available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Efficient and stable Ru(III)-choline chloride catalyst system with low Ru content for non-mercury acetylene hydrochlorination

Hang Li^a, Botao Wu^a, Jianhui Wang^b, Fumin Wang^{a,*}, Xubin Zhang^{a,#}, Gang Wang^c, Haichao Li^c^a School of Chemical Engineering & Technology, Collaborative Innovation Center of Chemical Science and Chemical Engineering (Tianjin), Tianjin University, Tianjin 300350, China^b Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, China^c College of Chemistry and Chemical Engineering, Qinghai Nationalities University, Xining 810007, Qinghai, China

ARTICLE INFO

Article history:

Received 16 May 2018

Accepted 6 June 2018

Published 5 November 2018

Keywords:

Acetylene hydrochlorination

Catalytic activity

Heterogeneous catalysis

Ionic complex

Ruthenium

ABSTRACT

Herein, we report an excellent, supported Ru(III)-ChCl/AC catalyst with lower Ru content, where the ionic complex ChRuCl_4 serves as the active component for acetylene hydrochlorination. The prepared heterogeneous Ru-10%ChCl/AC catalyst shows excellent activity and long-term stability. In this system, ChCl provides an environment for the ChRuCl_4 to be stabilized as Ru(III), thus suppressing the reduction of the active species and the aggregation of ruthenium species during the reaction. The interaction between reactants and catalyst species was investigated by catalyst characterizations in combination with DFT calculations to disclose the effect of the ChRuCl_4 complex and ChCl on the catalytic performance. This inexpensive, efficient, and long-term catalyst is a competitive candidate for application in the hydrochlorination industry.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Vinyl chloride monomer (VCM) is a significant commodity chemical with over a million tons being consumed annually for the increasing global production of polyvinyl chloride (PVC) [1]. Industrial VCM can be manufactured by the oxychlorination of ethylene derived from petroleum, or hydrochlorination of acetylene obtained from coal [2]. The coal-based acetylene route is economically advantageous relative to ethylene oxychlorination because of the rich coal reserves in China. Currently, the acetylene hydrochlorination reaction is typically catalyzed by carbon-supported mercuric chloride. However, mercury-based catalysts exhibit deactivation, which leads to a

decrease in activity, and volatilization of mercury, which is a significant problem due to mercury's toxic nature. For example, it was reported that about 8×10^5 kg of HgCl_2 is consumed annually for PVC production in China, with over 25% HgCl_2 failing to be recycled, thereby leading to the leakage of more than 2×10^5 kg of HgCl_2 during the reaction [3–5]. To reduce the consumption of Hg in the PVC industry by 2020, China has been one of the signatories of the Minamata Convention on mercury [6]. Therefore, the development of Hg-free green catalysts for the acetylene hydrochlorination reaction has become imperative for a sustainable PVC industry in China.

Over the past two decades, many researchers have screened numerous non-mercury metal chloride catalysts such as

^{*} Corresponding author. Tel/Fax: +86-22-27890041; E-mail: wangfumin@tju.edu.cn[#] Corresponding author. Tel/Fax: +86-22-27890041; E-mail: tjzxb@tju.edu.cn

This work was supported by the National Basic Research Program of China (2012CB720302) and the National Key R&D Program of China (2016YFF0102503).

DOI: 10.1016/S1872-2067(18)63121-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 11, November 2018

Au(III), Pt(II), Pd(II), Ru(III), Rh(III), Cu(II), and Bi(III), and many of these were found to be active for acetylene hydrochlorination [7–13]. The Au-based catalysts developed by Hutchings's group [14] have already been successfully tested in a pilot evaluation for over 3000 h, and the catalyst conversion was suppressed by 85% throughout the operation of the pilot plant. Zhao et al. [15] reported that the less toxic and recyclable organic aqua regia (OAR) can be used as a greener alternative solvent to conventional aqua regia to activate Au/AC catalysts in the acetylene hydrochlorination reaction. However, the scarce resources and high cost are becoming the obstacles limiting the large-scale application of Au catalysts, and prompt researchers to develop other efficient and cost-effective non-mercury catalysts for acetylene hydrochlorination [16,17]. In recent years, Ru-based catalysts have been considered as alternatives to Au-based catalysts due to their high activity, low price, and environmental friendliness, and a wide variety of methods have been adopted to improve the activity and stability of Ru-based catalysts. In 2013, Zhang et al. [18] reported that the $\text{Ru}_1\text{Co}_3/\text{SAC}$ catalyst showed more than 95% acetylene conversion within 48 h under the conditions of 170 °C and C_2H_2 GHSV (gas hourly space velocity) of 180 h^{-1} . In 2015, Li et al. [19] found that Ru metal supported inside carbon nanotubes showed good catalytic performance. Hou et al. [20] observed that a nitrogen-doped Ru/SAC-N700 catalyst exhibited better catalytic activity and stability for acetylene hydrochlorination, and that the N-dopants effectively reduce the coke deposition on the catalyst. Subsequently, Zhang et al. [21] revealed that the acetylene conversion reached 99% with the $\text{Ru}_1\text{Co(III)}_3\text{Cu(II)}_1$ catalyst at 170 °C and a GHSV (C_2H_2) of 180 h^{-1} , and that no obvious decline was observed in 500 h under the reaction conditions of 170 °C and a GHSV (C_2H_2) of 90 h^{-1} .

As mentioned above, considering the practical applications, the long-term stability of metal chloride catalysts is still a great challenge in developing non-mercury catalysts. These metal salt catalysts inevitably encounter the problem of deactivation because the metallic cations are easily reduced to zero-valent states by the reductive C_2H_2 gas during the reaction, which results in the rapid deactivation of the reaction [22–24]. Additionally, Nkosi and other researchers have found that the coking effect which originates from the adsorbed vinyl chloride monomer or oligomerization of the acetylene and vinyl chloride is another problem for the catalysts [25–27]. It should also be pointed out that the Ru content in most of the ruthenium-based catalysts mentioned above is 1 wt%, which is still too high for their application. Thus, the enhancement of activity and lifetime of Ru-based catalysts is still a challenge in the acetylene hydrochlorination reaction.

Recently, ionic liquids (ILs) have attracted significant attention for application in the acetylene hydrochlorination reaction regardless of whether the system is homogeneous or heterogeneous [25,28,29]. Xing et al. [28] reported that the active and stable metal nanoparticles (NPs) in a surfactant IL system showed excellent performance for the gas-liquid acetylene hydrochlorination reaction. Zhao et al. [29] was the first to describe a supported gold imidazolium-based IL ([Prmim]Cl) complex catalyst for gas-phase acetylene hydrochlorination in a

fixed-bed reactor, which demonstrated excellent catalytic activity and long-term stability. Shang et al. [25] reported that the efficient Ru@TPPB catalyst showed excellent activity and stability. It was found that TPPB provides a solvent environment for active ruthenium species such as RuCl_3 and RuO_2 . However, the toxicology of both imidazolium-based and quaternary phosphonium salt ILs have not yet been fully studied. Also, the high cost of these ionic liquids limits their applications in the PVC industry [30]. Choline chloride as an analog of ionic liquids has been used as the catalyst for Diels-Alder reactions and Fischer indole annulation reactions [31,32]. In addition, choline chloride is more inexpensive, non-toxic, and easier to store than most ionic liquids because choline is a naturally occurring bio-compatible compound [33]. To our knowledge, this cleaner analog of ionic liquids has not been used in acetylene hydrochlorination reactions.

Herein, a highly efficient Ru(III)-ChCl catalyst system with lower Ru content, which remains highly active and stable in a continuous gas-solid process for acetylene hydrochlorination, was successfully developed. The catalysts are composed of the active ruthenium complex (ChRuCl_4) stabilized as the Ru(III) form and excessive choline chloride (ChCl) on the carbon support. In this paper, the mechanism of the catalytic reaction in this Ru(III)-ChCl/AC system is discussed in detail via catalyst characterization combined with computational study.

2. Experimental

2.1. Material

Coconut-activated carbon (20–40 mesh) was purchased from Fujian Xinsen Activated Carbon Industry Science and Technology Co., Ltd. RuCl_3 (purity 99%) was purchased from Sigma-Aldrich. Choline chloride (ChCl) was purchased from J&K Scientific Ltd. C_2H_2 (gas, 99.99%) and HCl (gas, 99.99%) were purchased from Tianjin Hexagonal Industrial Gases Distribution Co., Ltd. All reagents and materials were directly used without further purification.

2.2. Catalyst preparation

The supported Ru(III)-ChCl/AC catalysts were prepared using an incipient wetness impregnation technique. Activated carbon (AC) was used as the solid porous support for this Ru(III)-ChCl system. Firstly, RuCl_3 precursor (0.02 g) and ChCl (0.05 g) were dissolved in deionized water (10 mL) under stirring until complete dissolution. Then, the activated carbon (5.0 g) was added to the solution with agitated stirring, followed by ultrasonication in an ultrasonic bath for 10 min. Subsequently, the system was aged at 60 °C for 10 h and dried at 80 °C in a vacuum oven for 12 h to obtain the catalysts, denoted as Ru-1%ChCl/AC, where 1% represents the mass percentage of ChCl in the activated carbon support. The Ru content in all samples was fixed at 0.2 wt%. Similar methods were applied to prepare catalysts labeled as Ru-5%ChCl/AC, Ru-10%ChCl/AC, and Ru-20%ChCl/AC with different contents of ChCl. Furthermore, the same process was adopted to prepare the

10%ChCl/AC and the monometallic Ru/AC.

Due to the low solubility of the complex in ethanol, for the sake of separation, the ruthenium complex (ChRuCl_4) was synthesized by dissolving RuCl_3 in a ChCl-ethanol solution for better separation, where the mole ratio of ChCl to RuCl_3 is 2:1, resulting in the rapid formation of a maroon-colored solid, followed by stirring for 10 min, aging for 12 h at 60 °C and finally, evaporating the solvents.

The carbon-supported $\text{ChRuCl}_4/\text{AC}$ catalyst was also prepared using an incipient wetness impregnation technique. Firstly, ChRuCl_4 (0.03 g) was dissolved in deionized water (10 mL), and carbon (5.0 g) was added to the solution under agitated stirring, followed by ultrasonication in an ultrasonic bath for 10 min. Thereafter, the system was maintained at 60 °C for 10 h and dried at 80 °C in a vacuum oven for 12 h to obtain the catalysts. Notably, the active ruthenium complex exists as ChRuCl_4 in the Ru(III)-ChCl/AC catalyst system, which is further discussed below.

2.3. Catalytic performance evaluations

The catalyst performance in the hydrochlorination reaction was evaluated in a fixed-bed micro-reactor (10 mm diameter). The temperature of the reactor was measured by a temperature controller (CKW-1100). The experimental setup for the continuous reaction is presented in Fig. S1.

Firstly, nitrogen was fed through a filter into the heated reactor containing 5 mL catalysts corresponding to the catalyst (0.9 g) before the reaction in order to remove trace impurities. Hydrogen chloride was fed into the reactor using a calibrated mass flow controller for 40 min in the initial reaction. Then, acetylene was fed into the reactor to ensure a $V_{\text{HCl}}/V_{\text{C}_2\text{H}_2}$ volume ratio of 1.15/1 to obtain a GHSV (C_2H_2) of 900 h^{-1} (C_2H_2 : 75.0 mL/min, HCl: 86.3 mL/min) or 540 h^{-1} (C_2H_2 : 45 mL/min, HCl: 51.8 mL/min) [4,9,34]. The effluent gas mixture was passed through NaOH solution to remove the unreacted hydrogen chloride and then analyzed by gas chromatography (GC; Beifen-Ruili SP-3420A) to determine the acetylene conversion and VCM selectivity values. The conversion of acetylene (X_A) and the selectivity to VCM (S_{VC}) were calculated according to the formula below using $N_{\text{A}0}$ as the volume fraction of acetylene in the feed gas, N_A as the remaining acetylene, and N_{VC} as the volume fraction of the vinyl chloride gas in the product mixture gas, with all these values determined by GC analysis.

$$X_A(\%) = \left(1 - \frac{N_A}{N_{\text{A}0}}\right) \times 100$$

$$S_{\text{VC}}(\%) = \frac{N_{\text{VC}}}{1 - N_A} \times 100$$

2.4. Characterization

Nitrogen adsorption/desorption isotherms were evaluated at −196 °C with a Bjbuilder analyzer. The catalysts were degassed at 200 °C for 6 h, and then measured using liquid nitrogen adsorption at −196 °C. TEM analysis was performed using a transmission electron microscope (TEM; Tecnai G2 F30) with an accelerating voltage of 300 kV. The catalyst samples were

dispersed in ethanol and then deposited onto Cu grids covered with Holey carbon film. The morphology of the catalysts was characterized by SEM with a Philips XL-30 scanning electron microscope. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/DSC instrument in the temperature range from 20 to 900 °C at the rate of 5 °C/min with an air flow of 10 mL/min. X-ray photoelectron spectroscopy (XPS) was performed using a PHI-5000 Versaprobe II System to determine the surface chemical compositions. The binding energy was calibrated to the C 1s level of 284.8 eV, and the step size of the XPS spectra was 0.1 eV. The raw spectra were fitted using the XPSPEAK 4.1 fitting program adopting mixed Gaussian (80%)-Lorentzian (20%) functions. Temperature-programmed desorption (TPD) experiments were performed on a Quantachrome Instruments AMI-90 to analyze the adsorption capacity of the catalysts for reactants and products. For the HCl-TPD and C_2H_2 -TPD profiles, the catalysts first adsorbed under HCl and C_2H_2 atmospheres for 4 h at 170 °C, respectively. Next, the catalysts were kept in a pure helium atmosphere for 30 min and the profiles were recorded in the temperature range of 50–700 °C at a heating rate of 10 °C/min. CO-TPD was conducted in this instrument, with the samples pretreated at 400 °C under H_2/Ar atmosphere, and thereafter, the CO uptake profile measured using a TCD detector. X-ray diffraction (XRD) measurements were conducted using a D8 Focus X-ray diffractometer with monochromatized Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$) operating in the 2θ scan range 30° to 75°.

The total ruthenium content in the catalysts was determined by inductively coupled plasma mass spectrometry (ICP-MS) with a PerkinElmer ELAN DRC-e. In order to measure the Ru content, the catalysts were calcined at 600 °C for 2 h, and the rest was dissolved in the mixed acid containing 20 mL HCl, 5 mL HNO_3 , and 0.5 mL HF to form an aqueous solution. The electrospray mass spectra (ESI-MS) of the active ruthenium complex were recorded on a micrOTOF-Q II instrument (Bruker Daltonics, Billerica, MA, USA) using water as the solvent. Fourier transform infrared spectroscopy (FTIR) was performed on a Bruker VERTEX 70 FT-IR spectrophotometer with a DTGS detector (UV-2550, Japan).

2.5. Computational details

All calculations were carried out using Gaussian 09 package at the gas phase. The B3LYP functional combined with the LanL2dz basis set and effective core potential were used for Ru, and the 6-31G(d,p) basis set was employed for other atoms in geometry optimization of all stable point and transition states [35–40]. Frequency calculations were performed at this level with a temperature of 170 °C, wherein the frequency correction factors were used for thermal corrections to Gibbs free energy [41]. Natural bond orbital (NBO) analysis was also performed at the same level [42]. Single-point electronic energy calculations were performed by using the M06 functional combined with the mixed basis set of def2-TZVP for Ru and 6-311+G(3df,2pd) for other atoms, and an ultra-fine integration grid was employed, containing a DFT-D3 correction to describe the dispersion effects [43–45]. The computed structures were il-

illustrated using CYL View [46]. The figure of wavefunction analysis was prepared by Multiwfn and VMD [47,48].

3. Results and discussion

3.1. Characterization of the ChRuCl_4 complex

The Ru(III)-ChCl/AC catalyst system consists of ruthenium species stabilized in the cationic form by the formation of the ChRuCl_4 complex. ESI-MS characterization using water as the solvent was conducted to confirm the synthesized ChRuCl_4 complex as an ionic complex, which contains RuCl_4^- and $[\text{C}_5\text{H}_{14}\text{NO}]^+$ (negative mode ESI-MS found: $m/z = 241.77$, 243.77, 245.77; calcd. for RuCl_4^- 242.87. positive mode ESI-MS found: $m/z = 104.11$; calcd. for $\text{C}_5\text{H}_{14}\text{NO}^+$ 104.17, as shown in Fig. 1). The nature of the obtained ChRuCl_4 complex was characterized by FT-IR (Fig. S2) as well as UV-Vis (Fig. S3). From these characterizations, the formation of tetra-coordinated RuCl_4^- via a Lewis acid-base reaction was confirmed. A similar behavior was also observed for metal chlorides such as FeCl_3 , ZnCl_2 , and AlCl_3 in the ChCl system [49].

3.2. Catalytic performance of Ru(III)-ChCl/AC for acetylene hydrochlorination

To provide a preliminary evaluation of different catalysts, their catalytic performance was evaluated in a fixed-bed reactor at 170 °C and high C_2H_2 GHSV of 900 h^{-1} . Fig. 2 shows the catalytic performance of the Ru-10%ChCl/AC catalyst and the corresponding Ru/AC, AC, and 10%ChCl/AC catalysts for comparison. It should be noted that the Ru content in all catalysts was fixed at 0.2 wt%. The Ru/AC catalyst showed a lower catalytic activity and poor stability with an acetylene conversion of 9.0% observed after 25 h of reaction, while both activity and stability were significantly increased for the Ru-10%ChCl/AC catalyst, which exhibited approximately 87.5% acetylene conversion. It should be noted that acetylene conversion values for the AC support and 10%ChCl/AC were only 6.8% and 5.2%, respectively, suggesting a negligible contribution from ChCl to

Fig. 1. ESI-MS spectra of (a) $\text{C}_5\text{H}_{14}\text{NO}^+$ (positive ion mode) and (b) RuCl_4^- (negative ion mode).

Fig. 2. Conversion of acetylene (a) and selectivity for VCM (b) in the acetylene hydrochlorination reaction for 0.2 wt% Ru catalysts over Ru-10%ChCl/AC, Ru/AC, 10%ChCl/AC, and AC catalysts. Reaction conditions: $T = 170$ °C, GHSV (C_2H_2) = 900 h^{-1} , and $V_{\text{HCl}}/V_{\text{C}_2\text{H}_2} = 1.15$.

the high activity of the Ru-10%ChCl/AC catalyst. Meanwhile, all prepared Ru-based catalysts demonstrated more than 99.3% VCM selectivity with only traces of byproducts.

Furthermore, systematic experiments were carried out to investigate the optimal ratio between Ru and ChCl, with the results shown in Fig. 3. The $\text{ChRuCl}_4/\text{AC}$ catalyst was also synthesized for comparison in order to investigate the catalytic activity of the active ruthenium complex in the catalysts. Remarkably, acetylene conversion reached nearly 99.3% for the $\text{ChRuCl}_4/\text{AC}$ catalyst in a short period of time even at the high

Fig. 3. Conversion of acetylene (a) and selectivity for VCM (b) in the acetylene hydrochlorination reaction for 0.2 wt% Ru catalysts with different ChCl contents. Reaction conditions: $T = 170$ °C, GHSV (C_2H_2) = 900 h^{-1} , and $V_{\text{HCl}}/V_{\text{C}_2\text{H}_2} = 1.15$.

GHSV of C_2H_2 ($900\ h^{-1}$). The high activity of the $ChRuCl_4/AC$ catalyst may be due to the enrichment of the active $ChRuCl_4$ complex on the surface of the support. Therefore, the $ChRuCl_4$ complex was identified as the active component in the $Ru(III)-ChCl/AC$ catalyst system. For the $Ru-xChCl/AC$ catalysts where x represents the weight percentage of $ChCl$ in the activated carbon support, it can be seen that neither an insufficient nor excessive content of $ChCl$ in the catalysts led to good catalytic activity and stability. The $Ru-10\%ChCl/AC$ catalyst showed optimum catalytic activity and excellent stability. We also calculated the TOF value to demonstrate the catalytic properties of the Ru -based catalysts, and the TOF value of $Ru-10\%ChCl/AC$ is about $40.7\ min^{-1}$, which makes it one of the most efficient catalytic materials based on TOF (detailed information is shown in Table S1, S2 and Fig. S4). It is worthwhile mentioning that the reaction was performed at lower C_2H_2 conversion when calculating the TOF value in order to eliminate the heat or mass transfer effect. The higher initial activity with low $ChCl$ loading might be due to the higher concentration of the active Ru complex species at the interface of the solid support. The catalysts with a lower $ChCl$ (1% and 5%) content had a relatively high initial acetylene conversion but showed rapid deactivation compared with that of the $Ru-10\%ChCl/AC$ catalyst. This may be caused by the deficiency of $ChCl$ in the catalyst system, which cannot provide adequate protection for the active $ChRuCl_4$ complex. On the other hand, the blockage of pores in the carbon support by excessive $ChCl$ leads to the low activity and poor stability of the $Ru-20\%ChCl/AC$ catalyst, as

observed in the SEM image (Fig. S5(d)) and pore structure parameter characterization (Table S3 and Fig. S6).

In addition, thermal stability evaluation of $ChCl$ was conducted using TG analysis. The TG results imply that decomposition occurs around $300\ ^\circ C$ (Fig. S7), which is $130\ ^\circ C$ higher than the reaction temperature, indicating that $ChCl$ is thermally stable under the reaction conditions. To confirm this excellent performance, the stability test was performed at a high GHSV (C_2H_2) of $540\ h^{-1}$ as a function of reaction time at high but not complete conversion in order to truly monitor stability. The results in Figure S8 show that acetylene conversion over the $Ru-10\%ChCl/AC$ catalyst decreases by 18.4% from 92.2% to 75.2% within 150 h, and the selectivity to VCM is maintained at more than 99.5% for 150 h, indicating that the $Ru-10\%ChCl/AC$ catalyst system exhibits high catalytic activity and stability despite low Ru content and shows great potential for industrial applications.

3.3. Effect of $ChCl$ on $Ru(III)-ChCl/AC$ in acetylene hydrochlorination

3.3.1. Valence change in the active component

XPS spectra were measured to determine the valence states of the ruthenium species in the fresh and used Ru -based catalysts. Deconvolution of the $Ru\ 3p$ profile was used to distinguish the ruthenium species because $Ru\ 3d$ signals overlap with $C\ 1s$ signals [50,51]. Fig. 4 shows the XPS spectra of the fresh and used Ru/AC catalysts and $Ru-10\%ChCl/AC$ catalysts.

Fig. 4. XPS spectra of $Ru\ 3p$ for the fresh and used catalysts. (a) Fresh Ru/AC , (b) used Ru/AC , (c) fresh $Ru-10\%ChCl/AC$, (d) used $Ru-10\%ChCl/AC$. Ru content 0.2 wt%.

Fig. 5. STEM image (a), EDX analysis (b) and elemental mapping images (c–h) of the fresh Ru-10%ChCl/AC catalyst.

For the fresh Ru/AC catalyst, there are more than one ruthenium species present, such as the dominant Ru(III) (463.3 ± 0.3 eV), Ru(> IV) (466.5 ± 0.3 eV), and metallic Ru(0) (461.4 ± 0.4 eV) [21,52,53]. The binding energies and relative contents are listed in Table S4, and are consistent with the observations in the literature [10,16,20,54]. In contrast, there is only one strong peak of Ru(III) in the spectrum of the fresh Ru-10%ChCl/AC catalyst, shown in Fig. 4(c), indicating that the active ChRuCl_4 complex is in the +3 valence state in the catalyst system and the Ru exists in the Ru(III) form due to the formation of the stable ChRuCl_4 complex. However, after 25 h of reaction, compared with that of the fresh Ru/AC catalyst, the relative content of high-valence ruthenium species gradually decreased in the used Ru/AC catalyst (Table S4), and the activity decreased accordingly [16]. However, as seen in Fig. 4(b), the Ru(III) peak shows no obvious change in the used Ru-10%ChCl/AC catalyst. It has been reported that acetylene, being a reductive gas, reduces the metal species in the course of the reaction and thereby causes the rapid deactivation of the catalysts [55]. This demonstrates that the addition of ChCl in RuCl_3 , resulting in the formation of the active ChRuCl_4 complex, can effectively suppress reduction by acetylene gas, and thus maintain its activity during acetylene hydrochlorination.

3.3.2. Catalyst sintering

It is well-known that the aggregation of the metal nanoparticles during the reaction leads to the rapid deactivation of the catalysts [56]. To observe the change in the morphology of the

catalysts before and after the reaction, TEM characterization was used to provide detailed images of the catalysts. The scanning transmission electron microscopy (STEM) image accompanied by the energy dispersive X-ray spectroscopy (EDS)

Fig. 6. TEM images of Ru-based catalysts. (a) Fresh Ru/AC, (b) used Ru/AC, (c) fresh Ru-10%ChCl/AC, (d) used Ru-10%ChCl/AC. Ru content 0.2 wt%.

Table 1

Coke deposition on the catalyst samples.

Sample	Amount of coke deposition (%)
Ru/AC	8.9
Ru-1%ChCl/AC	7.9
Ru-5%ChCl/AC	5.6
Ru-10%ChCl/AC	2.4
Ru-20%ChCl/AC	1.1

spectra suggest the presence of Ru elements, as well as heteroatoms originated from ChCl, such as N, O, and Cl, in the fresh Ru-10%ChCl/AC catalyst sample. It can also be concluded that most of the ruthenium compounds were homogeneously dispersed on the catalyst materials since crystalline nanoparticles were not observed by elemental mapping with STEM/EDS spectroscopy (Fig. 5). This is similar to results reported previously for Au catalysts prepared with a similar method [55,57].

Fig. 6 shows the TEM images of the used Ru/AC and Ru-10%ChCl/AC catalysts. Ru nanoparticles were detected in the used Ru/AC catalyst, as observed in Fig. 6(b). Two characteristic lattice fringes with lattice spacings of 0.21 and 0.23 nm are found in the HRTEM images, which can be attributed to the (101) and (100) crystal faces of Ru, respectively [10]. The appearance of metallic Ru nanoparticles indicates the sintering of the metal on the catalyst during the reaction and is also a reason for the rapid activity decrease of the Ru/AC catalyst. Interestingly, the Ru nanoparticles were not seen after the reaction, and the STEM mapping results show that the Ru, N, O, and Cl elements were still well separated and dispersed throughout the carbon support (Fig. S9). X-ray diffraction (XRD) analysis also showed that no characteristic peak of ruthenium species is detected in the fresh Ru-based catalysts (Fig. S10), which indicates that most ruthenium species are dispersed well or the concentration of Ru is too low to be detected by XRD. These findings confirm that the addition of ChCl inhibits the sintering of the Ru catalyst during the acetylene hydrochlorination reaction. Identical conclusions were also obtained in studies where the presence of ILs stabilized the oxidized metal complex, and thus prevented the agglomeration of the active species [56].

3.3.3. Coke deposition and loss of the active component

Coke deposits may originate from C_2H_2 , VCM, or their oligomers, because C_2H_2 and VCM may oligomerize during the reaction [58]. This would cover the active sites of the catalysts and hinder the access of reactants. Thermogravimetric (TG) analysis was performed to evaluate the degree of carbon deposition on the surface of the Ru-based catalysts. For the monometallic Ru/AC catalyst, the slight mass loss before 150 °C is mainly due to the evaporation of adsorbed water, and the rapid

mass loss above 400 °C is caused by the burning of the carbon support. Therefore, it is the mass loss from 150 to 400 °C that indicates that the variation on the catalyst is potentially caused by coke deposition during the hydrochlorination reaction [27,59]. In the case of the fresh Ru/AC catalyst, the mass loss in the temperature range of 150–400 °C is 1.3%, while it is 10.2% for the used catalyst. Thus, the amount of coke deposition is 8.9% for the Ru/AC catalyst after a 25 h reaction. The coke depositions on the catalysts after a 25 h reaction, determined by the above method, are shown in Fig. S11, and the amounts of coke deposition on the used catalysts are summarized in Table 1. In the Ru(III)-ChCl/AC catalysts, the amount of coke deposition is obviously reduced compared with that of the Ru/AC catalyst, and it decreases with increasing ChCl content. As listed in Table 1, the Ru-20%ChCl/AC catalyst has the least coke deposition of 1.1% but also shows a poor stability, which may be explained by the excessive ChCl on the catalyst, which partially covers the active sites of the $ChRuCl_4$ complex. This proves that ChCl efficiently inhibits the coke deposition, and thereby positively affects the stability of the catalyst in this case.

Additionally, inductively coupled plasma mass spectrometry (ICP-MS) was conducted to confirm the total Ru content of the fresh and used catalysts (Table 2). It can be seen that the Ru content of all the catalyst samples was consistent with the calculated amount, indicating that only a small amount of Ru was lost during the reaction and calcination processes. In addition, the elemental composition of the catalysts measured by XPS is listed in Table 2. The used Ru-10%ChCl/AC catalyst system is thermally stable because no drastic change in N content was observed during the reaction, which is also in good agreement with the TG experiment (Fig. S7) discussed above.

3.3.4. Adsorption properties of the reactants and product

TPD profiles were obtained to study the adsorption properties of the reactants and product on different catalysts. Fig. 7(a)–(c) show the TPD profiles of HCl, C_2H_2 , and VCM, respectively, of the Ru/AC, Ru-10%ChCl/AC, 10%ChCl/AC, and $ChRuCl_4$ /AC samples. The peak area in the TPD profiles reflects the adsorption capacity of active species, and the desorption temperature is correlated with the strength of the adsorbed species [60].

In the He-TPD profile, the strong peak observed at approximately 260 °C is related to the decomposition of ChCl under the test environment. As observed in Fig. 7(a), the HCl desorption peak in Ru-10%ChCl/AC moves to a higher temperature and the desorption area becomes significantly larger than that of the Ru/AC catalyst, indicating an increase in HCl adsorption in the Ru-10%ChCl/AC catalyst. Similarly, $ChRuCl_4$ /AC and 10%ChCl/AC also exhibit strong HCl adsorption, showing the

Table 2

Atomic ratios determined by XPS analysis and the Ru contents in the fresh and used catalysts calculated by ICP analysis.

Sample	Surface atomic composition of the catalysts (%)					Calculated loading (wt%)	Actual loading (wt%)
	C	N	O	Cl	Ru	Ru	Ru
Fresh Ru/AC	89.88	–	9.42	0.53	0.17	0.200	0.186
Used Ru/AC	90.60	–	8.79	0.45	0.16	0.200	0.179
Fresh Ru-10%ChCl/AC	86.79	3.44	5.58	3.97	0.22	0.200	0.180
Used Ru-10%ChCl/AC	87.53	3.41	4.80	4.05	0.21	0.200	0.175

Fig. 7. TPD profiles of the fresh catalysts. (a) HCl-TPD, (b) C₂H₂-TPD, (c) VCM-TPD, (d) He-TPD.

simultaneous contribution of ChRuCl₄ and ChCl species to the increased adsorption of HCl in this catalyst system. The C₂H₂- and VCM-TPD profiles of the 10%ChCl/AC and Ru-10%ChCl/AC samples show a smaller adsorption capacity compared with that of the Ru/AC catalyst, suggesting that excessive ChCl reduces, to some extent, the amount of coke deposition. In addition, it is worth noting that although the ChRuCl₄ serving as an active component in the catalysts has high reactant C₂H₂ adsorption to promote the hydrochlorination reaction, it also increases the probability of coke deposition during the reaction. This may explain why the ChRuCl₄/AC catalyst shows a relatively rapid deactivation under high C₂H₂ GHSV (Fig. 3). Song et al. [61] also proved that the adsorption of C₂H₂ is negatively correlated with catalyst stability. Based on the above reports, the favorable adsorption of HCl and weak adsorption of C₂H₂ on the Ru-10%ChCl/AC catalyst significantly contribute to the excellent stability of the catalysts. Therefore, sufficient HCl adsorbed in Ru(III)-ChCl/AC effectively supplements the consumption of reacted HCl, and reduces the possibility of C₂H₂ deposition on the carbon support. In conclusion, the deactivation by coking is suppressed under adequate HCl adsorption during acetylene hydrochlorination.

In order to explain the interaction between reactants (HCl or C₂H₂) and catalyst species (ChCl or ChRuCl₄) in the Ru(III)-ChCl/AC catalytic system, we carried out a series of DFT calculations. The RuCl₃ molecule was also considered here for comparison. The spontaneity of the adsorption can be investi-

gated by its Gibbs free energy change (ΔG_{ad}). The ΔG_{ad} for HCl

Fig. 8. Stable structure of HCl adsorbed on ChCl. (a) NPA (natural population analysis) charges; (b) DORI function. Green: chlorine, gray: carbon, silver: hydrogen, dark blue: nitrogen, red: oxygen, similarly hereinafter.

and C_2H_2 on $ChCl$, $ChRuCl_4$, and $RuCl_3$ are listed in Table S5. The ΔG_{ad} of C_2H_2 shows that it can be more easily adsorbed on $ChRuCl_4$ than $RuCl_3$ via π coordination (Fig. S14), which leads to a higher acetylene hydrochlorination activity. Additionally, as for HCl molecule, it should be pointed out that $ChCl$ and $ChRuCl_4$ species in this catalyst system both have stronger adsorption than $RuCl_3$, which is consistent with the results presented from HCl -TPD characterization. The structure of HCl adsorbed by $ChCl$ is mainly relying on hydrogen bonds and van der Waals forces (Fig. 8). A strong hydrogen bond is illustrated by the density overlap regions indicator (DORI) function with HCl acting as a hydrogen bond donor [62]. An HCl molecule tends to coordinate with $Ru(III)$ as a Cl^- ligand when it is adsorbed by the $ChRuCl_4$ complex (Fig. 9(a)). The coordination bond order between $Ru(III)$ and the Cl of HCl is 0.476 by Mayer bond order (MBO) calculation [63]. This is consistent with the calculation by the electron localization function (ELF) in Fig. 9(b), which is used to reveal binding and lone electron pairs in simple molecular systems as well [64,65]. Compared with that of the $RuCl_3$ catalyst, this system has an excellent performance in promoting the adsorption of HCl , which significantly improves the catalyst life in acetylene hydrochlorination. Moreover, $ChCl$ has a negative effect on the adsorption of C_2H_2 for $\Delta G_{ad} > 0$, indicating that $ChCl$ may reduce the aggregation of C_2H_2 in the system. Therefore, it is necessary to pretreat and activate the catalyst system with pure HCl to improve the stability of catalysts, which is consistent with the previous reports [4,9,34].

Table 3 shows the bond lengths, Mayer bond orders, and NPA charges of free and adsorbed HCl . The Mayer bond order

Table 3

Comparison of bond length, Mayer bond, and NPA charge of free and adsorbed HCl .

Status	Bond length (Å)	Mayer bond order	NPA charge
Free HCl	1.290	0.953	0.000
HCl adsorbed on $ChRuCl_4$	1.317	0.883	0.296
HCl adsorbed on $ChCl$	1.441	0.797	-0.113

indicates that the covalency of the $H-Cl$ bond decreased after adsorption by $ChCl$ or $ChRuCl_4$. The charge of HCl reveals that it loses electrons when it coordinates with the $ChRuCl_4$ complex and gains electrons from $ChCl$ as the hydrogen bond donor. $ChCl$ and the $ChRuCl_4$ complex simultaneously cause the activation of HCl in the $Ru(III)$ - $ChCl$ /AC system.

3.4. Pattern of catalytic mechanism in this system

The results of this study show that the activation of HCl is the key to improve the catalyst life in this reaction, which is in agreement with previous studies [7,25,66–68]. However, it remains challenging to enhance the adsorption or activation of HCl because the $H-Cl$ bond is sturdy (428 kJ/mol of bond energy) [69]. In this $Ru(III)$ - $ChCl$ /AC system, the enhanced adsorption of HCl has been confirmed by both the experimental and computational results above, where the addition of $ChCl$ and the formation of $ChRuCl_4$ are more effective than traditional $RuCl_3$ catalysts.

The activation of HCl is to facilitate the heterolytic cleavage process by increasing the molecular polarity. Compared with that of the typical covalent molecular bond before adsorption,

Fig. 9. Stable structure of HCl nucleophile adsorbed on $ChRuCl_4$. (a) NPA charges; (b) ELF figure. The plane of $Ru-H-Cl$ triatomic molecule was defined as the XOY plane (rectangular plane). Dark green: ruthenium, similarly hereinafter.

Fig. 10. The interaction between the HOMO of $ChCl$ and the LUMO of HCl (a), the LUMO of $ChRuCl_4$ and the HOMO of HCl (b).

Scheme 1. Proposed catalytic process in this system.

the activation in this system simultaneously enhances the properties of H^+ and Cl^- in the HCl molecule according to Table 3. Specifically, electrons transfer from the highest occupied molecular orbital (HOMO) of HCl to the lowest unoccupied molecular orbital (LUMO) of $ChRuCl_4$. Meanwhile, the LUMO of HCl accepts electrons of the HOMO of $ChCl$ (Fig. 10). It is conducive to reducing the energy barrier for the addition of HCl to C_2H_2 molecule. C_2H_2 can form a complex with $Ru(III)$ as a π ligand; thus, the $C-C$ triple bond is weakened, and can be attacked by nucleophiles or electrophiles [70,71]. A catalytic pathway for the formation of vinyl chloride is proposed in Scheme 1, which shows a synergistic process for this reaction.

As the active site of hydrochlorination reaction, $Ru(III)$ easily coordinates with the reactant C_2H_2 to promote the hydrochlorination reaction, reflecting the high catalytic activity of the catalysts. As has been discussed above, both $ChCl$ and $ChRuCl_4$ in this catalytic system are critical for the adsorption and activation of HCl to facilitate hydrochlorination reactions. Owing to the above advantages, this catalyst system greatly promotes the transformation of acetylene to vinyl chloride, and reduces the side effects such as reduction of the metal salts and carbon deposition on the active sites during the reaction. In consequence, this ionic complex is more effective than traditional metal salt catalysts for heterogeneous catalytic hydrochlorination.

4. Conclusions

In summary, a novel, efficient, and supported $Ru(III)$ - $ChCl$ /AC catalyst system for acetylene hydrochlorination was successfully developed. An active $ChRuCl_4$ ionic complex was obtained and stabilized in the $Ru(III)$ - $ChCl$ /AC system.

The Ru -10% $ChCl$ /AC catalyst realized an acetylene conversion of about 87.5% and a VCM selectivity surpassing 99.3% at 170 °C and C_2H_2 GHSV of 900 h^{-1} . The catalyst characterization showed that $ChCl$ provides adequate protection for the active $ChRuCl_4$ to be stabilized in the $Ru(III)$ form, thus suppressing the reduction of the active Ru complex as well the particle aggregation during the reaction. Furthermore, both experimental results and theoretical analysis revealed that the coordination of acetylene and the activation of HCl were simultaneously initiated, and had a significant synergistic effect on the activity and long-term stability of the Ru -based catalysts. Therefore, the excellent performance of this supported $Ru(III)$ - $ChCl$ /AC catalyst might promote further development of efficient and non-mercury green catalysts in the hydrochlorination industry.

References

- [1] X. Wei, H. Shi, W. Qian, G. Luo, Y. Jin, F. Wei, *Ind. Eng. Chem. Res.*, **2008**, 48, 128–133.
- [2] K. Zhou, W. Wang, Z. Zhao, G. Luo, J. T. Miller, M. S. Wong, F. Wei, *ACS Catal.*, **2014**, 4, 3112–3116.
- [3] H. Zhang, B. Dai, X. Wang, W. Li, Y. Han, J. Gu, J. Zhang, *Green Chem.*, **2013**, 15, 829–836.
- [4] M. Conte, A. F. Carley, C. Heirene, D. J. Willock, P. Johnston, A. A. Herzing, C. J. Kiely, G. J. Hutchings, *J. Catal.*, **2007**, 250, 231–239.
- [5] K. Zhou, J. Jia, C. Li, H. Xu, J. Zhou, G. Luo, F. Wei, *Green Chem.*, **2015**, 17, 356–364.
- [6] X. Li, X. Pan, X. Bao, *J. Energy Chem.*, **2014**, 23, 131–135.
- [7] T. V. Krasnyakova, I. V. Zhikharev, R. S. Mitchenko, V. I. Burkhovetski, A. M. Korduban, T. V. Kryshchuk, S. A. Mitchenko, *J. Catal.*, **2012**, 288, 33–43.
- [8] S. A. Mitchenko, T. V. Krasnyakova, R. S. Mitchenko, A. N. Korduban, *J. Mol. Catal. A*, **2007**, 275, 101–108.

Graphical Abstract

Chin. J. Catal., 2018, 39: 1770–1781 doi: 10.1016/S1872-2067(18)63121-3

Efficient and stable $Ru(III)$ -choline chloride catalyst system with low Ru content for non-mercury acetylene hydrochlorination

Hang Li, Botao Wu, Jianhui Wang, Fumin Wang*, Xubin Zhang*, Gang Wang, Haichao Li
Tianjin University; Qinghai Nationalities University

The supported $Ru(III)$ - $ChCl$ /AC catalyst system, where $ChCl$ provides an environment for the $ChRuCl_4$ to be stabilized as $Ru(III)$, shows superior activity and stability in acetylene hydrochlorination.

- [9] H. Zhang, B. Dai, W. Li, X. Wang, J. Zhang, M. Zhu, J. Gu, *J. Catal.*, **2014**, 316, 141–148.
- [10] Y. Pu, J. Zhang, L. Yu, Y. Jin, W. Li, *Appl. Catal. A*, **2014**, 488, 28–36.
- [11] H. Li, F. Wang, W. Cai, J. Zhang, X. Zhang, *Catal. Sci. Technol.*, **2015**, 5, 5174–5184.
- [12] K. Zhou, J. Jia, X. Li, X. Pang, C. Li, J. Zhou, G. Luo, F. Wei, *Fuel Process. Technol.*, **2013**, 108, 12–18.
- [13] S. A. Panova, G. K. Shestakov, O. N. Temkin, *J. Chem. Soc., Chem. Commun.*, **1994**, 977–977.
- [14] P. Johnston, N. Carthey, G. J. Hutchings, *J. Am. Chem. Soc.*, **2015**, 137, 14548–14557.
- [15] J. Zhao, B. Wang, X. Xu, Y. Yu, S. Di, H. Xu, Y. Zhai, H. He, L. Guo, Z. Pan, X. Li, *J. Catal.*, **2017**, 350, 149–158.
- [16] J. Zhao, S. Gu, X. Xu, T. Zhang, Y. Yu, X. Di, J. Ni, Z. Pan, X. Li, *Catal. Sci. Technol.*, **2016**, 6, 3263–3270.
- [17] K. C. O'Connell, J. R. Monnier, J. Regalbuto, *Appl. Catal. B*, **2018**, 225, 264–272.
- [18] J. Zhang, W. Sheng, C. Guo, W. Li, *RSC Adv.*, **2013**, 3, 21062–21068.
- [19] G. Li, W. Li, H. Zhang, Y. Pu, M. Sun, J. Zhang, *RSC Adv.*, **2015**, 5, 9002–9008.
- [20] L. Hou, J. Zhang, Y. Pu, W. Li, *RSC Adv.*, **2016**, 6, 18026–18032.
- [21] H. Zhang, W. Li, Y. Jin, W. Sheng, M. Hu, X. Wang, J. Zhang, *Appl. Catal. B*, **2016**, 189, 56–64.
- [22] M. Conte, A. F. Carley, G. J. Hutchings, *Catal. Lett.*, **2008**, 124, 165–167.
- [23] M. Conte, C. J. Davies, D. J. Morgan, T. E. Davies, D. J. Elias, A. F. Carley, P. Johnston, G. J. Hutchings, *J. Catal.*, **2013**, 297, 128–136.
- [24] M. Conte, A. F. Carley, G. Attard, A. A. Herzing, C. J. Kiely, G. J. Hutchings, *J. Catal.*, **2008**, 257, 190–198.
- [25] S. Shang, W. Zhao, Y. Wang, X. Li, J. Zhang, Y. Han, W. Li, *ACS Catal.*, **2017**, 7, 3510–3520.
- [26] H. Xu, K. Zhou, J. Si, C. Li, G. Luo, *Catal. Sci. Technol.*, **2016**, 6, 1357–1366.
- [27] B. Nkosi, N. J. Coville, G. J. Hutchings, M. D. Adams, J. Friedl, F. E. Wagner, *J. Catal.*, **1991**, 128, 366–377.
- [28] J. Hu, Q. Yang, L. Yang, Z. Zhang, B. Su, Z. Bao, Q. Ren, H. Xing, S. Dai, *ACS Catal.*, **2015**, 5, 6724–6731.
- [29] J. Zhao, Y. Yu, X. Xu, S. Di, B. Wang, H. Xu, J. Ni, L. Guo, Z. Pan, X. Li, *Appl. Catal. B*, **2017**, 206, 175–183.
- [30] A. Romero, A. Santos, J. Tojo, A. Rodriguez, *J. Hazard. Mater.*, **2008**, 151, 268–273.
- [31] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, V. Tambyrajah, *Green Chem.*, **2002**, 4, 24–26.
- [32] R. Calderon Morales, V. Tambyrajah, P. R. Jenkins, D. L. Davies, A. P. Abbott, *Chem. Commun.*, **2004**, 158–159.
- [33] A. Zhu, T. Jiang, B. Han, J. Zhang, Y. Xie, X. Ma, *Green Chem.*, **2007**, 9, 169–172.
- [34] K. Zhou, B. Li, Q. Zhang, J. Q. Huang, G. L. Tian, J. C. Jia, M. Q. Zhao, G. H. Luo, D. S. Su, F. Wei, *ChemSusChem*, **2014**, 7, 723–728.
- [35] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, M. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision C.01; Gaussian Inc.: Wallingford, CT, **2009**.
- [36] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta*, **1973**, 28, 213–222.
- [37] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.*, **1982**, 77, 3654–3665.
- [38] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, **1988**, 37, 785–789.
- [39] P. J. Hay, W. R. Wadt, *J. Chem. Phys.*, **1985**, 82, 299–310.
- [40] T. H. Dunning Jr, P. J. Hay, *Gaussian Basis Sets for Molecular Calculations*, Springer, New York, **1977**, 1–27.
- [41] J. P. Merrick, D. Moran, L. Radom, *J. Phys. Chem. A*, **2007**, 111, 11683–11700.
- [42] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.*, **1985**, 83, 735–746.
- [43] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B*, **2009**, 113, 6378–6396.
- [44] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.*, **2005**, 7, 3297–3305.
- [45] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.*, **2010**, 132, 154104.
- [46] C. Y. C. b. Legault, Legault, C. Y., Université de Sherbrooke, Canada, **2009**.
- [47] T. Lu, F. Chen, *J. Comput. Chem.*, **2012**, 33, 580–592.
- [48] W. Humphrey, A. Dalke, K. Schulten, *J. Mol. Graphics.*, **1996**, 14, 33–38.
- [49] A. P. Abbott, G. Capper, D. L. Davies, R. Rasheed, *Inorg. Chem.*, **2004**, 43, 3447–3452.
- [50] C. Wagner, A. Naumkin, A. Kraut-Vass, J. Allison, C. Powell, J. Rumble Jr, *National Institute of Standards and Technology: Gaithersburg, MD*, **2003**, 20899.
- [51] A. S. Arico, P. Creti, P. L. Antonucci, J. Cho, H. Kim, V. Antonucci, *Electrochim. Acta*, **1998**, 43, 3719–3729.
- [52] R. Chetty, S. Kundu, W. Xia, M. Bron, W. Schuhmann, V. Chirila, W. Brandt, T. Reinecke, M. Muhler, *Electrochim. Acta*, **2009**, 54, 4208–4215.
- [53] S. Sharma, Z. Hu, P. Zhang, E. W. McFarland, H. Metiu, *J. Catal.*, **2011**, 278, 297–309.
- [54] Y. Jin, G. Li, J. Zhang, Y. Pu, W. Li, *RSC Adv.*, **2015**, 5, 37774–37779.
- [55] Y. Jia, R. Hu, Q. Zhou, H. Wang, X. Gao, J. Zhang, *J. Catal.*, **2017**, 348, 223–232.
- [56] Q. Zhang, I. Lee, J. Ge, F. Zaera, Y. Yin, *Adv. Funct. Mater.*, **2010**, 20, 2201–2214.
- [57] J. Zhao, Y. Yu, X. Xu, S. Di, B. Wang, H. Xu, J. Ni, L. L. Guo, Z. Pan, X. Li, *Appl. Catal. B*, **2017**, 206, 175–183.
- [58] X. Li, P. Li, X. Pan, H. Ma, X. Bao, *Appl. Catal. B*, **2017**, 210, 116–120.
- [59] D. He, X. Jiao, P. Jiang, J. Wang, B. Q. Xu, *Green Chem.*, **2012**, 14, 111–116.
- [60] X. Li, M. Zhu, B. Dai, *Appl. Catal. B*, **2013**, 142, 234–240.
- [61] S. Chao, Q. Guan, W. Li, *J. Catal.*, **2015**, 330, 273–279.
- [62] P. de Silva, C. Corminboeuf, *J. Chem. Theory Comput.*, **2014**, 10, 3745–3756.
- [63] I. Mayer, *Chem. Phys. Lett.*, **1983**, 97, 270–274.
- [64] A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.*, **1990**, 92, 5397–5403.
- [65] A. Savin, R. Nesper, S. Wengert, T. F. Fässler, *Angew. Chem. Int. Ed.*, **1997**, 36, 1808–1832.
- [66] S. A. Mitchenko, T. V. Krasnyakova, R. S. Mitchenko, A. N. Korduban, *J. Mol. Catal. A*, **2007**, 275, 101–108.

- [67] Y. Han, M. Sun, W. Li, J. Zhang, *Phys. Chem. Chem. Phys.*, **2015**, 17, 7720–7730.
- [68] S. Wang, B. Shen, Q. Song, *Catal. Lett.*, **2010**, 134, 102–109.
- [69] B. d. B. Darwent, National Bureau of Standards, **1970**.
- [70] O. Eisenstein, R. Hoffmann, *J. Am. Chem. Soc.*, **1980**, 102, 6148–6149.
- [71] B. Wang, J. L. Jiang, H. Z. Yu, Y. Fu, *Organometallics*, **2017**, 36, 523–529.

一种高效稳定的低负载量的氯化-2-羟乙基三甲胺改性钌基催化剂 用于乙炔氢氯化反应

李 航^a, 吴博韬^a, 王建辉^b, 王富民^{a,*}, 张旭斌^{a,#}, 王 刚^c, 李海朝^c

^a天津大学化工学院, 天津化学化工协同创新中心, 天津300350

^b天津大学理学院化学系, 天津300072

^c青海民族大学化学化工学院, 青海西宁810007

摘要: 来自煤化工的乙炔氢氯化生产氯乙烯的工艺由于其经济优势成为我国生产PVC的主要路线。为了降低该工艺中汞触媒催化剂对环境的毒害, 开发高效环保的乙炔氢氯化无汞催化剂刻不容缓。但已有研究表明, 稳定性差和价格高昂成为制约乙炔氢氯化非汞催化剂工业化的瓶颈。由此, 我们选用价格低廉、催化活性良好的 RuCl_3 作为催化剂的前驱体, 采用浸渍法制备了低负载量的氯化-2-羟乙基三甲胺改性 RuCl_3 的催化剂, 其中活性组分在ESI-MS中观测到是一种离子型配合物, 其阴阳离子分别为 RuCl_4^- 和 $\text{C}_5\text{H}_{14}\text{NO}^+$ 。该催化剂在乙炔氢氯化反应中的测试结果表明, 氯化-2-羟乙基三甲胺的加入可以显著提高催化活性和稳定性。通过透射电镜(TEM)和扫描-透射电镜(STEM)表征表明, 该催化体系的活性组分具有良好的分散性, 季铵盐 $[\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}]\text{Cl}$ 不仅与 RuCl_3 形成配合物为活性组分, 其过量时也提供了一个溶剂环境, 能够稳定活性组分不团聚。透射电镜和X射线光电子能谱(XPS)结果共同表明, 相比于单一负载的 RuCl_3 催化剂, 该催化体系中Ru物种基本保持在+3氧化态, 不易在制备过程中被氧化或在反应过程中被还原性气体乙炔还原为金属颗粒, 表现出了良好的稳定性。程序升温脱附(TPD)结果表明, 氯化-2-羟乙基三甲胺这一季铵盐的加入能够大幅度提升体系对氯化氢的吸附, 降低体系对乙炔和产物氯乙烯的吸附, 从而促进乙炔氢氯化反应的进行, 减少体系吸附乙炔或氯乙烯过强导致的积炭现象。另一方面, 本工作中采用密度泛函理论方法研究了乙炔氢氯化非汞催化剂的性质、催化剂与反应物的吸附和相互作用模式。其中吸附能的计算结果表明, 活性组分和季铵盐都能够提升对氯化氢的吸附, 季铵盐还能够抑制体系对乙炔的吸附, 计算结果与TPD的结果基本一致。对反应物和催化剂之间的相互作用进行了考察, 发现该体系对氯化氢存在一个协同活化的作用, 能够促进H-Cl共价键的异裂, 有利于跨越传统催化剂对氯化氢吸附和活化的障碍。此外, 该催化体系对乙炔氢氯化过程也展现了一个协同催化的模式, 为乙炔氢氯化无汞非均相催化剂的设计提供了参考。

关键词: 乙炔氢氯化; 高活性; 非均相催化; 离子型配合物; 钌

收稿日期: 2018-05-16. 接受日期: 2018-06-06. 出版日期: 2018-11-05.

*通讯联系人. 电话/传真: (022)27890041; 电子信箱: wangfumin@tju.edu.cn

#通讯联系人. 电话/传真: (022)27890041; 电子信箱: tjzxb@tju.edu.cn

基金来源: 国家重点基础研究发展计划(2012CB720302); 国家重点研发计划(2016YFF0102503).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).