

Supported platinum–gallium catalysts for selective hydrodechlorination of CCl₄

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Abstract

The selective hydrodechlorination of tetrachloromethane (CCl₄) was performed over supported platinum–gallium catalysts with a support of MgF₂ to improve CHCl₃ selectivity and catalytic stability. In order to better understand the behavior of the Ga and MgF₂ 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 CHCl₃ selectivity and the conversion of CCl₄ 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 *CCl₃ species (a commonly accepted precursor to generate CHCl₃) under the assistance of hydrogen. The adsorption of reactant CCl₄ will be weakened on the catalyst surface and cause a lower conversion of CCl₄.

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1. Introduction

Tetrachloromethane (CCl₄) 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 CCl₄ have been restricted in developed countries since 1996, and the total phase out of CCl₄ should be fulfilled in developing countries by the year of 2010. Since CCl₄ 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 CCl₄. However, the combustion technique adopted presently is highly energy consuming and brings secondary contamination, e.g. dioxins, COCl₂ [2,3]. A more attractive and promising method

is proposed to convert CCl₄ to CHCl₃, 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 CCl₄ either in liquid phase [7–11] or gas phase [12–22]. In the pioneer work of the hydrodechlorination of CCl₄ over Pt/η-Al₂O₃ [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 *CCl₃ species to form CHCl₃ selectively and the second is a concerted addition of hydrogen atoms to adsorbed *CCl₃ with no desorption of intermediates to generate CH₄ eventually. However, this work has been marked with low selectivity to CHCl₃ 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 CCl₄, where 76.1% selectivity for CHCl₃ 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 MgCl₂ is observed, causing a considerable decrease in the surface area of the catalyst and the catalytic activities in terms of the hydrodechlorination of CCl₄. Then, Choi et al. synthesized Pt/ γ -Al₂O₃ 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 γ -Al₂O₃ support, and an optimum oxidation state of the Pt has been identified to be of the best selectivity to CHCl₃. 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/Al₂O₃ catalyst by treating the catalyst with a solution of NH₄Cl. In addition, Santo et al. [18] has reported organometallics-based platinum and palladium catalysts with MgO support for the hydrodechlorination of CCl₄. The phase change of MgO to MgCl₂ 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 CHCl₃ than the supported palladium in the gas phase selective hydrodechlorination of CCl₄. The higher selectivity to CHCl₃ 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 CCl₄ [22]. Palladium will rapidly deactivate in the reaction, exhibiting a rather poor selectivity to CHCl₃, 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 CHCl₃ selectivity in terms of the hydrodechlorination of CCl₄ 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 CCl₄. By adopting Ga component as a modifier, the catalytic stability and selectivity to CHCl₃ 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 γ -Al₂O₃ are susceptible to HCl, created inevitably in the hydrodechlorination of CCl₄, 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 CCl₄. Considering MgF₂ is quite stable in the hydrodechlorination of CCl₂F₂ [36], we attempt to use MgF₂ 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 H₂PtCl₆ and/or GaCl₃ (Aldrich) with appropriate amounts. Several commercial support materials including MgF₂ (BET surface area 70 cm² g⁻¹, pore volume 0.2 cm³ g⁻¹), ZSM-5 (Si/Al = 35, surface area 290 cm² g⁻¹ and pore volume 0.50 cm³ g⁻¹), Sm₂O₃ (Surface area 30 cm² g⁻¹ and pore volume 0.23 cm³ g⁻¹), γ -Al₂O₃ (BET surface area 220 cm² g⁻¹ and pore volume 0.45 cm³ g⁻¹) 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 H₂PtCl₆, 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⁻¹ 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 H₂PtCl₆ solution into a H₂PtCl₆ and GaCl₃ solution mixture, according to a similar procedure.

The catalyst precursor was sieved in the 500- to 100- μ m mesh range and was reduced directly in a 30 cm³ min⁻¹ stream of dry Ar containing 4.94% H₂ at 10 K min⁻¹ 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⁻¹ stream of N₂ 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 α 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 1.33×10^{-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

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