Hydrodechlorination of Tetrachloromethane over Supported Pt Catalysts

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In the selective hydrodechlorination of tetrachloromethane to chloroform, long catalytic life as well as high selectivity to chloroform is achieved over a platinum catalyst supported on MgO.

Tetrachloromethane is a versatile chemical that has been used as a raw material, a reagent, and a solvent in chemical and semiconductor industries.[1–3] However, it was classified as group IV material in the London conference in 1990 to be banned due to its potential impact on ozone depletion. Hydrodechlorination[4] and decomposition[5] of CCl_4 are known to be possible methods to reduce the disposal problem of CCl_4. In view of the value of products, selective hydrodechlorination of CCl_4 to chloroform or dichloromethane seems to be the more desirable method than decomposition.

In this communication, we report our results on the selective hydrodechlorination of CCl_4 to chloroform over Pt catalysts deposited on various supports. A Pt catalyst supported on MgO was found to be a stable and selective catalyst for the reaction.

Pt (0.5 mass%) catalysts were prepared by an incipient wetness impregnation with an aqueous solution of chloroplatinic acid (H_2PtCl_6, Aldrich) of various supports such as γ-Al_2O_3 (Strem, BET surface area S_g = 95 $m^2\ g^{-1}$), MgO (Aldrich, 169 $m^2\ g^{-1}$), TiO_2 (Aldrich, 11 $m^2\ g^{-1}$), NaY (Strem, 670 $m^2\ g^{-1}$), ZrO_2 (Aldrich, 80 $m^2\ g^{-1}$), SiO_2 (Aldrich, 483 $m^2\ g^{-1}$) and SiO_2–Al_2O_3 (Tosoh, 511 $m^2\ g^{-1}$). The impregnated samples were dried at 100 °C and calcined with O_2 at 300 °C, and then reduced with H_2 at 300 °C for 2 h. The catalysts were characterized by hydrogen chemisorption, N_2 adsorption for measurement of BET surface area (Micrometrics Accusorb 2100E), X-ray diffraction (XRD, Rigaku DMAX-B, CuKα radiation), transmission electron microscopy (TEM, Jeol, JEM 200CX) and X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5400). Gas-phase hydrodechlorination of CCl_4 was carried out with 200 mg of Pt catalysts in a continuous flow, fixed bed reactor at atmospheric pressure and 140 °C. Before the reaction the catalyst was re-reduced with hydrogen (42 μmol s^{-1}) at 300 °C for 2 h. A reaction mixture with $H_2 : CCl_4$ mol ratio of 5 : 1 was generated by bubbling hydrogen (21 μmol s^{-1}) through a CCl_4 saturator kept at 30 °C. Reaction products were analysed by on-line GC equipped with an FID detector and a 12 ft long, 1/8 inch stainless steel column packed with 60–80 mesh of OV101.

Table 1 shows the catalytic performance of Pt catalysts supported on various carriers in hydrodechlorination of CCl_4 at 140 °C, atmospheric pressure, and $H_2 : CCl_4$ mol ratio of 5 : 1. Major reaction products were chloroform, methane and C_2 compounds such as hexachloroethane (C_2Cl_6) and tetrachloroethylene (C_2Cl_4). Catalytic activity and product distributions depend strongly on the support. Pt catalysts in Table 1 could be classified into two groups according to their activity pattern and product distributions. One group including Pt/MgO, Pt/γ-Al_2O_3 and Pt/TiO_2 exhibited an induction period to reach the maximum activity and showed low selectivity for C_2 compounds. The other group such as Pt/ZrO_2, Pt/SiO_2, Pt/SiO_2-Al_2O_3 and Pt/NaY deactivated rapidly with time on stream and produced greater than 50% of C_2 compounds. Especially, the selectivity of C_2 compounds was greater than 90% over Pt/NaY catalyst. Hence, Pt catalysts supported on zeolite or silica–alumina are not appropriate for hydrodechlorination of CCl_4 because of their high selectivity to C_2 compounds and rapid deactivation. Considering the catalytic life and high yields of chloroform, Pt/MgO and Pt/γ-Al_2O_3 appear to be proper catalysts. Especially, Pt/MgO catalyst showed little deactivation for more than 30 h. Moreover, Pt/MgO catalyst showed the highest selectivity for chloroform among all catalysts.

All the catalysts deactivated during the reaction as shown in Table 1 recovered their initial activities when the catalysts were regenerated by O_2 treatment at 300 °C for 2 h. The major gas component that evolved during this regeneration process was CO_2 as determined by an on-line mass spectrometer. Chemical analysis of Pt/MgO and Pt/Al_2O_3 before and after 12 h of the reaction (Table 2) indicated that *ca.* 2 mass% of carbon had been deposited over Pt/Al_2O_3 while none was deposited over Pt/MgO. Other possible causes of catalyst deactivation would be the sintering of metal particles and poisoning by chlorine. There was no indication of sintering as observed by TEM analysis. For the catalyst poisoning by chlorine, it has been reported that Rh/SiO_2 catalyst deactivated by chlorine in the hydrodechlorination of trichloroethylene is easily regenerated after re-reduction by hydrogen.[6] However, it was impossible to recover the activity of our deactivated catalyst by hydrogen treatment at 300 °C for 2 h. These results indicate that catalyst deactivation is mostly

Table 2 Carbon analysis for Pt/MgO and Pt/Al_2O_3 before and after the hydrodechlorination of CCl_4 at 140 °C for 12 h

	Pt/MgO		Pt/Al_2O_3	
	Before	After	Before	After
Mass% carbon	0.1	0.1	0.1	2.0

Table 1 Performance of supported Pt catalysts in hydrodechlorination of CCl_4 at 140 °C, atmospheric pressure and $H_2 : CCl_4$ mol ratio of 5 : 1

	CTC conversion (%)									Product distribution[a] (mol %)		
Catalyst	0.1 h	1.5 h	3.0 h	4.5 h	6.0 h	8.0 h	10 h	18 h	34 h	$CHCl_3$	CH_4	C_2
Pt/MgO	8.6	29.4	52.0	45.6	45.5	$\underline{45.2}$	51.4	50.6	45.6	76.1	19.6	4.3
Pt/Al_2O_3	16.2	43.1	82.4	82.1	66.9	$\underline{60.4}$	38.8	21.5	—	66.1	26.2	7.7
Pt/TiO_2	11.2	16.7	21.3	20.7	20.7	$\underline{19.9}$	17.8	12.3	—	59.5	27.3	13.2
Pt/ZrO_2	31.7	$\underline{20.2}$	11.9	9.0	6.9	5.3	—	—	—	31.1	10.6	58.3
Pt/SiO_2	74.7	$\underline{18.9}$	15.7	11.7	9.23	—	—	—	—	19.3	14.4	66.3
Pt/Si-Al	40.0	$\underline{36.2}$	36.1	37.0	19.6	—	—	—	—	13.8	6.2	80.0
Pt/NaY	23.1	$\underline{8.6}$	7.8	3.1	—	—	—	—	—	4.4	4.4	91.2

[a] Obtained at the conversion underlined.

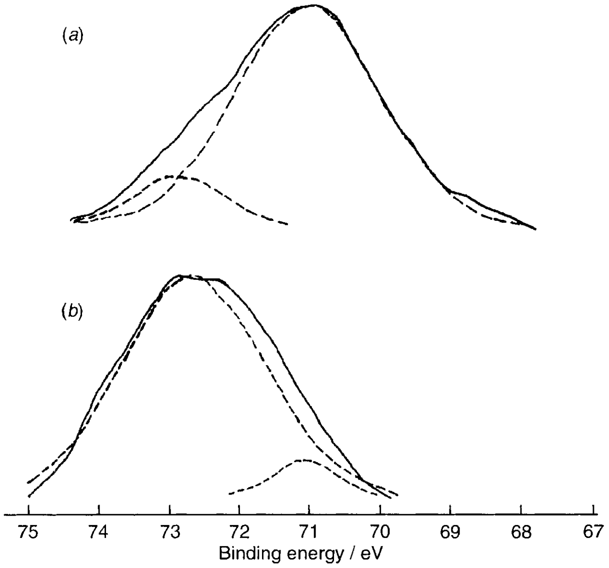

Fig. 1 XPS of Pt/MgO catalyst before (*a*) and after (*b*) the hydrodechlorination of CTC at 140 °C for 12 h. The dotted curves are deconvolutions of experimental spectra (solid curves) assuming that only Pt^0 and Pt^{II} are present. Note that majority of Pt^0 species present in the fresh catalyst turned to Pt^{II} after the reaction.

due to coking of the catalyst during hydrodechlorination of CCl_4. It is highly likely that coke is formed by an oligomerization reaction catalysed by acid sites on the supports. Indeed, as evident in Table 1, rapidly deactivating catalysts are mostly supported on acid supports and show high selectivity for C_2 compounds that are also the products of oligomerization of CCl_4. The excellent activity maintenance of Pt/MgO is believed to be due to the basic property of MgO which retards the coking. XRD spectra of the Pt/MgO after the reaction indicated that *ca.* 40% of MgO ($2\theta = 42.90°$) was transformed into $MgCl_2$ ($2\theta = 21.65°$) after the reaction.

The average size of Pt particles in the fresh Pt/MgO catalyst after reduction at 300 °C was *ca.* 3 nm as determined by hydrogen chemisorption and TEM. No activity was observed for MgO or $MgCl_2$ alone, which indicates that metal site is a main active site for hydrodechlorination over Pt/MgO catalyst. Platinum was present predominantly as Pt^0 prior to the reaction, while about 95% of Pt was present as Pt^{II} (binding energy = 73.6 eV) in the used catalyst as indicated by XPS spectra of Pt/MgO shown in Fig. 1. The induction period of Pt/MgO disappeared when reaction was conducted after Pt/MgO had been pretreated with 18% $HCl-H_2$ gas (7 μmol s^{-1}) and re-reduced with hydrogen (42 μmol s^{-1}) at 300 °C for 2 h, respectively. The performance was similar to the steady-state performance of Pt/MgO without the pretreatment. Thus, it appears that Pt^{II} (probably chloride) is the major active species for hydrodechlorination of CCl_4 over Pt/MgO.

In conclusion, a long catalyst life and high selectivity to chloroform in the hydrodechlorination of CCl_4 have been achieved over Pt supported on MgO. Basicity of MgO seems to be responsible for retarding the coke formation and suppression of C_2 oligomers. A Pt^{II} species is believed to be a dominant active species.

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