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Catalytic Behavior of Au Confined in Ionic Liquid Film: A Kinetics Study for the Hydrochlorination of Acetylene

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Abstract: A systematic study of the kinetics of supported-ionic-liquid-phase (SILP) Au catalysis (Au-IL/AC) has been established in the continuous gas-phase hydrochlorination of acetylene. We reveal that the effect of ionic liquid (IL) film on substrate diffusion can be eliminated. The reaction order of the catalyst indicates that Au is confirmed to exist as a monomer in the IL film of the Au-IL/AC system, which is different from the fast equilibrium of the “Au dimer and monomer” for the classical Au/AC catalyst. The homogeneous reaction micro-environment is confirmed for Au-IL/AC since the activation energy was little changed under both heterogeneous and homogeneous catalysis, further verifying the monatomic characteristics of Au in Au-IL/AC. Due to the supported IL film, the reaction order of hydrogen chloride was decreased from 1 to 0.5 while creating a hydrogen chloride enrichment system around Au, which provides the possibility of producing vinyl chloride with an equal substrates feed ratio. This kinetic-perspective-based revelation of the catalytic behavior of the metal active sites confined in IL film enriches and expands the SILP catalytic system for acetylene hydrochlorination.

Keywords: kinetics; SILP; ionic liquid film; reaction order; acetylene hydrochlorination



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1. Introduction

Polyvinyl chloride (PVC) is a widely used plastic in the world because of its high resistance to photo and chemical degradation [1–5]. During the past decade, acetylene hydrochlorination has dominated about 70% of total PVC production in China [3–5]. The acetylene hydrochlorination reaction, catalyzed by mercuric chloride (HgCl₂), is a dominant process in manufacturing vinyl chloride monomer (VCM). However, the strong exothermic nature of the reaction promotes the sublimation of HgCl₂, resulting in a severe waste of resources and ecological damage [6]. Thus, exploring an environmentally friendly catalytic system is imperative. Most studies have concentrated on Au-based catalysts to replace Hg-based catalysts in acetylene hydrochlorination since the commercialization of this catalyst in China by the Hutchings group [2]. Contemporaneously, Hutchings showed that the intrinsically active surface species is the Au monomer entity, which is unstable and easily deactivated due to the reduction of Auⁿ⁺ ($n = 3, 1$) by C₂H₂ [1].

To restrain the reduction of the oxidized Au species while enhancing the activity of the Au catalyst, some strategies were adopted to stabilize the oxidized Au as well as improve the dispersion of Auⁿ⁺. For example, choosing Au complexes with higher stability constants, such as Na₃Au(S₂O₃)₂ (stability constants: 5·10²⁸ compared to 10²⁶ of AuCl₃), as the precursor has been successfully verified as an effective method [2]. Reducing the valence state of gold species from Au³⁺ to Au⁺ (AuCl₃ → AuCl) is also a feasible method [7]. In addition, the modification of Au-based catalysts by adding a second metal component (Bi [7], Cu [8–10], Ba [11], Co [12], Ni [13], La [12], Cs [14,15], Sn [16], Y [17], Co [18], La [19], and Ir [20]) may be an effective strategy as well. Despite the promising initial catalytic activity, to date, there has been no public announcement of any process for the installation of the

above catalysts. One important reason that should not be ignored is that the price required to run a full catalytic life cycle with these catalysts is not attractive to existing industrial systems [1,2,21]. The substantial research on Au-based catalysts suggests that the efforts to construct an efficient and stable gold-based catalyst for acetylene hydrochlorination should circumvent the sintering of Au while increasing the concentration of effective active species and maintaining a higher oxidation state since the activity of the highly active catalysts comprising cationic Au monomers correlates with the ratio of Au^{n+} [1,22,23].

In our previous works, a highly active supported-ionic-liquid-phase (SILP) Au catalyst was first reported for acetylene hydrochlorination, showing superior activity and stability after immobilizing a thin ionic liquid film onto activated carbon support because of the high dispersion of gold [24,25]. In this system, the active Au species was confined in the supported ionic liquid film. Although this experimentally demonstrated that such systems (SILP systems) may exhibit outstanding catalytic performance compared to the uncoated analogy, the inevitable cause-and-effect relationship between the origins of such effects and the thin ionic liquid film and its related kinetics is not yet understood. In this work, the kinetics of the Au-SILP system were studied on how the ionic liquid interacts with the active centers and effective concentrations of the substrates, including the mass transport limitations in the ionic liquid film, the activation energy (E_a), the homogeneous nature of the catalyst, the kinetic reaction orders for the catalyst, C_2H_2 , and HCl, and the solubility of gaseous reactants in the ionic liquid film. The results illustrate that Au-IL/AC is a promising mercury-free catalyst for acetylene hydrochlorination reactions.

2. Results and Discussion

2.1. Activity and Stability

The Au-IL/AC and Au/AC catalysts were tested at the temperature of 463 K for 10 h with a 1,2-feed mole ratio of HCl to C_2H_2 . The activity of the catalysts and the selectivity of VCM were in good agreement with our previous reports [24,25]. During the test time of 10 h on stream, the C_2H_2 conversion of the Au-IL/AC catalyst remained unchanged, as shown in Figure 1, which implied that the addition of ionic liquid (IL) not only caused the higher activity of C_2H_2 but also accelerated the reaction at the initial stage of the reaction. It should be highlighted that for both Au-based catalysts, the selectivity for the formation of VCM was above 99.8%, corroborating the performance of a typical Au system catalyst in this field. Hutchings mentioned that the induction period for Au-based catalysts was allotted to the redox coupling of the $\text{Au}^{3+}/\text{Au}^+$ sites [1]. Our recent results have shown that the ultra-high $\text{Au}^{3+}/\text{Au}^+$ contents in the Au-SILP system should be a necessary factor for its high activity compared with reference Au/C [25]. However, the kinetic effect on catalytic performance should not be ignored when the Au species is confined in IL film, which is lacking in the existing IL catalytic system.

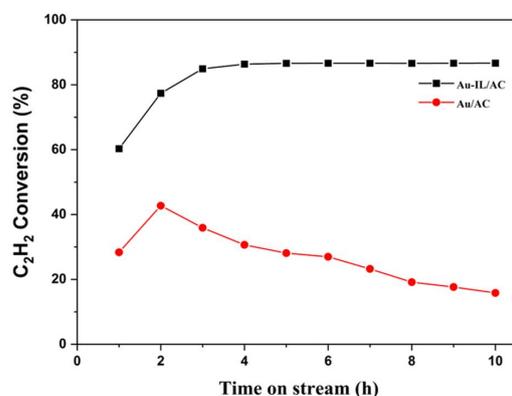


Figure 1. Comparison of catalytic performance between 1 wt.% Au-IL/AC and 1 wt.% Au/AC. Reaction conditions: $T = 463$ K, $\text{GHSV} (\text{C}_2\text{H}_2) = 370 \text{ h}^{-1}$, $V(\text{HCl})/V(\text{C}_2\text{H}_2) = 1.2$. The standard deviations (SDs) for the black and red data are 8.43 and 8.36, respectively.

2.2. Kinetics

2.2.1. Effect of IL Film on Substrate Diffusion

The concept of catalytic SILP materials may be influenced by mass transport limitations in two-phase systems [26,27] because of the relatively long diffusion film of substrate molecules to the active center compared to conventional heterogeneous catalysts, which may play an important role in the effective reaction rate. In the typical SILP system, the Mears criterion, C_{Mears} , is often used to evaluate the effect of IL film on substrate diffusion according to Equation (1) [28].

$$C_{Mears} = \frac{r_{eff} \cdot \rho_{Cat} \cdot \frac{d_p}{2} \cdot n}{C_{bulk} \cdot k_{film}} \leq 0.15 \quad (1)$$

The reaction rate r_{eff} is calculated from the molar substrate flow, the conversion, and the catalyst mass according to Equation (2).

$$r_{eff} = \frac{n \cdot X}{m_{Cat}} \quad (2)$$

The molecular diffusion coefficient can be estimated from Equation (3) [29].

$$D_{i,IL} = 5.28 \times 10^{-18} \frac{T}{\eta_{IL}^{0.66} V_{mol,i}^{1.04}} \quad (3)$$

The film diffusion rate constant k_{film} is calculated from the mass flow density J_{12} using correlations in Equations (4) and (5) [30,31].

$$J_{12} = 0.84 \cdot Re^{-0.51} \quad (4)$$

$$J_{12} = \frac{Sh}{Re \cdot Sc^{0.33}} = \frac{k_{film} \cdot \eta^{0.67}}{u \cdot D_{i,IL}^{0.67}} \quad (5)$$

All necessary calculation parameters are shown in Table 1.

Table 1. The data points for film diffusion estimations.

Parameter	Symbols	Unit	Value
Temperature	T	K	463.15
Pressure	P	Pa	101,325
Gas mixture concentration	C	$\text{mol} \cdot \text{m}^{-3}$	26.31
Particle diameter	d_p	m	$1.78 \cdot 10^{-4}$
Viscosity of gas mixture	η	$\text{m}^2 \cdot \text{s}^{-1}$	$1.35 \cdot 10^{-5}$
Gaseous density	ρ_g	$\text{kg} \cdot \text{m}^{-3}$	0.83
Inner tube diameter	d_R	m	0.01
Gas velocity	u	$\text{m} \cdot \text{s}^{-1}$	1.43
Reynolds number	Re	/	880.38
Gas mixture volume	$V_{mol,i}$	$\text{m}^3 \cdot \text{mol}^{-1}$	$3.40 \cdot 10^{-5}$
Molecular diffusion coefficient	$D_{i,IL}$	$\text{m}^2 \cdot \text{s}^{-1}$	$1.77 \cdot 10^{-7}$
Porosity	ϵ_p	/	0.50
Film diffusion rate constant	k_{film}	$\text{m} \cdot \text{s}^{-1}$	$2.07 \cdot 10^{-3}$
gas mixture molar flow	\dot{n}	$\text{mol} \cdot \text{s}^{-1}$	$7.44 \cdot 10^{-10}$
gas mixture conversion	X	/	0.20
gas mixture molar mass	M	$\text{kg} \cdot \text{kmol}^{-1}$	31.65
Mass SILP catalyst	m_{Cat}	kg	$2.00 \cdot 10^{-4}$
Mass-related effective reaction rate	r_{eff}	$\text{mol} \cdot \text{kgcat}^{-1} \text{ s}$	$7.43 \cdot 10^{-7}$
Density of catalyst bed	ρ_{cat}	$\text{kg} \cdot \text{m}^{-3}$	100
Reaction order	n	/	1.50
Mears criterion	C_M	/	$1.82 \cdot 10^{-4}$

The calculated Reynolds number Re was 880.38, which was sufficiently little to ensure the flow properties are approximately laminar flow [32]. Additionally, the calculated $C_{Mears} = 1.82 \cdot 10^{-4}$ was smaller than the lower limit of the standard value. In this case, the effect of substrate diffusion in the IL film can be completely eliminated [28]. This result is meaningful because it shows that the distribution of the substrates in the IL film during the reaction of the SILP system (where the gas first contacts the IL film and then reacts with the active center) is negligible, even if the Au species is dissolved in the IL phase instead of being exposed on the surface of the carbon carrier.

2.2.2. Effect of IL Film on the Dispersion of Active Sites

To intuitively compare the catalytic activity of the Au-IL/AC and Au/AC catalysts, as well as to further study the relationship between the ionic liquid and the active center, the activation energy (Ea), rather than turnover frequencies ($TOFs$), has been selected for measurement [33]. It is due to the fact that a suitable method has not been identified to accurately calculate the active sites on the Au-IL and Au/AC catalysts. To determine the values of Ea over Au-IL/AC and Au/AC, respectively, the VCM formation rate (R) was measured as a function of temperature (T) in the range of 443.15–493.15 K under ambient pressure with the HCl/C₂H₂ molar ratio of 1.2 [28,32]. The kinetic parameters of Ea were calculated based on the Arrhenius plots ($\ln(R)$ versus $1/T$) for the Au-IL/AC (black line) and Au/AC (red line) catalysts, shown in Figure 2. The straight line indicates that the mass transfer limitations were negligible [33], which verified that the reaction was kinetics-controlled under the above conditions. A relatively steeper slope was observed for the Au/AC catalyst, corresponding to $Ea_{Au/AC} = 50$ kJ/mol. By contrast, the Au-IL/AC catalyst significantly promoted the acetylene hydrochlorination reaction with $Ea_{Au-IL/AC} = 26$ kJ/mol.

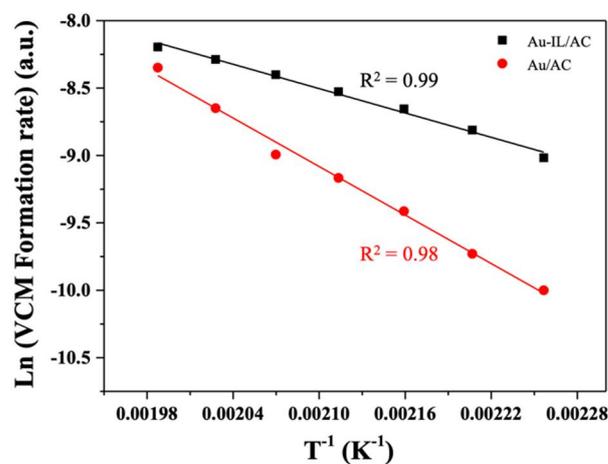


Figure 2. Arrhenius plot for the VCM formation rate over the 1 wt.% Au-IL/AC (black) and Au/AC (red) catalysts. The SDs for the black and red data are 0.29 and 0.52, respectively.

It is well-known that in SILP catalysis, transition metal dissolves in the ionic liquid phase, supported on a solid surface, which then works as a homogeneous catalyst [24,25,28,34,35]. Hence, proving the homogeneous nature of this SILP catalysis is more important than usual. Although this area is not yet highly developed, some useful spectroscopic methods, such as IR spectroscopy, have successfully proven that Rh-SILP catalysts behaved similarly to analogous rhodium-xanthene catalysts dissolved in the homogeneous phase for the hydroformylation of propene [36]. However, few studies have reported the homogeneous nature of SILP catalysts by kinetic experiments. In Figure 2, the effective activation energy for the gas-liquid Au-IL catalyst is calculated to be 30 kJ/mol (Figure S2), similar to 26 kJ/mol for the Au-IL/AC SILP system, suggesting the active Au center over the Au-IL/AC surface is homogeneous, presenting a catalytic characteristic of “macro-heterogeneous and micro-homogeneous”.

As shown in Figure 1, the addition of ionic liquid plays a dramatic promotion role in both the activity and stability of the catalyst, with a C_2H_2 conversion increase of 30–70% during the entire evaluation time. As previously stated, the catalytic activity depends on the number of active sites [24]. We conjectured that the addition of ionic liquid may have a positive influence on the number of active surface sites. Thus, the above hypothesis was validated by determining the reaction order to the concentration of the catalyst. As shown in Figure 3, $\ln R$ was plotted against $\ln[Cat.]$ ([Cat.]: concentration of catalyst). For the Au/AC catalyst, the linear fitting was 0.5. According to the literature, a 0.5 catalyst order implies that a fast equilibrium between the Au dimer and the active Au monomer [37,38] exists on the surface of the Au/AC catalyst. The Au monomer has been determined as the active site for acetylene hydrochlorination [1–3]. For the typical Au/AC, it has been confirmed that the Au dimer exists without the participation of IL [1]. Similar results have been proven in other catalytic reactions, such as the Fe-catalyzed allylic amination of olefins [39], Ir-catalyzed borrowing-hydrogen processes [40], Rh-catalyzed selective partial hydrogenation of alkynes [41], Pd-catalyzed arene C-H acetoxylation [42], and Cu-catalyzed phosphodiester hydrolysis [43], demonstrating that an equilibrium between the active monomer species and its dimer species exists.

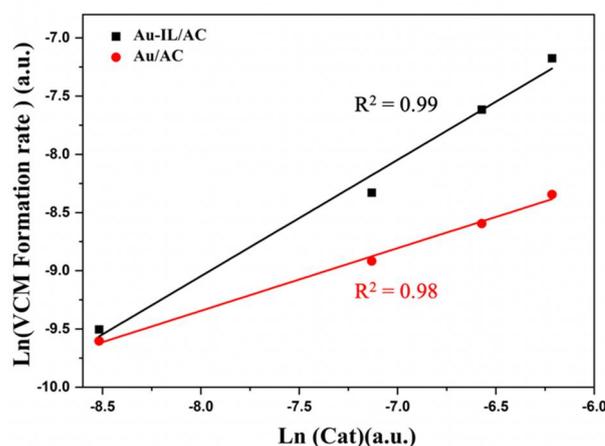


Figure 3. Changes in the natural logarithm of the VCM formation rate with the natural logarithm of the catalyst concentration. The SDs for the black and red data are 1.01 and 0.54, respectively.

In comparison, IL was added to the Au/AC catalyst. In this case, the fitting result (the black line shown in Figure 3) indicated that the reaction order to Au-IL/AC was 0.99, which can be approximately regarded as 1. This significant result implies that an interaction between IL and $AuCl_3$ exists [24,25], restraining the self-aggregation of $AuCl_3$ and further avoiding the formation of the non-active dimer entirely. Adding IL to the Au/C system avoids the self-aggregation of the active Au species, ensuring the existing state of the Au monomer. The homogeneous distribution of Au was confirmed in Au-IL/AC (Figure S1). This result confirms our speculation that the studied Au-IL/AC system follows the characteristics of “macro-heterogeneous and micro-homogeneous”.

2.2.3. Effect of IL Film on the Enrichment of Substrates

The kinetic reaction orders for C_2H_2 and HCl with respect to the formation rate of VCM were determined under the following reaction conditions: 463K, 16.8 mL/min HCl, and the molar ratio of C_2H_2 /HCl was adjusted from 0.3, 0.5, 0.7, 0.9 to 1.0. The value of $n(C_2H_2)$ for Au-IL/AC was calculated according to the slope, which can be easily obtained from the $\ln R - \ln(C_2H_2)$ relationship (Figure 4). The reaction order of C_2H_2 over Au-IL/AC was 1, corroborating the reaction mechanism proven in previous literature [32]: the reaction process is triggered by C_2H_2 adsorption [1,2,44]. Measuring the reaction order to HCl, all reaction factors except the molar ratio of HCl/ C_2H_2 were kept constant. The molar ratio

of HCl/C₂H₂ varied from 0.3 to 1.0. The reaction order of HCl, $n(\text{HCl})$, was 0.5 over the Au-IL/AC system, which was different from C₂H₂.

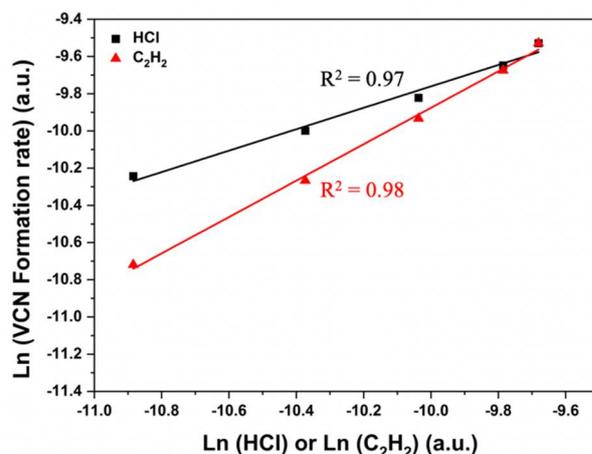


Figure 4. Changes in the natural logarithm of the VCM formation rate with the natural logarithm of the reactant concentrations. The SDs for the black and red data are 0.28 and 0.47, respectively.

To our knowledge, IL can modify the effective concentrations of the substrates [34,35] so that the solubility of gaseous reactants in IL differs in an appropriate manner from that in the initial gas-phase concentration. As mentioned above, the kinetic reaction order for C₂H₂ and HCl were 1 and 0.5, respectively, probably due to the solubility of the substrates in IL film. Additionally, some reports have shown that C₂H₂ and HCl could be physically and chemically adsorbed into ILs. Meanwhile, ILs with relatively strong basicity often show impressive performance in the substrate molecule's solubility and activate C₂H₂ and HCl effectively [45–47]. Specifically, the hydrogen-bond interaction between anions of ionic liquid and reaction gas (C₂H₂ and HCl) forms C₂H₂-Cl and [HCl₂][−] species [48–51]. The two advantages may facilitate the different reaction orders for C₂H₂ and HCl. In view of this, gas solubility was tested in this work. The solubility evaluation of C₂H₂ and HCl in Prmim-Cl, with the test temperatures and pressures, were 5.58 and 0.14 mol/L, and the ratio of the solubility of HCl to C₂H₂ was nearly 40 (see the supporting information for more details). Obviously, the ultra-high enrichment ratio obtained means that HCl is enriched, decreasing the reaction order of HCl in the supported IL film. This HCl-enriched strategy provides the possibility of producing vinyl chloride with an equal acetylene/hydrogen chloride feed ratio of 1:1.

3. Materials and Methods

Catalyst Preparation: The supported Au catalysts were prepared using a wet impregnation technique. A series of carbon-supported gold-based catalysts were prepared via a wet impregnation method. Firstly, HAuCl₄·xH₂O (Alfa Aesar, 99.9%) was dissolved in hydrochloric acid (Fisher, 32 wt.%). Then, 1-propyl-3-methylimidazolium chloride (Prmim-Cl, Lanzhou Greenchem Co., Ltd., Lanzhou, China, 99%) was added to the Au-containing solution and mixed uniformly. After that, the previous mixture was added dropwise into activated carbon (10 g) under vigorous stirring. Subsequently, the impregnated sample was laid overnight. Finally, the sample was dried at 393 K for 16 h under nitrogen flow to obtain the catalyst, labeled as Au-IL/AC, with a nominal total metal loading of 1 wt.%. The IL loading in all the catalysts was fixed at 10 wt.%. Due to the nature of the catalyst preparation procedure used, wet impregnation, with no filtration of the carbon or catalyst washing, was carried out; the metal loading should be considered equal to the nominal amount of metal impregnated into the hosts.

Activity Tests and Kinetic Experiments: The catalytic performance was determined in a tubular reactor setup. After 0.2 g of the catalyst was loaded into the reactor, the reactor was heated up to the reaction temperature at a ramp rate of 10 K/min and held for

30 min under a nitrogen atmosphere. Then, the C₂H₂/HCl (Jingong Special Gas Co., Ltd., Hangzhou, China) mixed gas was fed into the reactor and reacted under the catalysis of the Au-based catalyst. The off-gas from the reactor was sent through a bubbler containing aqueous sodium hydroxide solution to neutralize the free hydrogen chloride, then analyzed using gas chromatography. Kinetic experiments were performed at the range of the reaction temperature, from 443 to 493 K. The feed ratio of HCl to C₂H₂ was modulated by changing the volume flow of each gas, which was controlled by a gas mass flow controller. The catalyst activity is presented in terms of the VCM formation rate, R [mol·min⁻¹·g Cat⁻¹], representing the moles of VCM formation on 1 g of catalyst in one minute.

4. Conclusions

In conclusion, the following results of a supported-ionic-liquid-phase Au catalyst for acetylene hydrochlorination were revealed from kinetic experiments:

- (I). Gas diffusion in the ionic liquid film was negligible.
- (II). The reaction activation energy, $E_{a-Au-IL/AC} = 26 \text{ kJ mol}^{-1}$, is consistent with the activation energy for the gas-liquid catalyst, $E_{a-Au-IL} = 30 \text{ kJ mol}^{-1}$, confirming a homogeneous reaction micro-environment for the Au-SILP system.
- (III). The addition of ionic liquid produces an increase in the reaction order with respect to the concentration of the catalyst, which, in turn, partially avoids the self-aggregation of the active gold species.
- (IV). A hydrogen chloride enrichment system around Au is created, providing the possibility of producing vinyl chloride with an equal substrates feed ratio.

In perspective, we believe that the results presented in this article are of extreme importance for the development of new SILP catalysts for acetylene hydrochlorination.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12091012/s1>. Figure S1: High-angle annular dark-field images together with the elemental mapping of Au-IL/AC catalyst, Figure S2: Arrhenius plot for the VCM formation rate over the Au-IL/AC (black) and Au-IL (blue) catalysts.

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