

# Supported platinum–gallium catalysts for selective hydrodechlorination of CCl<sub>4</sub>

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Received 10 June 2005; received in revised form 3 August 2005; accepted 3 August 2005

Available online 6 September 2005

## Abstract

The selective hydrodechlorination of tetrachloromethane (CCl<sub>4</sub>) was performed over supported platinum–gallium catalysts with a support of MgF<sub>2</sub> to improve CHCl<sub>3</sub> selectivity and catalytic stability. In order to better understand the behavior of the Ga and MgF<sub>2</sub> support, hydrogen chemisorption, temperature programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS) measurements were conducted to characterize the catalysts. It was found that the electron-deficient Pt species are formed on the catalyst surface during the hydrodechlorination reaction due to the adsorption of active chlorine. The addition of Ga into the catalysts results in forming Pt–Ga assemblies such as PtGa alloys on the catalyst surface, and generates a Pt–Ga interaction as confirmed by TPR and XPS. The Ga addition will significantly increase the dispersion of Pt and create more Pt sites exposed to the reaction atmosphere on the catalyst surface in effect. The influence of Ga on the CHCl<sub>3</sub> selectivity and the conversion of CCl<sub>4</sub> can be ascribed to the modification of Ga to the electronic properties of the Pt active sites by changing the electronic environment surrounding the Pt atoms via the Pt–Ga interaction. The modified Pt species are believed to be beneficial to form a fast desorption step for the adsorbed \*CCl<sub>3</sub> species (a commonly accepted precursor to generate CHCl<sub>3</sub>) under the assistance of hydrogen. The adsorption of reactant CCl<sub>4</sub> will be weakened on the catalyst surface and cause a lower conversion of CCl<sub>4</sub>.

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**Keywords:** Supported platinum catalyst; Gallium; Modification; Hydrodechlorination; Tetrachloromethane; Chloroform

## 1. Introduction

Tetrachloromethane (CCl<sub>4</sub>) possesses negative effects on the environment, particularly, has the potential to deplete the ozone layer by delivering chlorine to the stratosphere [1]. According to the Montreal Protocol and its amendments, the use and sale of CCl<sub>4</sub> have been restricted in developed countries since 1996, and the total phase out of CCl<sub>4</sub> should be fulfilled in developing countries by the year of 2010. Since CCl<sub>4</sub> is a byproduct in several chlorine industrial processes, such as the manufacture of tetrachloroethylene, a surplus of it is continuously created. Hence, effective methods are quite necessary to eliminate CCl<sub>4</sub>. However, the combustion technique adopted presently is highly energy consuming and brings secondary contamination, e.g. dioxins, COCl<sub>2</sub> [2,3]. A more attractive and promising method

is proposed to convert CCl<sub>4</sub> to CHCl<sub>3</sub>, which is an important intermediate product in organic synthesis, through a catalytic hydrodechlorination [4–6].

Supported noble metal catalysts have been used for the hydrodechlorination of CCl<sub>4</sub> either in liquid phase [7–11] or gas phase [12–22]. In the pioneer work of the hydrodechlorination of CCl<sub>4</sub> over Pt/η-Al<sub>2</sub>O<sub>3</sub> [12], some details on the reaction pathway are given, suggesting that the reaction proceeds by two parallel routes: one route is a single step addition of hydrogen to an adsorbed \*CCl<sub>3</sub> species to form CHCl<sub>3</sub> selectively and the second is a concerted addition of hydrogen atoms to adsorbed \*CCl<sub>3</sub> with no desorption of intermediates to generate CH<sub>4</sub> eventually. However, this work has been marked with low selectivity to CHCl<sub>3</sub> and poor catalytic stability. More investigations have been performed in terms of this reaction since the middle of the 1990s. Choi et al. [14,15] reported their results on the hydrodechlorination of CCl<sub>4</sub>, where 76.1% selectivity for CHCl<sub>3</sub> at a 45.2% conversion was obtained after 8 h on stream of reaction on a Pt/MgO catalyst. The basicity of the MgO support

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improves catalytic stability by retarding the formation of the coke and the oligomers. However, a phase change of MgO to MgCl<sub>2</sub> is observed, causing a considerable decrease in the surface area of the catalyst and the catalytic activities in terms of the hydrodechlorination of CCl<sub>4</sub>. Then, Choi et al. synthesized Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by using different Pt precursors and characterized them using XANES method [16]. It is found that the product distribution is mainly affected by the oxidation state of the Pt on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, and an optimum oxidation state of the Pt has been identified to be of the best selectivity to CHCl<sub>3</sub>. However, carbon and chlorine are easy to deposit on the surface of the used catalysts, leading to the deactivation of catalysts. Thus, Zhang et al. [17] reported a method to improve the stability of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst by treating the catalyst with a solution of NH<sub>4</sub>Cl. In addition, Santo et al. [18] has reported organometallics-based platinum and palladium catalysts with MgO support for the hydrodechlorination of CCl<sub>4</sub>. The phase change of MgO to MgCl<sub>2</sub> during the hydrodechlorination reaction is also observed. More recently, Legawiec-Jarzyna et al. [21,22] carried out a comparative study on the selective removal of chlorine from dichlorodifluoromethane, carbon tetrachloride and 1,2-dichloroethane.

It is generally understood that the supported platinum shows the more attractive catalytic behavior such as high selectivity to CHCl<sub>3</sub> than the supported palladium in the gas phase selective hydrodechlorination of CCl<sub>4</sub>. The higher selectivity to CHCl<sub>3</sub> on the supported platinum catalysts is ascribed to the less strong binding of the Pt to the chlorine and the chlorine-containing organic intermediate species produced in the hydrodechlorination of CCl<sub>4</sub> [22]. Palladium will rapidly deactivate in the reaction, exhibiting a rather poor selectivity to CHCl<sub>3</sub>, and giving a variety of products including longer hydrocarbons [21–25]. Nevertheless, Pd-containing catalyst seems to be readily available under liquid phase conditions [7–11,26,27]. The catalytic stability and the CHCl<sub>3</sub> selectivity in terms of the hydrodechlorination of CCl<sub>4</sub> are of wide concern still.

Many researchers studied the effect of metal dispersions, particle sizes [20], reaction conditions [19] and catalyst modifications on the catalytic performance for the selective hydrodechlorination reaction. Particularly, Rh/Sn [28], Re [29], Bi/Tl [30], Fe/Co/Ag [31,32] and Fe [33], etc., have been extensively investigated to modify the supported palladium catalysts. On the other hand, Sn and Sn/Pb/Ge/Al/Zn have been used to modify the platinum catalysts for the hydrodechlorination of 1,2,3-trichloropropane [34], and the hydrodechlorination of *p*-chloronitrobenzene [35], respectively.

In this report, we will investigate the modification of platinum catalysts with non-noble metals, particularly Pt–Ga bimetallic catalysts, for the selective hydrodechlorination of CCl<sub>4</sub>. By adopting Ga component as a modifier, the catalytic stability and selectivity to CHCl<sub>3</sub> can be enhanced significantly. On the other hand, the catalytic performance is deeply related to the properties of the support. As the traditional oxide supports, e.g. MgO and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are susceptible to HCl, created inevitably in the hydrodechlorination of CCl<sub>4</sub>, it is instructive to choose a more stable support for the preparation of catalysts to obtain a higher structural and catalytic stability under the severe reaction condi-

tions in terms of the hydrodechlorination of CCl<sub>4</sub>. Considering MgF<sub>2</sub> is quite stable in the hydrodechlorination of CCl<sub>2</sub>F<sub>2</sub> [36], we attempt to use MgF<sub>2</sub> as the support of supported Pt catalysts.

## 2. Experimental

### 2.1. Catalyst preparation and activation

The supported platinum catalyst precursors were prepared by a standard impregnation method by using H<sub>2</sub>PtCl<sub>6</sub> and/or GaCl<sub>3</sub> (Aldrich) with appropriate amounts. Several commercial support materials including MgF<sub>2</sub> (BET surface area 70 cm<sup>2</sup> g<sup>-1</sup>, pore volume 0.2 cm<sup>3</sup> g<sup>-1</sup>), ZSM-5 (Si/Al = 35, surface area 290 cm<sup>2</sup> g<sup>-1</sup> and pore volume 0.50 cm<sup>3</sup> g<sup>-1</sup>), Sm<sub>2</sub>O<sub>3</sub> (Surface area 30 cm<sup>2</sup> g<sup>-1</sup> and pore volume 0.23 cm<sup>3</sup> g<sup>-1</sup>),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (BET surface area 220 cm<sup>2</sup> g<sup>-1</sup> and pore volume 0.45 cm<sup>3</sup> g<sup>-1</sup>) were used as the support of catalysts. The supports were dried in air at ca. 423 K for 24 h and then were subjected to the impregnation. In detail, a support was impregnated into an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub>, and the obtained mixture was stirred constantly for 3.0 h before the water was removed in a rotary evaporator in vacuo to obtain a solid. The solid was dried overnight in an air oven at 403 K, and was subsequently heated from 403 to 743 K at 10 K min<sup>-1</sup> in air, which was maintained at 743 K for 4 h to result in a catalyst precursor. The Pt loading of the catalyst precursor was determined by ICP-AES using aqua regia to dissolve the samples. The supported Pt–Ga catalyst precursor was prepared by changing the H<sub>2</sub>PtCl<sub>6</sub> solution into a H<sub>2</sub>PtCl<sub>6</sub> and GaCl<sub>3</sub> solution mixture, according to a similar procedure.

The catalyst precursor was sieved in the 500- to 100- $\mu$ m mesh range and was reduced directly in a 30 cm<sup>3</sup> min<sup>-1</sup> stream of dry Ar containing 4.94% H<sub>2</sub> at 10 K min<sup>-1</sup> to 673 K, which was maintained at 673 K for 3 h. After reduction as above, the temperature was declined to a desired value for a subsequent hydrodechlorination procedure. If necessary the catalyst was flushed for 0.5 h in a 25 ml min<sup>-1</sup> stream of N<sub>2</sub> before the catalyst was put in contact with a reaction atmosphere.

### 2.2. Characterization

X-ray photoelectron spectroscopy (XPS) method was employed to determine the nature of platinum and gallium species on the surface of catalysts. The spectra were recorded on a VG ESCALAB MK spectrometer using a monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV). The spent sample was protected from exposition to the atmosphere during the transferring from a reactor to the preparation chamber of the spectrometer by purified hexane. Prior to data acquisition, the sample was outgassed for several hours to minimize the surface contamination. The pressure of the measurement chamber was maintained below  $1.33 \times 10^{-6}$  Pa. Spectra were recorded at room temperature. C 1s peak at 284.6 eV was used as an internal standard for the energy correction. The data analysis involving a background subtraction used either a Shirley or linear-type integral profile and a curve fitting procedure by using a non-linear least-squares method. The FWHMs of two components of each doublet of Pt were assumed to be equal. The ratio of the peak areas was

maintained at 4:3 (4f<sub>7/2</sub>:4f<sub>5/2</sub>) with a 3.36 eV peak separation. The surface atomic ratios were estimated from the peak areas of the XPS spectra by using sensitivity factors. The reproducibility of the results was tested as good by parallel measurements.

Metal dispersions were determined by hydrogen chemisorption at the room temperature using the double isotherm method on an OMNisorp 100CX instrument according to the method described in Ref. [37].

Temperature programmed reduction (TPR) was recorded with a GR–GC system (a gas reactor and gas chromatography assembled system): the samples (ca. 0.2 g) were heated in a U-shaped quartz cell (10 cm × 4.2 mm i.d.) in a 25 ml min<sup>-1</sup> stream of Ar containing 4.94% H<sub>2</sub> by volume to 1073 K at 10 K min<sup>-1</sup> and the effluent gas was passed through a cool trap; H<sub>2</sub> consumption was monitored by a thermal conductivity detector (TCD) with data acquisition/manipulation using the N2000 software. The H<sub>2</sub> uptake values were reproducible to within ±5%; the values quoted in this paper are the mean.

### 2.3. Test of catalytic performance

The hydrodechlorination of CCl<sub>4</sub> (from Aldrich with purity of 99.6%) was carried out in a gas phase fixed-bed micro-reactor system (i.d. 10 mm) at a required temperature under atmospheric pressure. The catalytic reactor has been previously described in detail elsewhere [37,38] but some features for a typical reaction, pertinent to this study, are given below. The CCl<sub>4</sub> was fed by means of bubbling a flow of ultra-pure H<sub>2</sub> through a saturator maintained at 273 K: the flow rate was monitored using a digital flow meter and the partial pressure of CCl<sub>4</sub> was calculated according to the Antoine Equation [39]:

$$\log P_{\text{mmHg}} = a - \frac{b}{T + c}$$

where  $P$  is the partial pressure of CCl<sub>4</sub>,  $T$  the temperature with unit °C, Antoine constants  $a$ ,  $b$  and  $c$  are adopted as 6.89410, 1219.580 and 227.170, respectively. The catalytic activity and selectivity were assessed at a fixed inlet molar H<sub>2</sub>/CCl<sub>4</sub> ratio of 9:1 (argon was used as a balance gas to adjust the H<sub>2</sub>/CCl<sub>4</sub> ratio), where the gas hourly space velocity (21 000 ml (STP) gcat<sup>-1</sup> h<sup>-1</sup>) was kept constant. Pd-A molecular sieve was used to purify the H<sub>2</sub> and Ar. The products and remained CCl<sub>4</sub> were determined by using a gas chromatography equipped with a HP-5 capillary column (30 m × 0.32 mm) and a FID. The identification of the products was conducted on a HP 5890-5973 GC–MS system with a separation column of the same type. Repeated catalytic runs with different samples from the same batch of catalyst have reproducibility within ±5%.

## 3. Results and discussion

### 3.1. Catalytic performance

The effect of supports on the catalytic performance of several supported platinum catalysts in the hydrodechlorination of CCl<sub>4</sub> are recorded in Table 1. The main products are found to be CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>4</sub> but minor products of C<sub>2</sub>Cl<sub>4</sub> and

Table 1

Effect of supports on the hydrodechlorination of CCl<sub>4</sub> over supported platinum catalysts<sup>a</sup>

Catalyst	Pt loading	Conversion (%)		Selectivity <sup>b</sup> (%)		
		3 h	9 h	CH <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>
Pt/ZSM-5	1.0	50.4	46.9	33.5	5.9	60.6
Pt/Sm <sub>2</sub> O <sub>3</sub>	1.0	42.0	23.2	32.5	9.8	57.7
Pt/MgF <sub>2</sub>	1.0	82.3	82.8	33.4	3.9	62.7
Pt/γ-Al <sub>2</sub> O <sub>3</sub>	1.0	98.5	82.6	41.6	9.4	49.0

<sup>a</sup> Reaction temperature: 400 K; H<sub>2</sub>/CCl<sub>4</sub>(v/v)=9:1; space velocity: 21 000 ml(STP) gcat<sup>-1</sup> h<sup>-1</sup>.

<sup>b</sup> The selectivities are deduced after the 9 h on stream of reaction; minor products of C<sub>2</sub>Cl<sub>4</sub> and C<sub>2</sub>Cl<sub>6</sub> (with selectivities below 0.5%, generally) are excluded here for the convenience of calculation.

C<sub>2</sub>Cl<sub>6</sub> can also be detected sometimes with selectivities below 0.5%. For those catalysts with different supports, Pt/γ-Al<sub>2</sub>O<sub>3</sub> shows a deactivation behavior at the first stage of the reaction. The conversion of CCl<sub>4</sub> decreases from ca. 98.5% to 82.6% over a period of 9 h, where Pt/γ-Al<sub>2</sub>O<sub>3</sub> shows an increase in CHCl<sub>3</sub> selectivity at the first stage of the reaction (over 3 h on stream) and a decrease tendency to converge at ca. 49% subsequently (see Fig. 1 also). Although the CHCl<sub>3</sub> selectivity on Pt/ZSM-5 and Pt/Sm<sub>2</sub>O<sub>3</sub> are relatively higher than that on Pt/γ-Al<sub>2</sub>O<sub>3</sub> (~58% versus 49%), the conversions of CCl<sub>4</sub> over these catalysts are less than 50% after the 9 h on stream of reaction (end

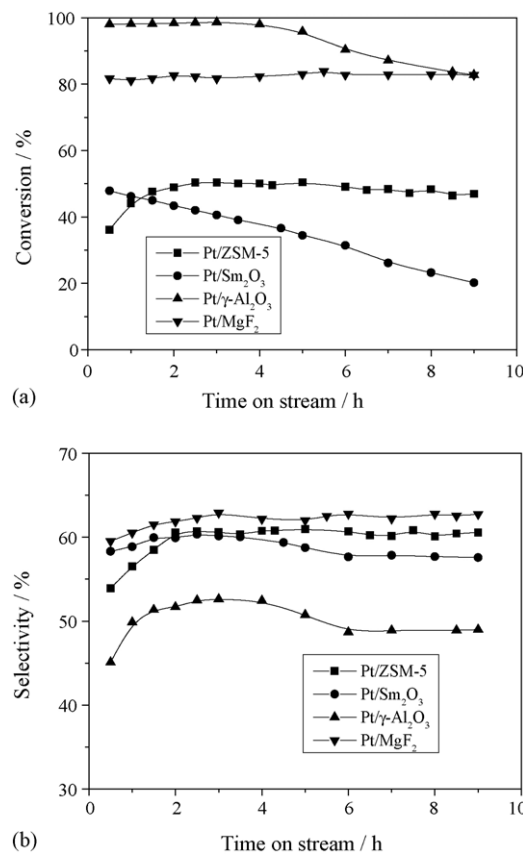


Fig. 1. Time on stream behaviors of the hydrodechlorination of CCl<sub>4</sub> over supported platinum catalysts with different supports: (a) conversion; (b) selectivity (for reaction conditions, see Table 1).

Table 2

Comparison of the catalytic performance of Pt/MgF<sub>2</sub> and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with different Pt loading in the hydrodechlorination of CCl<sub>4</sub><sup>a</sup>

Catalyst	Pt loading	Conversion (%)		Selectivity <sup>b</sup> (%)		
		3 h	9 h	CH <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>
Pt/MgF <sub>2</sub>	0.5	26.1	26.5	31.2	6.0	62.8
Pt/MgF <sub>2</sub>	1.0	82.3	82.8	33.4	3.9	62.7
Pt/MgF <sub>2</sub>	1.5	96.2	96.3	35.8	2.4	61.8
Pt/MgF <sub>2</sub>	2.0	98.5	98.6	36.7	2.1	61.2
Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	0.5	81.0	65.5	36.6	9.2	54.2
Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	1.0	98.5	82.6	41.6	9.4	49.0
Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	1.5	100	99.5	48.8	3.4	47.8
Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	2.0	100	100	51.0	3.8	45.2

<sup>a</sup> For reaction conditions, see Table 1.

<sup>b</sup> For the calculation method, see Table 1.

points in Fig. 1) and deactivation behaviors are also observed. On the other hand, Pt/MgF<sub>2</sub> can catalyze a stable hydro-conversion of CCl<sub>4</sub>. The Pt/MgF<sub>2</sub> catalyst of 1.0% Pt exhibits a ~82% conversion of CCl<sub>4</sub>, a comparative value with that on Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after the 9 h on stream of reaction, and a 62.7% selectivity to CHCl<sub>3</sub> under the same reaction conditions (Table 1 and Fig. 1).

The effect of Pt loading on the catalytic performance of Pt/MgF<sub>2</sub> and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts are listed in Table 2. For Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, the CHCl<sub>3</sub> selectivity decreases from 54.2% to 45.2% (after the 9 h on stream of reaction), where an increase of conversion from 65.5% to ~100% has been shown also, as the Pt loading increases from 0.5% to 2.0%, but a common character has been exhibited that the deactivation behavior of the hydrodechlorination of CCl<sub>4</sub> on Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts irrespective of Pt loading is visible as reported by Choi et al. [16,19], where the deactivation has been assigned to the carbon and chlorine deposits leading to a relatively hydrogen-deficient environment on the surface of catalysts. The conversion on the Pt/MgF<sub>2</sub> catalyst increases to more than 98%, which has been accompanied with a slightly decrease of CHCl<sub>3</sub> selectivity (from 62.8% to 61.2% as the Pt loading increases from 0.5% up to 2.0%). The selectivity to CH<sub>4</sub> has been increased with five percentages; manifesting the secondary reaction of reaction products, e.g. CHCl<sub>3</sub> is enhanced to cause a deep dechlorination. In fact, Malinowski et al. [36] firstly reported MgF<sub>2</sub> as an excellent catalyst support in the hydrodechlorination of CCl<sub>2</sub>F<sub>2</sub>. The interesting catalytic behavior in the hydrodechlorination of CCl<sub>4</sub> due to MgF<sub>2</sub> arouses us to investigate this catalyst system further by adjusting the modifier of the catalysts.

Vadlamannati et al. [40], in studying the hydrodechlorination of 1,2-dichloroethane over Pt–Cu/C catalyst, observed that Cu/Pt essentially affect the selectivity: a higher Cu/Pt ratio results in a higher selectivity towards ethylene by reducing the formation of ethane and monochloroethane. Bi has been reported to be modifier to the supported Pd catalyst for the hydrodechlorination of several CFCs by Ohnishi et al. [30,41], where the selectivity and catalytic activity were ameliorated to some extent. Gallia has been also reported as a support modifier of supported Pt catalyst in benzene hydrogenation reaction; the high selectivity of cyclohexane (~100%) has been linked to the addition of gallia to the alumina [42]. Diaz et al. [43], on the other

Table 3

Effect of additives on the hydrodechlorination of CCl<sub>4</sub> over supported platinum catalyst Pt/MgF<sub>2</sub><sup>a</sup>

Catalysts <sup>b</sup>	Conversion (%)	Selectivity <sup>c</sup> (%)		
		CH <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>
Pt/MgF <sub>2</sub>	57.3	33.0	4.0	63.0
PtCu <sub>0.30</sub> /MgF <sub>2</sub>	25.4	23.9	8.3	67.8
PtBi <sub>0.23</sub> /MgF <sub>2</sub>	1.1	23.2	20.6	56.3
PtGa <sub>0.28</sub> /MgF <sub>2</sub>	49.0	26.8	4.1	69.1

<sup>a</sup> Reaction temperature: 380 K; H<sub>2</sub>/CCl<sub>4</sub>(v/v)=9:1; space velocity = 21000 ml(STP) g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>; the conversions and selectivities are calculated after the 5 h on stream of reaction.

<sup>b</sup> Pt loading: 1.0% by weight; the subscript represents atomic ratio of the corresponding element to Pt.

<sup>c</sup> Minor products of C<sub>2</sub>Cl<sub>4</sub> and C<sub>2</sub>Cl<sub>6</sub> (with selectivities below 0.5%, generally) are excluded here for the convenience of calculation.

hand, gave the evidence of a Pt–Ga interaction in Pt/H[Ga]ZSM-5 catalyst. In this paper, we expect to find an effective promoter of supported Pt catalysts by investigating the behavior of the above-mentioned metals in the hydrodechlorination CCl<sub>4</sub>.

The effect of modifiers on the catalytic performance has been shown in Table 3. The addition of Cu into the Pt/MgF<sub>2</sub> catalyst significantly decreases the conversion of CCl<sub>4</sub> but the selectivity of CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> has been improved to some extent. Bi exhibits a negative effect on the performance of the supported Pt catalyst: resulting in a sharp decrease in the conversion of CCl<sub>4</sub> (from 57.3% for Pt/MgF<sub>2</sub> to 1.1% for PtBi<sub>0.23</sub>/MgF<sub>2</sub>) and the selectivity of CHCl<sub>3</sub> (from 63.0% for Pt/MgF<sub>2</sub> to 56.3% for PtBi<sub>0.23</sub>/MgF<sub>2</sub>) after the 5 h on stream of reaction. Fig. 2 has compared the dependence of the catalytic performance of catalysts modified by different modifiers on time-on-stream. The results show that the Pt–Cu/MgF<sub>2</sub> has suffered a significant deactivation with time-on-stream accompanied with an increase of CHCl<sub>3</sub> selectivity at the first 4 h of reaction. In contrast, the catalytic activity and selectivity on Pt–Ga/MgF<sub>2</sub> are quite stable in the hydrodechlorination of CCl<sub>4</sub> over a period of 8 h on stream.

As shown in Table 4, the effect of Ga modifier on the performance of supported Pt catalysts is found to be two-sided: the selectivity of CHCl<sub>3</sub> is markedly improved due to the addition of Ga but a negative effect of the Ga addition on the conversion of CCl<sub>4</sub> is also observed, where the conversion of CCl<sub>4</sub> decreases from 76.2% to 40.4% as the Ga/Pt ratio mounts up to 1.86 under identical experimental conditions (see Fig. 3 also); additionally, the selectivity of CH<sub>2</sub>Cl<sub>2</sub> is almost kept constant (see Table 4). It is worthy to note that the Ga/MgF<sub>2</sub> catalyst without addition of Pt does not show any catalytic activities in the hydrodechlorination of CCl<sub>4</sub> under the present reaction conditions. The hydrodechlorination of CCl<sub>4</sub> over PtGa<sub>1.86</sub>/MgF<sub>2</sub> catalyst modified with gallium, as shown in Fig. 4, exhibits a stable catalytic activity with time on stream and the associated CHCl<sub>3</sub> selectivity generally attains higher than 80% over the whole period we investigated, indicative of a stable catalytic behavior of the Ga promoted catalysts. We also find that if treat the used PtGa<sub>1.86</sub>/MgF<sub>2</sub> catalyst (after more than 7 h reaction in this case) in a flow of N<sub>2</sub> for 0.5 h, the CHCl<sub>3</sub> selectivity increases further with a slightly decrease of conversion, where



Table 4

Catalytic performance, Pt dispersion and hydrogen consumption at the low temperature region of the time programmed reduction (TPR) spectra of supported Pt–Ga/MgF<sub>2</sub> catalysts<sup>a</sup>

Catalysts	Conversion (%)	Selectivity <sup>b</sup> (%)			Dispersion (%)	H <sub>2</sub> consumption <sup>c</sup> (×10 <sup>5</sup> mol/gcat)	
		CH <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>		H <sub>a</sub>	H <sub>b</sub>
Pt/MgF <sub>2</sub>	76.2	36.1	2.5	61.4	28	15.4	0
PtGa <sub>0.37</sub> /MgF <sub>2</sub>	75.8	35.3	2.5	62.2	33	18.5	3.1
PtGa <sub>0.74</sub> /MgF <sub>2</sub>	60.5	27.0	2.6	70.4	36	20.6	5.2
PtGa <sub>1.11</sub> /MgF <sub>2</sub>	46.3	20.4	2.5	77.1	41	22.6	7.2
PtGa <sub>1.86</sub> /MgF <sub>2</sub>	40.4	16.0	2.6	81.4	48	25.8	10.4
Ga/MgF <sub>2</sub>	0.0	N/D <sup>f</sup>	N/D	N/D	N/D	0.0	0.0

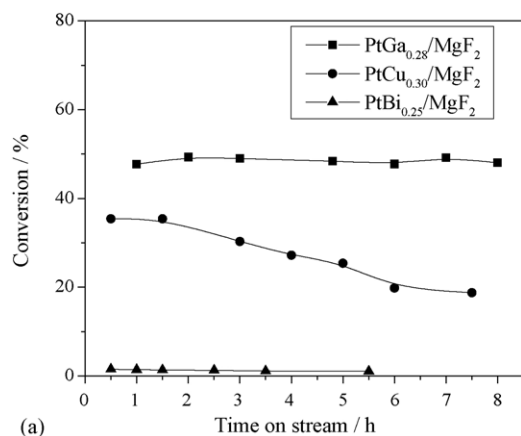
<sup>a</sup> Pt loading: 1.5% by weight; the subscript represents atomic ratio of Ga to Pt; for other conditions, see Table 3.

<sup>b</sup> For the calculation method, see Table 3.

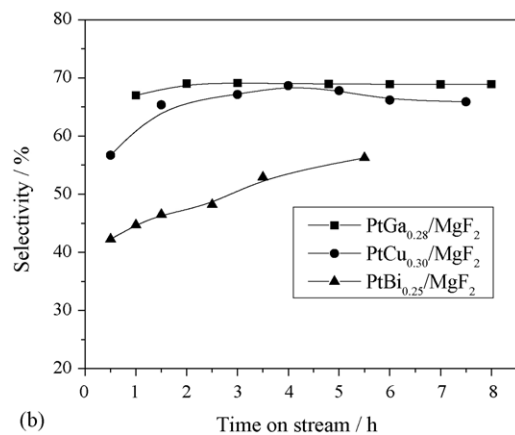
<sup>c</sup> Assuming the hydrogen consumed by Pt remains constant, independent of the Ga addition. H<sub>a</sub> denotes as the total H<sub>2</sub> consumption and H<sub>b</sub> denotes as the H<sub>2</sub> consumed by Ga reduction.

<sup>f</sup> N/D: not detectable.

the steady state conversion of CCl<sub>4</sub> and CHCl<sub>3</sub> selectivity converge at ca. 34% and 87%, respectively (Fig. 4). However, if one uses N<sub>2</sub> to sweep the PtGa<sub>1.86</sub>/MgF<sub>2</sub> after fresh reduction under identical operation conditions, there are no significant effects on the stability and selectivity to be found (not shown here). We did not find analogous behaviors derived N<sub>2</sub> treatment on the MgF<sub>2</sub> supported platinum catalyst without the modification of gallium.



(a)



(b)

Fig. 2. Effect of additives on the catalytic stability of the hydrodechlorination of CCl<sub>4</sub> over supported platinum catalysts: (a) conversion; (b) selectivity (for reaction conditions, see Table 3).

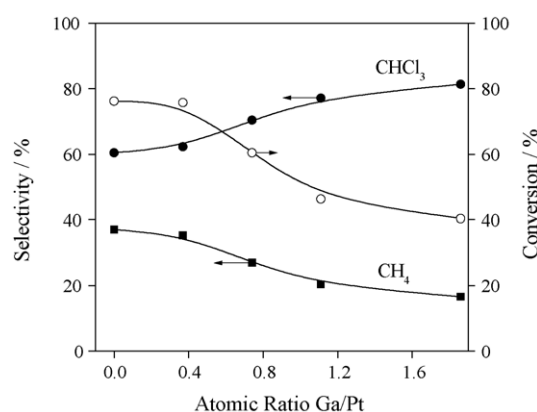


Fig. 3. Effect of the Ga loading on the selectivity of CHCl<sub>3</sub> and CH<sub>4</sub> over supported platinum catalysts (for reaction conditions, see Table 4).

This effect is not well understood yet, and need further investigation. According to the results from Fig. 5, it is also found that the loss of conversion upon the loading of gallium, as shown in Fig. 3, is accompanied with an almost linear increase of apparent activation energies in the hydrodechlorination of CCl<sub>4</sub>.

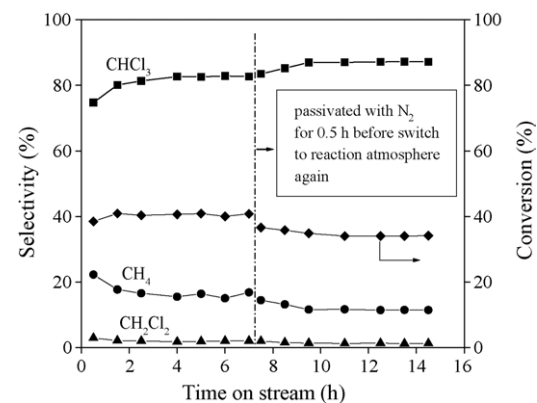


Fig. 4. Time on stream behaviors of the catalytic hydrodechlorination of CCl<sub>4</sub> over the supported platinum catalysts modified with gallium (for reaction conditions, see Table 4).

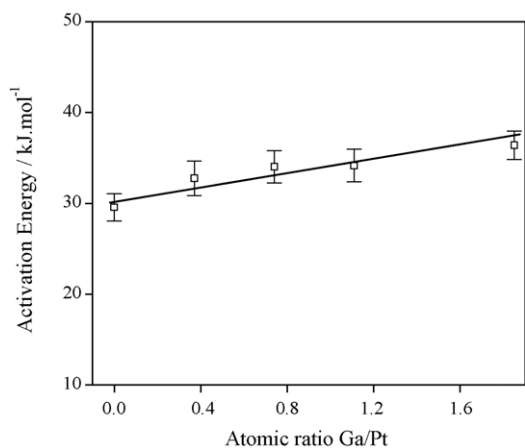


Fig. 5. Effect of the Ga loading on the apparent activation energy of the hydrodechlorination reaction of  $\text{CCl}_4$  over supported platinum catalysts (for reaction conditions, see Table 4).

### 3.2. Characterization of catalysts

#### 3.2.1. The dispersion of platinum

The dispersion of Pt determined by hydrogen chemisorption as listed in Table 4 is meaningful in terms of gaining an insight into the effect of Ga addition on the particle size and subsequently electronic properties of Pt. The results indicate that the catalysts with the addition of Ga have higher dispersion of Pt than  $\text{Pt/MgF}_2$ . A positive dependence of the dispersion of Pt on the contents of Ga element is observed: the dispersion of Pt increases from 28% for  $\text{Pt/MgF}_2$  to 48% for  $\text{PtGa}_{1.86}/\text{MgF}_2$ .

#### 3.2.2. The temperature programmed reduction (TPR)

The temperature-programmed reduction (TPR) can shed some light on changes in the electronic properties of supported metal particles [44]; the TPR profiles generated for the  $\text{MgF}_2$  supported Pt catalyst precursors are shown in Fig. 6. The TPR conditions match those used for actual catalyst activation prior to the hydrodechlorination of  $\text{CCl}_4$ . The reduction of the  $\text{Pt/MgF}_2$  generates two maximum  $\text{H}_2$  consumption peaks with characteristic temperature ( $T_{\text{max}}$ ) at ca. 550 and  $>1000$  K, respectively: the lower temperature peak is assigned to the reduction of Pt oxide species and the higher temperature peak is ascribed to the reduction of support  $\text{MgF}_2$  (the pure  $\text{MgF}_2$  exhibits a mono-reduction peak at  $\sim 1073$  K (Fig. 6(a)).  $\text{Ga/MgF}_2$  shows a similar TPR behavior to the pure  $\text{MgF}_2$  (Fig. 6(g)), indicating that the reduction of the oxide species of Ga occurs at the high temperature region ( $\sim 1050$  K). The TPR profile associated with the  $\text{PtGa}_x/\text{MgF}_2$  catalysts of different Ga loadings exhibits a bimodal characteristic like that for  $\text{Pt/MgF}_2$ , while the  $T_{\text{max}}$  of the high temperature peak shifts somewhat to a correspondingly lower temperature value of ca. 1000 K, as compared with that for the pure support. This indicates there exists an interaction between Pt (not Ga) and  $\text{MgF}_2$ , affecting the reduction behavior of the latter. Indeed, if compared the TPR profile for  $\text{Ga/MgF}_2$  with that for pure  $\text{MgF}_2$ , one will find that Ga mono-component only has limited effect on the reduction of  $\text{MgF}_2$ .

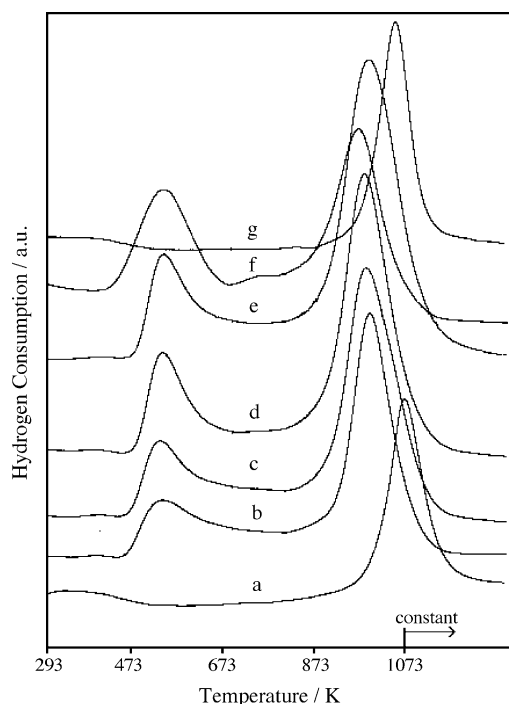
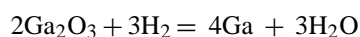


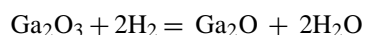
Fig. 6. TPR spectra of supported platinum catalysts: (a)  $\text{MgF}_2$ ; (b)  $\text{Pt}_{1.00}/\text{MgF}_2$ ; (c)  $\text{PtGa}_{0.37}/\text{MgF}_2$ ; (d)  $\text{PtGa}_{0.74}/\text{MgF}_2$ ; (e)  $\text{PtGa}_{1.11}/\text{MgF}_2$ ; (f)  $\text{PtGa}_{1.86}/\text{MgF}_2$ ; (g)  $\text{Ga/MgF}_2$ .

We can obtain some important information from the areas of the reduction peaks emerging in the low temperature region of TPR patterns for the  $\text{PtGa}_x/\text{MgF}_2$  catalysts. As summarized in Table 4, the areas of the low temperature peaks, which represents the hydrogen consumption, increases gradually with increasing the loading of Ga, indicate that an interaction between the Ga and the Pt to form  $\text{PtGa}$  assemblies such as  $\text{PtGa}$  alloy is caused as a consequence of the synchronous reduction of the Pt and Ga oxide species as suggested in Ref. [44]. It is believed that Pt can promote the reduction of Ga species.

When assume the amount of hydrogen consumed by the Pt species to be constant and independent of the Ga loading, in fact this assumption is reasonable because the Pt loading of  $\text{PtGa}_x/\text{MgF}_2$  catalysts is kept constant, we can figure out the hydrogen consumption consumed by the Ga species for each  $\text{Pt-Ga/MgF}_2$  catalyst in the low temperature region (see Table 4). Fig. 7 plots the hydrogen consumptions of Ga against the Ga contents of the  $\text{Pt-Ga/MgF}_2$  catalysts. The  $\text{H}_2/\text{Ga}$  molar ratio associated with the  $\text{Pt-Ga/MgF}_2$  catalysts is found to be lower than 1.5, a value of the theoretical molar ratio for a complete reduction of  $\text{Ga}_2\text{O}_3$ :



It is worthy noting that another reaction for the reduction of  $\text{Ga}_2\text{O}_3$  is thermodynamically feasible:



where the theoretical molar ratio of  $\text{H}_2/\text{Ga}$  is 1. The results in Fig. 7 shows that with increasing the Ga loading of catalysts,

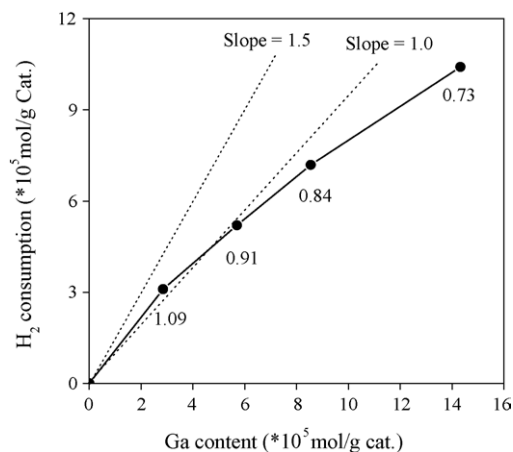


Fig. 7. Dependence of hydrogen consumptions in TPR spectra of Pt-Ga/MgF<sub>2</sub> on gallium contents.

the molar ratio of H<sub>2</sub>/Ga decreases gradually from 1.09 for PtGa<sub>0.37</sub>/MgF<sub>2</sub> to 0.73 for PtGa<sub>1.86</sub>/MgF<sub>2</sub>.

From the TPR pattern and hydrogen consumption of PtGa<sub>0.37</sub>/MgF<sub>2</sub>, it can be probably estimated that the reduced Ga species are of an electron-deficient state like Ga<sup>δ+</sup>, where 0 ≤ δ < 1, because the amount of hydrogen is sufficient for the reduction of the Ga species to form Ga(I) species but cannot afford a complete reduction of all the Ga species to generate a metallic state in the low temperature region.

Since the electron-deficient Ga<sup>δ+</sup> (0 ≤ δ < 1) species are the main reduction products in the low temperature region, a part of Ga species will preserve as a state of Ga(III) after the low temperature reduction (matches the activation conditions of the actual catalysts) for the other PtGa<sub>x</sub>/MgF<sub>2</sub> catalysts (indeed, the H<sub>2</sub>/Ga ratios are less than 1.0 as determined by TPR). However, we cannot quantitatively differentiate the Ga(III) species from the reduction peaks in the high temperature region of the TPR profiles, because the reduction reaction of Mg species occurs at the same region. Nevertheless, it is instructive to note that a little peak appears at 713 K for the PtGa<sub>1.86</sub>/MgF<sub>2</sub> catalyst may be ascribed to the reduction of Ga(III) species (Fig. 6(f)). This is in good agreement with the previous report [45,46]. Ga(III) can be reduced to Ga (I) at a temperature range of 373–673 K

over a Ga<sub>2</sub>O<sub>3</sub>/HZSM-5 catalyst [45] and the partially reduction of Ga(III) can be completed at 823 K to generate Ga<sup>δ+</sup>-H sites for a silica supported gallium(III) oxide [46]. We cannot completely exclude the possibility to form metallic Ga in the low temperature region of TPR, if consider the promotion effect of Pt to the Ga reduction like in the case of Pt/MgF<sub>2</sub>, where a lower T<sub>max</sub> for the MgF<sub>2</sub> reduction occurs, although the formation of the metallic Ga needs higher temperature (T<sub>max</sub> = 780 K) for a Ga/H-MFI catalyst [47]. Hence, the hypothesis on the formation of electron-deficient Ga<sup>δ+</sup> (0 ≤ δ < 1) needs some more direct evidences to support.

### 3.2.3. X-ray photoelectron spectroscopy (XPS)

We have performed XPS measurements on the PtGa<sub>x</sub>/MgF<sub>2</sub> catalysts to check the variety of Pt 4f<sub>7/2</sub> and Ga 3d lines as summarized in Table 5. The results manifest that the surface atomic ratio of Ga to Pt, which increases from 0.51 to 2.44 depending on the increase of the Ga loading determined by ICP-AES, is somewhat higher than the corresponding bulky Ga/Pt ratio, indicating that the Ga species have been enriched on the surface of catalyst by the hydrogen reduction. The Ga 3d transition associated with the reduced catalysts has a value of binding energy (BE) at 19.1–19.3 eV, which is believed to be ascribed to the formation of electron-efficient Ga<sup>δ+</sup> (0 ≤ δ < 1) species. Ga 3d has been reported having a binding energy at 19.0 and 20.6 eV for Ga<sub>2</sub>O and Ga<sub>2</sub>O<sub>3</sub>, respectively [48]. The XPS results are in good agreement with those from TPR.

Ga 3d has a binding energy at ~19.5 eV in the spent catalyst, somewhat higher than that in the catalysts as reduced. This suggests that, some changes have taken place for the Ga during the hydrodechlorination of CCl<sub>4</sub>, where a number of active chlorine was generated. The Ga<sup>δ+</sup> (0 ≤ δ < 1) species may interact with the active chlorine under the present reaction conditions to form Ga-Cl<sub>ads</sub> species. We can take the electronegativity as a means of estimating the electronic influence of the active chlorine. Indeed, chlorine is more electronegative than Ga, and an inductive effect between the adsorbed active chlorine and the Ga<sup>δ+</sup> (0 ≤ δ < 1) species will render the electrons around Ga atoms generate an excursion to the adsorbed chlorine atoms. The electron density of Ga atoms in the spent catalyst is accordingly

Table 5  
The XPS results<sup>a</sup>

Catalyst	Pt 4f <sub>7/2</sub> (eV)		Ga 3d (eV)		Ga/Pt ratio
	As reduced	Used	As reduced	Used	
Pt/MgF <sub>2</sub>	71.8(30), 70.8(70)	72.8(50), 71.0(50)			
PtGa <sub>0.37</sub> /MgF <sub>2</sub>	72.0(40), 70.9(60)	72.7(60), 71.1(40)	19.2	19.6	0.51
PtGa <sub>0.74</sub> /MgF <sub>2</sub>	72.1(45), 70.9(55)	72.7(70), 70.9(30)	19.3	19.5	0.96
PtGa <sub>1.11</sub> /MgF <sub>2</sub>	71.9(50), 71.0(50)	72.7(85), 70.8(15)	19.3	19.5	1.54
PtGa <sub>1.86</sub> /MgF <sub>2</sub>	72.1(55), 71.1(45)	72.8(85), 70.9(15)	21.5(10), 19.2(90)	21.7(15), 19.6(85)	2.44
Ga/MgF <sub>2</sub>			21.5(90), 19.1(10)	21.7	
Ga <sub>2</sub> O <sup>b</sup>			19.0		
Ga <sub>2</sub> O <sub>3</sub> <sup>b</sup>			20.6		
Pt/H[Ga]ZSM-5 <sup>c</sup>	72.8, 71.6, 70.8				

<sup>a</sup> Values denote binding energies in eV; values in the parentheses denote peak ratios.

<sup>b</sup> Data taken from [47].

<sup>c</sup> Data taken from [48].

lower than that in the catalyst as reduced, it would result in a higher BE value for Ga 3d in the spent catalyst. Nevertheless, the form of Ga(III) is not remarkable because, in general, Ga(III) has a BE value exceeding 20.5 eV [48,49].

The Ga 3d line in the PtGa<sub>1.86</sub>/MgF<sub>2</sub> catalyst as reduced can be deconvoluted into two parts: one has BE around 19.2 eV, and the other has BE around 21.5 eV (attributable to Ga(III) with octahedral coordination environment). This suggests that the Ga species are not fully reduced to the Ga of a relatively lower electrovalence, especially when the catalyst have a high Ga loading as in the case of PtGa<sub>1.86</sub>/MgF<sub>2</sub> (a proportion of the Ga(III) species in the catalyst as reduced is estimated to be ~10% by XPS measurement). It is also observed previously that the degree of the reduction of the Ga depends upon the loading of Ga according to the results from TPR. Similar phenomena as in the case of PtGa<sub>1.86</sub>/MgF<sub>2</sub> for the XPS spectra are not observed for the other catalysts having relatively lower Ga loadings. One may assume that it is fairly difficult to detect or differentiate trace Ga species by XPS spectra but the results from XPS are still helpful for us to get a basic understanding on the reduction behavior of Ga species, when combine XPS with TPR patterns (Figs. 6 and 7). It's worthy noting that in the case of the Ga/MgF<sub>2</sub> catalyst, only small amount of Ga species has been converted to a state possessing a lower BE value under the present activation conditions (Table 5).

The XPS results of Pt 4f<sub>7/2</sub> transitions are also listed in Table 5. According to the deconvolution of XPS spectra, two sets of Pt 4f doublet are found by fitting the experimental signal: the Pt 4f<sub>7/2</sub> transition at *ca.* 72.0 eV is denoted as A line, and the one at *ca.* 71.0 eV is denoted as B line. In contrast to the results in the Pt/H[Ga]ZSM-5 catalyst reported by Diaza et al. [43], the peak at 72.8 eV has not been found in this case, and the peak at 71.6 eV (corresponding to A line), which was assigned to the dispersed Pt particles interacting with surface O groups by the authors [43], shifts slightly to around 72.0 eV. The B line can be assigned to the Pt in metallic state in this case [49]. However, the BE value of A line is somewhat higher than that for metallic Pt, and lower than that for PtO (representative value generally falls into the range of 73.3–73.8 eV [49]). It should be noted that the Pt 4f<sub>7/2</sub> peak of a BE value at 71.8 eV has also been assigned to a surface Pt–O<sub>ads</sub> interaction [50]. The support in this case contains a high electronegative element of F, we ascribe A line herein to the formation of a Pt–F interaction like the Pt–O interaction in the case of the Pt/H[Ga]ZSM-5 catalyst [43].

As listed in Table 5, the A line associated with Ga-containing catalysts is slightly higher than that in the case of Pt/MgF<sub>2</sub> by a factor of ~0.2 eV, likely due to the effect of the Ga addition. The ratio of A line to B line slightly increases upon the Ga loading, indicative of an increase in the amount of the Pt sites involved in the Pt–F interaction due to the Ga addition. It is found that Ga atom can migrate and then be incorporated into Pt cluster during the process of reduction in the case of a Pt/Ga/H-Beta zeolite [51]. Ga can diffuse into the crystal lattices of platinum metal to form PtGa alloys of various compositions [52]. Indeed, a higher dispersion of Pt is observed if we increase the Ga loading in the MgF<sub>2</sub> supported catalysts. The higher dispersion of Pt is beneficial to generate more Pt sites, exhibiting a linear relationship

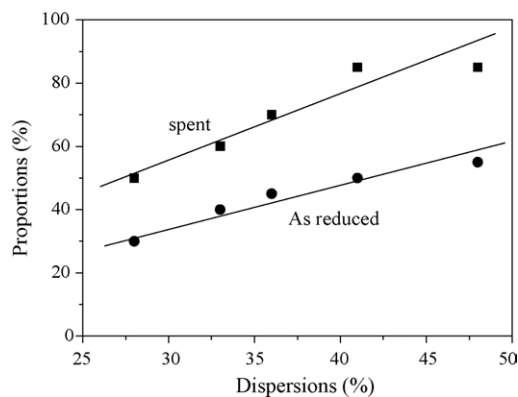


Fig. 8. Plots of the proportion of the Pt species of high electrovalence against Pt dispersions.

with the proportion of the A lines ( $R=0.97$ , slope = 1.218, see Fig. 8).

On the other hand, in the case of the spent Pt/MgF<sub>2</sub> catalyst, the two lines at 72.8 and 71.0 eV indicate that the metallic character of the Pt is decreased and about 50% of the Pt is transferred to the species of higher electrovalence during the hydrodechlorination of CCl<sub>4</sub>. We ascribe this to the formation of Pt–Cl species due to the adsorption of the active chlorine as in the case of Ga. In general, halogens are highly electronegative elements and their adsorption onto metal surface is expected to modify its electronic structure significantly. The effect of the chlorine has not been addressed directly for the supported Pt catalysts in the hydrodechlorination of CCl<sub>4</sub>. Nevertheless, Cl atoms co-adsorbed on the catalyst surface do affect the reaction of hydrogen-assisted dechlorination of vicinal chlorocarbons over Pt/SiO<sub>2</sub> catalysts [34,53]. The catalytic active phase has found to be a surface Pt(II) species with Cl ligands in the hydrodechlorination of CCl<sub>4</sub> over Pt/MgO, while the bulk remained as Pt metal [15]. Similar behavior can also be observed for the catalysts with the addition of Ga promoter, where a relatively higher proportion of the Pt species of high electrovalence is found. The increase of the proportion can be also explained by the increase of the Pt dispersion due to the addition of Ga promoter, where the amount of Pt sites exposed to the reaction atmosphere is increased accordingly. Indeed, the proportion of the Pt species of higher electrovalence in the spent catalysts is well related to the Pt dispersions (Fig. 8) with an  $R=0.94$  and a slope = 1.895.

The slope in this case is higher than that in the case of the catalysts as reduced (1.895 versus 1.218), manifesting that in addition to the increase of the number of Pt sites interacting with Cl directly, another factor will also result in the formation of Pt sites of higher electrovalence, and this factor also depends on the Ga loading in the catalysts. We have ascribed the increase of Ga 3d binding energy to the adsorption of the active chlorine on the site of Ga to form Ga–Cl<sub>ads</sub> species. Most likely, the electron attracting effect of these adsorbed Cl atoms can be transferred to the Pt atoms in the vicinity of the Ga (in a form of PtGa assemblies or PtGa alloy as described in the TPR) by an inductive effect to create an electron-efficient environment around Pt.



### 3.3. Discussion

It is reported that the oxidation state of Pt will essentially affect the catalytic performance in the hydrodechlorination of  $\text{CCl}_4$  [16], and the Pt active phase in the same reaction is a surface Pt(II) species [15]. For Gómez-Sainero et al. [10], the Pd species of high Lewis acid character were explained as the active sites to activate  $\text{CCl}_4$  effectively. Malinowski et al. [36] have firstly reported  $\text{MgF}_2$  as a support of palladium catalysts for the hydrodechlorination of  $\text{CCl}_2\text{F}_2$  (CFC-12). They speculated that the Lewis acidity of  $\text{MgF}_2$  would decrease the electron density in neighboring Pd sites, resulting in higher  $\text{CH}_2\text{F}_2$  selectivity in effect. It is believed that the  $\text{MgF}_2$  support will also modify the catalytic active sites by creating electron-deficient Pt species to some extent. This is supported by the XPS results (Table 5). On the other hand, unlike  $\text{MgO}$  and  $\gamma\text{-Al}_2\text{O}_3$ , the  $\text{MgF}_2$  is not susceptible to  $\text{HCl}$ , an inevitably product in the hydrodechlorination of  $\text{CCl}_4$ , and is beneficial to maintain a stable framework and to promote the structural stability of catalysts. Furthermore, the  $\text{MgF}_2$  support is also helpful to retard the formation toxic  $\text{COCl}_2$ , which produced by reacting  $\text{CCl}_4$  with the oxygen from oxide supports as identified by IR spectroscopic [54].

The most interesting aspect in terms of the present system is the promotion effect of Ga on the improvement of the  $\text{CHCl}_3$  selectivity for the selective hydrodechlorination of  $\text{CCl}_4$  over supported Pt catalysts. The reduction and migration of gallium are dramatically promoted by interacting with Pt in both Ga/H-ZSM-5 and Ga-silicate supported platinum catalyst [55], in good agreement with the TPR results in our case, where PtGa assemblies or PtGa alloys were supposed to be formed on the catalyst surface. It is reported that for Pt/Ga/H-beta zeolites, the PtGa bimetallic species are formed with inter-atomic distance of 2.51–2.54 Å upon reduction as determined by EXAFS analyses, and the sintering of Pt are prevented to aggregate into large particles by the Ga [51]. Thus, the dependence of dispersion on the Ga loading as shown in Table 4 can be well understood by considering the formation of PtGa assemblies, where Ga atoms may cover or be attached on the surface of Pt particles or even be incorporated into the Pt lattice to form PtGa alloys, and a similar preventing effect is expected to occur during the forming of Pt particles as in the case of reference [51].

In the present case, the addition of the Ga results in an increase in the  $\text{CHCl}_3$  selectivity (from ~60% to >80% with the Ga/Pt ratio increasing to 1.86), however, the conversion of  $\text{CCl}_4$  declines with a factor of ~2 (76.2% for Ga/Pt = 0 and 40.4% for Ga/Pt = 1.86). This means with the increase of  $\text{CHCl}_3$  selectivity, the yield of the  $\text{CHCl}_3$  is decreased obviously (up to ~30%). In general, the  $\text{CHCl}_3$  selectivity negatively depends on the conversion of  $\text{CCl}_4$ . Indeed, similar behavior has been observed over the Pt/ $\text{MgF}_2$  and Pt/ $\gamma\text{-Al}_2\text{O}_3$  catalysts (Table 2). It is instructive to mention herein that the Pt/ $\gamma\text{-Al}_2\text{O}_3$  catalysts suffered a sharp deactivation with the time on stream. However, for the  $\text{MgF}_2$  supported Pt system, the effect from the conversion changes on the  $\text{CHCl}_3$  selectivity retains at a limited level. Thus, the promotion effect of Ga on improving the  $\text{CHCl}_3$  selectivity can be well confirmed. In addition, the influence of the Ga addition on the  $\text{CHCl}_3$  selectivity and the conversion of  $\text{CCl}_4$  can be ascribed

to the modification of Ga to the electronic properties of the Pt active sites by changing the electronic environment surrounding the Pt atoms via a Pt–Ga interaction, particularly, when the electron-deficient Ga species are generated on the catalyst surface during the hydrodechlorination of  $\text{CCl}_4$ . The modified Pt species are believed to be beneficial to form a fast desorption step for the adsorbed  $^*\text{CCl}_3$  species (a commonly accepted precursor to generate  $\text{CHCl}_3$ ) under the assistance of hydrogen. At the same time, the adsorption of reactant  $\text{CCl}_4$  is weakened on the catalyst surface and results in a lower conversion of  $\text{CCl}_4$ . Detail works are in progress to improve the conversion of  $\text{CCl}_4$  by optimizing the present catalyst system.

The depositing of carbon and chlorine, which is due to a homolytic cleavage of C–Cl bond confirmed by using a linear free energy method [56–58], on the catalyst surface, where a relatively hydrogen-deficient environment is generated, has been suggested to be an important reason responsible for the deactivation in terms of the hydrodechlorination of  $\text{CCl}_4$  by Choi et al. [16,19]. Most likely, the excellent stability exhibited in terms of the hydrodechlorination of  $\text{CCl}_4$  can be ascribed to the weakened maintenance capacity of the present catalyst system for the chlorine and the deeply de-chlorinated carbon species, because the electron-deficient environment of Pt favors the adsorption of electron-donor molecules such as  $\text{H}_2$ .

### 4. Conclusion

The selective hydrodechlorination of  $\text{CCl}_4$  over Pt–Ga/ $\text{MgF}_2$  yields  $\text{CHCl}_3$  with selectivity higher than 80%. The catalysts exhibit excellent stability as compared with the traditional Pt/ $\gamma\text{-Al}_2\text{O}_3$  catalyst, and this is ascribed to the weakened maintenance capacity of the catalysts for the chlorine and carbon species. The electron-deficient Pt species are formed on the surface of catalyst due to the adsorption of active chlorine according to the results by XPS. The Ga serves to increase the dispersion of Pt and then to modify the electronic properties of Pt by the Pt–Ga interaction. The modified Pt species are believed to be beneficial to form a fast desorption step for the adsorbed  $^*\text{CCl}_3$  species (a commonly accepted precursor to generate  $\text{CHCl}_3$ ) under the assistance of hydrogen. At the same time, the adsorption of reactant  $\text{CCl}_4$  is weakened on the catalyst surface and results in a lower conversion of  $\text{CCl}_4$ .

### Acknowledgements

The authors would thank the reviewers for their valuable comments. The authors also wish to thank professor Atsushi Shibayama, Department of Material-Process Engineering and Applied Chemistry for Environment, Faculty of Engineering and Resource Science, Akita University, Japan, for his unselfish supports on this work.

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