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Improved catalyst recovery combined with extracting alumina from Na_2CO_3-catalyzed gasification ash of a high-aluminium coal char

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ABSTRACT

The catalyst recovery from Na_2CO_3-catalyzed steam gasification ash of Sunjiahao (SJH) high-aluminium coal char was investigated using water leaching method combined with extracting alumina by means of $Ca(OH)_2$ thermal activation. The recovery efficiency of sodium catalyst from Na_2CO_3-catalyzed gasification ash (NCGA) with single water leaching method was as low as 39.5 wt%, which resulted from the formation of water insoluble sodium aluminosilicate during Na_2CO_3-catalyzed gasification. In order to improve sodium recovery, the water-washed NCGA was activated by means of $Ca(OH)_2$ thermal activation for simultaneous recovery of sodium and alumina. The recovery efficiency of sodium from the water insoluble sodium aluminosilicate is 63.6 wt%, thus the total sodium recovery can be remarkably improved and reach 72 wt%. Meanwhile, the extraction efficiency of alumina from NCGA can reach 88.46 wt%. The low sodium recovery with $Ca(OH)_2$ thermal activation is attributed to the formation of Na_2CaSiO_4 during $Ca(OH)_2$ calcination. Extracting alumina process from NCGA of SJH high-aluminium coal can effectively promote the recovery of sodium catalyst and the process economy.

1. Introduction

With the increasing demand of natural gas, the production of synthetic or substitute natural gas (SNG) has been given much attention in the past decades [1,2]. Among the modern production technologies of SNG, catalytic coal gasification may be the most suitable candidate for the production of SNG. The reason is that it is easy for catalytic coal gasification to convert solid carbon fuels into gaseous fuels, besides that catalytic coal gasification has several remarkable advantages [3–6], such as (I) catalytic gasification can strikingly lower the reaction temperature [7–9]; (II) it can remarkably enhance the gasification reaction rate [7]; (III) moreover, catalytic gasification is in favor of the production of methane [10]. Catalytic coal gasification, therefore, is a promising technology for SNG production.

Although catalytic coal gasification has a research history of decades, it has not been put into effect in industry so far. This indicates that some crucial technical and economic challenges in the field of catalytic coal gasification remain for further investigation. The decisive challenge is the catalyst recovery process which mainly influences the economic evaluation of the integral catalytic gasification process and results in environmental pollution caused by water-soluble alkali metal compounds existing in ash without catalyst recovery treatment. Thus, commercial-scale catalytic coal gasification processes have rarely been put into operation at present. There are two main reasons accounting for the stagnant status of catalytic coal gasification in commerce. On one hand, catalyst recovery may markedly increase the investment costs of the entire gasification process. On the other hand, the risk of environmental pollution (such as groundwater pollution and soil pollution) may be increased by the remaining water-soluble alkali metal compounds existing in the catalytic gasification ash. Hence, with the rapid development of catalytic coal gasification technology, the catalyst recovery technology should be concurrently developed and will play a major part in the impending future.

Unfortunately, few efforts toward the recovery of the gasification catalyst applied in the catalytic coal gasification have been made [6]. It is the deficiencies of the gasification catalyst recovery that severely hinder the development of the industrial-scale catalytic coal gasification processes. Therefore, it is indispensable to further investigate gasification catalyst recovery to commercialize the catalytic coal gasification process. With respect to the gasification catalyst recovery, extensive research with Illinois coal was carried out in a lab- and bench-scale reactor by Exxon Research and Engineering Co. [11]. Not only the

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Table 1
Proximate and ultimate analyses of SJH coal, SJHC and SJHAC.

Sample	Proximate analysis (wt.% ad)				Ultimate analysis (wt.% daf)				
	V	FC	A	M	C	H	N	S	O*
SJH coal	29.6	51.2	16.9	2.3	78.8	4.9	1.5	0.8	14.0
SJHC	2.4	77.1	20.1	0.4	94.4	0.9	1.3	0.8	2.6
SJHAC	2.4	92.4	4.8	0.4	94.2	1.2	1.2	0.8	2.6

ad: air dried basis; daf: dry ash-free basis; *: by difference.

influence of different experimental conditions on catalyst recovery efficiency but also the effect of two catalyst recovering methods (water washing and limewater washing) on catalyst recovery efficiency [12] has been investigated in detail. In order to sufficiently recover the gasification catalyst, Sheth et al. [13] applied various extraction schemes, such as water extraction, H_2SO_4 extraction, and acetic acid extraction. Among the different extraction methods, H_2SO_4 extraction is the best recovery method. Zhang et al. [14] utilized a new approach to recover and reuse the calcium catalyst in coal gasification instead of aqueous acid solution. With the purpose of recovering and regenerating the gasification catalyst, they used the crude vinegars derived from the rapid pyrolysis of forestry and agricultural residuals to leach the catalytic coal gasification ash. Their investigation showed that the calcium catalyst could be completely regenerated and reused by the extraction of the gasification residues with crude vinegars. However, this recovery method cannot be easily commercialized due to the limitation of the production of crude vinegars. Unlike the solvent extraction methods, Kim et al. [15] reclaimed the catalyst from the catalytic coal gasification ash according to size and magnetic properties. Yuan et al. [16,17] used the combination of water washing and limewater washing to recover the gasification catalyst from the catalytic coal gasification residue. Their study result indicated that the optimal catalyst recovery efficiency could reach 84.69% by conducting three washes with the combined washing method. The investigation [18] reported that the highest recovery efficiency of the potassium catalyst used in the catalytic coal gasification could reach 92.14% after six limewater washings and 93.37% after three limewater washings, respectively. Unfortunately, the results of the forementioned catalyst recovery processes could not achieve a satisfactory result.

As far as catalytic coal gasification is concerned, a fluidized-bed reactor may be the appropriate gasification reactor due to the mild gasification temperature. However, the addition of alkali metal catalyst in the course of catalytic coal gasification may remarkably lower the ash fusion point, which can increase the slagging risk of fluidized gasifier. Thus, it is indispensable to use the coals with high ash fusion point to conduct fluidized catalytic coal gasification. It is generally considered that high-aluminium coals have high ash fusion point which may be the alternative to fluidized catalytic coal gasification. Nevertheless, the interaction between alkali metal catalyst and aluminium in the high-aluminium coal during catalytic coal gasification, makes it difficult to recover the gasification catalyst effectively. According to Bayer process in alumina production technology, the alkali metal such as Na_2CO_3 is involved. A satisfactory result may be obtained if the recovery of alkali metal catalyst and the extraction of alumina can be combined and conducted simultaneously. The profit of the extracted alumina will make up for the loss of gasification catalyst, even if the gasification catalyst recovery cannot reach a gratifying level. Therefore, this paper aims at the simultaneous recovery of both alkali catalyst and alumina during catalytic gasification of high-aluminium coal to explore the recovery of gasification catalyst.

However, few investigations have been reported about the catalytic steam gasification of high-aluminium coals and the recovery of catalyst. Consequently, in order to assess the concept of the simultaneous recovery of both alkali catalyst and alumina from the catalytic steam gasification ash of a high-aluminium coal and understand the possible mechanism, the recovery of gasification catalyst and the characterization of mineral transformation were conducted using a fixed bed reactor, a high temperature muffle and instrumental analyses. It is expected to provide fundamental understanding on the recovery process of gasification catalyst for the catalytic gasification of high-aluminium coals.

2. Experimental

2.1. Samples and reagents

SJH bituminous coal was collected from Inner Mongolia as the sample. The coal sample was first pulverized and sieved to a particle size of less than 120 μm. Then the sample was dried in an oven at 105 °C for 12 h, and finally stored in a desiccator for further use. SJH char (SJHC) and acid treated SJH char (SJHAC) were prepared according to our previous work [19]. The proximate and ultimate properties of SJH raw coal, SJHC and SJHAC are shown in Table 1. The ash compositions of SJH raw coal, SJHC and SJHAC are presented in Table 2.

All the analytical grade reagents used in this study are listed as follows: anhydrous Na_2CO_3 (Hengxing Chemical Reagent Co., Ltd. Tianjin), $Ca(OH)_2$ (Tianli Chemical Reagent Co., Ltd. Tianjin), NaOH (Hengxing Chemical Reagent Co., Ltd. Tianjin), aqueous ammonia (Beichenfangzheng Reagent Factory in Tianjin), Hydrochloric acid (Sinopharm Chemical Reagent Co., Ltd.), ethylene diamine tetraacetic acid (EDTA, Tianli Chemical Reagent Co., Ltd. Tianjin), KF (Beichenfangzheng Reagent Factory in Tianjin), $Zn(CH_3COO)_2$ (Beichenfangzheng Reagent Factory in Tianjin), CH_3COOH (Tianli Chemical Reagent Co., Ltd. Tianjin), anhydrous sodium acetate (Tianli Chemical Reagent Co., Ltd. Tianjin). Xylenol orange is a chemical grade reagent (Tianli Chemical Reagent Co., Ltd. Tianjin). All the water used in this study is deionized water.

2.2. Loading of Na_2CO_3 catalyst and preparation of Na_2CO_3-catalyzed steam gasification ashes

The detailed experimental procedures of Na_2CO_3 catalyst loading are carried out according to our previous work [19,20]. Na_2CO_3 catalyst was loaded by impregnating coal char sample with an aqueous solution containing different amount Na_2CO_3 on a dry basis of char sample. The mixture of coal char and Na_2CO_3 catalyst was stirred at 70 °C on a magnetic stirrer and dried at 105 °C for 24 h.

The preparation of Na_2CO_3-catalyzed steam gasification ashes was conducted in a fixed bed reactor in term of our previous work [19]. NCGA samples of SJHC and SJHAC were prepared in a horizontal quartz tube reactor at 800 °C under steam atmosphere (60 vol%, diluted

Table 2
Ash compositions of SJH coal, SJHC and SJHAC (wt%).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	SO_3	K_2O	Na_2O	P_2O_5
SJH coal	36.29	46.34	6.38	2.61	2.18	3.57	0.45	0.42	0.76	0.03
SJHC	36.09	46.64	6.58	2.51	2.08	3.50	0.43	0.27	0.42	0.04
SJHAC	10.21	52.28	32.50	0.83	0.46	0.67	0.88	0.02	0.09	0.06