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Experimental and modeling of fixed-bed reactor for yellow phosphorous tail gas purification over impregnated activated carbon

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Abstract

When yellow phosphorous tail gas will be used as chemical raw material gas to produce high accessional products such as formate, oxalate, methanol and so on, pretreatment process by its purifying could limit its application. In this paper, two kinds of impregnated activated carbon catalysts and catalytic oxidation reaction for purifying H_2S and PH_3 contained in tail gas have been studied in laboratory-scale and pilot-plant fixed-bed reactor. The concentration of both H_2S and PH_3 could be less than 10 mg/m^3 over these two kinds of catalysts. Reaction kinetics for the catalytic oxidation of H_2S and PH_3 over the mixed catalyst has also been studied on differential reactor, and kinetic model for both compounds have been formulated, which are subsequently implemented in the modeling of the pilot-plant fixed-bed reactor. A two-dimensional un-steady reaction model which includes both physical adsorption and catalytic reaction process was developed for binary gas mixture purification in fixed-bed. Results from model calculation are reasonably well agreement with the experimental data. It is helpful for a thorough explanation of the observed pilot-plant reactor performance and designing in industrial process.

Keywords: Yellow phosphorous tail gas; Catalytic oxidation; Impregnated activated carbon; Fixed bed; Modeling

1. Introduction

Yellow phosphorous is the main source for phosphorous chemical engineering. During the producing of yellow phosphorous by electric furnace method, about 2500–3000 m^3 tail gas will be let out when 1 t yellow phosphorous was produced, which is one of the main sources for air pollution in most cities in PR China [1]. The main contain of yellow phosphorous tail gas is about 85–95% carbon monoxide, which cause damage for environment and a huge waste of CO when it is exhaust into atmosphere. Since 1980’s, C_1 chemistry had got a great development especially in CO synthesizing technology. Many products such as methylformiate, dimethylether, ethanoic acid, methanol and methyl carbonate can be synthesized from CO. If yellow phosphorous tail gas can be used as raw material gas to synthesize chemically product, it cannot only avoid environmental pollution but also reduce the cost of yellow phosphorous production. However, by now only 20–25% yellow phosphorous tail gas has been used as fuel and the rest is let out into the air, few of them is used to produce some cheap products such as trimeric sodium phosphate, etc. [2]. The main reason to restrict wildly use of yellow phosphorous tail gas is that it contains phosphorous (PH_3, P_4), sulfur (H_2S), which can stark influence the reaction of carbonyl combination even at very low concentration. The heat value of tail gas is about 10,000 kJ/m^3. How to multipurpose use yellow phosphorous tail gas is one of the valuable things. It must obtain high purity CO when it is used as chemical raw material. Therefore, yellow phosphorous tail gas must be pretreated before it is used.

For the purposes of further products of yellow phosphorous tail gas, purifying technology have been researched for many years such as: washing with water to get rid of fly ash, SiF_4 and part of H_2S and HF; washing with water and sodium (NaOH 10–15%); purifying with the method of TSA-PSA [3,4], etc. For some high quality required of CO, deep desulfurization and dephosphorous (both sulfur and phosphorous contained less than 1 ppm) technologies are needed.

During the past several decades, most researches were focus on removing H_2S by adsorption and catalytic oxidation methods. Westmoreland and Harrison [5] researched that some metal oxide such as Fe, Zn, Mo, Mn, Sr, B, Co, Cu and W have better capacity for H_2S removal. Many works were focus on H_2S

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Nomenclature

b_i	Langmuir constant of i
c_i	i concentration in gas phase (kg/m^3)
c_i^*	i concentration at equilibrium (kg/m^3)
d	diameter of fixed bed (m)
D_{zi}	axial diffusion constant of i
D_{ri}	radius diffusion constant of i
k	reaction rate constant of PH_3 (1/min)
k_1	reaction rate constant of H_2S (kg/s Pa)
k_2	reaction rate constant of H_2S (1/Pa)
K	adsorption mass transfer constant (m^3/kg s)
Q_{mi}	monolayer maximum adsorption amount (kg/kg)
r	radius of fixed bed (m)
R_i	reaction rate of i (kg/s m^3)
S_{cat}	catalytic surface area per unit catalyst volume (m^2/m^3)
t	time (s)
u	flow velocity (m/s)
W_S	amount of S loading on catalyst (kg/kg)
X_i	i loading in activated carbon (kg/kg)
z	length of fixed bed (m)
Greek letters	
ε	viodage of fixed bed
ρ_c	density of activated carbon (kg/m^3)
Superscript	
$*$	at equilibrium
Subscript	
i	compound index of gas

removal from coal gas by limestone adsorbents [6–10]. However, less report had been found about PH_3 removal from gas phase except chemical vapor deposition [11,12]. Among various methods for H_2S and PH_3 removal reported in the literature, catalytic oxidation at low temperature is less reported [13–16]. To our knowledge, there is no systematic study of binary mixture gas purification contained both H_2S and PH_3 at very low concentration, and this is the sticking point for yellow phosphorous tail gas purification.

In the previously work of our group, it has been found that activated carbon impregnated with metal and other solution has better adsorption capacity for sulfur and phosphorous removing from tail gas. During this process, catalytic oxidation reaction for H_2S and PH_3 take place over impregnated activated carbon. Therefore, it can be assumed that physical adsorption and catalytic oxidation reaction occur simultaneously. In the present work, adsorption isotherm, dynamic behavior and chemical kinetics have been studied over impregnated activated carbon for desulfurization and dephosphorous. The influences of operating variables on catalytic oxidation in both laboratory-scale and pilot-plant fixed bed were investigated. For the purpose of optimal designing of gas–solid reactor and seeking for the optimal operation condition, a simulation model also has been given for predicting the process of both physics adsorption and chemical reaction for mixture gas in fixed-bed reactor.

2. Mechanism

The mechanism of removing H_2S has been studied including adsorption-clause process, liquid redox process and direct oxidation at lower temperature in presence of a catalyst [17,18]. Highly removal efficient and high sulfur capacity up to 60% (g/g cat.) are obtained by catalytic oxidation over impregnated activated carbon [19]. Whereas less study has been found about the removal of PH_3 from mixed gases.

The prior investigation for catalytic reaction on activated carbon was

$$H_2S\,(g) + \tfrac{1}{2}O_2 \rightarrow H_2O\,(g) + S\,(s).$$

Elemental sulfur formed in the oxidation is deposited on carbon catalyst which causes the continuous change in effectiveness factor due to the texture of catalyst changing as a result of sulfur deposition and gradual decrease in the number of active sites due to their physical covering by sulfur [20]. The amount of sulfur formed on is plotted against the reciprocal of time to processing the data. For removal of H_2S in yellow phosphorous tail gas over impregnated activated carbon, catalytic oxidation reaction takes place at the existing of O_2. At the same time, reactions may take place simultaneously for P_4 and PH_3 existed in tail gas, which will be analyzed below.

An ample amount of O_2 contained in tail gas could be used in these catalyst oxidation reactions. Previous work in our group had shown that in addition to oxidation-reductive reaction of impregnated activated carbon bed, there were some H_2S and PH_3 reduction in tail gas through the carbon bed at different temperature. Therefore, it can be assumed that physical adsorption and catalytic oxidation reaction occur simultaneously over the impregnated activated carbon.

2.1. Equilibrium adsorption of gas mixture

Except H_2S and PH_3, yellow phosphorous tail gas contains about 85–90% CO, 2–5% N_2, 1–8% H_2O, 1–4% CO_2, O.5% H_2 and 0.3% CH_4 and 0.5% O_2. The measurement of mix-gas adsorption is certainly tedious. However, models or correlation for mixed-gas adsorption should be capable of predicting from pure gas isotherms. Langmuir isotherm for single-gas adsorption can readily be extended to an n-component mixture [21]. The Langmuir equation for single component is:

$$X = \frac{Q_m b y}{1 + b y} \tag{1}$$

When adsorption for a mixture gas, supposing each species maintains its own molecular area, and the area covered by one molecule that is not influenced by the presence of other species on the surface as in single-gas adsorption, the amount adsorbed for i in the mixture is:

$$X_i = \frac{Q_{mi} b_i c_i}{1 + \sum_i^n b_i c_i} \tag{2}$$