

Tin-sulfur based catalysts for acetylene hydrochlorination

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Abstract: In the present work, tin-sulfur based catalysts were prepared using Na_2SO_3 and $(\text{CH}_3\text{SO}_3)_2\text{Sn}$ and were tested in acetylene hydrochlorination. Based on the analysis of experiments results, the acetylene conversion of $(\text{CH}_3\text{SO}_3)_2\text{Sn}/\text{S}/\text{AC}$ is still over 90% after a 50 h reaction, at the reaction conditions of $T = 200^\circ\text{C}$, $V_{\text{HCl}}/V_{\text{CH}_2} = 1.1:1.0$ and $\text{C}_2\text{H}_2\text{-GHSV} = 15\text{ h}^{-1}$. According to the results of X-ray photoelectron spectroscopy (XPS), HCl adsorption experiments, and acetylene temperature programmed desorption ($\text{C}_2\text{H}_2\text{-TPD}$), it is reasonable to conclude that the interaction between Sn and S not only can retard the oxidation of Sn^{2+} in catalysts but also strengthen the reactant adsorption capacity of tin-based catalysts. Furthermore, results obtained from nitrogen adsorption/desorption and XPS proved that the CH_3SO_3^- can effectively decrease the coke deposition of $(\text{CH}_3\text{SO}_3)_2\text{Sn}/\text{AC}$ and thus prolong the lifetime of $(\text{CH}_3\text{SO}_3)_2\text{Sn}/\text{AC}$.

Key words: Sulfur, tin-based catalysts, acetylene hydrochlorination

1. Introduction

Poly vinyl chloride (PVC) with its good wear-proof and chemical erode resistant properties has been implemented in many aspects of human life and industrial production. Furthermore, PVC is predominately synthesized through free radical polymerization reactions of the vinyl chloride monomer (VCM). Because of the resource feature of rich-coal in many developing countries (e.g., China), they mainly adopted the activated carbon-supported mercury chloride as catalysts, which catalyze the acetylene hydrochlorination to manufacture vinyl chloride [1–3]. However, the higher toxicity, easily sublimation, and mercury abatement worldwide has prompted many scholars to research a series of novel catalysts using the green method, for the sustainable development of acetylene hydrochlorination [4–6].

The higher intrinsic activity of gold based catalysts than that of HgCl_2 catalysts for acetylene hydrochlorination was firstly reported by Hutchings et al., who also discovered that the deactivation of Au based catalysts originated from the reduction of Au^{3+} to Au^0 and the aggregations of Au species in catalysts [7–12]. However, the fatal problem for gold based catalysts is high cost. Later on, this problem was solved through nonprecious metals, such as Cu [13–16] and Sn [17–22]. Li et al. reported that the acetylene conversion of phosphorus-doped copper-based catalysts decreases from 99.0% to 97.2% after a 82 h reaction (reaction conditions: $\text{GHSV-C}_2\text{H}_2 = 30\text{ h}^{-1}$, $T = 140^\circ\text{C}$, $V_{\text{HCl}}/V_{\text{CH}_2} = 1.15:1.0$) [13]. Due to the introduction of phosphorus into the catalysts, which can effectively not only improve the dispersion but also lessen the aggregation of copper species, Cu-P/AC features better catalytic performance than the Cu/AC catalyst in acetylene hydrochlorination [13]. Additionally, when the reaction condition was maintained at $\text{GHSV-C}_2\text{H}_2 = 50\text{ h}^{-1}$ and $T = 200^\circ\text{C}$, Zhai et al. founded that carbon supported CsCuCl_4 as catalysts still exhibited 92% hydrochlorination activity over 200 h [14]. Recently, Ren et al. reported that the (methoxymethyl) triphenylphosphonium chloride (MOMTPPC) ionic liquid has a positive effect on the dispersion and stabilization of Cu species in catalysts [16]. Specifically, $\text{Cu}@\text{MOMTPPC}/\text{AC}$ still reached the 98.7% acetylene conversion after the 360 h stability test under the conditions of $\text{GHSV-C}_2\text{H}_2 = 36\text{ h}^{-1}$, $T = 180^\circ\text{C}$, $V_{\text{HCl}}/V_{\text{CH}_2} = 1.2:1$ [16]. Except for Cu catalysts, Deng et al. prepared $\text{SnCl}_4\text{-BiCl}_3\text{-CuCl}/\text{AC}$ that can catalyze acetylene hydrochlorination and found that the deactivation of catalysts mainly attributed to the loss of tin(IV) chloride in acetylene hydrochlorination [17]. Although the tin-based catalysts exhibited considerable activity in acetylene hydrochlorination [18–20], the stability as the drawback is significant enough to restrict further development. In our previous study, it was discovered that the Sn^{2+} species is easily oxidized to Sn^{4+} , which results in the loss of Sn species during catalysis of acetylene

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New Reactions And Chemicals Based On Sulfur And Acetylene

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