the reverse reaction of DEE to $\text{C}_2\text{H}_5\text{OH}$ and AA (see Table 4). Since the 3 wt.% Pd/AC pretreated with hydrogen flow at different temperatures (below 573 K) showed a negligible difference in conversion and products distribution (Runs 4, 22 and 23), the catalysts could be used just after drying at room temperature. The effects of the amount of loaded palladium on activated carbons

are shown in Runs 4, 24 and 25. With the increase in palladium loading from 1.0 to 5.0 wt.%, a slight increase in CCl_4 conversion and more significant increase in $\text{C}_2\text{H}_5\text{OH}$ conversion were observed. The selectivity to CHCl_3 did not show great change, but that of DEE showed a significant decrease. There was also an increase in the selectivity of C_2 compounds ($\text{C}_2\text{H}_x\text{Cl}_{4-x}$ and C_2Cl_6) as Pd loading was increased.

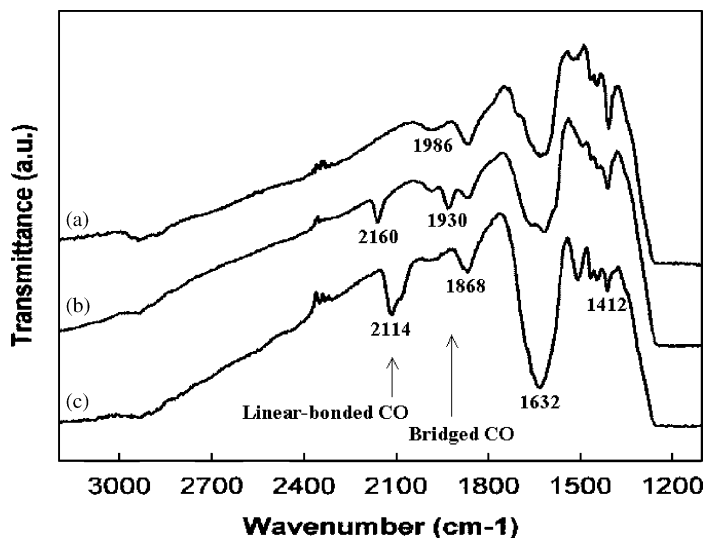


Fig. 3. FT-IR spectra of adsorbed CO on the various catalysts: (a) H-Mont; (b) Pd/Mont; (c) Pt/Mont. All catalysts were pretreated with He flow (20.5 $\mu\text{mol/s}$) at 373 K for 1 h, and CO molecules were adsorbed at room temperature for 0.5 h.

3.6. Addition of molecular oxygen

During the hydrodechlorination reactions with $\text{C}_2\text{H}_5\text{OH}$, generation of DEC was observed. This is unexpected because of the absence of carbon monoxide or phosgene in our system which are usual reac-

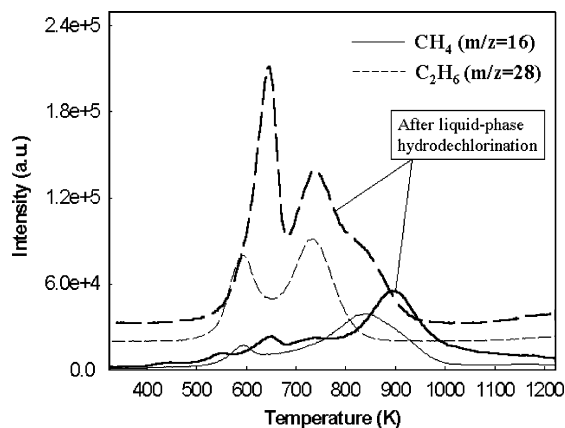


Fig. 4. TPSR profiles of Pd/Mont catalysts after and before reaction. Normal line: fresh one. Bold line: Pd/Mont reacted for 12 h at the same reaction conditions as mentioned in Fig. 1. TPSR conditions: ramping rate = 10 K/min; flow rate of H_2 = 20.5 $\mu\text{mol/s}$ with 0.04 g catalyst. The generation of CH_4 ($m/z = 16$) and C_2H_6 ($m/z = 28$) were continuously analyzed by GC-MSD (mass selective detector) 5973.

tants to synthesize DEC. We thought that dissolved oxygen might be involved in this reaction. To prove this hypothesis, air was intentionally introduced at the beginning of the reaction (Runs 26–31). When a small amount of air ($P(\text{O}_2) = 0.1$ MPa) was added at the beginning of the reaction (Runs 26–29), the formation of diethyl carbonate was greatly enhanced without much effect on hydrodechlorination of CCl_4 for all tested catalysts. Furthermore, with a much larger amount of air ($P(\text{O}_2) = 1$ MPa), the formation of DEC became the major reaction with a DEC selectivity as high as 52.1 mol% (Runs 30 and 31). The molecular oxygen in air could accelerate the formation of DEC by the oxidative cleavage of C=C double bonds in EVE precursors and the subsequent addition of ethoxy group (see Table 4 and Fig. 5). The real oxidizing agent may be hydrogen peroxide generated in situ on the transition metal by the reaction of dihydrogen and dioxygen [32,33]. When diluted hydrogen peroxide (30 wt.% H_2O_2 balanced with H_2O) was added ex situ at the beginning of the reaction (Run 34), the formation of DEC was also greatly enhanced. The oxidative cleavage of EVE precursors to produce DEC could be possible only in acidic media, but no reaction occurred with only $\text{C}_2\text{H}_5\text{OH}$ added even on the acidic support. To enhance the generation of DEC in our phosgene-free reaction conditions, the amount

Table 7

Conversion and product distribution: effects of hydrogen partial pressures and temperatures

Run #	Catalysts (variables)	Conditions	Conversion of CCl ₄	Product distribution (mol%)			Conversion of C ₂ H ₅ OH	Product distribution (mol%)			
				CHCl ₃	C ₂ H _x Cl _{4-x} ^a	C ₂ Cl ₆		DEE	AA	EVE	DEC
17	<i>P</i> (H ₂), 6 h), T = 323 K	3 MPa	27.9	91.0	1.5	7.5	14.6	66.2	18.7	12.4	2.7
18		4.5 MPa	33.7	91.4	1.5	7.1	15.1	79.3	11.0	9.4	0.3
19		6 MPa	35.5	91.2	1.5	7.3	13.3	83.6	10.7	5.2	0.5
20	<i>T</i> , 6 h), <i>P</i> (H ₂) = 3 MPa	338 K	46.6	93.9	1.8	4.3	22.1	78.0	15.1	6.1	0.8
21		353 K	62.8	92.5	4.6	2.9	11.7	10.6	67.3	22.0	0.1
22	(Red <i>T</i> , 12 h), <i>P</i> (H ₂) = 3 MPa	373 K	47.1	97.3	1.3	1.4	8.9	30.7	39.1	30.0	0.2
23		573 K	44.6	97.2	1.4	1.4	8.7	21.3	20.7	57.8	0.2
24	(wt.% of Pd, 12 h), <i>P</i> (H ₂) = 3 MPa	1.0 wt.%	42.8	97.9	1.0	1.1	6.4	49.2	26.4	24.3	0.1
25		5.0 wt.%	48.4	96.3	1.6	2.1	10.3	21.8	41.1	37.0	0.1

Effects of hydrogen pressures on Pd/Mont: Runs 17–19: same reaction conditions as Run 7 except for *P*(H₂) = 3–6 MPa and reaction for 6 h. Effects of reaction temperatures on Pd/Mont: Runs 20 and 21: same reaction conditions as Run 7 except for *T* = 323–353 K and reaction for 6 h. Effects of reduction temperatures on Pd/AC: Runs 4, 22 and 23: same reaction conditions as Run 4 except for Red *T* = 373–573 K. Effects of the loaded amount of palladium on Pd/AC: Runs 4, 24 and 25: same reaction conditions as Run 4 except for the amount of palladium loading.

^a C₂Cl₄ and C₂HCl₃ were the main products in C₂H_xCl_{4-x} (*x* = 0–2).

of reaction intermediates, chlorine-containing EVE precursors with the terminal vinyl group, should be an important variable. The conditions that would promote the formation of C₂H_xCl_{4-x} (mainly, *x* = 0 or 1) and in situ generated hydrogen peroxide, led to the

higher selectivity to DEC (Runs 26–31). Furthermore, the addition of H₂O during the hydrodechlorination (Runs 32 and 33) showed negative effects on conversion of reactants and selectivity to CHCl₃ and DEE. These negative effects were more severe when the

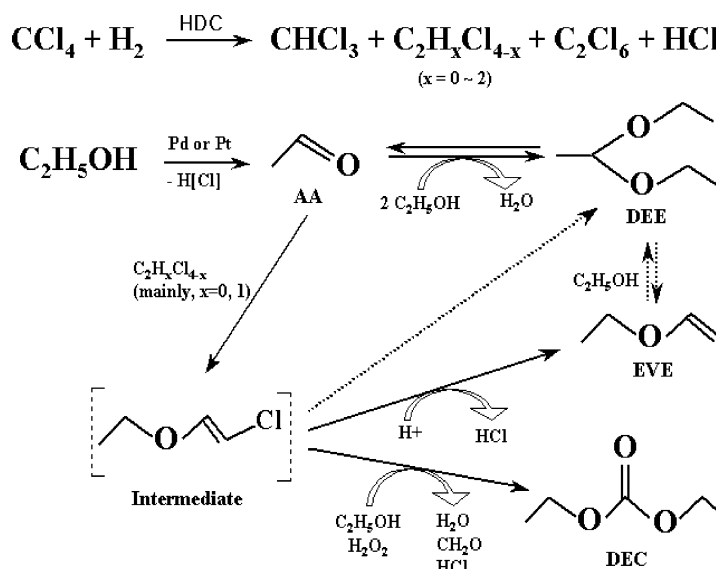


Fig. 5. A proposed possible reaction pathway.

amount of added water increased. The decrease in selectivity to CHCl_3 could be mainly from the reduction of hydrogen solubility in water-rich reaction solution. The partial molar volumes (solubility) of hydrogen at 298 K are as follows: $38 \text{ cm}^3/\text{mol}$ for carbontetrachloride, $35 \text{ cm}^3/\text{mol}$ for methanol and $26 \text{ cm}^3/\text{mol}$ for water [34]. With the decreased conversion of CCl_4 , acidity of the reaction solution could also be diminished resulting in decrease in DEE selectivity. When the formation rate of H_2O_2 was enhanced by introducing higher partial pressure of O_2 , the formation rate of C_2 compounds from the reaction of CCl_4 was accelerated probably due to the concomitant generation of H_2O (Runs 26, 30 and 27, 31).

3.7. A possible reaction pathway

With some control experiments shown in Table 4, a possible reaction pathway of the hydrodechlorination of CCl_4 in the presence of $\text{C}_2\text{H}_5\text{OH}$ and molecular oxygen is proposed as shown in Fig. 5. The final main product from the reaction of $\text{C}_2\text{H}_5\text{OH}$ with AA or EVE was mainly DEE with high conversion levels of reactants (Runs 35 and 36). The large amount of DEE could also be decomposed to $\text{C}_2\text{H}_5\text{OH}$, AA and EVE during the hydrodechlorination of CCl_4 (Run 37). In this scheme, catalytic hydrodechlorination of CCl_4 proceeds according to the well-known pathway over supported Pt or Pd catalysts to produce mainly CHCl_3 . As a protic solvent, $\text{C}_2\text{H}_5\text{OH}$ could donate the proton to the adsorbed chlorine produced in the HDC reaction, and turn itself to acetaldehyde on the supported Pd or Pt sites. The reaction of acetaldehyde with ethanol produces DEE by acid-catalyzed aldol condensation. Ethyl vinyl ether could be formed from the reaction of AA with $\text{C}_2\text{H}_x\text{Cl}_{4-x}$ (mainly, $x = 0$ or 1). Furthermore, chlorine-containing $\text{C}=\text{C}$ group in EVE intermediate could be easily dechlorinated to DEE by hydrogen mainly from the proton in $\text{C}_2\text{H}_5\text{OH}$ adsorbed on the catalyst surfaces. Diethyl carbonate is produced by the addition of oxygen to carbon–carbon double bonds [35] in an intermediate with the chlorine-containing $\text{C}=\text{C}$ group. To demonstrate the effects of $\text{C}_2\text{H}_x\text{Cl}_{4-x}$, the C_2 compounds such as C_2Cl_4 or $\text{C}_2\text{H}_4\text{Cl}_2$ was intentionally added to the reaction system. When C_2Cl_4 instead of CCl_4 was introduced with $\text{C}_2\text{H}_5\text{OH}$ and molecular oxygen under the hydrodechlorination conditions (Run 38),

the selectivity to DEC was greatly enhanced with the increased conversion of C_2Cl_4 . But the reactivity of $\text{C}_2\text{H}_4\text{Cl}_2$ with $\text{C}_2\text{H}_5\text{OH}$ under the same reaction conditions of Run 38 was negligible. Furthermore, under the same reaction conditions of Run 28 except for the extra addition of C_2Cl_4 , a little enhancement in the selectivity to DEE was observed. The reaction pathway shown in Fig. 5 is consistent with the above results and could be one of the possible routes for the formation of DEC and DEE. Although the possible reaction routes for the synthesis of DEE and for hydrodechlorination of CCl_4 over supported Pt or Pd was known [1–6,13,22], the formation of DEC in the presence of molecular oxygen was first reported in our previous communication [36]. The strong acidic environments and generation of $\text{C}_2\text{H}_x\text{Cl}_{4-x}$ ($x = 0$ or 1) induced from the hydrodechlorination of CCl_4 were very important requirements for the formation of DEC under aerobic oxidation conditions.

4. Conclusion

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. The catalytic activity and selectivity to CHCl_3 during the hydrodechlorination of CCl_4 was greatly enhanced in the presence of $\text{C}_2\text{H}_5\text{OH}$. This promotional effect could be due to the retarded deactivation induced by strongly adsorbed chlorine on active sites and the facile formation of HCl. The catalyst stabilization could be enhanced in the solvent by a facile reaction between adsorbed chlorine and proton from protic solvent to form HCl. The formation rate of DEE was much influenced by the acidity of catalysts and that of DEC was affected by the in situ generated chlorine-containing intermediate as well as oxidative cleavage of its $\text{C}=\text{C}$ group by in situ generated H_2O_2 .

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References

- [1] A.H. Weiss, B.S. Gambhir, R.B. Leon, *J. Catal.* 22 (1971) 245.
- [2] S.Y. Kim, H.C. Choi, O.B. Yang, K.H. Lee, J.S. Lee, Y.G. Kim, *J. Chem. Soc., Chem. Commun.* (1995) 2169.
- [3] H.C. Choi, S.H. Choi, J.S. Lee, K.H. Lee, Y.G. Kim, *J. Catal.* 161 (1996) 790.
- [4] H.C. Choi, S.H. Choi, J.S. Lee, K.H. Lee, Y.G. Kim, *J. Catal.* 166 (1997) 284.
- [5] Z.C. Zhang, B.C. Beard, *Appl. Catal. A* 174 (1998) 33.
- [6] J.W. Bae, E.D. Park, J.S. Lee, K.H. Lee, Y.G. Kim, S.H. Yeon, B.H. Sung, *Appl. Catal. A* 217 (2001) 79.
- [7] C.D. Thompson, R.M. Rioux, N. Chen, F.H. Ribeiro, *J. Phys. Chem. B* 104 (2000) 3067.
- [8] L.M. Gomez-Sainero, A. Cortes, X.L. Seoane, A. Arcoya, *Ind. Eng. Chem. Res.* 39 (2000) 2849.
- [9] L. Lassova, K.H. Lee, T.S. Andy Hor, *J. Mol. Catal. A* 144 (1999) 397.
- [10] V.A. YaKovlev, V.V. Terskikh, V.I. Simagina, V.A. Likholobov, *J. Mol. Catal. A* 153 (2000) 231.
- [11] M.A. Aramendia, V. Borau, I.M. Garcia, C. Jimenez, F. Lafont, A. Marinas, J.M. Marinas, F.J. Urbano, *J. Catal.* 187 (1999) 392.
- [12] M.A. Aramendia, V. Borau, I.M. Garcia, C. Jimenez, J.M. Marinas, F.J. Urbano, *Appl. Catal. B* 20 (1999) 101.
- [13] J.W. Bae, E.J. Jang, I.G. Kim, J.S. Lee, K.H. Lee, *Appl. Catal. A*, in press.
- [14] M.A. Pacheco, C.L. Marshall, *Energy Fuels* 11 (1) (1997) 2.
- [15] V. Raab, M. Merz, J. Sundermeyer, *J. Mol. Catal. A* 175 (2001) 51.
- [16] M.S. Han, B.G. Lee, I. Suh, H.S. Kim, B.S. Ahn, S.I. Hong, *J. Mol. Catal. A* 170 (2001) 225.
- [17] S.T. King, *J. Catal.* 161 (1996) 530.
- [18] K.T. Jung, A.T. Bell, *J. Catal.* 204 (2001) 339.
- [19] K. Tomishige, Y. Ikeda, T. Sakaihorii, K. Fujimoto, *J. Catal.* 192 (2000) 355.
- [20] K. Tomishige, Y. Furusawa, Y. Ikeda, M. Asadullah, K. Fujimoto, *Catal. Lett.* 76 (1–2) (2001) 71.
- [21] J.X. Zhen, S.Y. Hua, C.S. Hua, *Catal. Lett.* 69 (2000) 153.
- [22] M.R. Capeletti, L. Balzano, G. de la Puente, M. Laborde, *Appl. Catal. A* 198 (2000) L1.
- [23] E.J. Jang, K.H. Lee, J.S. Lee, Y.G. Kim, *J. Mol. Catal. A* 144 (1999) 431.
- [24] F.C. Carey, R.J. Sundberg, *Advanced Organic Chemistry. Part A*, third ed., Plenum Press, New York, 1993, p. 233.
- [25] S.H. Choi, J.S. Lee, *J. Catal.* 193 (2000) 176.
- [26] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy*, Physical Electronics, USA, 1995, p. 234.
- [27] L.M. Gomez-Sainero, X.L. Seoane, J.L.G. Fierro, A. Arcoya, *J. Catal.* 209 (2002) 279.
- [28] J.R. Sohn, J.T. Kim, *Langmuir* 16 (2000) 5430.
- [29] J.B. Giorgi, T. Schroeder, M. Baumer, H.J. Freund, *Surf. Sci.* 498 (2002) L71.
- [30] N. Sheppard, C. De La Cruz, *Catal. Today* 70 (2001) 3.
- [31] K. Balakrishnan, J. Schwank, *J. Catal.* 138 (1992) 491.
- [32] C. Shen, E.A. Garcia-Zayas, A. Sen, *J. Am. Chem. Soc.* 122 (2000) 4029.
- [33] E.D. Park, J.S. Lee, *Catal. Commun.* 2 (2001) 187.
- [34] R.C. Reid, J.M. Prausnitz, B.E. Poling, *The Properties of Gases & Liquids*, fourth ed., McGraw-Hill, New York, 1988, p. 336.
- [35] F.C. Carey, R.J. Sundberg, *Advanced Organic Chemistry. Part B*, third ed., Plenum Press, New York, 1993, p. 624.
- [36] J.W. Bae, J.S. Lee, K.H. Lee, E.J. Jang, *Chem. Lett.* 10 (2002) 1020.