## A Novel Method of CCl<sub>4</sub> Disposal by Disproportionation with CH<sub>4</sub> 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.<sup>1</sup> Catalytic combustion and hydrodechlorination are useful methods for disposal of these harmful chlorinated compounds including CCl<sub>4</sub>.<sup>2-7</sup> Compared to highly exothermic gas-phase hydrodechlorination of CCl<sub>4</sub>, 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 ( $\Delta H$  values of ca. -177 kJ/mol for hydrodechlorination of CCl<sub>4</sub>, and -11.197 kJ/mol for the perfect disproportionation of CCl<sub>4</sub> and CH<sub>4</sub>). Chlorohydrocarbon products such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>Cl, useful for solvents and intermediates can be obtained by this reaction. Chlorination of methane i.e., catalytic reaction of CH<sub>4</sub> with Cl<sub>2</sub>, has been found to show a very high selectivity to CH3Cl over solid super-acid and supported noble metal catalysts.<sup>8–11</sup> Although disproportionation<sup>12</sup> of chlorofluoromethane with CCl<sub>4</sub> and catalytic reaction<sup>13</sup> of methane with CBrF3 were studied, there has been no report, to our best knowledge, on the disproportionation of CCl<sub>4</sub> and CH<sub>4</sub> 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<sub>2</sub>PtCl<sub>6</sub> as a platinum precursor. Various supports were employed including activated carbon (specific surface area, Sg = 1500 m<sup>2</sup>/g), SrCO<sub>3</sub> (4.8 m<sup>2</sup>/g), SiO<sub>2</sub> (300 m<sup>2</sup>/g), MgO (45.3 m<sup>2</sup>/g), ZSM-5 (350 m<sup>2</sup>/g, Si/Al = 150), TiO<sub>2</sub> (11 m<sup>2</sup>/g), MgAl<sub>2</sub>O<sub>4</sub> (prepared from 10 wt% Mg/Al<sub>2</sub>O<sub>3</sub> by calcination at 1127 K, Sg = 65.1 m<sup>2</sup>/g), and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (103 m<sup>2</sup>/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<sub>4</sub>) through a mass flow controller (Brooks), and CH<sub>4</sub>/CCl<sub>4</sub> mole ratio of 20 was adjusted by bubbling helium (3.5 µmol/s) through a CCl<sub>4</sub> 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<sub>4</sub> with CH<sub>4</sub> 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<sub>4</sub> exceeded 10% above 800 K at a total reactant feed rate of 7.38 µmol/s. Typical product distribution (mole%) at CCl<sub>4</sub> conversion of 36.6% at 823 K was as follows; 42.3% for CH<sub>3</sub>Cl, 1.2% for CH<sub>2</sub>Cl<sub>2</sub>, 28.6% CHCl<sub>3</sub>, 4.6% for C<sub>2</sub>Cl<sub>4</sub>, and 23.2% for C<sub>2</sub>H<sub>x</sub>Cl<sub>y</sub>. As the reaction temperature increased above 770 K, the selectivity for C<sub>2</sub>H<sub>x</sub>Cl<sub>y</sub> (C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, C<sub>2</sub>HCl<sub>3</sub>, and unidentified by-products) increased abruptly probably by free radical reactions. Hence, performance of each catalyst for disproportionation of CCl<sub>4</sub> and CH<sub>4</sub> was studied below 773 K where the gas phase homogeneous reaction could be neglected.

Table 1 shows the conversion of CCl<sub>4</sub> 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 CH4. Although support itself showed some catalytic activity for disproportionation of CCl<sub>4</sub> and CH<sub>4</sub>, selectivity to CH<sub>3</sub>Cl 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<sub>4</sub> conversion indicated by parenthesis in Table 1. Products distribution and catalyst stability were affected strongly by the nature of support. Carbon- and TiO<sub>2</sub>-supported platinum showed high initial CCl<sub>4</sub> conversions, but the conversions decreased rapidly and continuously with time on stream. Pt/ SrCO<sub>3</sub> 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<sub>2</sub>, and Pt/MgAl<sub>2</sub>O<sub>4</sub> showed initial increase in CCl<sub>4</sub> conversions followed by levelingoff 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 :  $K_2PtCl_6$ 

Catalusta	Conversion of CCl <sub>4</sub> /%									
Catalysis	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	-
<sup>a</sup> 1.0 wt%Pt/SrCO <sub>3</sub>	99.7	99.9	98.3	55.9	52.8	50.8	51.0	50.5	50.9	(51.2)
1.0 wt%Pt/SiO2	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	<b>`57.9</b> ´	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/TiO2	95.6	87.0	79.5	64.8	(56.8)	48.8	45.1	-	-	38.0
1.0 wt%Pt/MgAl <sub>2</sub> O <sub>4</sub>	22.8	34.5	47.1	56.8	(56.6)	54.5	55.5	-	-	-
0.5 wt%Pt/Al <sub>2</sub> O <sub>3</sub>	61.9	67.3	70.1	74.3	(75.0)	77.4	-	-	-	-

<sup>a</sup>WHSV = 600 L/kgcat./hr and CH<sub>4</sub>/CCl<sub>4</sub> mole ratio of 10, H<sub>2</sub>PtCl<sub>6</sub> Products distribution in Figure 1, was obtained at the parenthesized conversion.



Figure 1. Products distribution over 1.0 wt% Pt catalysts supported on various supports: WHSV = 1200 L/kgcat./h based on CH<sub>4</sub>; 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.<sup>10</sup> After reaction, Pt/SrCO<sub>3</sub> and Pt/MgO also showed the change in the phase of supports from oxides to chlorides such as SrCl<sub>2</sub> and MgCl<sub>2</sub>·6H<sub>2</sub>O 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<sub>2</sub> and 1146 K for SrCl<sub>2</sub>. In any case, platinum supported on SiO<sub>2</sub>, MgO, SrCO<sub>3</sub> and MgAl<sub>2</sub>O<sub>4</sub> showed stable CCl<sub>4</sub> conversions and could become candidate catalysts for a novel disposal process of ozone-depleting CCl<sub>4</sub> by disproportionation with CH<sub>4</sub>. Supported platinum catalysts could be classified into two groups according to their products distribution shown in Figure 1. Pt/carbon, Pt/SrCO<sub>3</sub>, and Pt/SiO<sub>2</sub> showed the selectivity of CH<sub>3</sub>Cl close to 50% and comparable amounts of CHCl<sub>3</sub>. Substantial amounts of C<sub>2</sub> products were also formed over Pt/SrCO<sub>3</sub>, and Pt/SiO<sub>2</sub>. Other catalysts produced predominantly CH<sub>3</sub>Cl. In particular,  $Pt/MgAl_2O_4$ , and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts exhibited CH<sub>3</sub>Cl selectivity values higher than 90%. An ideal disproportionation of CCl<sub>4</sub> with CH<sub>4</sub> should have the following stoichiometry:

$$CH_4 + CCl_4 \rightarrow CH_3Cl + CHCl_3$$
(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;

$$3CH_4 + CCl_4 \rightarrow 4CH_3Cl \tag{2}$$

Figure 2 compares temperature-programmed oxidation (TPO) of adsorbed CH<sub>4</sub> on fresh Pt/SiO<sub>2</sub> and Pt/MgAl<sub>2</sub>O<sub>4</sub> 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<sub>4</sub> 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<sub>2</sub>O<sub>4</sub> showing a high selectivity to CH<sub>3</sub>Cl, a larger amount of a more reactive carbonaceous species is present compared to Pt/SiO2. CO2 evolution temperature was as low as around 750 K. It appears that facile dissociative adsorption of CH<sub>4</sub> promotes the selective formation of CH<sub>3</sub>Cl. CCl<sub>4</sub> could adsorb dissociatively on any supported platinum at a temperature as low as 323 K.<sup>14</sup> 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<sub>2</sub>O<sub>4</sub> with 4CH<sub>4</sub>/CCl<sub>4</sub>. As shown in Table 2, most (ca. 85%) of CH<sub>3</sub>Cl originates from methane. This higher value than expected from equation 2 (75%) suggested that the reaction



**Figure 2.** Temperature-programmed oxidation of adsorbed CH<sub>4</sub> at 723 K: (a) 1.0 wt%Pt/MgAl<sub>2</sub>O<sub>4</sub>. (b) 1.0 wt%Pt/SiO<sub>2</sub>. Pt precursor, K<sub>2</sub>PtCl<sub>6</sub>; Red T = 773 K (3 h); CH<sub>4</sub> adsorbed at 723 K for 1 h with a flow rate of 7.03  $\mu$ mol/s; flow rate of 1.0%O<sub>2</sub>/He = 20.1  $\mu$ mol/s; ramping rate = 10 K/min.

 Table 2.
 <sup>13</sup>C labeled content in products from catalytic reactions of <sup>13</sup>C-lableled methane with CCl<sub>4</sub> on 1.0 wt%Pt/MgAl<sub>2</sub>O<sub>4</sub> at 723 K and 4CH<sub>4</sub>/CCl<sub>4</sub>

 Reactants
 Contents of <sup>13</sup>C fraction in each chlorocarbone/<sup>0</sup>/<sup>4</sup>

Reactants	Contents of	C fraction in each chiorocarbons/%					
<sup>13</sup> CH <sub>4</sub> +	<sup>13</sup> CH <sub>3</sub> Cl	$^{13}CH_2Cl_2$	<sup>13</sup> CHCl <sub>3</sub>	$^{13}C_{2}Cl_{4}$			
CCl <sub>4</sub>	~ 85	~ 70	~ 40	0			

<sup>a</sup>The balance is <sup>12</sup>C fraction for the sauce chloromethane.

pathway should be more complicated than indicated by equations 1 and 2. As chlorine content increases in chloromethanes, the contribution of CCl<sub>4</sub> increases (30% for CH<sub>2</sub>Cl<sub>2</sub> and 60% for CHCl<sub>3</sub>). C<sub>2</sub>Cl<sub>4</sub> comes exclusively from CCl<sub>4</sub>. Thus the reaction on the catalyst surface is very complicated comprising reactions 1 and 2 and others. As mentioned, dissociative adsorption of CCl<sub>4</sub> is facile under the current reaction conditions. The selectivity to CH<sub>3</sub>Cl depends on the availability of adsorbed CH<sub>2</sub> species on the surface. When chlorine from adsorbed CCl<sub>4</sub> is readily picked up by the CH<sub>3</sub> species, dominant formation of CH<sub>3</sub>Cl results. Otherwise, more chlorinated chloromethanes or dimers are preferentially formed due to the extended residence of adsorbed CCl<sub>4</sub> 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.

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