Chemical Engineering Journal 295 (2016) 461–467

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Influence mechanism of H_2S on the reactivity of Ni-based oxygen carriers for chemical-looping combustion

Yuchuan Feng, Xing Cai, Xin Guo *, Chuguang Zheng

State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

HIGHLIGHTS

- The adsorption mechanism of H_2S on NiO(001) perfect and defect surface was investigated.
- The oxygen defect surface exhibits the high reactivity to the sequential dehydrogenation reaction of H_2S.
- The influence mechanism of H_2S on the CO adsorption and the diffusion of the O anion on NiO(001) surface is proposed.

ARTICLE INFO

Article history:
Received 15 January 2016
Received in revised form 11 March 2016
Accepted 12 March 2016
Available online 18 March 2016

Keywords:
Density functional theory
H_2S
Adsorption
Influence
Diffusion

ABSTRACT

First-principle calculations based on the density functional theory (DFT) were used to clarify the influence mechanism of H_2S on the reactivity of Ni-based oxygen carriers. A systematic investigation about the adsorption behaviors of H_2S on NiO(001) perfect and defect surface was firstly performed. H_2S molecule is very likely to produce the sequential dehydrogenation reaction on NiO(001) defect surface, while this phenomenon was not observed on NiO(001) perfect surface. Then the mechanism of CO adsorption on the H_2S pre-adsorption NiO(001) perfect and defect surface was clarified. It was revealed that the existence of H_2S could notably restrain the CO adsorption process on NiO(001) surface. The H_2S influence on the diffusion of the O anion in the NiO slab was also studied in detail. Results showed that the presence of H_2S would lead to the higher thermodynamic driving force required for the O anion diffusion, limiting the rate of the diffusion.

1. Introduction

Owing to its contribution to the increase of global average temperature, great attention has been given to CO_2 emission. Fossil fuel combustion is the primary source of anthropogenic CO_2 emission. In a convention combustion system, CO_2 separation is energy-intensive due to low concentration in the flue gas. Chemical looping combustion (CLC) is a promising approach used to combine fuel combustion and CO_2 separation with low cost and energy consumption [1]. The CLC system is composed of two interconnected fluidized bed reactors, an air reactor and a fuel reactor. The oxygen is transferred from the air reactor to the fuel reactor by means of an oxygen carrier, which is usually in the form of a metal oxide, avoiding the dilution of flue gases with the N_2 of the air. The oxygen carrier is circulating between the air reactor, where it is oxidized by the air, and the fuel rector, where it is reduced back to its initial state by the fuel. In this way, the fuel is oxidized to CO_2 and H_2O in the fuel reactor and then almost pure CO_2 can be obtained by condensing the water without requiring any energy for separation or purification.

Gaseous fuels in the chemical-looping combustion process, such as natural gas, refinery gas or synthesis gas from coal gasification, may contain different amounts of sulfur compounds, such as H_2S. Natural gas usually contains a few of H_2S about 20 vppm [2]. H_2S concentration in the refinery gas can vary depending on the site and reach up to 800 vppm in some sites, while this value may even rise substantially to 8000 vppm for the raw synthesis gas [3]. The sulfur compounds could react with the oxygen carrier to form sulfides or sulfates, decreasing the reactivity of the oxygen carrier and the combustion efficiency [4–9]. In addition, the low melting point of some sulfides could result in agglomeration, affecting the solid circulation pattern between the interconnected fluidized bed reactors [10]. Considering a large number of the existing experimental studies about the influence of H_2S on the reactivity of Ni-based oxygen carrier, which could be used as the evidence of our calculations, we chose the NiO as the oxygen carrier. Previous experimental studies [11–14] have found that H_2S can react with Ni-based

---

* Corresponding author. Tel./fax: +86 27 87545526.
E-mail address: guoxin@mail.hust.edu.cn (X. Guo).

http://dx.doi.org/10.1016/j.cej.2016.03.058
1385-8947/

oxygen carriers, affecting the performance of oxygen carrier reactivity. Garcia-Labiano et al. [11] have investigated the fate of sulfur during CH_4 combustion in a 500 Wth CLC prototype with a nickel-based oxygen carrier. It was found that Ni_3S_2 was formed in the fuel reactor, which resulted in the oxygen carrier deactivation and lower combustion efficiency. Ksepko et al. [12] reported that the presence of H_2S decreases reduction reaction rates of Ni-based oxygen carriers significantly. Shen et al. [13] studied the reactivity of NiO/Al_2O_3 oxygen carrier reduction with a gas mixture of CO/H_2 and H_2S. The results showed that the rate of NiO reduction with H_2S is higher than that with CO. Dueso et al. [14] explored that effect of H_2S on the behavior of an impregnated NiO-based oxygen-carrier for chemical-looping combustion (CLC). It was revealed that H_2S could obviously affect the Ni-based oxygen-carrier behavior.

Despite the enormous experimental efforts on the influence of H_2S on the reactivity of Ni-based oxygen carriers, theoretical calculations about it at the atomic level have not been reported yet. Hence, a systematic theoretical study is necessary and urgent in order to gain an insight into the effect of H_2S.

Adsorption is the primary step of the chemical reaction for gas on the solid surface and the degree of reaction is closely related to the adsorption process. Moreover, the diffusion process of the O anion of oxygen carrier plays an important role in the CLC. Therefore, in this work, first-principle calculations based on density functional theory (DFT) was employed to clarify the influence mechanism of H_2S on the CO adsorption and the diffusion of the O anion on NiO surface. Firstly, we investigated the adsorption behaviors of H_2S on NiO(001) perfect and defect surface. Then based on the calculations of CO adsorption on NiO(001) perfect surface in our previous study [15], the corresponding data are directly quoted for comparison to analyze the H_2S effect upon the CO adsorption on NiO surface. Moreover, we presented the H_2S influence on the diffusion of the O anion in the NiO slab.

2. Computational details

All the DFT calculations were carried out with the CASTEP (Cambridge Sequential Total Energy Package) [16,17] in Materials Studio of Accelrys Inc. The generalized gradient approximation functional proposed by Perdew, Burke, and Ernzerhof, known as GGA-PBE [18,19] for the treatment of electron exchange and correlation was performed in the calculations. The electron density functions were expanded in a plane wave basis set and ultrasoft pseudopotential was employed to describe ionic cores [20].

Nickel oxide crystal, which adopts the rock salt structure, is an antiferromagnetic material with a lattice parameter $a_0 = 4.17$ Å. NiO(001) surface is regarded as the near perfect bulk termination among the different surface terminations according to the experimental technique [21] and previous calculations [22], so all the calculations in this work were based on NiO(001) surface.

The condition with low oxygen pressures, which is easily provided in CLC fuel reactor, may result in the formation of oxygen vacancy [23]. In addition, the O anion of NiO surface could participate in the reaction in CLC, which may also bring about considerable concentrations of the oxygen vacancy. Therefore, a six-layer slab with a (2×2) periodic supercell was used to model NiO (001) surface, including both the perfect and defect surface with the oxygen vacancy. For the defect surface, the central O atom of the first layer was removed from the perfect surface [15,24]. A vacuum layer of 15 Å [25] thickness was utilized to reduce the interaction between the periodic slabs. The top two layers and the adsorbates were relaxed, while the bottom four layers were fixed during geometry optimization and transition state (TS) search.

The spin-polarized formalism was applied for the NiO unit cell due to the antiferromagnetic properties of nickel oxide [15,26]. Considering the convergence tests for the k point sampling, a $3 \times 3 \times 1$ Monkhorst–Pack k-point mesh for the Brillouin zone integrations was chosen in all the calculations [15]. The previous research showed the Hubbard parameter (U) could accurately describe the strong electron correlation effects that arise from the localized Ni 3d states, then $U = 6.3$ eV, in agreement with previously reported U value [15,27,28], was suggested to simulate NiO in present work. We use a cutoff energy of 330 eV in the expansion of the plane wave basis set to ensure the convergence of the total energy for the primitive cell of NiO bulk [15]. The dipole correction [29] has been taken into consideration in our calculation for the defect slab models and the CO adsorbed surfaces. The convergence criteria for geometry optimization was set to the tolerance for energy, SCF, maximum force as well as a maximum displacement of 2.0×10^{-5} eV/atom, 2.0×10^{-6} eV/atom, 0.05 eV/Å, and 0.002 Å, respectively. More detailed discussions about computational methods have been presented in our previous study [15].

The adsorption energy (E_{ads}) was calculated with the formula:

$$E_{ads} = E_{adsorbates/substrate} - (E_{adsorbates} + E_{substrate})$$

where $E_{adsorbates/slab}$ is the total energy of the substrate together with adsorbates, while E_{slab} and $E_{adsorbates}$ are the total energy of the substrate surface and the free adsorbates, respectively. Under this convention, a more negative value of adsorption energy represents stronger adsorption.

The TS searches were employed to find the TS configurations and to obtain the reaction energy (ΔH) as well as the activation barrier (E_b) of the reaction with the complete LST/QST (linear/quadratic synchronous transit) method [30]. ΔH and E_b were defined as

$$\Delta H = E_{pro} - E_{react}$$

$$E_b = E_{TS} - E_{react}$$

where E_{pro}, E_{react}, E_{TS} represent the energies of the products, the reactants and the TS, respectively.

3. Results and discussion

3.1. H_2S effect upon the CO adsorption on NiO(001) perfect surface

3.1.1. H_2S adsorption on NiO(001) perfect surface

H_2S and CO molecules were optimized in a 10 Å cubic crystal cell to obtain their equilibrium geometry. The bond length and bond angle of H_2S molecule were calculated to be 1.353 Å and 91.138°, which are in great agreement with the reported experimental results of 1.328 Å and 92.2° [31], respectively. Similarly, the computed bond length of CO is 1.153 Å, consistent with the corresponding experimental value of 1.128 Å [32].

The NiO(001) perfect surface recorded as P(001) surface is shown in Fig. 1. In order to comprehensively research the adsorption behaviors of H_2S on P(001) surface, four high-symmetry adsorption sites (Ni-top, O-top, bridge and hollow) were considered on P(001) surface. Meanwhile, three different adsorption directions of H_2S molecule were also respectively taken into account: (a) H_2S is perpendicular to the surface with the S atom down towards the surface; (b) H_2S is parallel to the surface; (c) H_2S is perpendicular to the surface with the S atom up towards the surface. Therefore, there are twelve initial structures at a coverage of 0.25 ML.

After optimization, the most stable configuration of H_2S on P (001) surface recorded as H_2S/P(001) surface is displayed in