

# Liquid-phase hydrodechlorination of CCl<sub>4</sub> in a medium of ethanol with co-production of acetal (1,1-diethoxyethane) and diethyl carbonate

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Catalytic hydrodechlorination (HDC) of CCl<sub>4</sub> in gas phase seemed to be a useful method for the disposal of this ozone-depleting compound [1-3], however, an obstacle in practicing HDC of CCl<sub>4</sub> in a large scale is the difficulty in controlling reaction temperature due to a large exotherm of the reaction. 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. [3,4] showed the reactivity of CCl<sub>4</sub> itself (without solvent) in the liquid phase HDC over some supported metal catalysts and they have finally recommended palladium supported on carbon as the best catalyst. In this study, the palladium catalysts grafted to montmorillonite (Pd/Mont) were prepared by ion exchange of H-montmorillonite with (CH<sub>3</sub>CN)<sub>2</sub>PdCl<sub>2</sub> [5]. We investigated a reaction system that gives not only the HDC of CCl<sub>4</sub> but also co-production of DEC and DEE with the presence of oxygen.

## Results and Discussion

The conversion of CCl<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>OH as well as product distribution over Pd/Mont with time on stream are shown in Figure 1. The selectivity to CHCl<sub>3</sub> from the reaction of CCl<sub>4</sub> increased with time on stream and vice versa for C<sub>2</sub> compounds, but the conversion of CCl<sub>4</sub> showed steady value after around 12 h. This could be mainly from catalyst deactivation due to the strong adsorption of the generated chlorine sources on active sites and the water generated could inhibit further conversion of CCl<sub>4</sub> (Run 3).

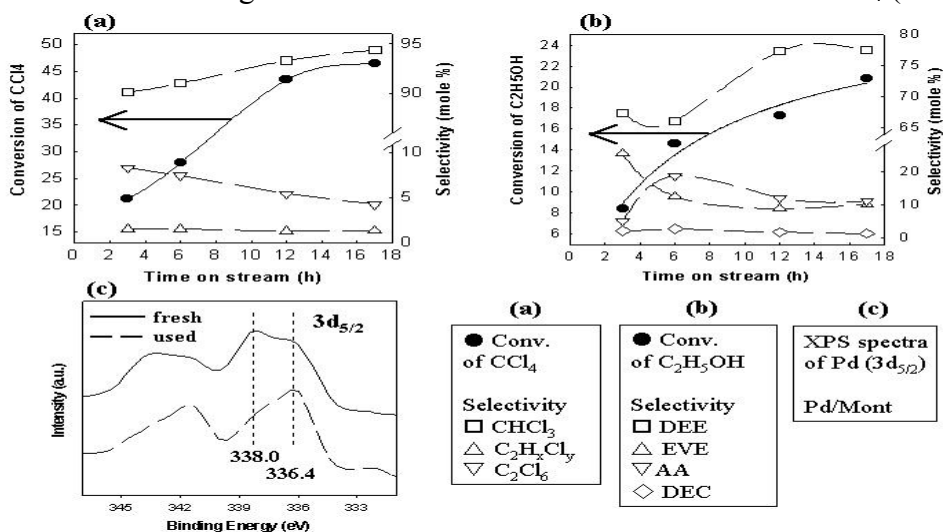


Figure 1. Conversion of CCl<sub>4</sub> (a) as well as C<sub>2</sub>H<sub>5</sub>OH (b) and product distribution over Pd/Mont. 2.8wt%Pd/Mont; T = 323 K; P(H<sub>2</sub>) = 3 MPa; CCl<sub>4</sub> = 64.5 mmol; C<sub>2</sub>H<sub>5</sub>OH = 217.4 mmol; internal standard (n-undecane) = 1.3 mmol; catalyst = 0.1 g. The conversions of CCl<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>OH approached the steady values after 15 h reaction possibly due to reverse reactions of products formed with C<sub>2</sub>H<sub>5</sub>OH. To correlate catalytic activity

change with the states of supported palladium, X-ray photoelectron spectroscopy (XPS) of the fresh Pd/Mont and the used ones are also investigated. The changes in oxidation states of supported palladium after reaction could be the main reason for the variation of selectivity to  $\text{CHCl}_3$  and  $\text{C}_2$  compounds with time on stream (Figure 1(a)). This is in line with the previous observations [3,4] and the activity changes in HDC of  $\text{CCl}_4$  were correlated with the oxidation states of grafted palladium in liquid-phase system.

Table 1. Conversion and products distribution on 2.8wt%Pd/Mont catalyst

Run	Effects	Conv. of $\text{CCl}_4$	Product distribution (mole %)			Conv. of $\text{C}_2\text{H}_5\text{OH}$	Product distribution (mole %)			
			$\text{CHCl}_3$	$\text{C}_2\text{H}_x\text{Cl}_{4-x}$ <sup>a</sup>	$\text{C}_2\text{Cl}_6$		DEE	AA	EVE	DEC
1	-	43.5	93.3	1.3	5.4	17.3	77.4	12.1	8.8	1.7
2	$\text{O}_2$	36.7	91.9	2.5	5.6	20.0	67.4	14.0	7.4	11.2
3	$\text{H}_2\text{O}$	36.3	88.5	1.9	9.6	4.6	55.0	26.4	16.8	1.8
4	$\text{H}_2\text{O}_2$	21.1	79.7	2.6	17.7	6.4	42.0	41.1	7.1	9.8

Reaction conditions: T = 323 K; P( $\text{H}_2$ ) = 3 MPa;  $\text{CCl}_4$  = 64.5 mmol; n-undecane = 1.3 mmol; catalyst = 0.1 g; reaction for 12 h. <sup>a</sup>  $\text{C}_2\text{Cl}_4$  and  $\text{C}_2\text{HCl}_3$  were the main products. **Run 2:** Effect of  $\text{O}_2$  (P = 0.1 Mpa); **Run 3:** Effect of  $\text{H}_2\text{O}$  ( $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 0.2$ ); **Run 4:** Effect of  $\text{H}_2\text{O}_2$  ( $\text{H}_2\text{O}_2$ (30wt% in  $\text{H}_2\text{O})/\text{C}_2\text{H}_5\text{OH} = 1.0$ ). Abbreviation: DEE=1,1-diethoxyethane; AA=acetaldehyde; EVE=ethyl vinyl ether; DEC=diethyl carbonate.

During the hydrodechlorination with  $\text{C}_2\text{H}_5\text{OH}$ , generation of DEC was observed. 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 (Run 2). When a small amount of air (P( $\text{O}_2$ ) = 0.1 MPa) was added at the beginning of the reaction, the formation of diethyl carbonate was greatly enhanced without significant effect on hydrodechlorination of  $\text{CCl}_4$ . 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. The real oxidizing agent may be hydrogen peroxide generated *in-situ* on the transition metal by the reaction of dihydrogen and dioxygen [6,7]. When hydrogen peroxide (30wt% $\text{H}_2\text{O}_2$  balanced with  $\text{H}_2\text{O}$ ) was added at the beginning of reaction (Run 4), the formation of DEC was also greatly enhanced. Catalytic hydrodechlorination of  $\text{CCl}_4$  over supported Pd in the presence of ethanol gives not only the selective synthesis of  $\text{CHCl}_3$ , but also co-production of valuable diethyl carbonate and 1,1-diethoxyethane (acetal). The formation rate of DEE was 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 C=C group by *in-situ* generated  $\text{H}_2\text{O}_2$ .

## References

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