Research Article

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Liquid-phase hydrogenation of carbon tetrachloride catalyzed by three-dimensional graphene-supported palladium catalyst

Abstract: In this article, a three-dimensional graphene (3DGN)-supported palladium metal catalyst was prepared by the impregnation method with noble metal palladium as the active component, aiming to synthesize a catalyst with high activity and high selectivity. Its catalytic performance in liquid-phase hydrochlorination of carbon tetrachloride (TTCM) was investigated. The influences of different Pd loadings, reduction temperatures, and reaction temperatures on the catalytic hydrogenation reaction were studied. The purpose is to explore the best operating conditions for the preparation of chloroform. The results show that the 3DGN-supported palladium catalyst exhibits excellent catalytic performance and high selectivity to chloroform in the hydrogenation of TTCM. When the Pd loading was 1.0 wt%, the reduction temperature was 773 K, and the hydrochlorination reaction temperature was 398 K, the conversion of TTCM was as high as 98.12%, and the selectivity of chloroform was 85.23%. The main by-product is dichloromethane. The selectivity of chloroform is affected by the increasing temperature but remains above 80%.

Keywords: carbon tetrachloride, hydrochlorination, palladium/three-dimensional graphene catalyst, selectivity

1 Introduction

Carbon tetrachloride (TTCM) has been widely used as a fire extinguishing agent, a chlorinating agent for organic substances, and an organic solvent, but its production is now restricted due to its toxicity and destruction of the ozone layer. After the Montreal Protocol (1987), the cooperation further reduced the manufacture and use of chlorofluorocarbon and the production market for TTCM gradually declined. It has been listed among the compounds banned from emission after several years at the London Conference in 1990. TTCM is a by-product of many industrial chlorination processes, so the green conversion of TTCM is essential. Catalytic hydrochlorination has become one of the most promising green conversion methods compared to other methods. Delannoy et al. studied the hydrochlorination of TTCM on Group VI metal carbides (WC, W$_2$C, and Mo$_2$C). These carbides were prepared by temperature-programmed carburizing of WO$_3$ and MoO$_3$ in 10–20% CH$_4$/H$_2$ mixtures. Mo$_2$C and W$_2$C were rapidly deactivated with time, independent of temperature, whereas WC showed good stability at 393 K [1]. Lu et al. obtained the lower surface activation energy of Pt(111) by studying its surface adsorption and hydrogenation. It shows that a platinum catalyst has high catalytic activity for the TTCM hydrogenation reaction [2]. Bonarowska et al. found that alumina-supported platinum’s catalytic activity is strongly dependent on metal dispersion. At 343–363 K, the catalytic activity of Pt/Al$_2$O$_3$ in TTCM hydrochlorination was inversely proportional to the dispersion of platinum [3]. A report on multimetallic catalysts found that the activated carbon-supported Pd–Au catalyst exhibited much better performance than the monometallic Pd sample in the hydrochlorination of TTCM. Pd–Au mixing was critical to obtain this synergistic effect [4]. The synergistic effect of the alloy will effectively improve the performance of the catalyst. Similarly, Karpinski et al. studied the hydrogenation of TTCM on SiO$_2$-supported Pd–Au alloy, and the reasonably mixed Pd–Au particles showed better catalytic performance in about 60 h. At the same time, the single metal palladium and palladium-rich catalysts would be inactivated rapidly [5]. Bae et al. studied tin’s effect on Pt–Sn/y-Al$_2$O$_3$ in TTCM hydrochlorination reaction [6]. It is concluded that the Pt–Sn/y-Al$_2$O$_3$ catalyst with an appropriate amount of tin exhibits enhanced catalytic stability.
and selectivity to CHCl₃ in the hydrochlorination of TTCM [6]. Although the catalysts studied above have a certain catalytic effect, their selectivity to chloroform is still low. The catalyst synthesis process was complicated because the catalyst was easily deactivated and had poor stability. Therefore, the preparation of catalysts with high activity and selectivity is of great significance for industrial applications.

Metallic palladium is a catalyst for hydrogen activation to form free atomic hydrogen, which is a reducing agent for dechlorination and hydrogenation of organic halogens [7–9]. Pd-based catalysts exhibit high catalytic activity and selectivity at lower reaction temperatures. Three-dimensional graphene (3DGN) as a carrier can provide a larger specific surface area, improve the dispersibility of metal particles, and reduce the agglomeration of metal particles in the hydrochlorination reaction. Notably, the conjugated structure of 3DGN can provide a better ability to adsorb molecules and higher electron mobility on the surface. It is conducive to the transfer of electrons on the carrier surface, thereby improving the catalytic activity of metals [10]. Both refer to three-dimensional graphene and palladium metal.

In order to improve the selectivity of chloroform and optimize the reaction process, this article combines the excellent properties of 3D graphene and palladium metal. A series of catalysts with different Pd loadings were prepared using the self-made 3D graphene as the carrier. The catalytic performance of 3DGN-loaded palladium metal catalysts (Pd/3DGNs) in the TTCM hydrogenation reaction was investigated using intermittent reactions.

## 2 Materials and methods

### 2.1 Reagents and materials

Expanded graphite (purity ≥99.7%) was purchased from Jiangsu Xianfeng Nanomaterials Technology Co., Ltd. Sodium nitrate (NaNO₃, 99.5%), H₂SO₄ (98%), potassium permanganate (KMnO₄, 98.0%), H₂O₂ (30%), HCl (5%), palladium chloride (PdCl₂), TTCM (CCL₄, 99%), and n-hexane (98%) were purchased from Guangzhou Ruoyang Huabo Instrument Co., Ltd. Hydrogen (high purity hydrogen, 99.9999%) was purchased from Guangzhou Danoutong Trading Co., Ltd.

### 2.2 Preparation of 3DGN

Graphene oxide (GO) was prepared using expanded graphite as raw material by the classical modified Hummers method [11]. The obtained GO is put into the stainless-steel hydrothermal reactor lined with 50 mL polytetrafluoroethylene. It was placed in a muffle furnace and heated to 180°C for 24 h. After cooling to room temperature, the samples were soaked in deionized water for 12 h. The samples were then freeze-dried in a freeze dryer (model SR-A10N-50) at −50°C for 48 h to obtain 3DGNs.

### 2.3 Preparation of 3DGN-supported palladium metal catalyst

The catalyst precursors with different Pd mass fractions (0.2, 0.3, 0.5, 1.0, and 1.5 wt%) were obtained after 12 h impregnation of 3DGN carriers using different concentrations of aqueous H₂PdCl₄ solutions (prepared from 0.02, 0.03, 0.05, 0.10, and 0.15 g anhydrous PdCl₂ and concentrated HCl). The catalyst precursors with different Pd mass fractions were obtained. After drying at 393 K for 48 h, the Pd catalyst precursor was placed in a tube furnace. The samples were reduced at 523, 573, 773, and 973 K for 6 h under an H₂/Ar (95%) mixed gas flow rate of 20 mL·min⁻¹. After the reaction was completed, it was cooled to room temperature, taken out, and sealed for later use. The catalysts were then labeled as 0.2, 0.3, 0.5, 1.0, and 1.5 Pd/3DGNs, respectively.

### 2.4 Characterization of catalyst

The molecular structures of GO, 3DGNs, and catalysts were analyzed by UV laser Raman spectroscopy (LabRAM hr800). X-ray diffraction (XRD) patterns were collected on an X-ray Diffractometer model (D8 ADVANCE) to analyze the crystalline phases of GO, 3DGNs, and catalysts. The morphology and microstructure of GO and 3DGNs were analyzed by field emission scanning electron microscopy (JSM-7001F, SEM). The porous structure of 3DGNs was characterized by specific surface area and micropore physical adsorption analyzer (ASAP2020). High-resolution transmission electron microscopy (TEM) was used to determine the structure of 3DGNs using the model HT7700. X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi) was used to determine the surface composition of the catalyst and the compound state of the elements.

### 2.5 Evaluation of catalyst

The catalyst’s performance was evaluated by the hydrogenation and dechlorination of TTCM. The reaction was
carried out in a fully automated parallel reactor produced in France (TOP HPHT 200). The equipment was installed after adding 50 mL of CCl₄, 6 g of Pd/3DGN catalyst, and 50 mL of n-hexane solvent to the autoclave in sequence. Before the reaction, the entire system was replaced with 1 MPa nitrogen five times and then replaced with 1 MPa hydrogen five times. After passing hydrogen to the pressure of 3 MPa, the temperature was raised to the set reaction temperature. The reaction products were analyzed quantitatively and qualitatively by gas chromatography (Agilent 7820 GC) on a P/N 19091J-413, HP-5 capillary column of 30 m × 320 μm × 0.25 μm.

3 Results and discussion

3.1 Characterization of catalyst

In order to study the morphology and surface microstructure of GO, 3DGNs, and catalysts, they were characterized by SEM and TEM, and the results are shown in Figure 1. Figure 1a shows the SEM image of GO. It can be seen that the appearance of GO is a monolithic structure with a wrinkled surface. Figure 1b and c shows the 3DGNs after high-temperature hydrothermal reduction. Its interior presents a highly cross-linked network structure with many holes, which provides a prerequisite for the high dispersion of metal atoms in the active center of the catalyst. The irregular internal structure of 3DGNs can be seen from the TEM image of 3DGNs in Figure 1d. The darker color parts exhibit a high degree of aggregation of nanostructures. Figure 1e and f shows the TEM images of the 1.0 Pd/3DGN catalyst at different magnifications, respectively. It can be seen that the palladium metal is evenly distributed along the folds and edges of the carrier. This indicates a strong interaction between palladium metal and 3DGN support [12–15]. In order to further explore the specific surface area of the 3DGN support, it was characterized by Brunauer, Emmett and Teller (BET) and compared with other catalyst supports, as shown in Table 1. It can be seen that the specific surface area of the self-made 3DGN carrier is 358 m²·g⁻¹, which is higher than that of the other carriers in the table. This enables the metal crystals to attach and disperse on the surface and mass transfer during the reaction, providing more active sites. Graphene as a catalytic carrier can provide a larger specific surface area and excellent morphological stability and effectively improve dispersibility [16,17]. At the same time, the dispersibility and stability of palladium metal on the surface of the carrier are effectively improved.

To reveal the extent of reduction of GO, 3DGNs, and 1.0 Pd/3DGN catalysts, they were characterized by Raman

Table 1: Comparison of specific surface areas of different catalyst supports

| Catalyst support | S_BET (m²·g⁻¹) | Average pore diameter (nm) | Reference |
|------------------|----------------|----------------------------|-----------|
| 3DGNs            | 358            | 28.8                       | —         |
| Al₂O₃             | 180            | —                          | [33]      |
| AlF₃              | 72             | —                          | [34]      |
| MgO              | 152            | 10.5                       | [35]      |

Figure 1: SEM and TEM results: (a) SEM image of GO, (b and c) SEM images of 3DGNs, (d) TEM image of 3DGNs, (e and f) TEM images of 1.0 Pd/3DGN catalyst.
spectroscopy. The results are shown in Figure 2. It can be seen from Figure 2 that all samples have two peak bands at 1,350 and 1,590 cm$^{-1}$. They are called D-peak and G-peak, respectively. The D peak is the defect peak of carbon lattice sp$^3$ hybridization, and the G peak is the carbon–carbon double bond peak [18,19]. The D/G band intensity ratio reflects the degree of graphitization [20,21]. The smaller the $I_D/I_G$ ratio, the higher the degree of graphitization and reduction. From the data obtained in the figure, it can be calculated that the corresponding $I_D/I_G$ of GO, 3DGNs, and 1.0 Pd/3DGN catalysts are 1.33, 1.21, and 1.02, respectively. It shows that compared with GO and 3DGNs, the degree of graphitization of 1.0 Pd/3DGN catalyst is increased, and the reduction effect is better. In addition, a peak at 2,700 cm$^{-1}$ appeared on the spectrum of the 1.0 Pd/3DGN catalyst. This is the 2D band of graphene, and the appearance of the 2D band proves the better quality and properties of graphene [22,23].

In order to conduct phase analysis of GO, 3DGNs, and 1.0 Pd/3DGN catalysts, they were examined by XRD with loadings of 0.2, 0.3, 0.5, 1.0, and 1.5 wt%. The result is shown in Figure 3. It can be seen that the diffraction peak of GO appears at $2\theta = 10.3^\circ$. According to Bragg’s law (Eq. 1), the distance between the GO layers is calculated to be 0.86 nm [24]. In addition, at 26.4$^\circ$, both the 3DGNs and the reduced catalyst have this characteristic peak. The chemically reduced graphene sheets are re-stacked to form a regular and periodic graphitic-like layered structure. The sp$^2$ hybrid graphene network was re-established in the reduction. These phenomena can be confirmed from the SEM images. This characteristic peak can be found in the XRD patterns of the Pd/3DGN catalyst, which proves that the high-temperature reduction does not destroy the three-dimensional structure of the support. The characteristic peaks of palladium metal crystals appear on the (111), (200), and (220) planes. From the XRD pattern of the Pd/3DGN catalyst, it can be seen that the metal crystal peaks are prominent, and more crystals are attached to the surface of the material. When the loading of palladium metal is within 1.0 wt%, relatively broad diffraction peaks are obtained, indicating that the metal crystal size is minimal. Due to the small percentage and particle size, the diffraction signal of metallic palladium cannot be detected [25]. It shows that the metal palladium crystals form a monolayer or sub-monolayer dispersion on the 3DGN support. This dispersed state is a thermodynamically stable state, which will be beneficial to improving the activity and stability of the catalyst [26]. When the loading of palladium metal is 1.5 wt%, the characteristic peaks of metal crystals are more prominent due to the agglomeration of metal palladium. This is probably one of the reasons why the catalyst activity of the supported amount is not very high.

$$2d \sin \theta = n\lambda$$  

(1)

3.2 Evaluation of catalyst

3.2.1 Effects of Pd loading and reaction temperature on the reaction performance of Pd/3DGN catalyst

The catalyst’s performance was investigated by changing the loading of palladium metal and the reaction temperature. The results are shown in Table 2. The metal loading shows that the conversion rate of TTCM and the selectivity of chloroform of 1.0 wt% Pd catalyst are high, and the selectivity of
3.2.2 Effect of reduction temperature on the reaction performance of Pd/3DGN catalyst

In order to study the effect of reduction temperature on the reaction performance of the catalyst, the valence state of the metal on the catalyst was characterized by XPS. The results are shown in Figure 4. It can be seen that Pd$^{2+}$ peaks appear at 338 and 343 eV, and Pd$^{0}$ peaks appear at 335.8 and 337.7 eV on Pd/3DGNs [27]. There are two reasons for the appearance of the Pd$^{2+}$ peak after the catalyst is reduced at a high temperature to obtain Pd$^{0}$. First, the catalyst is not fully reduced, as there is still a tiny amount of Pd$^{2+}$. Second, due to the fact that the catalyst is exposed to air after reduction, an oxide film is formed on the surface of Pd$^{0}$. The reduction temperature rises from 523 to 973 K. The content of palladium metal increases continuously. The higher the reduction temperature, the more palladium metal Pd$^{0}$ is obtained. It can be seen from Table 3 that the selectivity of chloroform varies with the surface atomic ratio of Pd$^{0}$/Pd$^{2+}$. TTCM showed lower chloroform selectivity in catalysts with a Pd$^{0}$/Pd$^{2+}$ ratio higher or lower than 1. When the Pd$^{0}$/Pd$^{2+}$ atomic ratio is close to 1, the chloroform selectivity is higher. The Pd/3DGN catalyst at the reduction temperature of 773 K has the best selectivity of chloroform.

As mentioned before, chloroform was the main product in all reactions, and its reactivity was very low (Table 2). The sum of the selectivities for chloroform and dichloromethane was approximately constant throughout the reaction. This experimental result confirms that dichloromethane was converted from chloroform. Therefore, the TTCM reaction is a continuous dechlorination reaction.

The first step of the reaction is the adsorption of TTCM and hydrogen on the catalyst surface. The results given in Table 3 show that the reduction temperature changes the valence state of the metal Pd on the catalyst surface. The reduction temperature affects the distribution of Pd$^{0}$ and Pd$^{2+}$, thereby affecting the catalytic activity of the catalyst. When the reduction temperature is 523 K, the Pd$^{0}$/Pd$^{2+}$ ratio is 0.01, and the selectivity of chloroform is only 80.65%. When the reduction temperature

Table 2: Comparison of activity and selectivity of different catalytic systems for hydrogenation of carbon tetrachloride

| Catalyst          | Reaction temperature (K) | CCl₄ conversion rate (%) | CHCl₃ selectivity (%) | CH₂Cl₂ selectivity (%) |
|-------------------|--------------------------|--------------------------|-----------------------|------------------------|
| 0.2 Pd/3DGNs      | 398                      | 50.32                    | 80.16                 | —                      |
| 0.3 Pd/3DGNs      | 398                      | 55.15                    | 80.57                 | —                      |
| 0.5 Pd/3DGNs      | 398                      | 70.63                    | 80.69                 | —                      |
| 1.5 Pd/3DGNs      | 398                      | 98.08                    | 83.01                 | —                      |
| 1.0 Pd/3DGNs      | 358                      | 80.36                    | 81.32                 | 9.12                   |
| 1.0 Pd/3DGNs      | 378                      | 85.49                    | 80.79                 | 10.56                  |
| 1.0 Pd/3DGNs      | 398                      | 98.12                    | 85.23                 | 12.69                  |
| 1.0 Pd/3DGNs      | 418                      | 98.09                    | 82.45                 | 14.98                  |
| Pt/Al₂O₃ [36]     | —                        | 97.6                     | 69.0                  | —                      |
| Pd/MgO–MgF₂ [35]  | —                        | 100                      | <62.7                 | —                      |
| Ir/SiO₂ [37]      | —                        | 92.50                    | 92.43                 | —                      |

chloroform is 85.23%. It can be seen that the high loading of Pd has a favorable effect on the reaction rate. However, when the loading of Pd was set at 1.5 wt%, the conversion rate of TTCM did not improve much. This is because of the agglomeration of palladium metal, which was confirmed by the XRD results. Since palladium is a precious metal, its loading should not be too large. Otherwise, the cost of the catalyst is too high, and when the loading is too large, a part of the active components agglomerates or stays in the deep pores of the support. The hydrogenation activity of the catalyst will be reduced, so the loading amount of 1.0 wt% is the most suitable. The effect of temperature on TTCM conversion was investigated at 358, 378, 398, and 418 K using a 1.0 wt% Pd/3DGN catalyst. The increase in reaction temperature results in the enrichment of by-products. The selectivity of dichloromethane was as high as 14.98% at the reaction temperature of 418 K. From the point of view of reaction time and reaction conditions, 398 K is the most suitable reaction temperature, with low cost and high chloroform selectivity. It can be seen from Table 2 that the selectivity of chloroform varies with the reaction temperature. However, when the temperature is too low, a part of the active components is not exposed to air after reduction, an oxide film is formed on the surface of Pd$^{0}$. The reduction temperature rises from 523 to 973 K. The content of palladium metal increases continuously. The higher the reduction temperature, the more palladium metal Pd$^{0}$ is obtained. It can be seen from Table 3 that the selectivity of chloroform varies with the surface atomic ratio of Pd$^{0}$/Pd$^{2+}$. TCCM showed lower chloroform selectivity in catalysts with a Pd$^{0}$/Pd$^{2+}$ ratio higher or lower than 1. When the Pd$^{0}$/Pd$^{2+}$ atomic ratio is close to 1, the chloroform selectivity is higher. The Pd/3DGN catalyst at the reduction temperature of 773 K has the best selectivity of chloroform.
reached 773 K, the ratio of Pd\(^0\)/Pd\(^{n+}\) increased to 0.98, and the selectivity of chloroform increased to 85.23%. When the reduction temperature increased to 973 K, the ratio of Pd\(^0\)/Pd\(^{n+}\) reached 2.96, but the selectivity of chloroform decreased to 81.63%. The above discussion shows that Pd\(^0\) and Pd\(^{n+}\) are necessary for the catalytic dechlorination reaction. The active centers of Pd/3DGN catalysts in this reaction are formed by the combination of adjacent metal and electron-deficient palladium species \([\text{Pd}^0 + \text{Pd}^{n+}]\), which can be confirmed in many kinds of literature \([28,29]\).

\[
\text{2Pd}^0 + \text{H}_2 \rightarrow 2\text{H}^-\text{Pd}^0 \quad (2)
\]

\[
\text{Pd}^{n+} + \text{Cl} \cdots \text{CCl}_3 \rightarrow [\text{Cl}−\text{Pd}]^{n+} + \text{*CCl}_3 \quad (3)
\]

\[
\text{H}−\text{Pd}^0 + \text{*CCl}_3 \rightarrow \text{CHCl}_3 + \text{Pd}^0 \quad (4)
\]

As shown in Eqs. 2 and 3, Pd\(^0\) adsorbs H\(_2\) and dissociates into adatom H\(^−\)Pd\(^0\), while TTCM adsorbs on a single Pd\(^n+\) site. As shown in Eqs. 4 and 5, the adsorbed TTCM is hydrogenated to form chloroform. Cl\(^−\) is rapidly and gradually replaced by hydrogen atoms to form HCl.

This synergistic mechanism has also been reported in other literature \([30]\). A truly continuous process in which the adsorbed phases on the same active center occur via a “rake” mechanism is considered a synergistic mechanism \([31]\). Therefore, the high selectivity of chloroform can be understood as the high selectivity of Pd\(^{n+}\) to chloroform radicals.

\[
[\text{Cl}−\text{Pd}]^{n+} + \text{H}−\text{Pd}^0 \rightarrow \text{HCl} + \text{Pd}^{n+} + \text{Pd}^0 \quad (5)
\]

The second step of the reaction is the adsorption of chloroform and hydrogen on the catalyst surface. The chloroform generated by the first-step reaction regenerates the activation center and reacts with H−Pd\(^0\) to form dichloromethane, as shown in Eqs. 6 and 7. But in the reaction from chloroform to dichloromethane, the energy required to remove one chlorine atom increased from 285.9 to 349.0 kJ\(\cdot\)mol\(^−1\) \([32]\). Therefore, the difficulty of generating dichloromethane increases. It is proved by experiments that the selectivity of dichloromethane

| Reduction temperature (K) | \(\text{Pd}^0/\text{Pd}^{n+}\) | \(S_{\text{TCM}}\) (%) |
|--------------------------|-----------------|------------------|
| 523                      | 0.01            | 80.65            |
| 573                      | 0.35            | 82.96            |
| 773                      | 0.98            | 85.23            |
| 973                      | 2.96            | 81.63            |

Note: catalyst, 1.0 Pd/3DGNs; reaction temperature, 398 K; and hydrogen pressure, 3 MPa. \(S_{\text{TCM}}\) indicates chloroform selectivity.
increases with the increase in reaction temperature. The reason is that the temperature increase promotes the reaction (Eq. 6). Therefore, the concentration of dichloromethane increases. It can be seen that the formation of dichloromethane is due to the adsorption and dissociation of a small part of chloroform on the Pd/3DGN catalyst. Therefore, in order to improve the selectivity of chloroform, the reaction temperature should be in a moderate range.

4 Conclusion

In this study, a 3DGN catalyst carrier was successfully synthesized. The support has a larger specific surface area and porous structure to provide more active sites with a higher degree of graphitization. The palladium metal is more fully and stably attached to the surface of the carrier. The TEM and SEM results show that 3DGNs as metal particles. The results showed that the selectivity of TTCM to chloroform was higher at a Pd loading of 1.0 wt%, a reduction temperature of 773 K, and a hydrochlorination reaction temperature of 398 K. The main by-product of the reaction is methane chloride. The higher the reaction temperature, the higher the dichloromethane content as a by-product and the lower the selectivity of chloroform, but it always remained above 80%.

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