Acetylene hydrochlorination over tin nitrogen based catalysts: effect of nitrogen carbon-dots as nitrogen precursor

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Abstract: The catalysts comprising the main active compounds of Sn-N were synthesized using trichlorophenylstannane ((C₆H₅)ClSn), nitrogen carbon-dots (NCDs), and activated carbon (AC) as starting materials, and the activity and stability of catalysts was evaluated in the acetylene hydrochlorination. According to the results on the physical and chemical properties of catalysts (TEM, XRD, BET, XPS and TG), it is concluded that NCDs@AC can increase (C₆H₅)ClSn dispersity, retard the coke deposition of (C₆H₅)ClSn/AC and lessen the loss of (C₆H₅)ClSn, thereby further promoting the stability of (C₆H₅)ClSn/AC. Based on the characterization results of C₆H₅Sn-TPD and HCl adsorption experiments, we proposed that the existence of Sn-N can effectively strengthen the reactants adsorption of catalysts. By combing the FT-IR, C₆H₅-TPD and Rideal-Eley mechanism, the catalytic mechanism, in which C₆H₅ is firstly adsorbed on (C₆H₅)ClSn to form (C₆H₅)ClSn-Cl-C₆H₅ and then reacted with HCl to produce vinyl chloride, is proposed.

Key words: Trichlorophenylstannane, nitrogen carbon-dots, vinyl chloride, acetylene hydrochlorination

1. Introduction

Organotin compounds (OTCs), as one of organometallic compounds [1], have been widely applied to many areas, encompassing anticancer therapy [2–4], biocides [5], stabilizer [6], and catalysts [7–11]. Currently, scientists have proved that alkyl-organotin not only can be used as stabilizer in polymerization vinyl chloride fabrication (PVC) but also can catalyze acetylene hydrochlorination to manufacture vinyl chloride [6,11,12]. The production of PVC in many regions mainly depends on the carbon-supported HgCl₂ catalytic acetylene hydrochlorination reaction [13]. However, the prevention and governance of mercury pollution is still a serious problem around the world [14,15]. Therefore, the nonmercuric catalytic acetylene hydrochlorination process for PVC production need to be urgently explored.

Great attentions have been paid to study the tin-based catalysts in the hydrochlorination of acetylene, especially inorganic tin in the past few years. Researchers founded that metal compounds additives, including BiCl₃, ZnCl₂, CuCl₂, CeCl₃, CoCl₂ and LiCl [21] can effectively improve the stability of inorganic tin-based catalysts. Basing from the study by Deng reported that the deactivation of SnCl₃/AC catalysts for acetylene hydrochlorination is due to the high volatility of SnCl₃ [16]. Gao et al. reported that the CoCl₂ and BiCl₃ promoters can effectively lessen the coking formation of SnCl₃/AC in acetylene hydrochlorination and improve the stability of SnCl₃/AC catalysts [17]. Although SnCl₃/AC can rival the catalytic activity of Hg-based catalysts, the key scientific and technological issue of SnCl₃/AC catalysts is to improve its stability [16]. Later on, Guo et al. founded that the synergistic effect of SnCl₃-ZnCl₂ and Tb₂O₃ can strengthen the catalytic performance of SnCl₃/AC in the hydrochlorination of acetylene [20]. In our previous work, we reported that LiCl-promoted SnCl₃ catalysing acetylene hydrochlorination with considerable stability, originating from the synergistic effect between Sn and Li [21]. Moreover, organotin catalysts, as another kind of tin-based catalysts in acetylene hydrochlorination, have been studied [11,12,22]. There is no research regarding the catalytic mechanism of organotin as catalysts for acetylene hydrochlorination.

Owing to the specified electronic properties and unique chemical characteristics, a series of nitrogen-doped carbon materials as catalyst carries is grabbing more attention in acetylene hydrochlorination [23–25]. For example, Dai et al. synthesized g-C₃N₄/AC as a novel nonmetallic catalyst, which can catalyze acetylene to produce vinyl chloride [23].

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Afterward, scientists reported that the coexistence of pyridinic nitrogen and pyrrolic nitrogen in nitrogen-doped carbons could strengthen the adsorption of the reactants [24]. Furthermore, Li et al. studied that the enhancement of AuCl$_2$/PPy-MWCNT catalytic performance was due to the electron transfer from N atom in PPy to the Au$^{3+}$ and, thus, improve the hydrogen chloride adsorption [25].

In this paper, nitrogen-carbon quantum dots (NCDs) with distinctive physical and chemical properties [26–30] is used as nitrogen sources in the preparation of tin nitrogen based acetylene hydrochlorination catalysts. Specifically, the aims of this work are to study the effect of NCDs on the performance of (C$_5$H$_5$)$_2$Sn-based catalysts for acetylene hydrochlorination and the catalytic mechanism of (C$_5$H$_5$)$_2$Sn/AC in acetylene hydrochlorination.

2. Materials and methods

2.1. Materials

Coal-based activated carbon (φ=1.5 mm, l=5 mm) was obtained from Shanxi Xinhua Chemical Company. Trichlorophenylstannane (98.0%) was purchased from TCI (Shanghai) Development Co., Ltd. Citric acid (99.5%), urea (99.0%), ammonium hydroxide (25–28%), and ethanol (99.5%) were obtained from Tianjin Kermel Technology Development Co., Ltd.

2.2. Catalyst preparation

2.2.1. Preparation of NCDs

N-doped carbon quantum dots (NCDs) were prepared by citric acid and urea [31,32]. Specifically, citric acid (2.0 g) and urea (2.0 g) were dissolved in distilled water (15 mL). Then, the mixture was transferred to a Teflon coated stainless-steel autoclave and heated at 160 °C for 7 h. Afterward, the obtained NCDs solution was mixed with ethanol and centrifuged at 8000 rpm for 20 min. Finally, the samples were dried overnight at 80 °C to obtain the purified NCDs powders.

2.2.2. Preparation of NCDs@AC

NCDs (1.0 g), AC (9.0 g) and ammonium hydroxide was mixed in deionized water (20 mL), and the mixture was stirred at a room temperature for 30 min. Then, the mixture was transferred to a Teflon coated stainless-steel autoclave and heated at 200 °C for 8 h. The obtained samples was washed by deionized water and dried at 100 °C overnight. The final solid sample was labeled as NCDs@AC. Carbon support was pretreated by the same procedure, and the obtained carbon sample was denoted as AC.

2.2.3. Preparation of (C$_5$H$_5$)$_2$Sn-based catalysts

(C$_5$H$_5$)$_2$Sn/NCDs@AC was synthesized using NCDs@AC as support and (C$_5$H$_5$)$_2$Sn as active compounds, respectively. Specifically, (C$_5$H$_5$)$_2$Sn (1.5 g) was dissolved in the appropriate amount of ethanol, and then this impregnation solution was slowly added to NCDs@AC (8.5 g). The obtained heterogeneous solid was dried at 80 °C to get 15%(C$_5$H$_5$)$_2$Sn/NCDs@AC. The similar procedure was repeated to prepare the (C$_5$H$_5$)$_2$Sn/AC catalysts for comparisons.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were carried out on Shimadzu XRD-6000 with Cu Ka radiation (0.15418 nm). All samples were taken at range of 10–80°. Catalysts were degassed at 150 °C for 4 h, before the nitrogen adsorption/ desorption isotherms at –196 °C were analyzed using Quantachrome NOVA 2000e. Fourier transform infrared (FT-IR) spectra were recorded by a Biorad Excalibur FTS 3000 equipped with a DTGS detector. Transmission electron microscopy (TEM) was performed on JEM-2100F instruments at an acceleration voltage of 200 kV, used to study the dispersion of Sn species, and it characterized the morphology of Sn-based catalysts. X-ray photoelectron spectroscopy (XPS) was conducted on EscaLab 250Xi instruments using Al Ka X-ray source and analyzed the valence of element on the surface of support. The spectra were analyzed using XPSPEAK software pack and corrected for changing in using C1s binding energy (BE) as the reference at 284.8eV. Acetylene-temperature programmed desorption (C$_2$H$_2$-TPD) measurements were performed on a FINESORB-3010 chemisorption analyzer. Briefly, the samples (50 mg) were first treated with Ar gas at 200 °C for 1.5 h. After cooling, it was continually flushed with a C$_2$H$_2$ flowing at a rate of 25 mL·min$^{-1}$ and heated from room temperature to 500 °C at a heating rate of 10 °C·min$^{-1}$. The coke deposition of spent catalysts were determined by thermogravimetric (TG) instruments (NETZSCH STA 449F3) over the temperature from atmosphere temperature to 800 °C at a heating rate of 15 °C·min$^{-1}$ and an air flow rate of 30 mL·min$^{-1}$. HCl adsorption experiments were analyzed by titration method [22].

2.4. Catalyst tests

The hydrochlorination of acetylene tested in the fixed-bed micro-reactor (i.d.10 mm). The reaction temperature was regulated using a temperature controller (Yudian Al-808H). When the reactor temperature initially was maintained at 180 °C, the hydrogen chloride firstly fed into the reactor containing 4 mL catalysts to get rid of moistures and air in reaction
system for 30 min. The mole ratio of \( \text{C}_2\text{H}_2/\text{HCl}=1.0:1.1 \) was calibrated by mass flow controller with a given \( \text{C}_2\text{H}_2 \)-GHSV of 30 h\(^{-1} \). Then, the product mixture gas was getting through the medical soda lime to remove the unreacted hydrogen chloride. The final product gas was analyzed by an online gas chromatograph (GC900) using TCD as the detector for gas chromatograph, which equipped with a packed column (GDX301).

3. Results and discussion

3.1. Physicochemical properties of NCDs

Figure 1a shows that the XRD patterns of NCDs displays a broad peak at 23.8°, suggesting that NCDs is mainly composed of amorphous carbon [33–35]. Figure 1b shows the FT-IR spectra of NCDs, with four characteristic peaks at 3195, 3055, 1651 and 1567 cm\(^{-1} \) inferring the bonding formation of -CO-NH- [26]. The composition of NCDs was studied by XPS. The full scan spectra of XPS confirm the existence of C, N and O in NCDs (Figure 1c). The high-resolution N \(_1\)s is depicted in Figure 1d, three peaks at 399.6 eV, 400.5 eV and 401.7 eV that commonly correspond to C-N-C, N-(C)\(_2\) and N-H, respectively [27,36] (Figure 1e). In the XPS-C\(_{1s}\) spectra of NCDs, the deconvoluted three peaks at 284.5 eV, 286.0 eV, and 288.4 eV can be assigned to C=C, C-N, and N-C=N, respectively [26,36]. Moreover, two types oxygen species at 531.8 eV (C=O) and 533.3 eV (C-OH/C-O-C) are observed in the sample (Figure 1f) [36,37]. Based on both FTIR and XPS results, the successful synthesis of NCDs was confirmed.

3.2. Catalytic performance

The effect of NCDs on the performances of \((\text{C}_2\text{H}_2\text{Cl})\text{Sn/AC}\) catalysts was evaluated at a temperature of 180 °C with \( \text{C}_2\text{H}_2 \)-GHSV of 30 h\(^{-1} \), and the results is displayed in Figure 2a. The acetylene conversion of \(5\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/NCDs@AC}\), \(10\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/NCDs@AC}\), \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/NCDs@AC}\), and \(20\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/NCDs@AC}\) are 78.2%, 88.5%, 92.5%, and 87.3%, respectively, and \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/NCDs@AC}\) with highest acetylene conversion (92.5%) was selected for the following studies. The acetylene conversion of \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/NCDs@AC}\) and \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/AC}\) (90.2%) are similar, which prove that NCDs exhibits a little effect on the catalytic activity of \((\text{C}_2\text{H}_2\text{Cl})\text{Sn/AC}\). Comparing with \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/AC}\) (90.2%), only 8.9% \( \text{C}_2\text{H}_2 \) has been transformed to vinyl chloride over AC and NCDs@AC features 17.9% acetylene conversion, suggesting that \((\text{C}_2\text{H}_2\text{Cl})\text{Sn}\) can catalyze the acetylene hydrochlorination to generate vinyl chloride and NCDs doped-AC can enhance the catalytic performance of AC. At the same time, the VCM selectivity of five catalysts decrease in the following order: \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/NCDs@AC}\) (98.5%) > \(\text{NCDs@AC}\) (78.8%) > \(\text{AC}\) (76.5%) (Figure 2b). Experiments show that the higher VCM selectivity of catalysts is mainly attributed to the \((\text{C}_2\text{H}_2\text{Cl})\text{Sn}\).

As shown in Figure 2c, \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/NCDs@AC}\) features stable catalytic performance at first 12 h of the reaction. After 40 h since the reaction started, the acetylene conversion of \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/NCDs@AC}\) gradually decreases from 92.5% to 59.2%. However, \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/AC}\) reaches the acetylene conversion of 90.2% and then reduced by 66.1% 40 h after reaction. Furthermore, it is concluded that NCDs additives can prolong the lifetime of \((\text{C}_2\text{H}_2\text{Cl})\text{Sn/AC}\) catalysts for acetylene hydrochlorination. Figure 2d shows that the deactivation rate of \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/AC}\) (1.65 %•h\(^{-1} \)) is higher than that of \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/NCDs@AC}\) (0.82 %•h\(^{-1} \)), indirectly proving the above-mentioned conclusion.

3.3. Physical properties of catalysts

The specific surface area, pore volume, and pore size distribution of catalysts were analyzed by the nitrogen adsorption/desorption experiments. According to IUPAC classification (Figure 3a), all catalysts display the type-I langmuir isotherms and type H \(_4\) loop, which suggests the coexistence of micro- and mesopores in samples. This result is in compliance with the pore size distribution curves (Figure 3b). As listed in Table 1, the specific surface area of NCDs@AC, \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/AC}\) and \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/NCDs@AC}\) is 798 cm\(^2\) g\(^{-1} \), 712 cm\(^2\) g\(^{-1} \) and 631 cm\(^2\) g\(^{-1} \), respectively, which are all lower than that of AC (983 cm\(^2\) g\(^{-1} \)), indicating that additives successfully loaded into carbon support. As can be seen in Figure 3c, the two obvious diffraction peaks at 26.4 and 44.4 ° correspond to the (002) and (101) crystal planes of AC (PDF#41-1487), respectively [38]. However, there are no other discernible peaks in \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/NCDs@AC}\), inferring that \((\text{C}_2\text{H}_2\text{Cl})\text{Sn}\) homogeneously dispersed on the NCDs@AC surface [39]. We analyzed the \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/NCDs@AC}\) and \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/AC}\) through TEM images (Figure 3d and Figure 3e). As depicted in Figure 3d, \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/AC}\) has some black particles, which represent that \((\text{C}_2\text{H}_2\text{Cl})\text{Sn}\) dispersed on the carbon surface. In stark contrast, this phenomenon does not exist in \(15\%(\text{C}_2\text{H}_2\text{Cl})\text{Sn/NCDs@AC}\) surface. This result suggests that NCDs@AC carrier can promote the better dispersion of \((\text{C}_2\text{H}_2\text{Cl})\text{Sn}\).

3.4. Chemical properties of catalysts

The surface element composition of catalysts and the chemical effect of NCDs on \((\text{C}_2\text{H}_2\text{Cl})\text{Sn}\) were investigated by XPS techniques. To be specific, Figure 4a and Table 2 prove that the element of Sn, N, C and O exist in four \((\text{C}_2\text{H}_2\text{Cl})\text{Sn}\)-based catalysts.

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Figure 1. (a) XRD patterns of NCDs, (b) FTIR spectra of NCDs, (c) XPS patterns of NCDs, (d) High resolution XPS-C$_{1s}$ spectra of NCDs, (e) High resolution XPS-N$_{1s}$ spectra of NCDs, (f) High resolution XPS-O$_{1s}$ spectra of NCDs.
As shown in Figure 4b, the high resolution Sn$_{3d5/2}$ spectrum of 15%($C_6H_5$)$_3$Cl$_2$Sn/AC reaches two peaks at 485.5 eV and 486.9 eV, which are related to the presence of Sn-C and Sn-O, respectively [40–43]. However, the high resolution Sn$_{3d5/2}$ spectrum in the case of 15%($C_6H_5$)$_3$Cl$_2$Sn/NCDs@AC (Figure 4c) can be deconvoluted into three individual peaks corresponding to Sn-O (486.9 eV), Sn-C (485.5 eV) and Sn-N$_x$ (486.0~486.8 eV) [42-45], confirming that the presence of Sn-N$_x$ in catalysts is due to the interaction between ($C_6H_5$)$_3$Cl$_2$Sn and NCDs.

Because a number of oxygen-containing functional groups on the AC and NCDs surface are able to react with NH$_3$ under 200 ºC [46], fresh-15%($C_6H_5$)$_3$Cl$_2$Sn/NCDs@AC (10.75 wt.% surface) has the lower oxygen element content than that of fresh-15%($C_6H_5$)$_3$Cl$_2$Sn/AC (12.03 wt.%) (Table 2). However, in the catalytic acetylene hydrochlorination reaction, the reason of Sn-O in ($C_6H_5$)$_3$Cl$_2$Sn-based catalysts reacting with HCl may be to generate SnCl$_4$, which easily sublimes at 180 ºC, resulting in the loss of Sn species (Table 3). As listed in Table 2, the Sn content in ($C_6H_5$)$_3$Cl$_2$Sn/AC decreased from 5.65 to 1.17 wt.% after 40 h of reaction. Interestingly, the only Sn amount of 2.92 wt.% was leached from 15%($C_6H_5$)$_3$Cl$_2$Sn/NCDs@AC. Additionally, the Sn-N$_x$ content in the case of 15%($C_6H_5$)$_3$Cl$_2$Sn/NCDs@AC is reduced by 1.09 wt.% after 40 h (Table 4). The above analysis indicated that Sn-N$_x$ stabilizes the loss of Sn species during the reaction (Figure 2c).

### 3.4.2. N$_1s$

It can be seen in Figure 4d that there are four fitted peaks (C-N-C (399.6 eV), N-(C)$_3$ (400.5 eV), N-H (401.7 eV) and N$_x$-Sn (397.7 eV)), in the N1s spectra of 15%($C_6H_5$)$_3$Cl$_2$Sn/NCDs@AC [26,38,45], which represents that NCDs successfully dispersed on AC surface and also prove the existence of Sn-N$_x$. 

![Figure 2](image-url)
The effect of NCDs on the reactants adsorption of (C₆H₅)Cl₃Sn-based catalysts was investigated by C₂H₂-TPD and hydrogen chloride adsorption/desorption experiments, respectively. The acetylene adsorption amounts of four catalysts are as follows: 15%(C₆H₅)Cl₃Sn/NCDs@AC > 15%(C₆H₅)Cl₃Sn/AC > NCDs@AC > AC (Figure 5a). Particularly, 15%(C₆H₅)Cl₃Sn/AC shows the stronger acetylene adsorption ability than that of AC. This implies that (C₆H₅)Cl₃Sn displays a key role...
in acetylene adsorption. As illustrated in Figure 5b, 15%(C_6H_5)Cl_3Sn/NCDs@AC, 15%(C_6H_5)Cl_3Sn/AC, NCDs@AC, and AC feature the hydrogen chloride adsorption amount of 0.23 mmol·g\(^{-1}\), 0.21 mmol·g\(^{-1}\), 0.19 mmol·g\(^{-1}\) and 0.18 mmol·g\(^{-1}\), respectively (Table 5, 6, 7, 8). Compared to bare AC, the higher content of Pyridine N in NCDs@AC plays a key role on the hydrogen chloride adsorption [47,48]. Furthermore, the hydrogen chloride adsorption of 15%(C_6H_5)Cl_3Sn/NCDs@AC

Table 1. Texture parameters of catalysts and AC.

| Samples               | \(\text{BET}_{\text{total}}\) (cm\(^2\)·g\(^{-1}\)) | \(\text{BET}_{\text{meso}}\) (cm\(^2\)·g\(^{-1}\)) | \(\text{BET}_{\text{micro}}\) (cm\(^2\)·g\(^{-1}\)) | \(V_{\text{total}}\) (cm\(^3\)·g\(^{-1}\)) | \(D\) (nm) |
|-----------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-------------|
| AC                    | 983                                           | 129                                           | 854                                           | 0.48                                          | 1.90        |
| NCDs@AC              | 798                                           | 89                                            | 709                                           | 0.41                                          | 1.92        |
| 15%(C_6H_5)Cl_3Sn/AC | 712                                           | 106                                           | 606                                           | 0.38                                          | 2.00        |
| 15%(C_6H_5)Cl_3Sn/NCDs@AC | 631                                         | 103                                           | 528                                           | 0.30                                          | 2.20        |

Figure 4. (a) XPS pattern of different catalysts, (b) High resolution XPS spectra of Sn3d\(_{5/2}\) in fresh- and used 15%(C_6H_5)Cl_3Sn/AC, (c) High resolution XPS spectra of Sn3d\(_{5/2}\) in fresh- and used 15%(C_6H_5)Cl_3Sn/NCDs@AC, (d) High resolution XPS spectra of N1s in fresh- and used 15%(C_6H_5)Cl_3Sn/NCDs@AC.
AC is higher than that of 15%(C₆H₅)Cl₃Sn/AC. It is indicated that NCDs additives can promote the hydrogen chloride adsorption of (C₆H₅)Cl₃Sn/NCDs@AC, as result of the coexistence of Sn-Nₓ and Pyridine N (Figure 5b and Figure 4).

### 3.5. Deactivation reason

The specific surface area of 15%(C₆H₅)Cl₃Sn/AC and 15%(C₆H₅)Cl₃Sn/10%NCDs@AC is reduced by 447 cm² g⁻¹ and 328 cm² g⁻¹ after 40 h of reaction, respectively (Table 9) indicates indirectly that coke deposition is one of deactivation reason of

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**Table 2. The relative contents of different elements in catalysts.**

| Sample                                | Elements (wt%) |
|---------------------------------------|----------------|
|                                        | Sn  | N   | C   | O   | Cl  |
| Fresh 15%(C₆H₅)Cl₃Sn/AC              | 5.65| 0.44| 77.84| 12.03 | 4.04 |
| Used 15%(C₆H₅)Cl₃Sn/AC               | 1.17| 0.58| 79.72| 11.48 | 7.05 |
| Fresh 15%(C₆H₅)Cl₃Sn/NCDs@AC         | 5.69| 2.36| 78.01| 10.75 | 3.19 |
| Used 15%(C₆H₅)Cl₃Sn/NCDs@AC          | 2.92| 2.04| 79.95| 11.02 | 4.07 |

**Table 3. The relative contents of Sn-O in catalysts.**

| Sample                                 | Total Sn-O content (wt%) | Loss (wt %) |
|----------------------------------------|--------------------------|-------------|
|                                        | Fresh  | Used | △Sn-O |
| 15%(C₆H₅)Cl₃Sn/AC                     | 1.45   | 0.30 | 1.15  |
| 15%(C₆H₅)Cl₃Sn/NCDs@AC                | 1.93   | 0.60 | 1.33  |

**Table 4. The relative contents of Sn-Nₓ in catalysts.**

| Sample                                 | Total Sn-Nₓ content (wt%) | Loss (wt %) |
|----------------------------------------|---------------------------|-------------|
|                                        | Fresh  | Used | △Sn-Nₓ |
| 15%(C₆H₅)Cl₃Sn/AC                     | --     | --   | --     |
| 15%(C₆H₅)Cl₃Sn/NCDs@AC                | 3.07   | 1.98 | 1.09   |

**Figure 5.** (a) C₂H₂-TPD of catalysts, (b) HCl adsorption of catalysts.
Table 5. The different parameter of 15%(C₆H₅)Cl₃Sn/NCDs@AC.

| Numbers | Na₂CO₃ (mL) | Adsorption volume (mL) | Catalysts (g) | HCl adsorption capacity (mmol g⁻¹) |
|---------|-------------|------------------------|---------------|----------------------------------|
| 1       | 10530       | 250                    | 3.51          | 0.24                             |
| 2       | 10033       | 250                    | 3.49          | 0.23                             |
| 3       | 9652        | 250                    | 3.51          | 0.22                             |
| 4       | 10063       | 250                    | 3.50          | 0.23                             |

Table 6. The different parameter of 15%(C₆H₅)Cl₃Sn/AC.

| Numbers | Na₂CO₃ (mL) | Adsorption volume (mL) | Catalysts (g) | HCl adsorption capacity (mmol g⁻¹) |
|---------|-------------|------------------------|---------------|----------------------------------|
| 1       | 8625        | 250                    | 3.45          | 0.20                             |
| 2       | 9004        | 250                    | 3.43          | 0.21                             |
| 3       | 9082        | 250                    | 3.46          | 0.21                             |
| 4       | 8600        | 250                    | 3.44          | 0.20                             |

Table 7. The different parameter of NCDs@AC.

| Numbers | Na₂CO₃ (mL) | Adsorption volume (mL) | Catalysts (g) | HCl adsorption capacity (mmol g⁻¹) |
|---------|-------------|------------------------|---------------|----------------------------------|
| 1       | 8075        | 250                    | 3.40          | 0.19                             |
| 2       | 8099        | 250                    | 3.41          | 0.19                             |
| 3       | 8550        | 250                    | 3.42          | 0.20                             |
| 4       | 7695        | 250                    | 3.42          | 0.18                             |

Table 8. The different parameter of AC.

| Numbers | Na₂CO₃ (mL) | Adsorption volume (mL) | Catalysts (g) | HCl adsorption capacity (mmol g⁻¹) |
|---------|-------------|------------------------|---------------|----------------------------------|
| 1       | 7203        | 250                    | 3.39          | 0.17                             |
| 2       | 7225        | 250                    | 3.40          | 0.17                             |
| 3       | 7456        | 250                    | 3.41          | 0.19                             |
| 4       | 7650        | 250                    | 3.40          | 0.18                             |

(C₆H₅)Cl₃Sn/AC in the hydrochlorination of acetylene [49]. Additionally, all the number of tin species in different catalysts decreased promptly in Table 1, which shows that another deactivation occurs from the loss of tin species.

3.6. Catalysis mechanism

The C₂H₂-TPD, FT-IR, HCl adsorption/desorption experiments and Rideal–Eley mechanism [50,51] were used to investigate the reaction mechanism of (C₆H₅)Cl₃Sn/AC in acetylene hydrochlorination. In addition, (C₆H₅)Cl₃Sn/AC was separately pretreated with HCl, C₂H₂ and N₂ at 180 °C for 1 h. Later on, (C₆H₅)Cl₃Sn/AC-HCl, (C₆H₅)Cl₃Sn/AC-C₂H₂, (C₆H₅)Cl₃Sn/AC-N₂ were characterized by FT-IR techniques. Both SnCl₄ and HCl as electron-acceptor do not react with each other [52], and (C₆H₅)Cl₃Sn is more inclined to adsorb acetylene rather than HCl (Figure 5a, b). The above-mentioned two points infer that (C₆H₅)Cl₃Sn prefers to interact with C₂H₂ in the catalytic acetylene hydrochlorination process. However, only one characteristic adsorption bands at ~1610 cm⁻¹ is observed in (C₆H₅)Cl₃Sn/AC-C₂H₂, suggesting
that the existence of -C=C- consequently infers the interaction between gaseous C\textsubscript{2}H\textsubscript{2} and (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn (Figure 6) [53,54]. This result suggests that the (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn does interact with C\textsubscript{2}H\textsubscript{2}, and (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn/AC-C\textsubscript{2}H\textsubscript{2} is transition state of (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn in catalysis acetylene hydrochlorination reaction and then adsorbs HCl to generate vinyl chloride. Based on the analysis of previous studies, the reactant adsorption ability of catalysts displays a vital in acetylene hydrochlorination, but strong C\textsubscript{2}H\textsubscript{2} adsorption may result in deactivation of the catalysts [55–57]. Accordingly, it is proposed that coke deposition is main deactivation reason for (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn-based catalysts in the hydrochlorination of acetylene. It can be seen from Figure 4b, the binding energy of the Sn-C (Sn3\textsubscript{d}5/2) in (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn/NCDs@AC is centered at 485.7 eV, but (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn/AC is located at 485.9 eV. This negative shift is due to Sn-N (Figure 4c). Significantly, this results promote the hydrogen chloride adsorption of (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn/NCDs@AC and, therefore, improve the catalytic performance of (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn-based catalysts in the acetylene hydrochlorination reaction.

4. Conclusion

In conclusion, (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn/AC can catalyze the acetylene hydrochlorination process. The intermolecular force between (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn and NCDs induces the formation of Sn-N\textsubscript{x}, which can promote the (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn dispersion, reduce the (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn loss and lessen coke deposition, leading to the longer lifetime of (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn/AC. According to the Rideal–Eley mechanism and experiments results, we proposed that the (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn/AC-C\textsubscript{2}H\textsubscript{2} indicates a transition state of (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn in catalysis of acetylene hydrochlorination reaction and then adsorbs HCl to generate vinyl chloride. Thus, it is showed that the main deactivation reason of (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn/AC is coke deposition during the acetylene hydrochlorination. This work provides a novel application of (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn and NCDs for further studies on the organotin-based catalysts for acetylene hydrochlorination.

Table 9. Specific surface area of fresh- and used catalysts.

| Sample                  | S\textsubscript{BET}(cm\textsuperscript{2}g\textsuperscript{-1}) | S\textsubscript{BET}(cm\textsuperscript{2}g\textsuperscript{-1}) |
|------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
|                        | fresh                          | used          | fresh          | used          |
| 15%(C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn/AC | 712                            | 265           | 447            |                |
| 15%(C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn/NCDs@AC | 631                            | 303           | 328            |                |

Figure 6. FTIR spectra of different (C\textsubscript{6}H\textsubscript{5})Cl\textsubscript{3}Sn/AC.
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