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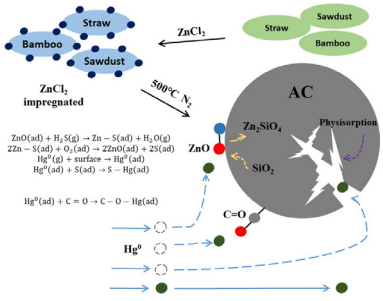
Full Length Article

Mercury removal mechanism of AC prepared by one-step activation with $ZnCl_2$

Dongyang Hong[a], Jinsong Zhou[a,*], Changxing Hu[b], Qixing Zhou[a], Juezhen Mao[a], Qianwen Qin[a]

[a] State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, Hangzhou 310027, China
[b] Institute of Energy and Environmental Engineering, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, China

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, activated carbon with ZnO laden on the surface was prepared by $ZnCl_2$-one-step activation of different types of biomass (corn straw, bamboo powder and sawdust) and employed for mercury removal in the coal gas. During the activation, a part of $ZnCl_2$ is converted into ZnO and laden on activated carbon, which greatly promotes the mercury removal performance with the presence of H_2S. The ZnO content varies greatly with the content of SiO_2 in the biomass due to its inactivation of ZnO and formation of Zn_2SiO_4. Carbonyl, which is important to mercury removal is largely retained after the activation at 500 °C and the amount of carbonyl seems to be positively correlated with the specific surface area (related to the lignin content). The temperature programmed desorption method was applied to further analyse the mercury adsorption in the coal gas. The results showed that ZnO and carbonyl play an important role in mercury removal, while the physisorption is not significant and only accounts for approximately 7% at 130 °C. The mechanism study showed that ZnO serves as a catalytic active site and catalyses the Hg^0 into HgS with the presence of H_2S. While the C═O group of carbonyl acts as adsorption sites and turns into C—O after the adsorption. This study provided a promising preparation method of mercury sorbents in the coal gas, and the influence of surface functional groups was also investigated in detail.

1. Introduction

Coal will comprise the largest source of Chinese energy consumption for a long time. By 2040, coal will still account for 36% of the Chinese energy infrastructure, which is 41% of the global coal demand [1]. Coal gasification technology is an important way to utilize coal resources and its comprehensive and clean application have drawn wide attention [2,3]. In the process of gasification, mercury in its

* Corresponding author.
E-mail address: zhoujs@zju.edu.cn (J. Zhou).

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Nomenclature

AC	activated carbon
AC-STR	the activated carbon activated from corn straw
AC-BAM	the activated carbon activated from bamboo
AC-SAW	the activated carbon activated from sawdust
SAW-900	AC-SAW after the calcination treatment at 900 °C in a N_2 atmosphere for 1 h
SAW-HCl-900	AC-SAW after the acid leaching with 0.1 mol/L hydrochloric acid for 24 h and calcination treatment at 900 °C in a N_2 atmosphere for 1 h
Hg^0	elemental mercury
Hg^{2+}	oxidized mercury
Hg^P	particle-bound mercury
ηT	the mercury removal efficiency of a period,%
Hg^T_{inTT}	the total adsorption quantity in a certain period, μg
Hg^T_{outTT}	the total mercury removal quantity, μg
Hg^T_{in}	the total mercury concentration at the inlet, μg/m^3
Hg^T_{out}	the total mercury concentration at the outlet, μg/m^3
Hg^T	the total mercury concentration, μg/m^3
V^t	the volume correction coefficient caused by the change in the thermodynamic state of the gas
k_i	the display peak intensity in the TPD diagram of peak i
k'_i	the theoretical peak intensity which is not affected by the adsorption of subsequent n-i peaks
$k“_i$	the real peak intensity which is not affected by all the peaks
$\eta_{i,j}$	the adsorption efficiency of the peak j when the peak i desorbs
v	the nitrogen blow velocity, m^3/min
m	the adsorbent weight, g
ρ	the adsorbent density, g/m^3
s	the adsorbent sectional area, m^2
$k_{j,unsa}$	the unsaturated intensity of the peak j

various forms (Hg^0, Hg^{2+}, Hg^P) will migrate to the gas phase and obstruct the clean utilization of coal gas. Most of the mercury released from coal is in the form of Hg^0, and the amount of Hg^0 in coal gas is even higher than that in coal-fired flue gas [4]. Hg^0 has high volatility and low water solubility, and it is difficult to remove using conventional flue gas treatment facilities. It has become a hot topic of current research to transform Hg^0 into Hg^{2+} which is easier to arrest and absorb from coal gas.

Biomass is a cheap and eco-friendly resource and its comprehensive utilization has wide developing prospect [5]. AC from biomass has well-developed pore structures and rich surface chemical groups, resulting in a strong specific adsorption ability that can remove mercury [6,7]. Increases in the specific surface area, total pore volume and the percentage of micro-pores are accompanied by an almost proportional increase in the mercury adsorption capacity [8–10]. In addition, the oxygen functional groups on the surface can greatly promote mercury removal [11]. However, due to the limited mercury adsorption capacity, an additional modification process is often required, such as sulphurization [12,13], adding halogen groups [14–16], loading metallic oxides and acid modification [17,18]. However, additional load and modification processes to obtain a high mercury removal efficiency are often complex and time-consuming. The optimization of the selection of raw materials and preparation methods of AC to enhance the mercury removal ability without an extra load and modification process is significant.

The production methods of AC mainly include physical and chemical activation. Under physical activation, material is activated by the activated gas and the temperature often reaches as high as 1000 °C. Activated gases are usually carbon dioxide, water vapor, air or their mixtures [19]. However, most of the surface functional groups on the surface of AC will be decomposed and lost due to this high activation temperature [20]. Chemical activation requires the addition of a chemical activator to raw material in a certain proportion and then activate in an inert gas medium. Common activators include KOH, NaOH, $ZnCl_2$,

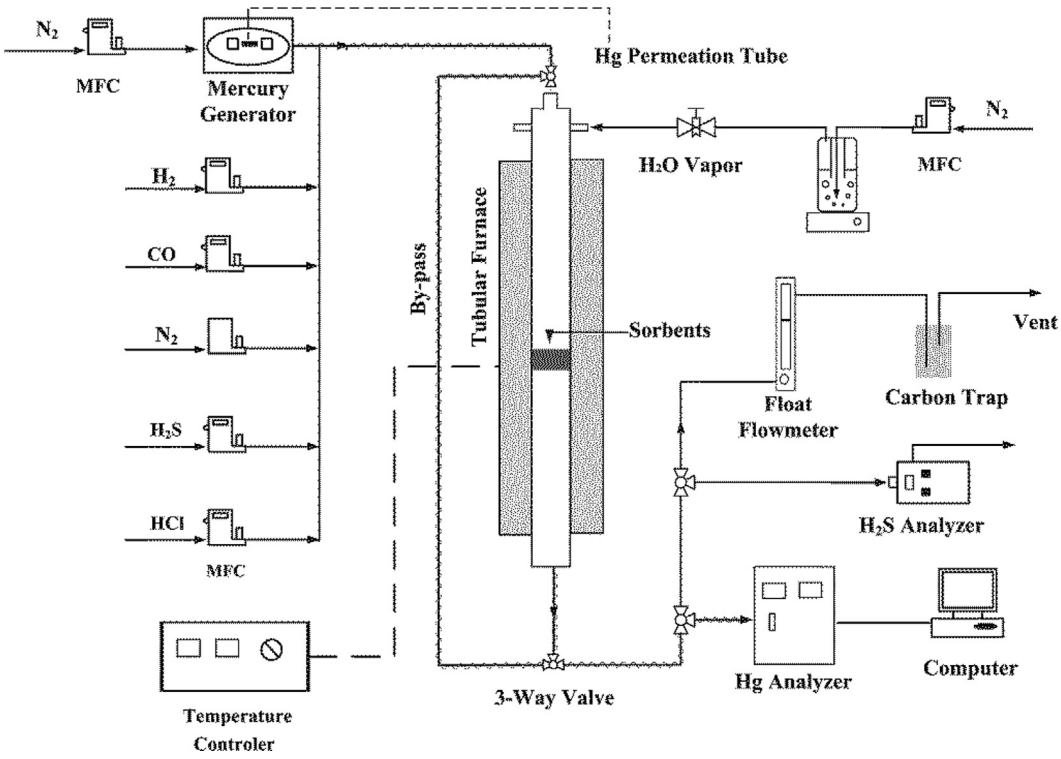

Fig. 1. Schematic diagram of the fixed bed reaction system.