A Novel Method of CCl_4 Disposal by Disproportionation with CH_4 over Pt on Various Supports

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In disproportionation of CCl_4 with CH_4 into CH_3Cl and $CHCl_3$, platinum supported on $SrCO_3$, SiO_2, MgO and $MgAl_2O_4$ showed stable activity and high selectivities around 700 K, providing a novel disposal method of ozone-depleting CCl_4.

Chlorinated-carbons are known as ozone-depleting compounds.[1] Catalytic combustion and hydrodechlorination are useful methods for disposal of these harmful chlorinated compounds including CCl_4.[2–7] Compared to highly exothermic gas-phase hydrodechlorination of CCl_4, which has a short-coming of rapid catalyst deactivation due to high exothermicity, disproportionation of CCl_4 with CH_4 is very attractive and novel method discharging much lower heat of reaction (ΔH values of ca. –177 kJ/mol for hydrodechlorination of CCl_4, and –11.197 kJ/mol for the perfect disproportionation of CCl_4 and CH_4). Chlorohydrocarbon products such as $CHCl_3$, CH_2Cl_2 and CH_3Cl, useful for solvents and intermediates can be obtained by this reaction. Chlorination of methane i.e., catalytic reaction of CH_4 with Cl_2, has been found to show a very high selectivity to CH_3Cl over solid super-acid and supported noble metal catalysts.[8–11] Although disproportionation[12] of chlorofluoromethane with CCl_4 and catalytic reaction[13] of methane with $CBrF_3$ were studied, there has been no report, to our best knowledge, on the disproportionation of CCl_4 and CH_4 to produce chloromethanes. In the present letters, we studied the reaction over various supported platinum catalysts as a novel method of CCl_4 disposal.

Supported platinum catalysts were prepared by the conventional wet impregnation methods with K_2PtCl_6 as a platinum precursor. Various supports were employed including activated carbon (specific surface area, Sg = 1500 m^2/g), $SrCO_3$ (4.8 m^2/g), SiO_2 (300 m^2/g), MgO (45.3 m^2/g), ZSM-5 (350 m^2/g, Si/Al = 150), TiO_2 (11 m^2/g), $MgAl_2O_4$ (prepared from 10 wt% Mg/Al_2O_3 by calcination at 1127 K, Sg = 65.1 m^2/g), and γ-Al_2O_3 (103 m^2/g). Before initiating reaction in quartz reactor at a desired temperature, a prepared catalyst (500 mg) was reduced at 773 K with hydrogen flow of 21.1 μmol/s for 3 h. Methane (Matheson, 99.99%) was introduced at 7.03 μmol/s (weight hourly space velocity (WHSV) of 1200 L/kgcat./h based on CH_4) through a mass flow controller (Brooks), and CH_4/CCl_4 mole ratio of 20 was adjusted by bubbling helium (3.5 μmol/s) through a CCl_4 saturator. Products were analyzed by HP GC 5890 series II equipped with a 60 m DB-5 capillary column and a flame ionization detector.

As a blank test, pyrolysis of CCl_4 with CH_4 without catalyst was investigated in a quartz reactor (o.d. = 1.27 mm, length = 100 mm). The reaction rates became measurable around 700 K, and conversion of CCl_4 exceeded 10% above 800 K at a total reactant feed rate of 7.38 μmol/s. Typical product distribution (mole%) at CCl_4 conversion of 36.6% at 823 K was as follows; 42.3% for CH_3Cl, 1.2% for CH_2Cl_2, 28.6% $CHCl_3$, 4.6% for C_2Cl_4, and 23.2% for $C_2H_xCl_y$. As the reaction temperature increased above 770 K, the selectivity for $C_2H_xCl_y$ ($C_2H_2Cl_4$, C_2HCl_3, and unidentified by-products) increased abruptly probably by free radical reactions. Hence, performance of each catalyst for disproportionation of CCl_4 and CH_4 was studied below 773 K where the gas phase homogeneous reaction could be neglected.

Table 1 shows the conversion of CCl_4 over 1.0 wt% platinum supported on various carriers at 723 K, a CH_4/CCl_4 mole ratio of 20, and a WHSV of 1200 L/kgcat./h based on CH_4. Although support itself showed some catalytic activity for disproportionation of CCl_4 and CH_4, selectivity to CH_3Cl was lower than Pt-supported catalyst and catalyst deactivation occurred rapidly (not shown). Figure 1 shows the product distribution of each catalyst at the CCl_4 conversion indicated by parenthesis in Table 1. Products distribution and catalyst stability were affected strongly by the nature of support. Carbon- and TiO_2-supported platinum showed high initial CCl_4 conversions, but the conversions decreased rapidly and continuously with time on stream. Pt/ $SrCO_3$ showed an initial rapid decrease in the conversion but the activity was stabilized after then. Other catalysts of Pt/MgO, Pt/ZSM-5, Pt/SiO_2, and Pt/$MgAl_2O_4$ showed initial increase in CCl_4 conversions followed by leveling-off or decrease. Alumina also showed a similar behavior although the variation was smaller. However, the catalyst formed solid deposits at the reactor outlet probably due to the low sublimation

Table 1. CCl_4 conversion on supported platinum catalysts in disproportionation of CCl_4 with CH_4 at 723 K; WHSV = 1200L/kgcat./h and CH_4/CCl_4 mole ratio of 20; Pt precursor : K_2PtCl_6

Catalysts	Conversion of CCl_4 / %									
	0.5 h	1.5 h	2.5 h	3.5 h	5 h	7 h	9 h	11 h	13 h	15 h
1.0 wt%Pt/carbon	98.7	96.8	93.1	87.7	(83.1)	80.0	75.2	68.5	60.8	-
[a]1.0 wt%Pt/$SrCO_3$	99.7	99.9	98.3	55.9	52.8	50.8	51.0	50.5	50.9	(51.2)
1.0 wt%Pt/SiO_2	27.9	34.4	37.6	57.4	61.2	66.1	(69.4)	69.6	69.3	69.3
1.0 wt%Pt/MgO	10.4	65.6	88.1	94.4	79.9	72.0	57.9	56.1	(57.0)	57.7
1.0 wt%Pt/ZSM-5	27.1	36.9	48.3	58.5	(61.9)	66.2	65.3	62.6	58.9	-
1.0 wt%Pt/TiO_2	95.6	87.0	79.5	64.8	(56.8)	48.8	45.1	-	-	38.0
1.0 wt%Pt/$MgAl_2O_4$	22.8	34.5	47.1	56.8	(56.6)	54.5	55.5	-	-	-
0.5 wt%Pt/Al_2O_3	61.9	67.3	70.1	74.3	(75.0)	77.4	-	-	-	-

[a]WHSV = 600 L/kgcat./hr and CH_4/CCl_4 mole ratio of 10, H_2PtCl_6 Products distribution in Figure 1, was obtained at the parenthesized conversion.

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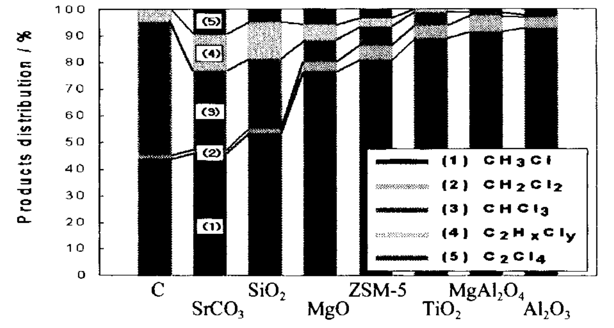

Figure 1. Products distribution over 1.0 wt% Pt catalysts supported on various supports: WHSV = 1200 L/kgcat./h based on CH_4; Reduction T = 573 K(3 h); T = 723 K; mole ratio CH_4/CCl_4 of 20; K_2PtCl_6; flow rate of CCl_4, 0.351 μmol/s; flow rate of CH_4, 7.03 μmol/s.

temperature of $AlCl_3$ (mp = 463 K) which might be formed during the chlorination reaction.[10] After reaction, Pt/$SrCO_3$ and Pt/MgO also showed the change in the phase of supports from oxides to chlorides such as $SrCl_2$ and $MgCl_2 \cdot 6H_2O$ as observed XRD. Despite this change, two catalysts showed stable catalyst activity and product distribution at 723 K for more than 30 h. These chlorides have high melting points, 987 K for $MgCl_2$ and 1146 K for $SrCl_2$. In any case, platinum supported on SiO_2, MgO, $SrCO_3$ and $MgAl_2O_4$ showed stable CCl_4 conversions and could become candidate catalysts for a novel disposal process of ozone-depleting CCl_4 by disproportionation with CH_4. Supported platinum catalysts could be classified into two groups according to their products distribution shown in Figure 1. Pt/carbon, Pt/$SrCO_3$, and Pt/SiO_2 showed the selectivity of CH_3Cl close to 50% and comparable amounts of $CHCl_3$. Substantial amounts of C_2 products were also formed over Pt/$SrCO_3$, and Pt/SiO_2. Other catalysts produced predominantly CH_3Cl. In particular, Pt/$MgAl_2O_4$, and Pt/Al_2O_3 catalysts exhibited CH_3Cl selectivity values higher than 90%. An ideal disproportionation of CCl_4 with CH_4 should have the following stoichiometry:

$$CH_4 + CCl_4 \rightarrow CH_3Cl + CHCl_3 \qquad (1)$$

The first group of catalyst, Pt/carbon in particular, appears to follow this route. However, we have to consider other stoichiometries in order to account for the dominant formation of CH_3Cl over the second group catalysts such as;

$$3CH_4 + CCl_4 \rightarrow 4CH_3Cl \qquad (2)$$

Figure 2 compares temperature-programmed oxidation (TPO) of adsorbed CH_4 on fresh Pt/SiO_2 and Pt/$MgAl_2O_4$ representing each group of catalysts. The catalyst (500 mg) was reduced at 773 K and purged in He flow at 873 K prior to CH_4 adsorption at 723 K. Then, TPO was executed with a ramping rate of 10 K/mim from 323 K to 1173 K. On Pt/$MgAl_2O_4$ showing a high selectivity to CH_3Cl, a larger amount of a more reactive carbonaceous species is present compared to Pt/SiO_2. CO_2 evolution temperature was as low as around 750 K. It appears that facile dissociative adsorption of CH_4 promotes the selective formation of CH_3Cl. CCl_4 could adsorb dissociatively on any supported platinum at a temperature as low as 323 K.[14] In order to investigate the source of carbon in each product, the reaction of labeled $^{13}CH_4$ with CCl_4 was studied over 1.0 wt%Pt/ $MgAl_2O_4$ with $4CH_4/CCl_4$. As shown in Table 2, most (ca. 85%) of CH_3Cl originates from methane. This higher value than expected from equation 2 (75%) suggested that the reaction pathway should be more complicated than indicated by equations 1 and 2. As chlorine content increases in chloromethanes, the contribution of CCl_4 increases (30% for CH_2Cl_2 and 60% for $CHCl_3$). C_2Cl_4 comes exclusively from CCl_4. Thus the reaction on the catalyst surface is very complicated comprising reactions 1 and 2 and others. As mentioned, dissociative adsorption of CCl_4 is facile under the current reaction conditions. The selectivity to CH_3Cl depends on the availability of adsorbed CH_3 species on the surface. When chlorine from adsorbed CCl_4 is readily picked up by the CH_3 species, dominant formation of CH_3Cl results. Otherwise, more chlorinated chloromethanes or dimers are preferentially formed due to the extended residence of adsorbed CCl_4 species on the catalyst surface. This overall picture is consistent with the product distribution in Figure 1 and the amounts of methane adsorption in Figure 2. A study of detailed reaction mechanism and optimization of reaction conditions are underway.

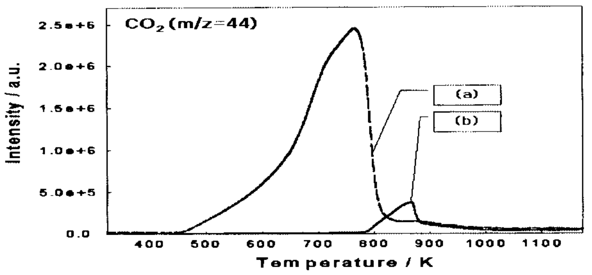

Figure 2. Temperature-programmed oxidation of adsorbed CH_4 at 723 K: (a) 1.0 wt%Pt/$MgAl_2O_4$. (b) 1.0 wt%Pt/SiO_2.
Pt precursor, K_2PtCl_6; Red T = 773 K (3 h); CH_4 adsorbed at 723 K for 1 h with a flow rate of 7.03 μmol/s; flow rate of 1.0%O_2/He = 20.1 μmol/s; ramping rate = 10 K/min.

Table 2. ^{13}C labeled content in products from catalytic reactions of ^{13}C-lableled methane with CCl_4 on 1.0 wt%Pt/$MgAl_2O_4$ at 723 K and $4CH_4/CCl_4$

Reactants	Contents of ^{13}C fraction in each chlorocarbons/%[a]			
$^{13}CH_4$ +	$^{13}CH_3Cl$	$^{13}CH_2Cl_2$	$^{13}CHCl_3$	$^{13}C_2Cl_4$
CCl_4	~ 85	~ 70	~ 40	0

[a] The balance is ^{12}C fraction for the sauce chloromethane.

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