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Synthesis and characteristics of organotin-based catalysts for acetylene hydrochlorination

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Abstract

Organotin-based catalysts prepared by a facile and green synthesis route were used in the acetylene hydrochlorination reaction. In detail, organotin-based catalysts were directly synthesized by supporting both organotin and nitrogen compounds on a coal-based columnar activated carbon (AC) using both incipient wetness impregnation and calcination methods. Interestingly, upon addition of nitrogen compounds, the resultant ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC catalysts showed higher activity and stability when compared to its ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC counterpart at 200 ºC and a gas hourly space velocity (GHSV, C_2H_2 based) of 30 h^{-1}. According to the results, organotin was demonstrated to be the active site, while the incorporation of nitrogen allowed to partly mitigate the loss of active components.

Keywords: organotin-based catalyst; organotin compounds; nitrogen compounds; acetylene hydrochlorination.

1. Introduction

Polyvinylchloride (PVC) plays a significant role in agriculture, industry, electronic science and national defense.[1] The industrial production of PVC is typically carried out by direct chlorination of ethylene, oxychlorination of ethylene, and acetylene hydrochlorination, the latter of which is widely used in coal-rich regions of China.[2] Nevertheless, the traditional mercury-based catalysts used to carry out this reaction are easily lost during the course of the

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reaction. Additionally, mercuric chloride constitutes a potential threat to the environment and to the human health. Thus, developing non-mercury catalysts represents a sustainable acetylene production route.

Hutchings et al. reported Au-based catalysts to have superior catalytic performance towards the hydrochlorination of acetylene and studied in detail the reaction mechanism of these materials. The reduction of Au^{3+} was associated with catalyst deactivation.[1,3,4] Although precious-metal catalysts show excellent catalytic performance, it is of great significance to explore non-precious metal catalysts with reduced cost. With this aim, numerous researchers have started to develop new-type catalysts.[5–13] Later, Dai et al prepared boron-and nitrogen-doped graphene catalysts that displayed superior catalytic activity towards acetylene hydrochlorination and demonstrated that boron and nitrogen can promote hydrogen chloride adsorption.[7] Additionally, the Dai's group also reported AC-supported transition metal nitrides to show better activity and selectivity towards acetylene hydrochlorination.[11]

In the past few years, tin compounds have been investigated as promoters to reduce coke deposition and therefore improve the catalytic activity and the stability of catalysts.[14–17] Moreover, numerous diorganotins and triorganotins have been widely used as stabilizers, catalysts and treatment materials for industrial and agricultural applications owing to their unique structure, low toxicity and superior activity.[18–22] In addition, Shinoda found that the hydrochlorination activities of metal chlorides correlate with the affinity of the metal cation, although their study did not include tin ions.[23] Moreover, Zhang et al. reported that the superior catalytic performance and relatively long lifetime of Au-Sn/AC catalysts can be improved by adding $SnCl_2 \cdot 2H_2O$, which prevented coke deposition.[8] At the same time, organotin has been scarcely studies as an active site for the hydrochlorination of acetylene. Having this in mind, the better activity of organotin motivated us to prepare organotin-based materials were applied in acetylene hydrochlorination.

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In this article, we successfully synthesized organotin-based catalysts using highly porous AC as a support. We simultaneously carried out thermogravimetry/differential thermal analysis (TG-DTA), scanning electron microscopycoupled withenergy dispersive X-ray spectrometry (SEM-EDS) elemental mapping and low-temperature nitrogen adsorption/desorption experiments to characterize the organotin-based catalyst.

2. Experimental

2.1 Catalyst preparation

The raw material (a coal-based columnar AC) was pre-treated with HCl (0.01mol/L) to remove impurities, thoroughly washed with distilled water until neutral pH, and finally dried at 120 ºC for 24 h.

The organotin-based catalyst was synthesized by an incipient wetness impregnation technique using AC as a support. The impregnating solution was prepared by dissolving dioctyldichlorotin (2.0 g) and tin (IV) chloride (2.0 g) in ethanol (100 mL) in a beaker. The solution was stirred at 80 ºC (water bath) for 30min. Subsequently, 16 g of fresh AC were gradually added under stirring, and the resulting mixture was stirred at 80 ºC or 2 h and finally dried in an oven at 100 ºC for 12 h. The product was heated to 200 ºC under flowing nitrogen for 4 h with a heating rate of 10 ºC/min to finally yield the catalyst. In addition, different samples were prepared by the same method for comparison. 20% ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC-200 indicates that the dioctyldichlorotin and tin (IV) chloride loading in all the catalysts was fixed at 20 wt% and the calcination temperature was 200 ºC.

2.2 Catalytic performance tests

The performance of the organotin-based catalyst was determined in a fix-bed glass reactor (i.d. =10mm) at atmosphericpressure. Before initiating the reaction, hydrogen chloride was passed through the fix-bed to remove air and water from the reaction system (60min). Once the reactor reached the desired temperature (150–200 ºC), the gas mixture (HCl/C_2H_2

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=1.1:1.0) was calibrated using mass flowmeters and fed into the reactor containing 3.2 mL of catalyst (gas hourly space velocity (GHSV) of 30 h^{-1}). The outlet gas was passed through a glass tube containing medical soda-lime to absorb the unreacted HCl and immediately analyzed on-line using a gas chromatograph (GC900) equipped with a GDX-301 column.

2.3 Catalyst characterization

The Brunauer–Emmett–Teller (BET) surface area and pore volume of the samples were measured by nitrogen adsorption at 77 K using a Quantachrome Nova 2000e gas sorption analyser. All the catalysts were degassed at 100 ºC for 5h before the analysis.

The weight loss and stability of the catalysts were analyzed by TG-DTA (NETZSCH STA 449F3) under a nitrogen flow of 30 mL/min and at a heating rate of 30 ºC/min within a temperature range of 25–800 ºC.

The SEM micrographs and the EDS elemental maps were recorded on a TEACAN MAIA3 microscope at an acceleration voltage of 15 kV.

3. Results and discussion

3.1 Catalytic performance

The surface area and pore volume of the different samples are listed in Table 1, while the catalytic performance of the catalysts is shown in Fig. 1. Fresh AC shows a negligible conversion despite showing the highest specific surface area (987.2 m^2/g). Upon calcination at higher temperature, the specific surface area and micropore volume of the 20% $C_2N_4H_4$/AC-550 sample decreased to 577.9 m^2/g and 0.30 cm^3/g, respectively, while the maximum acetylene conversion reached 22.5%. Owing to dicyandiamide is easily transformed into g-C_3N_4,[25] which was mostly dispersed on the micropores of the carbon material improving the acetylene conversion. Interestingly, 20% $C_{16}H_{34}Cl_2Sn$/AC-200 significantly increased its catalytic activity at 200 ºC and showed higher activity than $SnCl_4$/AC-200. This result, along

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with data in Table 1, confirmed that organotin was successfully loaded on AC and played an active site in the acetylene hydrochlorination reaction.

Fig. 1b shows the effect of the dioctyldichlorotin loading (5-25wt%) on the catalytic performance. The acetylene conversion gradually increased (from 36.3 to 86.4%) with the dioctyldichlorotin loading increasing from 5 to 25 wt%. The decrease in surface area and pore volume with the dioctyldichlorotin loading can be attributed to dioctyldichlorotin partly blocking the surface of the support. 20% $C_{16}H_{34}Cl_2Sn$/AC shows higher acetylene conversions than 25% $C_{16}H_{34}Cl_2Sn$/AC. Thus, the catalytic activity increased with the dioctyldichlorotin content up to 20 wt%.

Because of the activity of dioctyldichlorotin and tin (IV) chloride, we focused our investigations on the catalyst containing both components (i.e., ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC)) which showed better catalytic performance than $C_{16}H_{34}Cl_2Sn$/AC and $SnCl_4$/AC. Importantly, the mixture of dioctyldichlorotin and tin (IV) chloride can effectively reduce the cost of the organotin-based catalysts.

3.2 Catalytic performance of ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC

The Kocheshkov redistribution reaction is commonly carried out without solvent and thus it was necessary to investigatethe effect of the calcination temperature and mole ratio of tin compounds on the catalytic performance of the materials prepared.[26] As shown in Table 2, the external surface area of ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC gradually increased with the calcination temperature, indicating that dioctyldichlorotin reacted with tin (IV) chloride at an optimal calcination temperature of 200 ºC. As depicted in Fig. 2a, the optimum catalytic activity of ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC-200 was not ascribed to its specific surface and volume characteristics. Instead, the nature of the active site has a significant influence on the acetylene conversion. As shown in Fig. 2b, the $SnCl_4$:$C_{16}H_{34}Cl_2Sn$ mole ratio was 1.6:1.0, suggesting that tin (IV) chloride reacted with dioctyldichlorotin to generate octyltrichlorotin.

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This was further supported by the fact that tin (IV) chloride was easily volatilized at temperatures lower than the reaction temperature (114.5 ºC). As illustrated in Fig. 2a, the maximum acetylene conversion of ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC-200 was 89.1% at 200 ℃, at a $SnCl_4$:$C_{16}H_{34}Cl_2Sn$ mole ratio of 1.6:1.0. However, this catalyst showed the maximum weight loss rate at 230.6 ℃ (Fig. 5), and we tried to improve the stability of the catalyst by adding some components. For instance, Zhang et al. developed a nitrogen-modified carbon supported $AuCl_3$ catalyst with superior stability, which was ascribed to nitrogen inhibiting the Au^{3+} to Au^0 reaction and enhancing the adsorption of hydrogen chloride.[27] By temperature-programmed adsorption and density functional theory (DFT) calculations, Dai et al.revealed that the addition of nitrogen can improve the adsorption of HCl.[6] Therefore, we used dicyandiamide as a precursor of g-C_3N_4 for improving the lifetime of the ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC catalyst.

3.3 Catalytic performance of ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC

As shown in Table 3, the specific surface area and total pore volume of ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC were slightly higher than that of ($C_{16}H_{34}Cl_2Sn$+$SnCl_4$)/AC prepared at similar synthesis conditions, indicating that the active compounds were successfully loaded on the support. In addition, the catalytic performance of ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC (Fig. 2a and 3a) and ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC indistinctively changed over the temperature range of 150 – 300 ℃, showing that nitrogen compounds played a small effect on the acetylene conversion of organotin-based catalysts at lower calcination temperatures. Over the temperature range of 350-500 ℃ (Fig. 3b), ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC-400 shows the lowest specific surface and total volume values among the samples studied (233.0 m^2/g and 0.15 cm^3/g, respectively), indicating that dicyandiamide may have reacted with tin (IV) chloride and dioctyldichlorotin to produce molecules with larger molecular weight. Therefore, it is essential to study in detail the

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effect of the calcination temperature or nitrogen compounds on the conversion of acetylene. As shown in Fig. 3c, ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC-400 showed the best performance among the organotin samples with an acetylene conversion of 92.1%. Thus, the optimal calcination temperature of ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC was 400 ºC. The external surface seems to influence the catalytic performance to a larger extent as compared to the micropore surface (Table 3). With regard to the nitrogen-doped catalysts, ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC-400 showed slightly higher acetylene conversions than that of ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC-200 and ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC-400, illustrating that the addition of nitrogen has a positive effect on the acetylene conversion at higher calcination temperature, in line with results shown in Fig. 4a. The stability of both catalysts should be investigated in detail.

3.4 Stability of ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC and ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC

The catalytic performance and stability of ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC and ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC are illustrated in Fig. 4. By thermal condensation experiments, the addition of dicyandiamide showed a minimal effect on the catalytic activity and selectivity, whereas it dramatically improved the stability of the catalysts. As shown in Fig. 4a, ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC showed higher catalytic activity and longer lifetimes than ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC (92.1 versus72.1% acetylene conversion) after 36 h on stream.The acetylene conversion of ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC decreased from 89.1 to 49.5% after 36 h on stream, revealing poor stability towards the acetylene hydrochlorination reaction. As shown in Fig. 4b, the selectivity towards vinyl chloride monomer (VCM) was above 97.5%. This result demonstrated that organotin are highly active and selective species, while the addition of dicyandiamide can strengthen the catalytic stability of organotin-based catalysts during the hydrochlorination of acetylene. While the catalytic performance of the organotin-based

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catalysts was slightly poorer than that of 10%$HgCl_2$/AC, the organotin-based catalysts showed a better selectivity towards vinyl chloride.

The TGA results (Fig. 5) confirmed that the addition of dicyandiamide is the main factor affecting the catalytic stability. ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC showed a mass loss of 22.7%, in agreement with the loaded amount of active component. Nevertheless, ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC showed a mass loss close to 13.7%, while the maximum weight loss rates of the $SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC and ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC samples were found at 298.9 and 230.6 ºC, respectively. Fig. 5 and 6 confirmed that dicyandiamide was added to organotin via calcination, being transformed into a novel compound with a reduced maximum weight loss temperature.

We selected several areas to investigate the dispersion of tin and chlorine on the fresh and used catalysts via EDS elemental mapping. As shown in Fig. 6a and c, tin and chlorine were highly dispersed on the surface of the fresh-($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC and fresh-($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC samples. The distribution of tin in the used-($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC and used-($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC samples is shown in Fig. 6b and d.The results of Fig. 5 and 6a and 6c strongly confirmed that organotin was successfully loaded on the coal-based columnar AC. Table 4 indicated that a large amount of tin was dispersed on the surface of used-($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC versus used-($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC, because the incorporation of nitrogen effectively and significantly reduced the loss of tin during reaction. Combining the above results, it is concluded that organotin acted as a catalytic active site and the incorporation of nitrogen strongly enhanced the stability of organotin-based catalysts.

4. Conclusion

In this paper, we successfully synthesized organotin-based catalysts having superior catalytic performance and stability towards the hydrochlorination of acetylene. These

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catalysts were prepared by loading organotin and nitrogen compounds on an AC under optimal conditions. The characterization data demonstrated that the effective addition of dicyandiamide can prolong the lifetime of the organotin-based catalysts, and organotin played a positive effect in increasing the acetylene conversion.

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Tables

Table 1. Textural properties of the different catalysts.

[a] S_{BET} is the surface area calculated using the Brunauer–Emmett–Teller (BET) equation over the relative pressure range of 0.05–0.03. [b] Micropore surface area. [c] External surface area calculated by the t-plot method. [d] $V_{meso}= V_{total}-V_{mic}$($V_{mic}$, micropore volume) is also calculated by the t-plot method. [e] V_{total} (total volume) at P/P_0=0.99 is derived from the nitrogen adsorption isotherm.

Sample	Calcinations Temperature (℃)	S_{BET} $(m^2/g)^a$	S_{mic} $(m^2/g)^b$	S_{ext} $(m^2/g)^c$	V_{mic} (m^3/g)	V_{meso} $(m^3/g)^d$	V_{total} $(m^3/g)^e$
AC-200	200	987.2	864.5	122.7	0.12	0.36	0.48
20%$C_2N_4H_4$/AC-550	550	641.9	577.9	64.0	0.23	0.07	0.30
20%$SnCl_4$/AC-200	200	474.2	422.6	51.6	0.18	0.05	0.23
25%$C_{16}H_{34}Cl_2Sn$/AC-200	200	84.7	51.4	33.8	0.06	0.02	0.08
20%$C_{16}H_{34}Cl_2Sn$/AC-200	200	156.4	122.3	34.1	0.06	0.03	0.09
15%$C_{16}H_{34}Cl_2Sn$/AC-200	200	281.8	223.4	58.4	0.10	0.06	0.16
10%$C_{16}H_{34}Cl_2Sn$/AC-200	200	408.9	335.6	73.3	0.14	0.07	0.21
5%$C_{16}H_{34}Cl_2Sn$/AC-200	200	523.2	450.3	72.9	0.19	0.07	0.26

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Table 2. Textural properties of ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC at different calcination temperatures.The molar ratio of $SnCl_4$ and $C_{16}H_{34}Cl_2Sn$ was1.6:1.0.

Sample	Calcinations Temperature (℃)	S_{BET} (m^2/g)[a]	S_{mic} (m^2/g)[b]	S_{ext} (m^2/g)[c]	V_{mic} (m^3/g)	V_{meso} (m^3/g)[d]	V_{total} (m^3/g)[e]
($SnCl_4$+$C1_6H_{34}Cl_2Sn$)/AC-150	150	442.6	237.2	205.4	0.13	0.11	0.24
($SnCl_4$+$C1_6H_{34}Cl_2Sn$)/AC-200	200	243.5	143.0	100.5	0.11	0.04	0.15
($SnCl_4$+$C1_6H_{34}Cl_2Sn$)/AC-250	250	313.1	181.7	131.4	0.12	0.06	0.18
($SnCl_4$+$C1_6H_{34}Cl_2Sn$)/AC-300	300	378.5	338.4	40.1	0.29	0.02	0.31

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Table 3. Textural properties of ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC calcined at different temperatures. The molar ratio of $SnCl_4$, $C1_6H_{34}Cl_2Sn$, and $C_2N_4H_4$was1.6:1.0:4.9.

Sample	Calcinations Temperature (℃)	S_{BET} (m^2/g)[a]	S_{mic} (m^2/g)[b]	S_{ext} (m^3/g)[c]	V_{mic} (m^3/g)	V_{meso} (m^3/g)[d]	V_{total} (m^3/g)[e]
($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC-150	150	173.3	135.0	38.3	0.07	0.05	0.11
($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC-200	200	340.5	287.8	52.7	0.12	0.05	0.17
($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC-250	250	440.9	372.5	68.4	0.15	0.08	0.23
($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC-300	300	567.6	494.3	73.3	0.21	0.06	0.27
($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC-350	350	298.9	257.8	47.1	0.11	0.05	0.16
($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC-400	400	233.0	160.8	72.2	0.11	0.04	0.15
($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC-450	450	314.5	179.7	134.8	0.11	0.08	0.19
($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC-500	500	463.8	400.7	63.1	0.17	0.06	0.23
($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC-400	400	374.0	300.6	73.4	0.26	0.03	0.29
$HgCl_2$/AC	200	571.0	479.6	91.4	0.20	0.09	0.29

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Table 4. Mass percent of tin in the samples as detected by SEM-EDS.

Sample	Sn wt%
fresh-$C_{16}H_{34}Cl_2Sn+SnCl_4$)/AC	8.94
used-($C_{16}H_{34}Cl_2Sn+SnCl_4$)/AC	2.93
fresh-($C_{16}H_{34}Cl_2Sn+SnCl_4+C_2N_4H_4$)/AC	7.16
used-($C_{16}H_{34}Cl_2Sn+SnCl_4+C_2N_4H_4$)/AC	5.06

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Figures

Fig. 1 (**a**) Conversion of acetylene for the different catalysts. (**b**) Catalytic activity of the catalysts containing different amounts of dioctyldichlorotin.

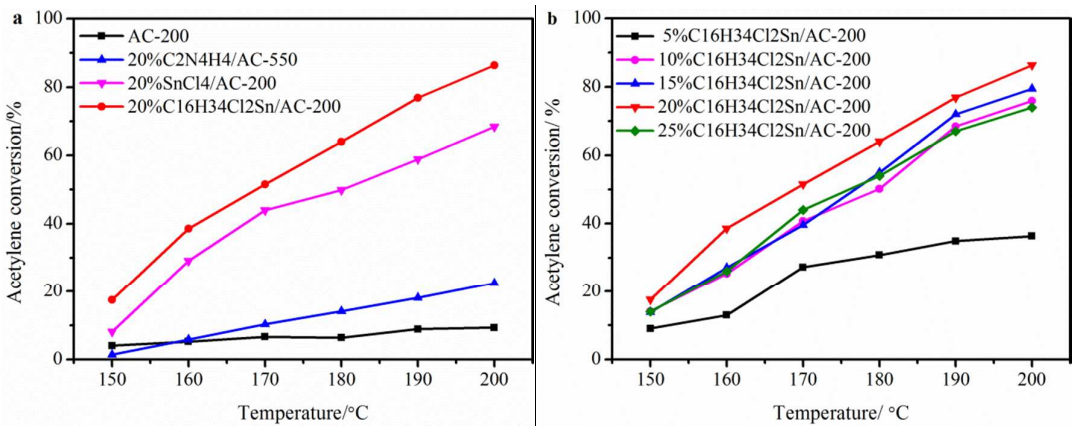

Fig. 2 Conversion of acetylene for ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC at (**a**) different calcinationtemperatures, and (**b**) various mole ratio of tin compounds. (1.0$SnCl_4$+1.0$C_{16}H_{34}Cl_2Sn$)/AC-150 with a $SnCl_4$:$C_{16}H_{34}Cl_2Sn$ molar ratio of 1.0:1.0. The calcination temperature was150 ºC.

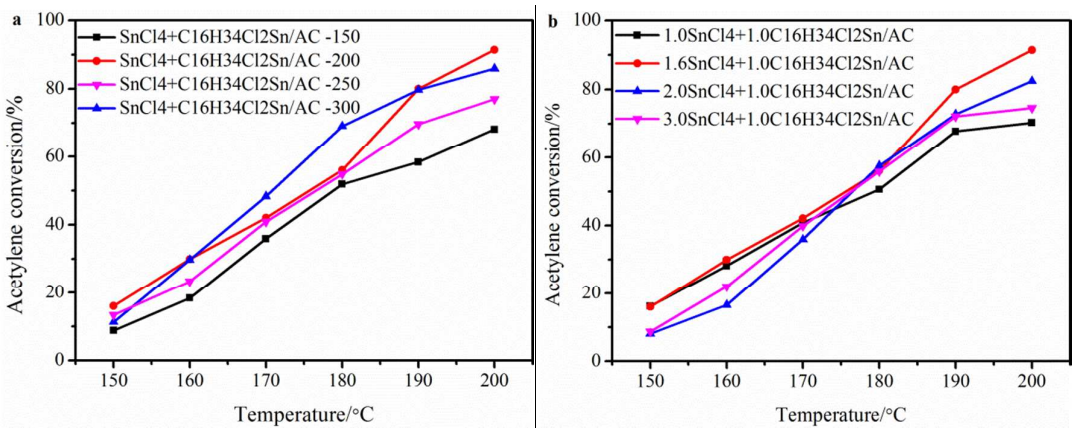

Fig. 3 Conversion of acetylene for ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC calcined at different temperatures.

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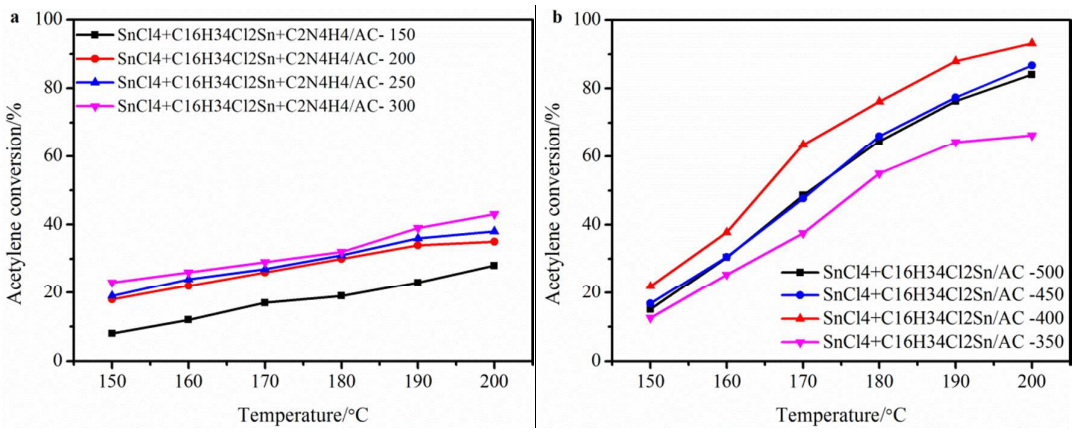

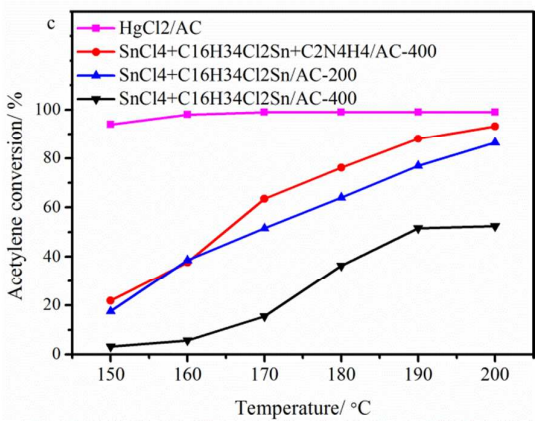

Fig. 4 Catalytic performance of $HgCl_2$/AC, ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC and ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$). (**a**) conversion of acetylene; (**b**) selectivity towards vinyl chloride monomer (VCM).

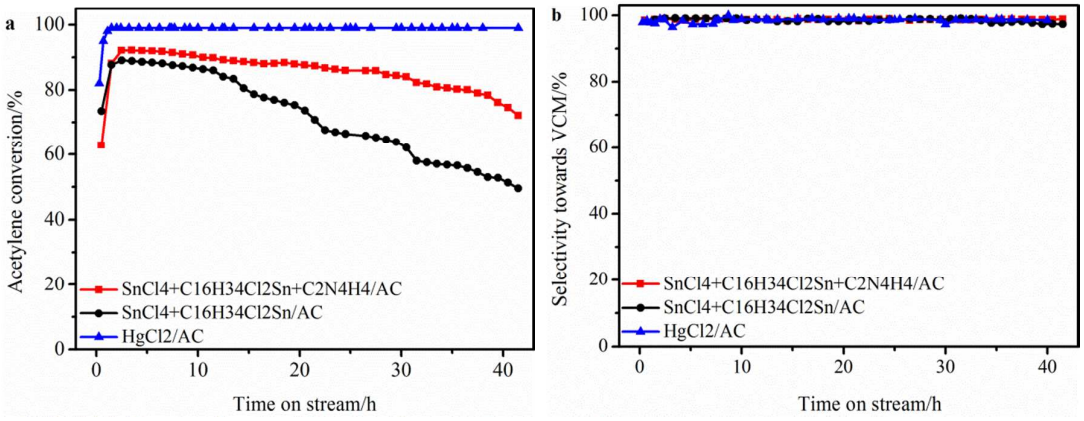

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Fig. 5 TGA and DTG curves of the ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC and ($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC catalysts.

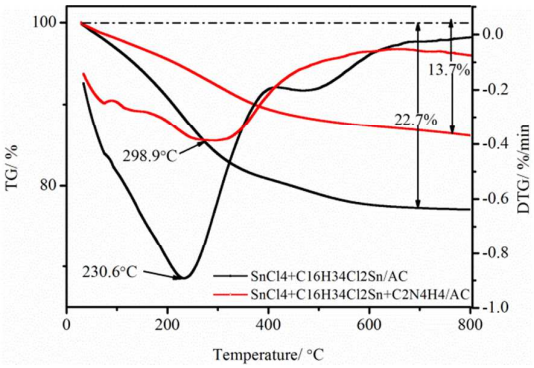
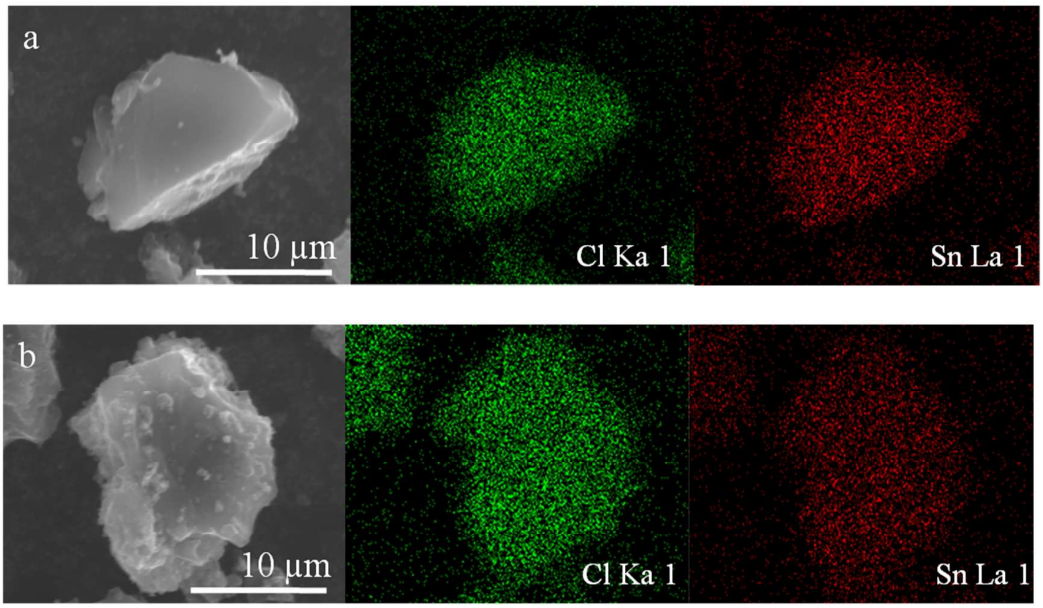


Fig. 6 SEM micrographs and tin and chloride EDS elemental maps of the fresh samples: (**a**) fresh-($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC and (**c**) fresh-($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC and after 36 h of reaction: (**b**) used-($SnCl_4$+$C_{16}H_{34}Cl_2Sn$)/AC and (**d**) used-($SnCl_4$+$C_{16}H_{34}Cl_2Sn$+$C_2N_4H_4$)/AC.



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