Catalytic Dechlorination of Carbon Tetrachloride in Liquid Phase with Methanol as H-Donor Over Ag/C Catalyst

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Catalytic hydrodechlorination of carbon tetrachloride (CCl₄) is an effective measure to remove CCl₄ due to its pollutant character. The dechlorination of CCl₄ to dichloromethane (CH₂Cl₂) and chloroform (CHCl₃) with a molar ratio of 3:2 was catalyzed by carbon-supported silver (Ag/C) catalyst in methanol solution. It was proposed from the catalytic results and characterization (X-ray diffraction, transmission electron microscopy and X-ray photoelectron spectroscopy) data that, the chloride ion is abstracted from adsorbed CCl₄ by Ag to form CCl₃ and CCl₂ radicals and silver chloride (AgCl), and meanwhile the dehydrogenation of methanol over Ag domains intrigues initial active Ag–H species and formaldehyde (HCHO); then the CCl₃ and CCl₂ radicals are combined with Ag–H to generate reaction products (CHCl₃ and CH₂Cl₂) and Ag, and the dehydrogenated product HCHO facilitates the regeneration of formed AgCl to Ag with formation of carbon monoxide and hydrogen chloride. The catalyst can be recovered and recycled, and there was no significant decrease in catalytic activity and selectivity after 4th recycling.

Keywords: Dechlorination, Carbon Tetrachloride, Ag/C Catalyst, Methanol, Ag Nanoparticles, Reaction Mechanism.

1. INTRODUCTION

Carbon tetrachloride (CCl₄) has been catalogued as group IV material and banned due to its potential ozone layer depletion. Catalytic hydrodechlorination of CCl₄ using supported or unsupported metal catalysts (Pt, Pd, Ni, Cu, Fe, Co, etc.) in gas phase has been intensively exploited to avoid the conventional expensive and polluting combustion process for its elimination.¹ Conversion of CCl₄ in liquid phase with bubble slurry reactor has been proved more advantageous than gaseous phase because of its high hydrophobicity, high heat capacity and low vapour pressure, and its easy fouling on the catalytic active sites causing rapid deactivation.^{2,3}

Here, we report the dechlorination of CCl₄ in liquid phase with sole supported silver (Ag) catalyst to the dechlorinated products (dichloromethane and chloroform) by the combination of methanol decomposition.

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2. EXPERIMENTAL DETAILS

2.1. Catalyst Preparation

The activated carbon (420–840 μm, Sinopharm Chemical Reagent Co., Ltd.) was washed by refluxing in nitric acid (1 mol/L) for 3 h prior to use, followed by drying in static air at 393 K overnight. The catalyst was prepared by incipient wetness impregnation of aqueous silver nitrate (AgNO₃) solution onto activated carbon support with the Ag content of 8 wt.%, followed by drying at 393 K for 12 h and reduction at 673 K in flowing hydrogen (H₂, 25 ml min^{−1}) for 3 h. The catalyst was hereafter abbreviated as Ag/C catalyst.

2.2. Catalyst Characterization

X-ray diffraction (XRD) patterns were obtained with a Rigaku D/MAX 2500 diffractometer with Cu Kα radiation. The particle size was calculated from Scherrer equation: $\tau = (K\lambda)/(\beta \cos \theta)$, where τ is the mean size of the ordered (crystalline) domains, K is the shape factor,

λ is the X-ray wavelength, β is the full width at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. Transmission electron microscopy (TEM) images were recorded on a JEM 2100 electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. The sample was ultrasonicated for 5 min in ethanol before the TEM measurement. Nitrogen sorption was determined at 77 K on a Micromeritics ASAP 2400 system in static measurement mode. The samples were outgassed at 673 K for 8 h prior to the sorption measurements. The total surface area (S_{BET}) and total pore volume (V_{total}) were calculated by the Brunauer–Emmett–Teller (BET) model and the Barrett–Joyner–Halenda (BJH) method, respectively. X-ray photoelectron spectroscopy (XPS) spectra of the samples were recorded at room temperature using a Thermo-Multilab2000 system with Mg-K α radiation. The C(1s) line at 284.6 eV was taken as a reference for binding energy (BE) calibration.

2.3. Dechlorination of CCl₄

The dechlorination of CCl₄ was conducted in a teflon-lined autoclave (100 ml) at 403 K. Typically, 5 ml of CCl₄ (Sinopharm Chemical Reagent Co., Ltd., AR), 25 ml of methanol (CH₃OH, Sinopharm Chemical Reagent Co., Ltd., AR) and 0.3 g catalyst were first loaded into the autoclave, followed by purging with nitrogen (N₂, Tianhong Chemical Industrial Co., Ltd., $\geq 99.9\%$) for 3 times. The reactor was then charged with 1.0 MPa nitrogen, followed by temperature increasing to 403 K. Liquid samples were collected at interval of 1–2 h and analyzed by a Varian CP-3800 gas chromatograph equipped with a FID detector and a SE-30 capillary column (30 m $\times$ 0.53 mm).

The conversion of CCl₄ and selectivities to chloroform (CHCl₃) and dichloromethane (CH₂Cl₂) were calculated as follows:

$$X_{\text{CCl}_4} (\%) = \left(1 - \frac{C_{\text{mol,CCl}_4}}{C_{\text{mol,CCl}_4} + C_{\text{mol,CHCl}_3} + C_{\text{mol,CH}_2\text{Cl}_2}} \right) \times 100$$

$$S_{\text{CHCl}_3} (\%) = \left(\frac{C_{\text{mol,CHCl}_3}}{C_{\text{mol,CHCl}_3} + C_{\text{mol,CH}_2\text{Cl}_2}} \right) \times 100$$

$$S_{\text{CH}_2\text{Cl}_2} (\%) = \left(\frac{C_{\text{mol,CH}_2\text{Cl}_2}}{C_{\text{mol,CHCl}_3} + C_{\text{mol,CH}_2\text{Cl}_2}} \right) \times 100$$

where $C_{\text{mol,CCl}_4}$, $C_{\text{mol,CHCl}_3}$ and $C_{\text{mol,CH}_2\text{Cl}_2}$ are the molar fractions of CCl₄, CHCl₃ and CH₂Cl₂ in liquid phase, respectively; X_{CCl_4} is the conversion of CCl₄, and S_{CHCl_3} and $S_{\text{CH}_2\text{Cl}_2}$ are the selectivities to CHCl₃ and CH₂Cl₂, respectively.

2.4. Recycling Test

The used catalyst was filtrated and then charged into an autoclave with additional 3 wt.% fresh Ag/C catalyst after each catalytic cycle (in order to compensate the loss of the used catalyst during the process of filtration and collection). 5 ml of CCl₄ and 25 ml of CH₃OH were then

loaded into the autoclave, followed by purging with N₂ for 3 times. The reactor was then charged with 1.0 MPa N₂, followed by temperature increasing to 403 K. Liquid samples were collected at interval of 1–2 h and analyzed by a Varian CP-3800 gas chromatograph equipped with a FID detector and a SE-30 capillary column (30 m $\times$ 0.53 mm).

3. RESULTS AND DISCUSSION

3.1. Characterization of Samples

The Ag/C catalyst with Ag loading of 8 wt.% was prepared by incipient wetness impregnation method. Briefly, AgNO₃ solution was added onto acid-washed activated carbon support, followed by drying and reduction with flowing hydrogen. The surface area and the pore volume of prepared catalyst are 924 m² g^{−1} and 0.45 ml g^{−1}, respectively, indicating the intact of support textural structure after Ag loading by comparison with activated carbon support with BET surface area of 1025 m² g^{−1} and pore volume of 0.49 ml g^{−1} (Table I). The XRD pattern of fresh catalyst (Fig. 1) indicates that Ag in the prepared catalyst is in metal form with particle size of 21 nm, calculated from Scherrer equation.

3.2. Dechlorination of CCl₄

The conversion of dechlorination of CCl₄ with Ag/C catalyst in methanol solution was measured in a teflon-line autoclave purged with N₂ and compressed with 1.0 MPa N₂. Samples were taken at an interval of 1–2 h, and analyzed with gas chromatography. Figure 2 shows the conversion of CCl₄ and selectivities to CH₂Cl₂ and CHCl₃ over Ag/C at 403 K. The conversion of CCl₄ increased with reaction time and selectivities to CH₂Cl₂ (60 mol%) and CHCl₃ (40 mol%) were kept nearly constant at all reaction time, indicating the independent formation pathways of CH₂Cl₂ and CHCl₃ from CCl₄, and the marginal contribution of consecutive reactions. Moreover, the direct formation of adsorbed: CCl₂ carbene during adsorption of CCl₄ onto Ag domains has been proved previously,⁴ which can be converted to CH₂Cl₂ by combination of active hydrogen species followed by desorption. The robustness of self-prepared Ag/C catalyst for the dechlorination of CCl₄ was examined by recycling the used catalyst, no significant decrease in catalytic activity and selectivity changes were observed after 4th recycling (Fig. 3).

It is well known that Ag catalyst can catalyze selective oxidation of ethylene to ethylene oxide and methanol to formaldehyde.⁵ Moreover, dihydrogen can be activated by Ag catalyst to form Ag–H species.^{6,7} Montoya et al.

Table I. Textural properties of activated carbon and Ag/C catalyst.

Sample	S_{BET} (m ² g ^{−1})	V_{total} (ml g ^{−1})
Activated carbon	1025	0.49
Fresh Ag/C catalyst	924	0.45

Figure 1. XRD patterns of (a) fresh Ag/C catalyst, (b) used Ag/C catalyst, (c) fresh Ag/C catalyst after reaction with 5 μl of CCl_4 for 0.5 h, and (d) fresh Ag/C catalyst after reaction with 10 μl of CCl_4 for 0.5 h.

reported that silver can catalyze dehydrogenation of alcohols in the absence of oxygen with formation of aldehydes.⁸ It was also reported that Ag is able to adsorb the chlorinated molecules such as chloromethane (CH_3Cl),⁹ CCl_4 ,¹⁰ and 1,2-dichloroethane¹¹ and break the C—Cl bond. Here, we speculate that applied methanol in CCl_4 dechlorination acts as not merely a solvent, but also a hydrogen providing reactant with the formation of active Ag—H species via dehydrogenation catalyzed by Ag catalyst with the formation of formaldehyde. The direct formation of formaldehyde from

Figure 2. Conversion of CCl_4 (●) and selectivities of CH_2Cl_2 (◆) and CHCl_3 (▲) on Ag/C catalyst (Reaction conditions: 0.3 g of catalyst, 5 ml of CCl_4 , 25 ml of CH_3OH , 1.0 MPa N_2 , 403 K).

Figure 3. Conversion of CCl_4 on Ag/C catalyst for the first run (●) and the fourth run (◆) (Reaction conditions: 0.3 g of catalyst, 5 ml of CCl_4 , 25 ml of CH_3OH , 1.0 MPa N_2 , 403 K).

adsorbed methoxide on Ag has been observed during temperature programmed desorption (TPD) at relatively low temperatures, i.e., 290 K.^{12,13} The hydrogen atoms will be converted to water or active hydrogen followed by desorption as H_2 regarding the reaction conditions.

3.3. Catalyst Changes After the Dechlorination of CCl_4

The XRD pattern of used Ag/C catalyst (Fig. 1) indicates that Ag phase was partially converted to silver chloride (AgCl) phase during catalyzing the dechlorination of CCl_4 . The particle size of AgCl phase in the used catalyst was 54 nm, calculated from Scherrer equation, which is consistent with TEM images of fresh and used catalysts (Fig. 4). The particle size increasing would be related to the densities of Ag (10.5 g cm^{-3}) and AgCl (5.6 g cm^{-3}), as

Figure 4. TEM images (left) and XPS (right) of (a) fresh Ag/C catalyst and (b), (c) used Ag/C catalyst.

Table II. Particle size of catalyst calculated from Scherrer equation.

Sample	<i>D</i> (nm)
Fresh Ag/C catalyst	21
Used Ag/C catalyst	54
Fresh Ag/C catalyst after reaction with 5 μ l of CCl ₄ for 0.5 h	41
Fresh Ag/C catalyst after reaction with 10 μ l of CCl ₄ for 0.5 h	47

Figure 5. Reaction scheme for dechlorination of CCl₄ by supported silver catalyst in the presence of methanol.

well as the incorporation of chloride ion (Cl^-) into the Ag domains. The rapid transformation of Ag to AgCl during the reaction was also illustrated by adding trace amounts of CCl₄ (5 and 10 μ l, respectively) into the reactor and reacting for 0.5 h, also shown in Figure 1. The AgCl particle size increases with CCl₄ amount monotonously (41 nm for 5 μ l of CCl₄ added and 47 nm for 10 μ l, Table II), indicating the incorporation of Cl^- into the Ag particles. The certain degree of aggregation of Ag particles was found in the used catalyst (Fig. 4(c)), implying the weak interaction of Ag domains with activated carbon support. But no very large Ag particles were observed, indicating the sintering of Ag did not occur during the reaction, evidenced from the identical performance of recycled catalysts. The chemical states of surface silver species of used Ag/C catalyst were determined by XPS,^{14,15} calibrated with C1s (284.6 eV). The XPS of used catalyst (Fig. 4) clearly shows that the coexistence of Ag and Ag^{1+} at the outer sphere of the reacted Ag particles, indicating the reduction of AgCl by formaldehyde (HCHO) with formation of carbon monoxide (CO) and hydrogen chloride (HCl), at elevated temperatures.

3.4. Reaction Mechanism

Here, we propose a plausible reaction mechanism for the dechlorination of CCl₄ over sole Ag catalysts with methanol as hydrogen donor, involving the dehydrogenation of methanol to formaldehyde with the formation of Ag–H active species and the abstraction of Cl^- from adsorbed CCl₄ by Ag to form CCl₃ and CCl₂ radicals, combined with Ag–H to generate reaction products, CHCl₃ and CH₂Cl₂. The regeneration of Ag from AgCl would be related to the HCHO intermediate (Fig. 5).

4. CONCLUSION

In summary, we reported here an efficient catalytic process for the dechlorination of CCl₄ to CH₂Cl₂ and CHCl₃ in liquid phase over sole silver catalysts, where methanol is taken as H-donor, and its dehydrogenated product, formaldehyde, facilitates the regeneration of formed AgCl to Ag.

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