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COMMUNICATION

Gas-liquid acetylene hydrochlorination under nonmercuric catalysis using ionic liquids as reaction media†

Gang Qin,[a,b] Yuhan Song,[a] Rui Jin,[a] Jun Shi,[a] Zhiyong Yu[c] and Shaokui Cao*[a]

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By using ionic liquids as reaction media, gas-liquid acetylene hydrochlorination proceeded efficiently under catalysis of nonmercuric metal chlorides.

Acetylene hydrochlorination is a very important industrial process for the production of vinyl chloride monomer (VCM), which is further used as the starting materials for poly(vinyl chloride) production.[1] Although VCM is also obtained by ethylene-based processes, acetylene hydrochlorination is of growing importance because of increasing petroleum prices, since acetylene is derived from coal industry. Currently, acetylene hydrochlorination is still widely applied in VCM production in China (about 7.21 million tons per year), which is primarily performed under the catalysis of $HgC1_2$ supported on activated carbon. However, the $HgC1_2$ catalysis has some inherent disadvantages, especially the catalyst toxicity and volatility.[2,3]

Thermodynamically, acetylene hydrochlorination is highly exothermic (ΔH = −110 kJ mol^{-1}). Even if the packed multitubular reactor with an external cooler is utilized in the current industrial process, the formation of local hot-spots with ultra-high temperature can not be avoided due to the fast reaction speed. Therefore, mercury volatilization and catalyst deactivation are induced to a serious extent, resulting in a severe shortening in catalyst lifetime and significant mercury consumption at high production rate,[4] which consequently is a severe environmental issue.

Nonmercuric catalytic systems for acetylene hydrochlorination have been the subject of research for a long time, and many transition metal compounds, such as Cu(I),[5] Au(III),[6] Pt(II),[7,8] Pd(II),[9] Sn(IV),[10] Rh(III)[11] and Bi(III),[12] have been found to be effective. Some of these nonmercuric catalysts have a similar initial activity and selectivity to $HgCl_2$. Most of these nonmercuric catalysts were investigated through a gas-solid reaction by loading the active component on activated carbon, analogous to the current industrial process with $HgCl_2$ catalysis, which appeared to show a steady decrease in catalytic activity derived from the surface carbonaceous deposition, the pulverization of solid catalyst, the hardening of activated carbon, and so on.[13]

Compared to gas-solid reactions, gas-liquid reaction processes in principle give better temperature control and heat removal.[14] Also, catalytic activity of the active component would be better developed in a homogeneous reaction medium. Gas-liquid reaction process for acetylene hydrochlorination have also been reported.[15–17] While the process has to be carried out at a much lower temperature than the current industrial process (150–180 °C) for the low boiling points of common organic solvents or water. Hence, we believe that ionic liquids (ILs) will resolve these problems very well. ILs have several unique characteristics, such as a polar but weakly coordinating character, non-volatility and are excellent solvents for organic, inorganic and organometallic compounds. Therefore, ILs have attracted enormous interest in many research fields in recent years, especially in the field of catalysis.[18–25]

Herein, we report our efforts in finding some novel reaction systems for acetylene hydrochlorination by using nonvolatile ILs as reaction media, such as [Bmim]Cl, $[Bmim]HSO_4$, $[Bmim]PF_6$, $[Emim]PF_6$, [EPy]Br and $[BPy]BF_4$. Several nonmercuric inorganic salts, specifically $CuCl_2$, $SnCl_4$, $MnCl_4$, H_2PtCl_6 and $HAuCl_4$, were investigated as environmentally benign catalysts; $HgCl_2$ was also evaluated for comparison. To the best of our knowledge, acetylene hydrochlorination with ILs as a reaction medium has not yet been reported.

The gas-liquid acetylene hydrochlorination was performed in a self-designed glass reactor shown in Fig. 1 similar to the bubbling reactor widely employed in gas-liquid reactions. The reactor consists of a gas mixer and two coaxial glass tubes with different diameters. The outer tube has a diameter of 15 mm and a height of 400 mm. The internal tube used as a concentric draft tube has a diameter of 12 mm. The inner tube is separated from the outer tube by 1.5 mm in order to achieve a long reaction path about 340 mm by using minimum amount of ILs. About 20 mL of the mixture of ILs and metal chloride was stored in the outer tube which was immersed in a thermostatic oil bath. Acetylene and hydrogen chloride with a certain ratio, which was controlled by a glass rotameter, were injected into the gas mixer for a uniform mixing and then bubble flowed from the

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[a] *School of Materials Science and Engineering, Zhengzhou University, Zhengzhou, 450052, China. E-mail: caoshaokui@zzu.edu.cn; Fax: +86-371-6676-3561; Tel: +86-371-6676-3561*
[b] *School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo, 454001, China*
[c] *Beijing Longzida Science and Technology Development Co., Ltd., Beijing, China*

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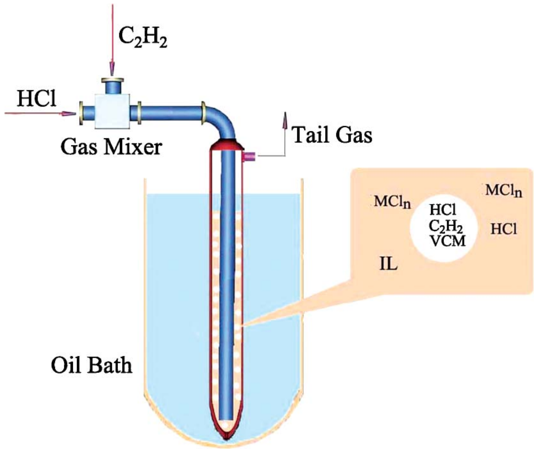

Fig. 1 Reactor illustration for a gas-liquid acetylene hydrochlorination.

reactor bottom. The outlet gas composition was measured by gas chromatography.

First of all, several ILs, specifically [Bmim]Cl, [Bmim]HSO_4, [Bmim]PF_6, [Emim]PF_6, [EPy]Br and [BPy]BF_4, were used as the reaction medium for VCM synthesis by acetylene hydrochlorination using $CuCl_2$ as a catalyst. The results are listed in Fig. 2, and indicate that the catalytic activity of $CuCl_2$ is influenced by the nature of ILs. Organic solvents were also examined for comparison, acetylene conversion and VCM selectivity are 4.5% and 71.5% respectively in PEG-10000 (column 1), and those in DMSO are 6.3% and 54.4%, respectively (column 2). Both acetylene conversion and VCM selectivity are much higher in all ILs examined, among which [Bmim]Cl (column 3) performs the best with 68.1% acetylene conversion and 97.5% VCM selectivity. Therefore, [Bmim]Cl was used as the reaction medium to investigate the catalytic behavior of other metal chlorides in the following experiments. Simultaneously, the anion of ILs also affects the catalytic activity in the order of $Cl^- > HSO_4^- > PF_6^-$, which corresponds to the solubility order of $CuCl_2$ in ILs.

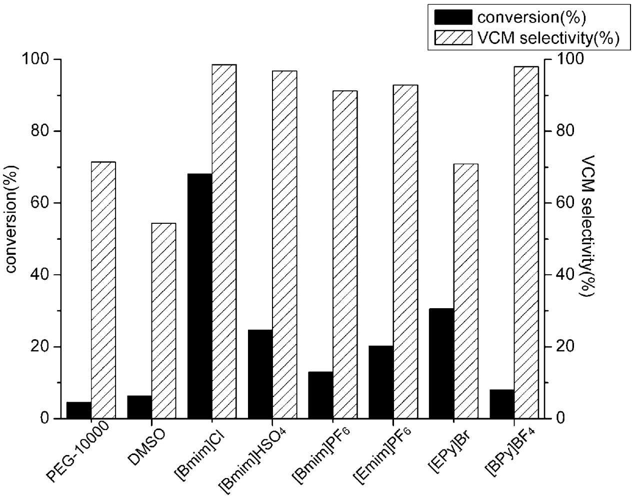

Fig. 2 Acetylene hydrochlorination in different liquid media using $CuCl_2$ as catalyst (reaction conditions: 160 °C; HCl: 0.4 L h^{-1}; C_2H_2: 0.3 L h^{-1}; $CuCl_2$: 0.058 mol L^{-1}).

Several metal chlorides were investigated as catalyst in [Bmim]Cl for acetylene hydrochlorination, and the results are shown in Fig. 3. It can be observed that both $HAuCl_4$ and H_2PtCl_6 gave the highest acetylene conversion, which are 78.5% and 79.5%, respectively. The conversion follows the order of Au ≈ Pt > Hg ≈ Cu > Mn > Sn, and all the metal chlorides showed high VCM selectivity, from 82.8% the lowest ($MnCl_4$) to 98.5% the highest ($HAuCl_4$).

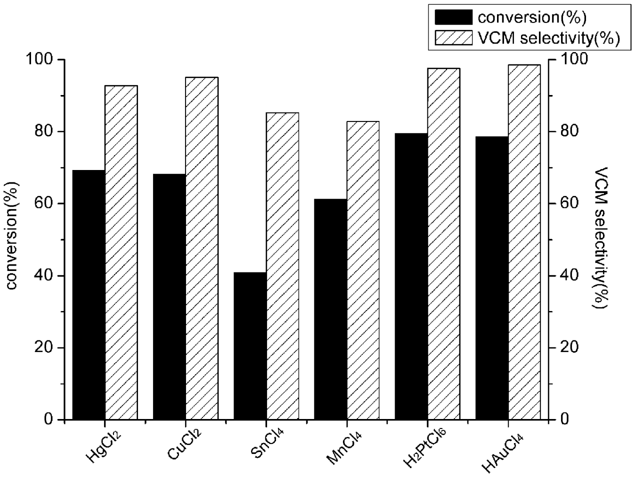

Fig. 3 Different metal chlorides as catalyst for acetylene hydrochlorination (reaction conditions: IL: [Bmim]Cl; 160 °C; C_2H_2: 0.3 L h^{-1}; HCl: 0.31 L h^{-1}; catalyst concentration: 0.069 mol L^{-1}).

Evidently, when ILs are used as the reaction media, the catalytic activity of metal chlorides for the gas-liquid reaction of acetylene hydrochlorination exhibits the same rule as the gas-solid reaction using metal chlorides supported on activated carbon as catalysts.[26,27] The catalytic activity of metal chlorides for acetylene hydrochlorination correlates significantly with the standard reduction potential of the metal cation. Essentially, a cation with higher standard reduction potential displays a higher catalytic activity. Au(III) and Pt(II) have the highest reduction potentials, which are 1.42 V and ~1.2 V respectively. Therefore, it is not a surprise that $HAuCl_4$ and H_2PtCl_6 exhibited the highest catalytic activity for the gas-liquid reaction of acetylene hydrochlorination in ILs observed in our experiments.

Considering $CuCl_2$ is much less expensive than $HAuCl_4$ and H_2PtCl_6 and exhibits reasonable catalytic behavior comparable to $HgCl_2$, $CuCl_2$ is believed to be the best candidate for industrial application for both economic and environment reasons. Hence, optimization of reaction conditions was concentrated on using $CuCl_2$ as catalyst and [Bmim]Cl as the reaction medium for the gas-liquid reaction of acetylene hydrochlorination, which may provide some valuable data for further scaling-up of the reaction.

Firstly, the effect of molar ratio of C_2H_2 with HCl on the reaction was investigated under two sets of conditions as shown in Fig. 4. Obviously, a slight excess of HCl is necessary for the reaction, and a good acetylene conversion can be achieved when the molar ratio of HCl to C_2H_2 is varied in between 1.03 : 1.00 and 1.50 : 1.00. Acetylene conversion decreases with further increase in HCl to C_2H_2 molar ratio, which might be ascribed to the dilution effect of HCl on C_2H_2 under higher molar ratio. Besides, VCM selectivity decreases gradually with the increase in HCl to C_2H_2 molar ratio, because of further excess HCl addition to VCM producing 1,2- or 1,1-dichloroethane. If

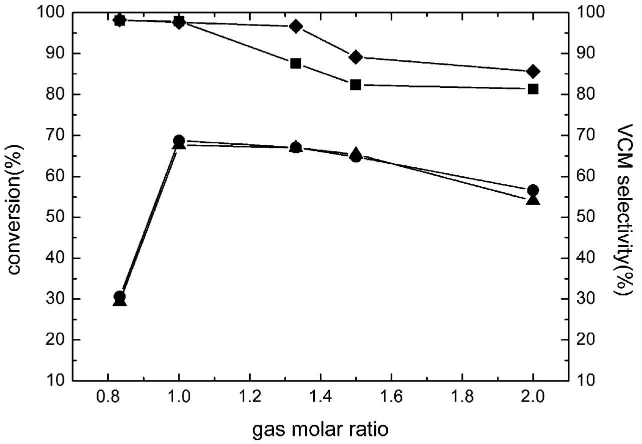

Fig. 4 Influence of HCl/C_2H_2 molar ratio on acetylene hydrochlorination in [Bmim]Cl (● acetylene conversion, ◆ VCM selectivity, 160 °C, $CuCl_2$: 0.319 mol L^{-1}; ▲ acetylene conversion, ■ VCM selectivity, 180 °C, $CuCl_2$: 0.664 mol L^{-1}).

C_2H_2 is in excess, the catalyst might be reduced by the excess C_2H_2, which is one of the reasons for metal halide catalyst deactivation.[28]

The effect of space velocity on acetylene hydrochlorination was also investigated under two sets of reaction conditions with fixed HCl to C_2H_2 molar ratio of 1.03 : 1.00 as illustrated in Fig. 5. Results indicated that acetylene conversion decreases from 71.5% to 36.7% (160 °C) and from 72.6% to 40.3% (180 °C) as the space velocity increases from 10 h^{-1} to 91.5 h^{-1}, which resulted from incomplete reaction because of the short residence time at higher gas space velocity. To ensure sufficient reaction with reasonable reactant residence time and gas space velocity, a slim reactor design or connected reactors in series would be preferred as shown above. Additionally, VCM selectivity is not affected evidently by the space velocity, which is kept above 90% all the time.

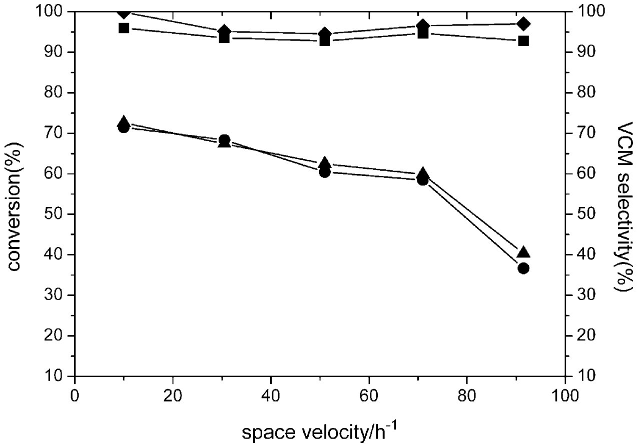

Fig. 5 Influence of space velocity on acetylene hydrochlorination in [Bmim]Cl (● acetylene conversion, ◆ VCM selectivity, 160 °C, $CuCl_2$: 0.051 mol L^{-1}; ▲ acetylene conversion, ■ VCM selectivity, 180 °C, $CuCl_2$: 0.172 mol L^{-1}).

The results illustrated in Fig. 6 show that the acetylene conversion changed little with the increase in the test range of $CuCl_2$ concentration and was constant at nearly 67% under two sets of reaction conditions. In current commercial VCM processes the $HgCl_2$ loading on activated carbon is typically 10–12% (weight percent) in general. Our dosage of metal chloride as catalyst in IL is far below this value. The lower limit for the $CuCl_2$ in this study loading was 0.7% (weight percent), which is equal to 0.05 mol L^{-1}. This may come from the easy formation of a six-membered ring active center from the cation of metal chloride in ILs.[29] In other words, IL may facilitate the catalytic active center formation and hence promote the acetylene hydrochlorination, which would be a topic for further research.

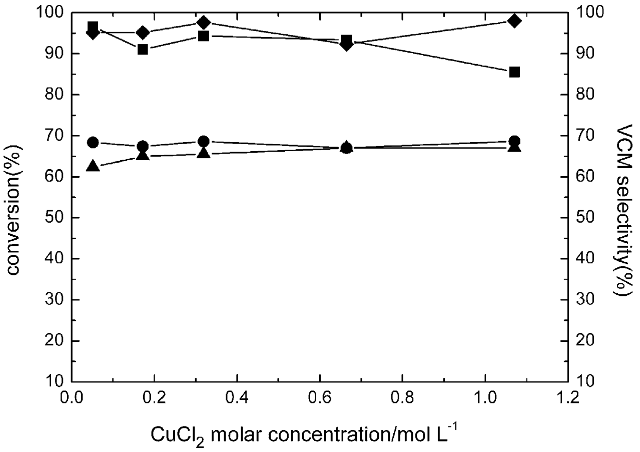

Fig. 6 Influence of $CuCl_2$ concentration on acetylene hydrochlorination in [Bmim]Cl (● acetylene conversion, ◆ VCM selectivity, 160 °C, HCl: 0.31 L h^{-1}; C_2H_2: 0.3 L h^{-1}; ▲ acetylene conversion, ■ VCM selectivity, 140 °C, HCl: 0.4 L h^{-1}; C_2H_2 0.3 L h^{-1}).

The results in Fig. 7 indicated that the acetylene conversion reaches a maximum value at around 160 °C and decreases below or above this temperature. This conversion change with reaction temperature is attributed to the exothermic character of acetylene hydrochlorination. On the other hand, the conversion rapidly declines above 180 °C, which is probably due to the catalyst deactivation. Interestingly, the VCM selectivity is nearly stabilized at 94.3%. The catalyst deactivation at higher

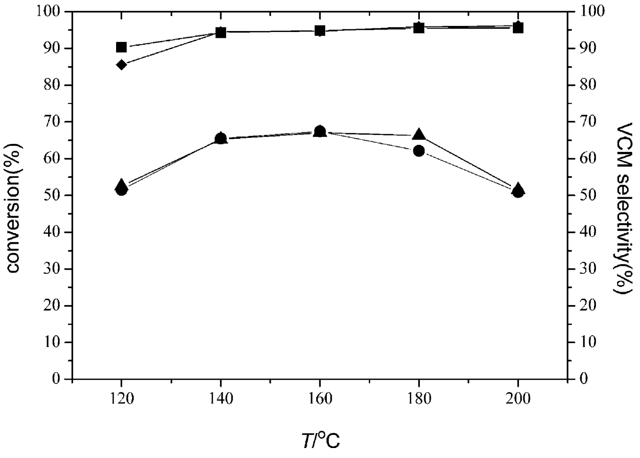

Fig. 7 Influence of temperature on acetylene hydrochlorination in [Bmim]Cl (● acetylene conversion, ◆ VCM selectivity, HCl: 0.31 L h^{-1}; C_2H_2: 0.3 L h^{-1}; $CuCl_2$: 0.051 mol L^{-1}; ▲ acetylene conversion, ■ VCM selectivity, HCl: 0.4 L h^{-1}; C_2H_2: 0.3 L h^{-1}; $CuCl_2$: 0.319 mol L^{-1}).

temperature is not related to the thermal decomposition of [Bmim]Cl which starts to decompose at 285 °C.

As illustrated in Fig. 8, the whole process of acetylene conversion and VCM selectivity with running time takes on S-shaped curves. The reaction is slowly going on during the initial section before 50 min. Thereafter, the conversion and selectivity are rapidly enhanced with the increase in running time and finally reach stable values of 62.5% and 99%, respectively, at around 160 min. Even when the reaction was carried out for 3 days, no decrease in catalytic activity was observed. This provides a distinct advantage over previously reported non-mercury catalysts, which present a short lifetime in the gas-solid reaction, for example, only several hours due to the fast deactivation generally derived from the carbon deposition and the regional hot-spot. The extended catalytic lifetime in ILs presents a promising prospect for practical industrial application.

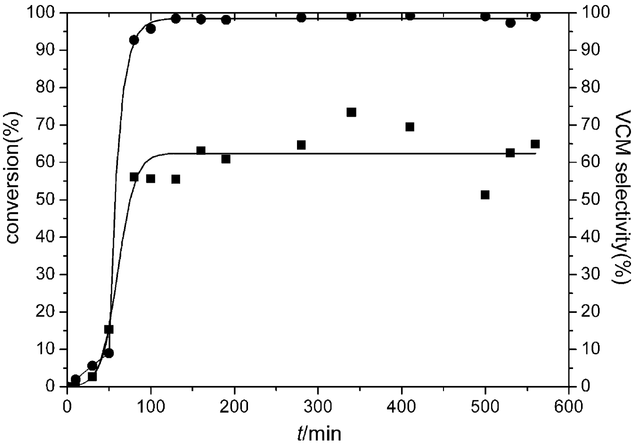

Fig. 8 Influence of running time on acetylene hydrochlorination in [Bmim]Cl (■ acetylene conversion, ● VCM selectivity. 140 °C, HCl: 0.4 L h^{-1}; C_2H_2: 0.3 L h^{-1}; $CuCl_2$: 0.058 mol L^{-1}).

In conclusion, when ILs were used as a reaction medium, the gas-liquid acetylene hydrochlorination reaction was successfully demonstrated. The use of alternative metal chloride catalysis was also carried out. The disadvantages of a gas-solid reaction, such as the carbon deposition and the regional hot-spot, could be overcome. The nonmercuric metal chlorides also provide good acetylene conversion and VCM selectivity. Therefore, the combination of ILs and nonmercuric metal chlorides provides an efficient, economic and environment-friendly approach for acetylene hydrochlorination. These significant results suggested a hopeful alternative approach for industrial VCM production.

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