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The ligand coordination approach for improving the stability of low-mercury catalyst in the hydrochlorination of acetylene☆



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ABSTRACT

Mercuric chloride supported on activated carbon ($HgCl_2/AC$) is used as an industrial catalyst for the hydrochlorination of acetylene. Loss of $HgCl_2$ by sublimating from the surface of activated carbon causes the irreversible deactivation of mercury catalyst and environmental pollution. In this work, a ligand coordination approach based on the Principle of Hard and Soft Acids and Bases (HSAB) was employed to design more stable low-mercury catalyst. The low-mercury catalysts (4% $HgCl_2$ loading) were prepared by using $HgCl_2$ and potassium halides (KX , $X = Cl, I$) as precursors. The $HgCl_2-4KI/AC$ catalyst showed best catalytic stability than $HgCl_2/AC$ and $HgCl_2-4KCl/AC$ in the hydrochlorination of acetylene. $HgCl_2$ could form more stable complex with KI , K_2HgI_4 as the main active component of the $HgCl_2-4KI/AC$ catalyst. The characterizations of XRD and EDX analysis illustrated that the active component of $HgCl_2-4KI/AC$ was highly dispersed on the surface of activated carbon. The sublimation rates of $HgCl_2$ from the catalysts verified that the active component with larger stability constant had better thermal stability. Using $Hg(II)$ complexes with high stability constant as the active component may be the research direction of developing highly stable low-mercury catalyst for the hydrochlorination of acetylene. © 2017 The Chemical Industry and Engineering Society of China, and Chemical Industry Press. All rights reserved.

1. Introduction

Vinyl chloride monomer (VCM) is mainly used for the production of polyvinyl chloride (PVC), which is one of the five general resins and widely applied in the fields of industry, agriculture, and building materials [1]. Generally, VCM is industrially synthesized by the dehydrochlorination of dichloroethane or the hydrochlorination of acetylene [2,3]. The hydrochlorination of acetylene has received much attention in countries with large reserves of coal [4]. For instance, the manufacture of PVC via the hydrochlorination of acetylene accounts for about 70% of the total PVC production capacity in China [5].

In the industrial process of the hydrochlorination of acetylene, acetylene (C_2H_2) reacts with anhydrous hydrogen chloride (HCl) to obtain VCM under the catalysis of mercuric chloride ($HgCl_2$) supported on activated carbon at optimum temperature range of 170–180 °C [6]. However, $HgCl_2$ (B. P. = 302 °C) volatilizes easily from the surface of activated carbon under reaction conditions [7]. Meanwhile, $HgCl_2$ is highly toxic. Loss of $HgCl_2$ not only leads to an irreversible deactivation of the catalyst but also threatens to the environment and human health. Therefore, it is urgent to explore new types of environment-friendly non-mercury catalysts to replace mercury catalyst from the view of sustainable development of PVC industry. Based on the correlation of

hydrochlorination activity of metal chlorides supported on activated carbon with the standard reduction potential [8], scholars focuses their attention on Au^{3+} [9–13], Pd^{2+} [14–16], Ru^{3+} [17,18], and Pt^{6+} [19,20], *et al.* Nevertheless, these non-mercury catalysts cannot simultaneously satisfy the requirements of high activity and favorable stability for industrial catalyst. Thus activated carbon supported mercuric chloride ($HgCl_2/AC$) has still been used as the catalyst for the hydrochlorination of acetylene by most of PVC enterprises. Consequently, aiming at the problems of the instability of $HgCl_2/AC$, it's necessary to make improvement in the stability of mercury catalyst. Herein, how to inhibit the sublimation of the mercury species is the key to improving the stability of mercury catalyst. Xin Huang employed carbon-mixing expanded multilayered vermiculite (EML-VMT-C) as the high-mercury catalyst support and the as-obtained catalyst showed good stability for acetylene hydrochlorination [21]. But vermiculite has low specific surface area [22], not in favor of the dispersion of active components. Furthermore, carbon deposition in the form of polymerization of acetylene would happen on non-carbon supports in the hydrochlorination of acetylene [23]. Besides, some kinds of metal chlorides such as $CdCl_2$ [24], $CsCl$ [25], $BiCl_3$, $CeCl_3$ and KCl [26], were used as additives to improve the stability of mercury catalyst and reduce the amount of $HgCl_2$ effectively. However, it is worth noting that loss of $HgCl_2$ still exists in the operating cycle of low mercury catalyst significantly [27]. Hence, to improve the stability of mercury catalyst for the hydrochlorination of acetylene presently should focus on designing more stable active component.

The catalyst stability also puzzles the development of Au-based catalyst in the hydrochlorination of acetylene. It has come to our notice

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that, in order to improve the stability of Au-based catalyst for acetylene hydrochlorination, Hutchings attempted to search or synthesize some gold complexes as the active precursor from the view of stability constant [28]. Using $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ with higher stability constant than AuCl_4^- as the active gold precursor could suppress the reduction of oxidized gold species effectively. Thus, we consider that whether this method to stabilize the gold species is valid for stabilizing mercury catalyst for acetylene hydrochlorination. Hg^{2+} can react with halogen anions (Cl^- , Br^- , I^-), forming a series of coordination ions (HgX_4^{2-} , $\text{X} = \text{Cl}, \text{Br}, \text{I}$) with different stability constants and the stability of the coordination ions is enhanced in the order of Cl , Br , and I [29]. In this paper, we have prepared some low-mercury catalysts (4% HgCl_2 loading), using potassium halides (KCl and KI) as additives. The results showed that the low-mercury catalyst HgCl_2 -4 KI /AC performed better stability than HgCl_2 -4 KCl /AC and HgCl_2 /AC under the acetylene hydrochlorination reaction conditions. The order of sublimation rates of HgCl_2 from the catalysts is: HgCl_2 -4 KI /AC < HgCl_2 -4 KCl /AC < HgCl_2 /AC, indicating that the HgCl_2 -4 KI /AC catalyst using K_2HgI_4 with larger stability constant as the main active component had better thermal stability.

2. Experimental

2.1. Pretreatment of activated carbon support

A commercial activated carbon (Norit ROX 0.8) was used as the support. Activated carbon was firstly washed with concentrated nitric solution (HNO_3 , 65%–68%) at room temperature for 1 h to remove the contained impurities, then filtered and washed with deionized water to neutral and dried at 110 °C for 12 h in the air.

2.2. Catalyst preparation

Taking into account the depletion and limited use of mercury resources, low-mercury (4 wt% HgCl_2 loading) catalyst was chose as the research object. The incipient wetness impregnation method was employed to prepare the catalysts. Firstly, HgCl_2 (0.2 g, GR, $\geq 99.9\%$, Xiya Reagent) and KX (0.2197 g KCl , or 0.4891 g KI , $n(\text{HgCl}_2):n(\text{KX}) = 1:4$, $\text{X} = \text{Cl}, \text{I}$) were dissolved in deionized water (9 ml). Then, the mixed solution was added dropwise to the pretreated activated carbon (5 g) with stirring. After placed overnight, the catalyst was dried at 110 °C for 12 h in the air. The as-prepared catalysts were labeled as HgCl_2 -4 KCl /AC and HgCl_2 -4 KI /AC, respectively. The same procedure was applied to prepare the pure HgCl_2 /AC catalyst.

2.3. Sublimation rate measurements of HgCl_2

The sublimation rate measurements of HgCl_2 were carried out as described in the chemical industry standard of the People's Republic of China HG/T 4192-2011 [30]. The fresh catalyst (0.6 g) was set into a tubular reactor ($\phi 10 \text{ mm} \times 400 \text{ mm}$) and heated up to 250 °C. Nitrogen with a flow rate of $6 \text{ ml} \cdot \text{min}^{-1}$ was fed into the reactor for 3 h before the catalyst was taken out to be analyzed. The content of HgCl_2 in the catalyst was analyzed by titration with $\text{C}_5\text{H}_{10}\text{NS}_2\text{Na}$. After ground, screened with 80 mesh sieve and dried to constant weight, the sample (0.5 g) was put into a 250 ml flask with a reflux condenser. 10 wt% NaCl solution (10 ml) and aqua regia (10 ml) were added before the flask was heated to boiling for 15 min. The mixture was filtrated and the obtained filtrate was titrated with standard $\text{C}_5\text{H}_{10}\text{NS}_2\text{Na}$ solution. Considering the easy sublimation of mercuric chloride and the high temperature during drying process, the real contents of HgCl_2 in fresh catalysts were determined by the same titration method above.

2.4. Catalyst characterization

X-ray diffraction (XRD) patterns of the catalysts were conducted on a PANalytical X'Pert diffractometer using a $\text{Cu K}\alpha$ radiation

($\lambda = 0.1541 \text{ nm}$) in a scanning range of $2\theta = 10^\circ - 80^\circ$ that was operated at the voltage of 40 kV and the current of 40 mA. The morphology and components of the catalysts was characterized by using a transmission electronic microscope (TEM, Philips-FEI Tecnai G2 F30 S-Twin) equipped with high-angle annular dark-field (HAADF) detector and EDX spectroscopy.

2.5. Catalytic performance evaluation

Catalytic performance was carried out in a fixed bed reactor (i.d. 10 mm). The temperature of the reactor was regulated by an AI-808P temperature controller (Xiamen Yudian Automation Technology Co., Ltd.). Firstly, nitrogen gas ($6 \text{ ml} \cdot \text{min}^{-1}$) was fed into the reactor containing catalyst (0.82 g) to eliminate water and air in the reaction system. After the reactor was heated up to 220 °C, switch nitrogen gas to HCl gas ($6 \text{ ml} \cdot \text{min}^{-1}$), which was controlled by a calibrated mass flow controller (Beijing Sevenstar Electronics Co., Ltd.), passing through the catalyst bed and activating the catalyst for 0.5 h. Then, pretreated by saturated $\text{K}_2\text{Cr}_2\text{O}_7$ solution and concentrated sulfuric acid successively to eliminate the contained H_2S and H_3P impurities, C_2H_2 ($5 \text{ ml} \cdot \text{min}^{-1}$) was fed through another calibrated mass flow controller and mixed with HCl before passing through the reactor. Here, the gas hourly space velocity (GHSV) of C_2H_2 is 180 h^{-1} . The exit gas mixture was passed through an absorption bottle containing saturated NaOH solution to absorb excess HCl . The compositions of the product were analyzed using an online gas chromatography (GC 9790, Zhejiang Fuli Analytical Instruments Co., Ltd.) equipped with flame ionization detection (FID). Chromatographic separation and identification of the compositions was determined by using a Porapak N packed column (6 ft. $\times$ 1/800 stainless steel). The conversion of C_2H_2 and the selectivity to VCM were defined by the following equations.

$$\text{C}_2\text{H}_2 \text{ Conv.} = \left(1 - \frac{F_A}{F_{A0}}\right) \times 100\% \quad (1)$$

$$\text{VCM Sel.} = \left(\frac{F_{\text{VCM}}}{1 - F_A}\right) \times 100\% \quad (2)$$

In the above equations, F_{A0} , F_A , and F_{VCM} represent the volume fraction of acetylene in the raw gas, the volume fraction of remaining acetylene in the product mixture gas, and the volume fraction of VCM in the product mixture gas, respectively.

3. Results and Discussion

3.1. Characterization

3.1.1. Crystal phase analysis

The X-ray diffraction patterns of the above three catalysts are shown in Fig. 1. It can be seen that there are no obvious detectable reflections of Hg species, such as HgCl_2 , K_2HgCl_4 , or K_2HgI_4 , in the patterns. It indicates that the active components are highly dispersed on the surface of activated carbon. According to Xie's findings [31], HgCl_2 , K_2HgCl_4 and K_2HgI_4 may disperse as a monolayer on the surface of the support because these substances are all salts. The extra KCl is generated when HgCl_2 reacts with excess KX . There were no diffraction peaks of KCl , suggesting that the extra KCl is also highly dispersed.

3.1.2. Morphology of HgCl_2 -4 KI /AC

In our previous study, when CsCl was used as an additive to be added into the low-mercury catalyst, the elements of Hg and Cl were homogeneously distributed on the surface of activated carbon [25]. Therefore, we speculate that the distribution of Hg and Cl on the HgCl_2 -4 KCl /AC catalyst is the same as that on Hg - Cs /AC catalyst. Fig. 2 shows the mapping photographs of several major elements on HgCl_2 -4 KI /AC. The mapping characterization displays that the elements of Hg and I are in homogeneous distribution on the surface of the support as well as K

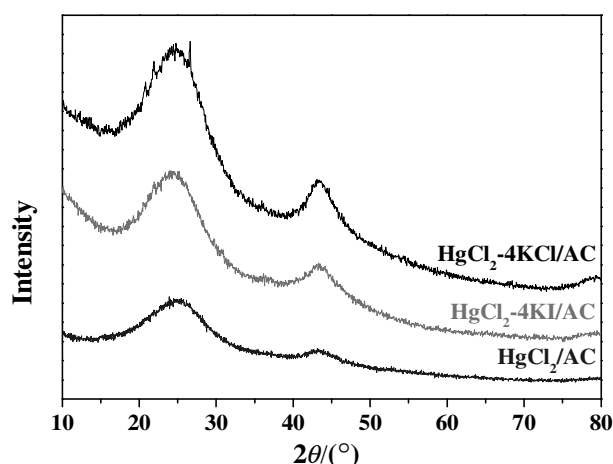


Fig. 1. X-ray diffraction patterns of HgCl_2/AC , $\text{HgCl}_2\text{-4KCl}/\text{AC}$, and $\text{HgCl}_2\text{-4KI}/\text{AC}$.

and Cl, and no obvious particles exist on the surface of activated carbon. It indicates that there are some interactions between HgCl_2 and excess KI, hinting the generation of K_2HgI_4 , which is the active component of the $\text{HgCl}_2\text{-4KI}/\text{AC}$ catalyst.

3.2. Catalytic properties

3.2.1. The effect of KX on the performance of HgCl_2/AC

In order to investigate the catalytic stability, the three catalysts were evaluated for 50 h under fixed acetylene hydrochlorination reaction conditions at 220 °C, an acetylene gas hourly velocity (C_2H_2) of 180 h^{-1} , and a fed volume ratio $V(\text{HCl})/V(\text{C}_2\text{H}_2)$ of 1.2. The catalytic performances of the three catalysts were shown in Fig. 3. The selectivity to

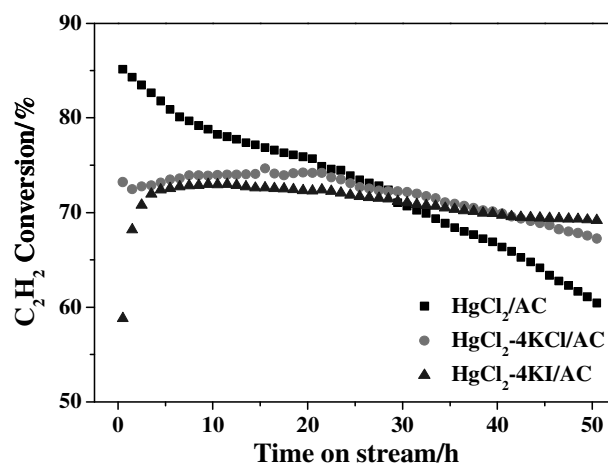


Fig. 3. The catalytic performances of three low-mercury catalysts in acetylene hydrochlorination. ($6 \text{ ml} \cdot \text{min}^{-1} \text{ HCl}$, $5 \text{ ml} \cdot \text{min}^{-1} \text{ C}_2\text{H}_2$, 0.82 g Cat. , $T = 220 \text{ }^\circ\text{C}$).

VCM was all above 99.5% over the three catalysts. Although HgCl_2/AC showed the highest hydrochlorination activity with C_2H_2 conversion of 85.12%, it deactivated rapidly with an average deactivation rate of $0.49\% \cdot \text{h}^{-1}$. The deactivation rates of $\text{HgCl}_2\text{-4KCl}/\text{AC}$ and $\text{HgCl}_2\text{-4KI}/\text{AC}$ were $0.30\% \cdot \text{h}^{-1}$ and $0.10\% \cdot \text{h}^{-1}$, respectively, smaller than that of HgCl_2/AC . $\text{HgCl}_2\text{-4KCl}/\text{AC}$ and $\text{HgCl}_2\text{-4KI}/\text{AC}$ exhibited better catalytic stability than HgCl_2/AC .

3.2.2. The effect of variation of the active species on the performance of HgCl_2/AC

Because of the formation of the excess KCl in $\text{HgCl}_2\text{-4KX}/\text{AC}$, in order to investigate the intrinsic stability of the active component K_2HgX_4 in

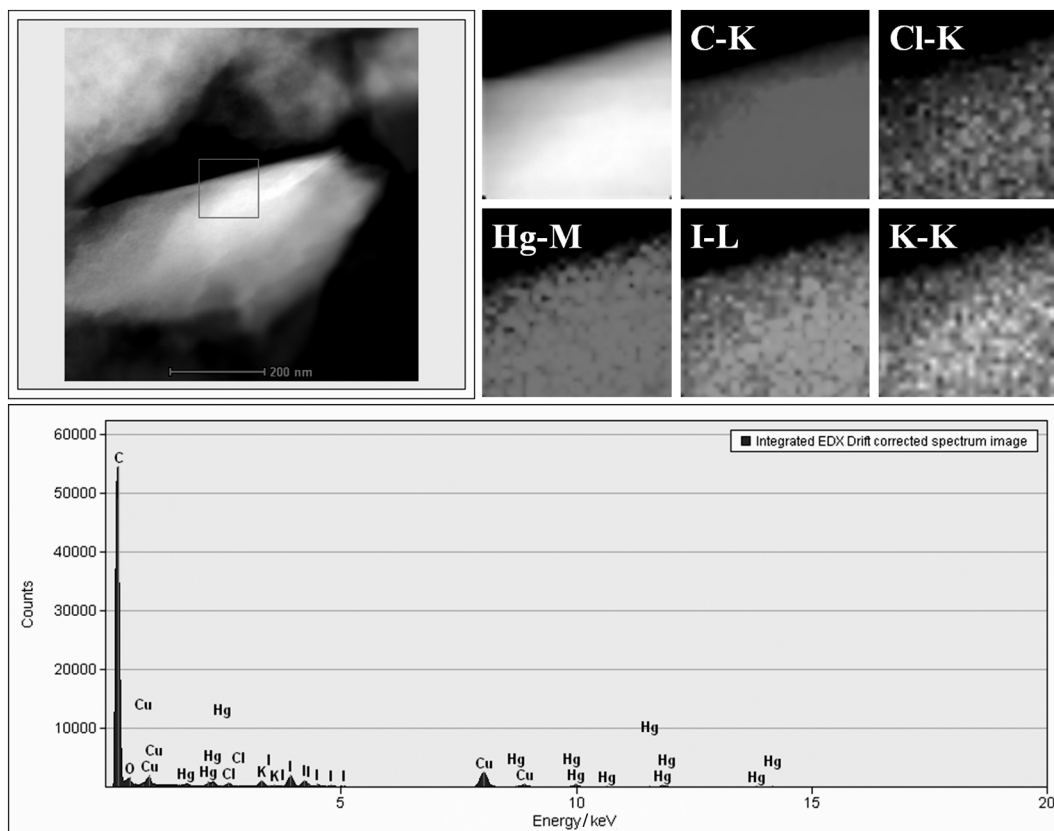


Fig. 2. HAADF image together with the EDS mapping of the $\text{HgCl}_2\text{-4KI}/\text{AC}$ catalyst.

the catalyst, we prepared some catalysts using pure K_2HgX_4 ($X = Cl, I$) as precursor without excess KCl. The K_2HgCl_4/AC catalyst was prepared using 0.2 g $HgCl_2$ and 0.1099 g KCl ($n(HgCl_2):n(KCl) = 1:2$) as precursor. The K_2HgI_4/AC catalyst was prepared as follows: Firstly, the red deposit HgI_2 was obtained by reacting 0.2 g $HgCl_2$ with 0.2446 g KI ($n(HgCl_2):n(KI) = 1:2$), and washed with deionized water to eliminate K^+ and Cl^- . Then, the K_2HgI_4/AC catalyst was got by using the as-prepared HgI_2 and 0.2446 g KI ($n(HgI_2):n(KI) = 1:2$) as precursor. The $K_2HgCl_4-K_2HgI_4/AC$ catalyst was prepared by step impregnating method. The catalytic performances of the three catalysts were shown in Fig. 4. We could see from Fig. 4 that the three catalysts showed similar highest activity, about 78%–80% of acetylene conversion at the C_2H_2 GHSV of $180\ h^{-1}$ and $220\ ^\circ C$. With the active component varying from K_2HgCl_4 to K_2HgI_4 , the stability of the catalyst was improved. The catalytic performances stated clearly that K_2HgI_4 had better stability than K_2HgCl_4 under acetylene hydrochlorination reaction conditions.

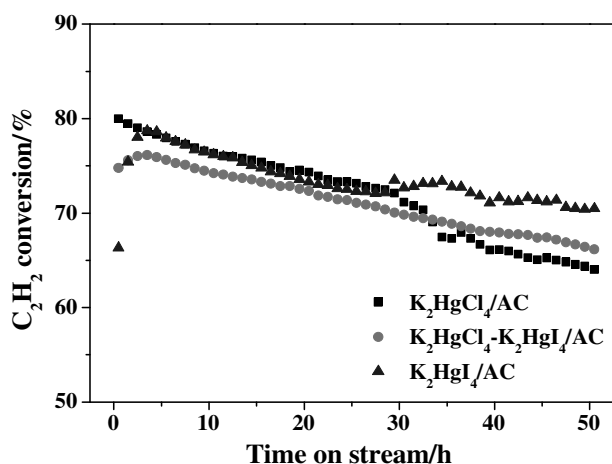


Fig. 4. The catalytic performances of K_2HgX_4/AC in acetylene hydrochlorination. ($6\ ml\cdot min^{-1}\ HCl$, $5\ ml\cdot min^{-1}\ C_2H_2$, $0.82\ g\ Cat.$, $T = 220\ ^\circ C$).

The reason why $HgCl_2-4KI/AC$ showed the best catalytic stability can be stated as below. Hg^{2+} can react with halogen anions (Cl^- , Br^- , I^-), forming a series of coordination ions (HgX_4^{2-} , $X = Cl, Br, I$) with different stability constants. The chemical equations for the reactions of Hg^{2+} and halogen ions to form a variety of coordination ions and corresponding stability constants of the coordination ions are listed in Table 1 [29]. As can be seen from Table 1, the active components of $HgCl_2/AC$, $HgCl_2-4KCl/AC$, and $HgCl_2-4KI/AC$ may be $HgCl_2$, K_2HgCl_4 and K_2HgI_4 , respectively. The stability constant of HgI_4^{2-} is 7.2×10^{29} , far greater than that of $HgCl_4^{2-}$, 1.6×10^{15} . According to the Principle of Hard and Soft Acids and Bases (HSAB) [32,33], hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases. Soft acids form stable complexes with bases that are highly polarizable. Hg^{2+} is a soft acid with high polarizability. I^- is a soft acid and Cl^- is a hard acid. The large radius and loose electron cloud of I^- results in high polarization degree of $Hg-I$ bond and the nature of $Hg-I$ bond is close to covalent bond. Cl^- has small ionic radius, difficult to form stable covalent bond. The high polarizability of Hg^{2+} makes the $Hg-Cl$ bond difficult

Table 1

The stability constants of coordination ions formed by reacting Hg^{2+} with Cl^- , Br^- , and I^- , respectively

Chemical equation	Stability constant of HgX_4^{2-} , K
$Hg^{2+} + 4Cl^- \rightarrow HgCl_4^{2-}$	1.6×10^{15}
$Hg^{2+} + 4Br^- \rightarrow HgBr_4^{2-}$	1.0×10^{21}
$Hg^{2+} + 4I^- \rightarrow HgI_4^{2-}$	7.2×10^{29}

to form stable ionic bond. Therefore, the stability of HgI_4^{2-} is better than that of $HgCl_4^{2-}$. Likewise, the order of the thermal stabilities of $HgCl_2/AC$, $HgCl_2-4KCl/AC$ and $HgCl_2-4KI/AC$ can be judged based on the stability constants.

3.3. The average sublimation rate of $HgCl_2$

The order of the sublimation rates of $HgCl_2$ for $HgCl_2/AC$, $HgCl_2-4KCl/AC$ and $HgCl_2-4KI/AC$ can be predicted based on the stability constants in Table 1. The specific sublimation rates of $HgCl_2$ for the three catalysts are also compared in Table 2. As we can see from Table 2, the sublimation of $HgCl_2$ for $HgCl_2/AC$ is the fastest with the average $HgCl_2$ sublimation rate of $47.78 \times 10^{-3}\ mg\cdot g^{-1}\cdot min^{-1}$ and the sublimation of $HgCl_2$ for $HgCl_2-4KI/AC$ is slower than $HgCl_2-4KCl/AC$ at $250\ ^\circ C$. The average $HgCl_2$ sublimation rate of $HgCl_2-4KCl/AC$ is $20 \times 10^{-3}\ mg\cdot g^{-1}\cdot min^{-1}$, about 5/12 of that of $HgCl_2/AC$. The average $HgCl_2$ sublimation rate of $HgCl_2-4KI/AC$ is $2.22 \times 10^{-3}\ mg\cdot g^{-1}\cdot min^{-1}$, about 1/22 of that of $HgCl_2/AC$ and 1/9 of that of $HgCl_2-4KCl/AC$. Loss percentage of $HgCl_2$ from the $HgCl_2-4KI/AC$ catalyst is 1.02%, less than 3% [30], which satisfies the requirement for industrial catalyst. The data in Table 2 reveal that the addition of KI further promotes the inhibition of sublimation of $HgCl_2$ from the low-mercury catalyst compared with the addition of KCl. The order of the average $HgCl_2$ sublimation rate is opposite to the order of stability constant of active components.

Table 2

Comparison of the average $HgCl_2$ sublimation rates of $HgCl_2/AC$, $HgCl_2-4KCl/AC$, and $HgCl_2-4KI/AC$

catalyst	HgCl ₂ content		Sublimation rate of HgCl ₂ /mg·g ⁻¹ ·min ⁻¹	Loss percentage of HgCl ₂ /wt%
	Initial	Treated		
HgCl ₂ /AC	3.77%	2.91%	47.78×10^{-3}	22.81
HgCl ₂ -4KCl/AC	3.78%	3.42%	20×10^{-3}	9.52
HgCl ₂ -4KI/AC	3.91%	3.87%	2.22×10^{-3}	1.02

Conditions: $6\ ml\cdot min^{-1}\ N_2$, $0.6\ g\ Cat.$, $T = 250\ ^\circ C$, $t = 180\ min$.

4. Conclusions

A ligand coordination approach was employed to enhance the stability of low-mercury catalyst for the hydrochlorination of acetylene. According to the Principle of Hard and Soft Acids and Bases (HSAB), a more stable low-mercury catalyst (4% $HgCl_2$ loading), $HgCl_2-4KI/AC$, was successfully prepared by using $HgCl_2$ and KI as precursors. The active component of the $HgCl_2-4KI/AC$ catalyst was K_2HgI_4 , highly dispersed on the surface of activated carbon. The $HgCl_2-4KI/AC$ catalyst showed better catalytic stability than $HgCl_2/AC$ and $HgCl_2-4KCl/AC$ for the hydrochlorination of acetylene under fixed acetylene hydrochlorination reaction conditions at $220\ ^\circ C$, an acetylene gas hourly velocity (C_2H_2) of $180\ h^{-1}$, and a fed volume ratio $V(HCl)/V(C_2H_2)$ of 1.2. The comparison of the $HgCl_2$ sublimation rates for three catalysts indicated that the $HgCl_2-4KI/AC$ catalyst had best thermal stability than $HgCl_2/AC$ and $HgCl_2-4KCl/AC$. This approach points out the direction to designing more stable mercury catalyst for the hydrochlorination of acetylene.

References

- [1] T. Yang, Production, application and prospect of PVC resin in China, *China Plast.* 22 (2) (2008) 1–8 (in Chinese).
- [2] Q.S. Han, F. Sun, Contrast analysis on PVC produced by ethylene method and acetylene method, *Polyvinyl Chloride* 37 (9) (2009) 5–7 (in Chinese).
- [3] F.Z. Xin, Contrast of vinyl chloride production processes, *Yunnan Chem. Technol.* 37 (1) (2010) 65–67 (in Chinese).
- [4] X.B. Wei, H.B. Shi, W.Z. Qian, G.H. Luo, Y. Jin, F. Wei, Gas-phase catalytic hydrochlorination of acetylene in a two-stage fluidized-bed reactor, *Ind. Eng. Chem. Res.* 48 (1) (2009) 128–133.
- [5] J.L. Bing, C.Z. Li, Review on development of China's PVC industry in the past 10 years and analysis on the trends in the year 2010, *Polyvinyl Chloride* 39 (5) (2001) 1–8 (in Chinese).

- [6] J.L. Zhang, N. Liu, W. Li, B. Dai, Progress on cleaner production of vinyl chloride monomers over non-mercury catalysts, *Front. Chem. Sci. Eng.* 5 (4) (2011) 514–520.
- [7] G.J. Hutchings, D.T. Grady, Effect of drying conditions on carbon supported mercuric chloride catalysts, *Appl. Catal.* 16 (1985) 411–415.
- [8] G.J. Hutchings, Vapor phase hydrochlorination of acetylene: Correlation of catalytic activity of supported metal chloride catalysts, *J. Catal.* 96 (1985) 292–295.
- [9] K. Zhou, W. Wang, Z. Zhao, G.H. Luo, J.T. Miller, M.S. Wong, F. Wei, Synergistic Gold-Bismuth catalysis for non-mercury hydrochlorination of acetylene to vinyl chloride monomer, *ACS Catal.* 4 (2014) 3112–3116.
- [10] K. Zhou, J.C. Jia, C.H. Li, H. Xu, J. Zhou, G.H. Luo, F. Wei, A low content Au-based catalyst for hydrochlorination of C_2H_2 and its industrial scale-up for future PVC processes, *Green Chem.* 17 (2015) 356–364.
- [11] J. Zhao, J.T. Xu, J.H. Xu, J. Ni, T.T. Zhang, X.L. Xu, X.N. Li, Activated-carbon-supported gold-cesium(I) as highly effective catalysts for hydrochlorination of acetylene to vinyl chloride, *ChemPlusChem* 80 (2015) 196–201.
- [12] J. Zhao, J.T. Xu, J.H. Xu, T.T. Zhang, X.X. Di, J. Ni, X.N. Li, Enhancement of Au/AC acetylene hydrochlorination catalyst activity and stability via nitrogen-modified activated carbon support, *Chem. Eng. J.* 262 (2015) 1152–1160.
- [13] J. Zhao, S.C. Gu, X.L. Xu, T.T. Zhang, Y. Yu, X.X. Di, J. Ni, Z.Y. Pan, X.N. Li, Supported ionic-liquid-phase-stabilized Au(III) catalyst for acetylene hydrochlorination, *Catal. Sci. Technol.* 6 (2016) 3263–3270.
- [14] S.A. Mitchenko, T.V. Krasnyakova, I.V. Zhikharev, Catalytic hydrochlorination of acetylene on mechanochemically-activated K_2PdCl_4 , *Theor. Exp. Chem.* 44 (5) (2008) 316–319.
- [15] L. Wang, F. Wang, J.D. Wang, X.L. Tang, Y.L. Zhao, D. Yang, F.M. Jia, T. Hao, Hydrochlorination of acetylene to vinyl chloride over Pd supported on zeolite Y, *React. Kinet. Mech. Catal.* 110 (2013) 187–194.
- [16] L. Wang, F. Wang, J.D. Wang, Non-mercury catalytic acetylene hydrochlorination over a NH_4F -urea-modified Pd/HY catalyst for vinyl chloride monomer production, *New J. Chem.* 40 (2016) 3019–3023.
- [17] Y.F. Pu, J.L. Zhang, L. Yu, Y.H. Jin, W. Li, Active ruthenium species in acetylene hydrochlorination, *Appl. Catal. A Gen.* 488 (2014) 28–36.
- [18] G.B. Li, W. Li, H.Y. Zhang, Y.F. Pu, M.X. Sun, J.L. Zhang, Non-mercury catalytic acetylene hydrochlorination over Ru catalysts enhanced by carbon nanotubes, *RSC Adv.* 5 (2015) 9002–9008.
- [19] S.A. Mitchenko, T.V. Krasnyakova, R.S. Mitchenko, A.N. Korduban, Acetylene catalytic hydrochlorination over powder catalyst prepared by pre-milling of K_2PtCl_4 salt, *J. Mol. Catal. A Chem.* 275 (2007) 101–108.
- [20] S.A. Mitchenko, E.V. Khomutov, A.A. Shubin, Y.M. Shul'ga, Catalytic hydrochlorination of acetylene by gaseous HCl on the surface of mechanically pre-activated K_2PtCl_6 salt, *J. Mol. Catal. A Chem.* 212 (2004) 345–352.
- [21] X. Huang, F. Yu, M.Y. Zhu, F.H. Ouyang, B. Dai, J.M. Dan, Hydrochlorination of acetylene using expanded multilayered vermiculite (EML-VMT)-supported catalysts, *Chin. Chem. Lett.* 26 (2015) 1101–1104.
- [22] J. Zhang, T.Y. Liu, R. Chen, X.H. Liu, Vermiculite as a natural silicate crystal for hydrogen generation from photocatalytic splitting of water under visible light, *RSC Adv.* 4 (2014) 406–408.
- [23] L.L. Xu, X.G. Wang, H.Y. Zhang, B. Dai, Z.Y. Liu, Q.F. Zhang, Application of a novel carbon carrier in acetylene hydrochlorination, *Chem. Ind. Eng. Prog.* 30 (2011) 536–541 (in Chinese).
- [24] M.H. Chen, K. Xu, J.X. Liao, X.H. Chen, Effects of Cd cocatalytic mechanism in multi-element catalytic system on performance of low-level mercury catalyst, *Polyvinyl Chloride* 42 (5) (2014) 26–29 (in Chinese).
- [25] X.L. Xu, J. Zhao, C.S. Lu, T.T. Zhang, X.X. Di, S.C. Gu, X.N. Li, Improvement of the stability of Hg/AC catalysts by CsCl for the high-temperature hydrochlorination of acetylene, *Chin. Chem. Lett.* 27 (2016) 822–826.
- [26] Y. Zhou, Q. Yang, Q. Luo, W.W. Jiang, Preparation and optimization of a new-type low-mercury catalyst for hydrochlorination of acetylene, *Appl. Chem. Ind.* 40 (12) (2011) 2147–2150 (in Chinese).
- [27] Z.Q. Chen, X.Y. Ma, Application of environmental low-mercury catalyst, *China Chlor-Alkali* 6 (2009) 9–11 (in Chinese).
- [28] P. Johnston, N. Carthey, G.J. Hutchings, Discovery, development, and commercialization of gold catalysts for acetylene hydrochlorination, *J. Am. Chem. Soc.* 137 (2015) 14548–14557.
- [29] X.J. Liu, Y.F. Zhu, F. Gao, Inorganic Element Chemistry, Science Press, Beijing, 2010 (in Chinese).
- [30] China Chlor-Alkali Industry Association, HG/T 4192–2011, Low-Level Mercury Catalyst for Chloroethylene Synthesis, Chemical Industry Press, Beijing, 2011 (in Chinese).
- [31] Y.C. Xie, N.F. Yang, Y.J. Liu, Y.Q. Tang, Spontaneous dispersion of some active components onto the surfaces of carriers, *Sci. Sinica* 26 (1983) 337–350.
- [32] R.G. Pearson, Hard and soft acids and bases, HSAB, part I fundamental principles, *J. Chem. Educ.* 45 (9) (1965) 581–587.
- [33] R.G. Pearson, Hard and soft acids and bases, HSAB, part II underlying theories, *J. Chem. Educ.* 45 (10) (1968) 643–648.