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Predicting the vanadium speciation during petroleum coke gasification by thermodynamic equilibrium calculation

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HIGHLIGHTS

- FactSage was used to investigate the reactions of V with associated mineral elements.
- V participates in the reactions with Ca, Fe and Na to form V-containing species.
- H_2S(g) suppresses the reactions of V with Ca and Fe due to the formation of sulfides.
- V_2O_5(s), FeV_2O_4(s) and VO_2(g) are formed with the presence of all mineral elements.

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ABSTRACT

High temperature gasification has been considered as one of the most promising routes for the clean and efficient utilization of high-sulfur petroleum coke (petcoke). However, petcoke usually contains high content of vanadium (V). It has been proven that V element in petcoke can lead to fouling or corrosion problems in the process of combustion, which captures the attention to the fate of V during petcoke gasification. In this paper, thermodynamic equilibrium calculations based on the FactSage were used to investigate the reaction mechanism of V with the main associated mineral elements (Si, Ca, Al, Fe, Ni and Na) during petcoke gasification. The influence of gasification temperature and atmospheres on the V species equilibrium composition was also evaluated. The results indicate that V reacts with the mineral elements of Ca, Fe and Na to form V-containing species $(CaO)_3V_2O_5$(s), FeV_2O_4(s), $(Na_2O)_3V_2O_5$(s) and $(Na_2O)_2V_2O_5$(l), respectively. The presence of H_2S(g) suppresses the reactions of V with Ca and Fe due to the formation of sulfides (CaS and FeS). In addition, it is verified that V does not participate in the reactions with Si, Al and Ni. However, the associated mineral elements may have remarkable co-effects on V species equilibrium composition. Ca reacts with Si or Al easily to form the Ca-containing minerals ($CaSiO_3$(s), $Ca_3Si_2O_7$(s), Ca_2SiO_4(s), $CaAl_4O_7$(s), $CaAl_2O_4$(s)), impeding the formation of $(CaO)_3V_2O_5$(s). Na combines with Al to generate Na-containing minerals ($NaAlO_2$(s), $Na_2Al_{12}O_{19}$(s)), inhibiting the formation of $(Na_2O)_3V_2O_5$(s) and $(Na_2O)_2V_2O_5$(l). When all of the main associated mineral elements are present, the V-containing species formed in the whole process of gasification are V_2O_3(s), FeV_2O_4(s) and a small amount of VO_2(g).

1. Introduction

The production of petcoke, especially high-sulfur petcoke, is increasing progressively with the trend of processing heavy crudes in refineries [1]. High-sulfur petcoke can be used as an alternative to the natural fuel, but the high content of sulfur inevitably causes considerable sulfur oxide emissions into the environment in the process of combustion [2]. Therefore, the efficient and environmentally-friendly utilization of petcoke has become an imperative problem [3,4]. The particular advantages of high calorific value and low ash [5], make the case of petcoke as a gasification feedstock more attractive and economical. Petcoke gasification for hydrogen production is beneficial to solve hydrogen deficiency for hydroprocessing units in refineries. It also offers a variety of product slates including steam, electricity and chemicals via synthesis gas route [6]. Moreover, the process of gasification is considered to be more responsible than that of combustion with regard to environmental factors.

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Petcoke usually contains high content of heavy metal vanadium (V) which might be found up to 1500 ppm in petroleum samples [7]. Previous studies [8–11] have demonstrated that the high content of V gives rise to various environmental and technological problems during combustion processes. For instance, vanadium pentoxide (V_2O_5) may lead to corrosion caused by acidic sulfates since it acts as a catalyst in the sulfuric acid production process [8]. V_2O_5 may also damage the refractories at high temperatures because the molten V_2O_5 is able to readily dissolve most refractories and metal oxides [9]. The fate of V element in petcoke during gasification may be obviously different to that which occurs during combustion. As an example, V is present in the form of V_2O_5 below 1077 °C under oxidizing conditions, whereas V_2O_3 is the major V-containing species below 1477 °C under reducing conditions [12]. Consequently, it is necessary to access to the information on the fate of V in the process of petcoke gasification.

However, the relevant information is quite limited compared to that from coal gasification. In terms of the fact that the chemical and physical property of coal is similar to that of petcoke, a large amount of references on the coal gasification can be applied to discussing the fate of V during petcoke gasification. The effect of V on the transformations of minerals in coal at reducing atmospheres was examined by Wang et al. [13]. It was shown that at high temperatures V_2O_5 could react with CaO to form calcium orthovanadate ($(CaO)_3V_2O_5$). Simultaneously, the reduction of V_2O_5 to form karelianite (V_2O_3) took place initially at 1100 °C. When the temperature was above 1400 °C, V_2O_3 was the only crystal containing V element.

In addition to the experimental techniques, thermodynamic equilibrium calculations using different computer programmes have also been successfully carried out to obtain the information on the fate of elements in the process of gasification [14]. One such study by Bunt and Waanders [15] investigated the trace elements behaviors in the Sasol–Lurgi MK IV FBDB gasifier. The V thermodynamic equilibrium results showed that at temperatures higher than 325 °C, V_2O_5 was reduced to V_2O_3 with no volatilization of the V species occurring. V_2O_3 existed stably in the rest process of gasification in thermodynamic equilibrium. Some volatilization of $VO_2(g)$ (0.1%) occurred with the temperature increasing to above 1225 °C. Frandsen et al. [12] studied the fate of trace elements in the thermal conversion calculation of coal. It was found that under standard reducing conditions solid V_2O_3 was the stable form of V below 1447 °C. When the temperature was above 1527 °C, a small amount of $VO_2(g)$ was present in the system. The distribution of V in gases from coal gasification was investigated by Diaz-Somoano and Martinez-Tarazona [16] using thermodynamic equilibrium calculation. It was observed that $V_2O_3(s)$ became the main condensed species above 500 °C. The formation of $VO_2(g)$ might occur at temperatures higher than 1400 °C and low pressures (<1 MPa). When the temperature was below 200 °C, V existed in the form of VC.

Note that, the effects of associated mineral elements in petcoke on the V speciation are not taken into account in the researches mentioned above. Si, Ca, Al, Fe, Ni and Na are the main mineral elements coexisting with V. The presence of these associated mineral elements may have remarkable influences on the V species equilibrium composition. Unfortunately, a detailed research on the reactions of V with associated mineral elements during gasification is not yet gained.

This study adopts FactSage thermodynamic equilibrium modeling based on Gibbs energy minimization. The objective is to predict the reactions of V with associated mineral elements between 100 and 1600 °C in different gasification atmospheres. The research focal points are: (1) simulating the equilibrium conditions for reactions of V with associated mineral elements, (2) assessing the effect of $H_2S(g)$ present in synthesis gas atmosphere on the V species equilibrium composition. On the basis of those predicted results, researchers can precisely ascertain the V speciation in the presence of associated mineral elements during petcoke gasification. Furthermore, the results can provide theoretical basis for petcoke efficient and environmentally-friendly utilization.

2. Calculation procedure and input data

2.1. Thermodynamic equilibrium modeling

FactSage software is the integration of two well-known F*A*C*T/Fact-Win and ChemSage thermochemical packages [17,18]. In this study, it is used as a modeling tool to predict the reactions of V with associated mineral elements in thermodynamic equilibrium during petcoke gasification because the built-in database includes thermodynamic properties for 4400 chemical species [19]. The original mode of occurrence of trace elements in petcoke is not taken into account in the FactSage and all the elements studied are assumed to get into equilibrium reaction freely. Once the total Gibbs energy of the reaction system is at its minimum value, all possible chemical reactions (homogeneous and heterogeneous) will reach equilibrium, and only stable chemical species and phases remain [15]. The Equilib module utilized with the FactPS and FToxid databases can detect the concentration of chemical species when specific elements or compounds react to equilibrium [20–22]. In our thermodynamic equilibrium calculations the number of potential chemical species exceeds 800, including 70 V-species, 110 Ca-species, and 130 Si-species. Besides, the number of Al-species, Fe-species, Na-species, and Ni-species is as many as 100, 80, 90, and 60, respectively. Many of possible chemical reactions occurring under petcoke gasification operating conditions would be much too slow at low temperatures (<800 °C) and may not actually reach equilibrium. FactSage software based on Gibbs energy minimization just identifies the possible chemical products in thermodynamic equilibrium during gasification processes. Consequently, there exists intrinsic differences between thermodynamic equilibrium calculations and actual gasifier operating results. Even so, Factsage equilibrium analysis does provide a computational approach that has proven to yield insight into the fate of trace elements [14,15].

2.2. Gasification condition and input data

Thermodynamic equilibrium calculations are performed in typical petcoke gasification atmospheres. The temperature ranges from 100 to 1600 °C, with the interval of 100 °C. The typical petcoke from Shengli Oilfields, China, is selected for this study. Its proximate and ultimate analysis is listed in Table 1.

There should be two assumptions. (1) All the sulfur in petcoke is presented in the vapor phase as $H_2S(g)$ initially because all of gasifiers produce $H_2S(g)$. The calculations are carried out under two sets of gasification atmospheres (atmosphere A and atmosphere B) which are controlled by varying the concentration of $H_2S(g)$. Consequently, the effect of $H_2S(g)$ on the V species equilibrium composition in the process of gasification is investigated. (2) The current knowledge regarding the mode of occurrence of trace elements in petcoke is little. Therefore, V and the associated mineral

Table 1
Proximate and ultimate analysis of petcoke.

Petcoke	Proximate analysis (wt%, ad)			Ultimate analysis (wt%, ad)				
	M	A	V	C	H	O	N	S
Shengli oilfields	0.67	0.80	9.81	88.80	3.61	1.38	1.14	3.60