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Communication

The origin of the extraordinary stability of mercury catalysts on the carbon support: the synergy effects between oxygen groups and defects revealed from a combined experimental and DFT study

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ABSTRACT

Thermal stability of HgCl_2 has a pivotal importance for the hydrochlorination reaction as the loss of mercuric compounds is toxic and detrimental to environment. Here we report a low-mercury catalyst which has durability over 10000 h for acetylene hydrochlorination under the industrial condition. The stability of the catalyst is carefully analyzed from a combined experimental and density functional theory study. The analysis shows that the extraordinary stability of mercury catalyst is resulted from the synergy effects between surface oxygen groups and defective edge sites. The binding energy of HgCl_2 is increased to be higher than 130 kJ/mol when adsorption is at the edge site with a nearby oxygen group. Therefore, the present study revealed that the thermal stability problem of mercury-based catalyst can be solved by simply adjusting the surface chemistry of activated carbon. Furthermore, the reported catalyst has already been successfully applied in the commercialized production of vinyl chloride.

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1. Introduction

Vinyl chloride monomer (VCM) is a major chemical intermediate for the manufacture of polyvinyl chloride (PVC), which is the third most important polymer in use today [1,2]. At present, the VCM is generally synthesized by hydrochlorination of acetylene in regions of the world where coal is abundant, especially in China. However, production of VCM in acetylene hydrochlorination units consumes about 1400 tons mercury per annum before the low-mercury catalyst was applied, which caused big environmental problems. With the implementation

of the mercury restriction, the solution of environment pollution problems involving mercury is one of the key technologies for vinyl chloride producing by calcium carbide method [3,4]. Although the gold based non-mercury catalyst invented by Hutchings' group shows superior performance and has been commercialized as mentioned in reference [5,6]. The wide application of the gold catalysts by the PVC enterprises still need much time due to its high cost. While other non-mercury catalyst like nitrogen doped catalysts are not active enough for application in industry [7–9]. Early in 2012, the Chinese government required the loading of HgCl_2 to be reduced from 10

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wt%–12 wt% to 4 wt%–6.5 wt%, which is called the low-mercury catalysts [10]. The fulfillment of the low-mercury catalyst in China has reduced more than 50% of the mercury consumption and the pollution of mercury has been greatly reduced in 2015. The low-mercury catalyst is still the major catalysts been used in the PVC factory nowadays before the mercury-free catalysts been mature and been widely applied. The stability of low-mercury catalysts should be different from the high-mercury catalyst due to the decreasing loading of HgCl_2 to 4%–6.5% will results in a single layer dispersion of HgCl_2 on carbon support [11]. However, the research work on the thermal stability of the low-mercury catalysts was neglected and rarely reported. The previous reports on the thermal stability of carbon supported mercury catalyst are mostly based on the high-mercury catalysts [12,13]. If the thermal stability is improved, the sublimation of HgCl_2 will be suppressed and thus the environmental pollution can be greatly reduced since the catalysts will not be consumed during reaction.

At present, the strategies for the improvement of the stability for activated carbon (AC) supported mercury chloride (HgCl_2/AC) catalysts mainly focus on two aspects: Firstly, alkali chloride was used as ligand as reported by Li et al. [14]. They observed that the thermal stability of the HgCl_2/AC catalyst can be obviously improved when CsCl is co-impregnated with HgCl_2 to AC support. Except for the addition of various promoters, there are also a few reports about the study on the carbon support. Wei et al. [15] and Xu et al. [16] studied on the coconuts based and coal based ACs including metal oxide supported low-mercury catalysts, but they didn't give a direct thermal stability test of catalysts and the mechanism study on the role of carbon surface chemistry. The identification of the role of surface functional groups on the supported metal catalysts such as Ru [17], Pt [18] and Au [19] etc. is receiving increasing interest in carbon materials research recently. It is clearly concluded that the interaction of supported active phase with the carbon supports plays an important role which will determine the dispersion and stability of active phases [20]. Several studies also indicated that defective sites are of great importance to the adsorption [21–23]. However, to our best knowledge there are no reports which have been devoted to understand the role of carbon-oxygen surface complexes or surface defects on the thermal stability of supported HgCl_2 catalyst. The present work will concentrate on thermal stability of the low-mercury catalysts, the interaction of carbon surface functional groups and

surface defects with HgCl_2 molecular by experimental and theory calculations.

The texture and surface structure of carbon supports were fully characterized and discussions are given in supporting information (Figs. S1–S7, Tables S1–S4). The coal and wood based commercialized activated carbons were used for study which is denoted as AC-C and AC-W, respectively. AC-W700 was prepared by calcination of AC-W under inert gas flow to remove the acidic functional groups. Briefly, all the activated carbons have a surface area higher than $1000 \text{ m}^2/\text{g}$ (Table 1), and the ash content is in range of 3.00%–3.25%. The impurities are mainly silica and alumina oxide with very few amount of calcium oxide. The elemental analyses of activated carbons are provided in Table S2. The main difference between these activated carbons is the surface structures and oxygen contents. AC-W has abundant oxygen containing surface functional groups (SFGs), the oxygen content is as high as 33% according to the CHNS elemental analysis. While the AC-W700 and AC-C has less SFGs, the oxygen content of AC-W700 is reduced to 16% and the oxygen content of AC-C is ca. 8%. As demonstrated by X-ray diffraction (XRD), thermogravimetric (TG), and Raman characterizations, although the graphitic degree of AC-W700 and AC-C is better than that of the AC-W, the $I(\text{D})/I(\text{G})$ value is higher for AC-W700 and AC-C than that of AC-W. This means that more surface defects are produced by the thermal treatment at 700°C . The AC-C has more surface defects than that of AC-W due to the less oxygen content. As reported by Lu et al. [21], graphene with rich surface defects can be obtained by using an oxidation step followed by a thermal decomposition method. As demonstrated by the TPD and FT-IR characterizations, AC-W contains much acidic functional groups such as carboxylic acids, phenols, and carboxylic anhydrides, while the AC-W700 and AC-C have more basic functional groups as lactones, ketone, and quinone which are more thermally stable.

The low-mercury catalysts were prepared by an incipient-wetness impregnation method. The isothermal curves and pore size distributions (Fig. S8) and XRD patterns (Fig. S9) of these catalysts are also similar to the ACs indicates a homogeneous dispersion of the HgCl_2 on the surface of ACs supports and no crystallite of HgCl_2 exist in the catalyst. The texture properties of these catalysts are given in Table 1. The decreasing of the surface area and pore volume of the catalysts compared with their corresponding ACs is small which indicates that the HgCl_2 molecule is monodispersed in the pore of ACs.

Table 1
Texture properties and TG analysis data of various catalysts and supports.

Samples	S. A. (m^2/g)	P. V. (cm^3/g)	Mass loss (%) ^a at different temperature range			Temperature ^b ($^\circ\text{C}$)	HgCl_2 (wt%)
			110–200 $^\circ\text{C}$	200–500 $^\circ\text{C}$	500–850 $^\circ\text{C}$		
AC-W	1364	0.92	0.6	5.4	13.7	—	—
AC-W700	1237	0.78	0.6	2.3	6.1	—	—
AC-C	1150	0.78	0.4	1.3	2.8	—	—
$\text{HgCl}_2/\text{AC-W}$	1152	0.80	0.6	12.7	7.5	302	6.3
$\text{HgCl}_2/\text{AC-W700}$	1180	0.75	0.4	9.2	5.6	360	6.4
$\text{HgCl}_2/\text{AC-C}$	1139	0.57	0.3	7.8	5.4	382	6.4

^aThe mass loss of different ACs and catalysts calculated based on TG analysis under argon flow.

^bThe temperature of fast weight loss (assigned to the loss of HgCl_2 on various catalysts).

TG techniques were conducted under argon flow to evaluate the thermal stability of various low-mercury catalysts supported on the above ACs. TG and DTG profiles of the $\text{HgCl}_2/\text{AC-W}$, $\text{HgCl}_2/\text{AC-W700}$ and $\text{HgCl}_2/\text{AC-C}$ catalysts are given in Fig. 1(a). For comparison, the TG and DTG profile of various ACs are also measured under same conditions, which are given in Fig. S10. The TG profile of HgCl_2 is provided in Fig. S11, the sublimation temperature is as low as 140 °C. From Fig. 1, it can be seen that the mass loss curves can be obviously divided into three temperature ranges. The mass loss occurs at ca. 100 °C is caused by the evaporation of physical adsorbed water. The amounts of water for all the samples are below 0.6% due to all the samples were dried before the TG experiments. The second mass loss occurs at 200–500 °C, there are obvious DTG peaks for all the catalysts. The peak of DTG profiles for $\text{HgCl}_2/\text{AC-W}$, $\text{HgCl}_2/\text{AC-W700}$ and $\text{HgCl}_2/\text{AC-C}$ catalysts are at 302, 360 and 382 °C, respectively. To eliminate the mass loss of the activated carbon, the subtracted data of the mass loss ratio at 200–500 °C of the catalysts and their related support are given in Table 1. The weight loss is in the range of 6.5%–7.3%, considering the experimental error, which is in the same level of the HgCl_2 loading. This confirms the mass loss peak in this temperature range can be assigned to the sublimation of the adsorbed HgCl_2 species. Since there is only one peak appears in TG curves for all the catalysts. It is in accord with the results characterized by the N_2 sorption and XRD techniques.

It is interesting to note that the sublimation temperature of HgCl_2 are all higher than the 200 °C, and the maximum weight loss temperature of HgCl_2 for $\text{HgCl}_2/\text{AC-W}$, $\text{HgCl}_2/\text{AC-W700}$ and $\text{HgCl}_2/\text{AC-C}$ are 302, 360 and 382 °C, respectively. The higher sublimation temperature of the HgCl_2 indicates a stronger interaction of HgCl_2 with carbon support. Moreover, the difference of the HgCl_2 sublimation temperature for various catalysts and HgCl_2 may indicate that the interaction of HgCl_2 molecular with activated carbons is different and there are properly strong interaction between the HgCl_2 and the carbon supports.

X-ray photoelectron spectroscopy (XPS) was used to characterize the status of HgCl_2 on various catalysts. The high-resolution Hg 4f spectra for $\text{HgCl}_2/\text{AC-W}$, $\text{HgCl}_2/\text{AC-W700}$ and $\text{HgCl}_2/\text{AC-C}$ catalysts were given in Fig. 1(b). It can be seen that the photoelectron spectra of Hg 4f clearly shows two doublet-peaks, the spin-orbit splitting of Hg 4f was 4.1 eV and intensity ratio was about 4:3 ($\text{Hg } 4f_{7/2} : \text{Hg } 4f_{5/2}$) [24]. For $\text{HgCl}_2/\text{AC-W}$, the main peak of $\text{Hg } 4f_{7/2}$ at 101.4 eV, which is attributed to Hg^{2+} species and there are apparently no Hg^+ and Hg^0 species [25–27]. For $\text{HgCl}_2/\text{AC-W700}$ and $\text{HgCl}_2/\text{AC-C}$, the main peaks are shifted to 100.8 eV. The fitting of the peaks shows there are two species exist in these samples with around 65% of mercury was ascribed to Hg^+ species (100.8 eV) and around 30% of mercury was ascribed to Hg^{2+} species (101.4 eV).

From above analysis, it is clearly indicated that $\text{HgCl}_2/\text{AC-W700}$ and $\text{HgCl}_2/\text{AC-C}$ catalysts are more stable than $\text{HgCl}_2/\text{AC-W}$. To further understand the origin of the enhanced stability, DFT calculations are performed to study the interactions between HgCl_2 molecule and carbon supports. One of the important differences between AC-W700, AC-C and AC-W is the oxygen group and surface defects as characterized by TPD and Raman techniques. The carboxylic and phenol groups are dominant on AC-W while AC-W700 and AC-C have more quinone and ketone groups. Therefore the binding energy of the HgCl_2 molecule at the different oxygen groups are calculated including quinone, ketone, carboxyl, lactone and phenol groups (Fig. S12, Table S5). It is clearly indicated that the binding energy of HgCl_2 is decreased along quinone, ketone, carboxyl, lactone and phenol groups. The quinone group is the most strong adsorption site for HgCl_2 while the phenol group is the weakest site among the investigated oxygen groups. Not only oxygen groups on the support but also defective sites such as vacancy and edge are considered in the calculations. The binding energy of HgCl_2 on defective site is indeed bigger than the strongest oxygen site (quinone) which are 49.20, 36.95 and 47.28 kJ/mol at zigzag, armchair edges and mono-vacancy re-

Fig. 1. (a) TG and DTG profiles and (b) Hg 4f XPS spectra for $\text{HgCl}_2/\text{AC-W}$, $\text{HgCl}_2/\text{AC-W700}$ and $\text{HgCl}_2/\text{AC-C}$ catalysts.

Fig. 2. The binding energy of HgCl₂ at various sites. (a) The E_b of HgCl₂ at Ketone zigzag; (b) The E_b of HgCl₂ at Ketone armchair.

spectively. The increased binding energy at defective sites is resulted from the saturated dangling bond. However, the binding energy of HgCl₂ at either oxygen site or edge site is still small and below 50 kJ/mol. Furthermore, the Mayer bond order of Hg–C and Hg–O is 0.37 and 0.2 respectively which indicate this is a weak intermolecular interaction. Interestingly, it is found the binding energy of HgCl₂ is up to 130 kJ/mol when adsorption takes place at the edge adjacent to a carbonyl group (ketone and quinone) as shown in Table S5. And the bond order is 0.64. It is suggested that the adjacent oxygen greatly enhances the binding energy at the edge site. As shown in our previous work, the insertion of oxygen group can decrease the aromaticity of the carbon materials and increase the reactivity [28]. Based on these discussions, the DFT results are consistent with the experimental observations. The calculations indicate either carbonyl groups or the nearby carbon atom at edge are the most stable binding sites for HgCl₂ molecule. This is well explained that the HgCl₂ catalysts on the AC-C and AC-W700 have a better stability.

Stability of the catalysts is an important issue for their application in industry, especially for the supported mercuric

chloride catalysts. Because the loss of volatile mercury ultimately finds its way into the environment thus cause severe pollution of the environment [29]. The enthalpy of hydrochlorination of acetylene reaction is –124.8 kJ/mol, which is strongly exothermic and it will generate a hotspot in the reactor which moves through the fixed bed reactor in the direction of the flow of the reactants [30]. The reaction temperature range in industry are controlled in a range of 80–180 °C, the space velocity of total reaction gas in the range of 15–100 h^{–1} for a better control of temperature of reaction. In order to give a fast screen of the thermal stability of the catalysts, the reaction temperature and space velocity in our experiments was set at 180 °C and 1000 h^{–1}. The time on stream catalytic performances of the above catalysts supported on various activated carbons (HgCl₂/AC-W, HgCl₂/AC-W700 and HgCl₂/AC-C) in acetylene hydrochlorination are shown in Fig. 3(a). It can be seen that the initial activity is similar for all the three catalysts. But the deactivation rate of these three catalysts was evidently differed with the order of HgCl₂/AC-W > HgCl₂/AC-W700 > HgCl₂/AC-C. This order is same with the thermal stability of these catalysts characterized above. Combining with the XPS results and catalytic performance, both Hg²⁺ and Hg⁺ could be involved as center of catalysis in this reaction. This is similar with Au/carbon catalysts, as reported by Hutchings et al. the redox couple of Au⁺/Au³⁺ has been suggested to be the active center in VCM [6].

To further test the stability of the mercury catalyst, an experiment simulated the industrialized reaction condition has been done in lab. The conversion of acetylene and selectivity to vinyl chloride with reaction time is given in Fig. 3(b). The initial conversion of acetylene is about 96%, after 10000 h running (ca. 417 d) still as high as 88.6%. This excellent catalytic performance confirmed that thermal stability is the key point to life time of mercury catalysts as demonstrated in reference by Hutchings group's early report [12,13]. According to TG characterization results, the initial evaporation of the most stable HgCl₂/AC-C catalyst is increased to above 300 °C. There are almost 120 °C improved. The sublimation of HgCl₂ will not occur under industry operation temperatures (80–180 °C).

Fig. 3. (a) Acetylene conversion vs reaction time over various catalysts at reaction temperature 180 °C and GHSV(C₂H₂) 1000 h^{–1}; (b) Acetylene conversion and selectivity to vinyl chloride vs reaction time over HgCl₂/AC-C catalysts at reaction temperature 140 °C and GHSV(C₂H₂) 30 h^{–1}.

Therefore, the leaching of HgCl_2 for mercury catalysts used in industry caused by the thermally unstable properties can be greatly solved.

The thermal stability improvement of mercury related catalysts insures a long service life of mercury based catalysts under reaction conditions. This has significant impact on the elimination of the environmental pollution problems for mercury related catalytic process in industry. For example, commercial production of VCM (ca. 20 million tons PVC per annum in China is based on the acetylene based process) in acetylene hydrochlorination units consumes about 1000 tonnes Hg per annum. The fulfilment of the low-mercury catalysts for PVC production required the loading of HgCl_2 decreased from 10 wt%–12 wt% to 4 wt%–6.5 wt% has reduced the almost half of the mercury consumption. Therefore, the release of mercury chloride for the application of new generation low-mercury catalysts can be diminished to quite low level. This thermally stable low-mercury catalyst has already been successfully commercialized and applied in PVC factories. The environmental problems caused by thermally unstable mercury catalysts are greatly reduced. The combination of fundamental and experimental research proved essential for the successful development of this robust technology.

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Graphical Abstract

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The origin of the extraordinary stability of mercury catalysts on the carbon support: the synergy effects between oxygen groups and defects revealed from a combined experimental and DFT study

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$\text{HgCl}_2/\text{carbon}$: Thermally unstable! Proper carbon support with more surface defects shows stronger C- HgCl_2 interaction, which greatly increases the thermal stability of mercury catalyst.

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超稳低汞催化剂的稳定机理：炭表面含氧基团及缺陷协同作用实验及理论研究

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摘要: 聚氯乙烯(PVC)作为五大工程塑料之首在材料领域应用广泛. 2017年, 中国PVC产能逾2600万吨, 占世界总产量的70%以上, PVC产业是我国重要支柱产业之一. 基于中国富煤少气缺油的能源格局, PVC产量的90%以上都是基于煤化工的乙炔法生产的, 而氯化汞催化剂是目前乙炔法氯乙烯工业上唯一实现产业化应用的催化剂. 但是由于氯化汞属于金属氯化物中唯一的共价化合物, 其热稳定极差, 涉汞催化剂的汞污染问题一直是氯乙烯行业的世界级难题. 中国电石法聚氯乙烯产业每年催化剂消耗量高达2.0万吨, 年耗汞近1000吨, 可回收不足40%, 占世界汞消耗量的70%. 而无汞催化剂由于成本高、使用寿命短等原因, 短期内实现工业化应用及推广仍有困难. 中国政府早在2014年开始限汞行动, 提出了氯乙烯产业汞催化剂减量化直至无汞化的战略目标. 根据2015年拟定的氯乙烯用低汞触媒的国标要求, 氯化汞负载量最高不得超过6.5%, 而高汞催化剂的氯化汞负载量在10%–12%之间, 在氯化汞负载量降低一半的情况下保持催化剂的高性能及高热稳定性对催化剂的制备技术提出了很大的挑战. 催化剂是参与化学反应而自身不会消耗的物质, 其在工业使用过程中理论上并不会消耗, 解决了催化剂的热稳定性问题, 不但可以延长催化剂使用寿命, 而且还可以缓解涉汞催化剂的资源消耗及环境污染问题.

活性炭具有较高的比表面积、可调控的表面化学性质和耐酸碱腐蚀性, 在工业中应用广泛. 氯乙烯单体合成的原料为氯化氢和乙炔, 由于氯化氢的腐蚀性, 活性炭基催化剂在工业化应用方面具有明显的优势. 而活性炭载体的表面性质调控及对负载型金属催化剂的相互作用研究一直是近年来多相催化领域的一个热点. 本文通过热处理的方法调控了活性炭的表面含氧基团, 研究了活性炭的表面结构的区别, 通过浸渍法制备了三种活性炭负载的低汞催化剂, 对比了三种不同的活性炭载体的乙炔氢氯化性能及稳定性, 发现表面基团的调控对低汞催化剂的稳定性具有较大的影响. 热重实验表明, HgCl₂/AC-C催化剂中氯化汞的最大失重温度提高到了380 °C以上. 该催化剂在反应温度140 °C, 乙炔空速30 h⁻¹条件下稳定运行10000 h, 乙炔转化率只下降了8%. DFT理论计算发现, 碳氧双键旁边的缺陷位和氯化汞可以形成强的化学吸附, 其吸附能可达120–130 kJ/mol, 而氯化汞在含氧基团的表面吸附能只有3–35 kJ/mol. 本文通过对活性炭表面结构的调控, 使氯化汞和炭表面活性位形成化学吸附, 可大大提高催化剂的耐热稳定性, 从理论上给出了低汞催化剂的热稳定性解决方案, 目前该催化剂已经成功实现了产业化应用, 在工业转化器上使用寿命超过12000 h, 性能表现卓越. 超稳低汞催化剂的工业化应用不仅能够降低氯乙烯单体生产过程中的单耗, 节约PVC生产成本, 还能够有效减少汞触媒使用过程中造成的重金属污染, 为我国电石法氯碱行业的节能减排及限汞公约履约提供了很好的技术支撑和保障.

关键词: 汞催化剂; 热稳定性; 缺陷; 含氧官能团; 乙炔氢氯化

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