DENSITY FUNCTIONAL THEORY (DFT) STUDY ON THE REACTION MECHANISM OF IN-SITU NO REDUCTION IN HYDROGEN RICH BLAST FURNACE

Based on density functional theory and classical transition state theory, the reaction mechanism of NO reduction by H_2 catalyzed by coke in hydrogen rich blast furnace was investigated. The results showed that the presence of active sites on the coke surface promoted the NO reduction reaction. Reactive oxygen species remaining on the coke edge inhibited the NO reaction after NO reduction. Both coke and H_2 can release edge sites by reducing reactive oxygen species, but reactive oxygen species reduction by H_2 requires a high barrier value of 634,3 kJ/mol, which is higher than that by coke.

Key words: blast furnace, hydrogen, coke, Gibbs free energy, NO reduction

INTRODUCTION

There is a large amount of nitrogen oxide generation in the production process of the steel industry. As one of the atmospheric pollutants, nitrogen oxides will cause the formation of haze, acid rain and ozone hole [1]. Due to the high temperature of coal powder combustion in the swing area, it would produce a large number of thermal NOx [2]. However, the front end of the swing area of the wind outlet in the blast furnace has a certain oxidation property, and other positions are basically in a reducing atmosphere [3]. The NOx generated in the front of the blast furnace can be reduced in situ through coke and the reductive atmosphere in the blast furnace. With the fact that carbon neutrality and carbon emission reduction targets, traditional blast furnaces gradually transform into hydrogen-rich blast furnaces [4]. For hydrogen-rich blast furnaces, the remaining H_2 in the ironmaking process can also be used as a NO reduction reducing agent.

In this study, Zigzag coke model was used and reaction mechanism of coke catalyzed NO reduction by H_2 was studied with density functional theory (DFT) and classical transition state theory (TST).

COMPUTING METHOD

Coke is mainly composed of 3-7 aromatic ring benzene rings. Zigzag coke was used in this study to simulate the reaction path of its catalytic NO reduction. The structure is shown in Figure 1.

The B3LYP/Lanl2dz level was adopted for the transition metal Ni atoms and the B3LYP/6-31G(d) level

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was adopted for the non-metallic atoms C, N and O [5,6]. Reactants, products, intermediates and transition state structures were optimized and the frequency were analyzed. The transition state in the reaction process was found by TS method, which ensures that the transition state has a unique virtual frequency. The intrinsic reaction coordinate analysis (IRC) was used to trace the reaction path to ensure the correctness of the structural connection before and after the reaction process. Quantum chemical calculation was carried out using Gaussian 09 package.
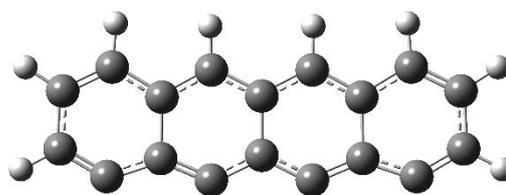
Figure 1 The coke structure employed in DFT simulation

RESULTS AND DISCUSSION

The adsorption behavior of NO should be the first step in the heterogeneous reduction of NO at the edge of coke. Zhang et al. [7] found that side-on adsorption at the edge of coke was easy for NO adsorption. Therefore, for the NO reduction by H_2 at the coke edge site, the adsorption of NO on the coke surface by side-on absorption is also the first step of the whole reaction. The geometries of intermediates and transition states during NO reduction are displayed in Figure 2. The Gibbs free energy of NO reduction is shown in Figure 3.

When NO molecules are adsorbed to the coke edge site, IM1 is formed, and the length of N(1)-O(1) bond increases from 1,16 Å in the free radical state to 1,71 Å.

Figure 2 The geometries of intermediates and transition states during NO reduction
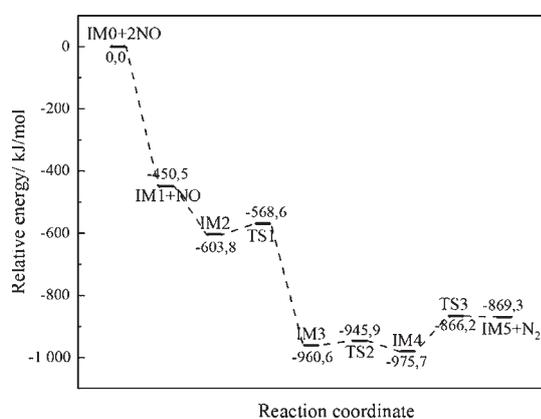
Figure 3 The Gibbs free energy of NO reduction

Subsequently, the second NO molecule is adsorbed on C(3) to form the stable state IM2. With the effect of coke, the bond length between N(1) and N(2) gradually decreases, from 2,71 Å (IM2) to 1,92 Å (TS1) to 1,19 Å (IM3). The energy barrier needs to overcome in this process is 14,7 kJ/mol, and the energy released is 15,1 kJ/mol. Subsequently, N(1)-N(2) rotates around C(3) to form IM4. The C(2)-N(1) bond length gradually elongates. And eventually forms N_2 molecules of gas by the transition state TS3. By comparing and analyzing the activation energy of each step in the above process, it can be found that the speed-controlled step for the formation of N_2 by the heterogeneous reduction of NO in coke is IM4→TS3, which needs to overcome the energy barrier of 109,5 kJ/mol.

In order to further explore the reduction mechanism of NO in blast furnace, the reaction paths of NO reduction by coke and H_2 are analyzed respectively. When N_2 is generated, reactive oxygen species (O*) produced by NO decomposition are still adsorbed on the edge of coke. However, coke can catalyze the reduction of O* and provide the active site again. The geometries of intermediates and transition states during O* reduction by coke is dis-
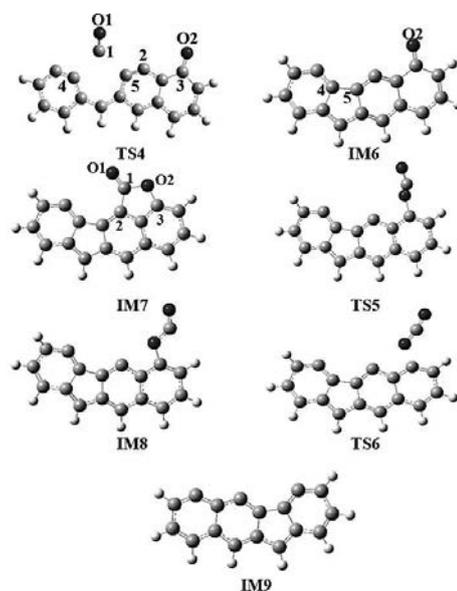
Figure 4 The geometries of intermediates and transition states during O* reduction by coke

played in Figure 4. The Gibbs free energy of O* reduction by coke is shown in Figure 5. From the stable state IM5, C(1) breaks the bond with C(4) and C(5) atoms under the action of O*, and the bond length of C(1)- C(4) increases, the bond length of C(1)- C(5) changes from 1,51 Å (IM5) to 2,37 Å (TS4). Finally, the C-C bond breaks to release gaseous CO molecules, and the C(4) and C(5) atoms rebond to form a stable structure IM6, in which needs to overcome 246,3 kJ/mol energy barrier. The gaseous CO molecules adsorbed on the O* remaining on the coke surface to form a stable structure IM7, where the C(1)- C(2) bond length is 1,48 Å. The C(1)-C(2) bond lengths gradually stretch and break, and rotate around C(3) to form IM8. The bond energy of C(3)-O(2) bond is gradually weakened, and finally CO_2 molecules are formed and desorbed to the surface of coke, which needs to overcome 24,6 kJ/mol energy barrier.

By comparing Figure 3 and Figure 5, it can be found that for the complete process of $C+NO→N_2+CO_2$, the rate-controlled step of the reaction is the generation of CO, and the activation energy required for this step is 524,9 kJ/mol, indicating the importance of the active site at the edge of coke.

For hydrogen-rich blast furnace, there is a large amount of unreacted hydrogen in the blast furnace. When coke reacts with NO to form N_2, O* can be reduced by H_2 remaining in the active site of coke and re-released the active site for NO reduction. The geometries of intermediates and transition states during O* reduction by H_2 is displayed in Figure 6. The Gibbs free energy of O* reduction by H_2 is shown in Figure 7. Due to the presence of H_2 in the reaction atmosphere, the active site on the coke surface is easily occupied by H atom. The H_2 molecules are first adsorbed on the coke to form a stable structure H-IM0. The H(1)-H(2) bond length stretches to 1,91 Å, and H(1)-O(1) bonds with a bond length of 0,97 Å. Then, the -OH radical rotates around the C(1) atom, forming the stable structure H-IM1. The -OH radical re-
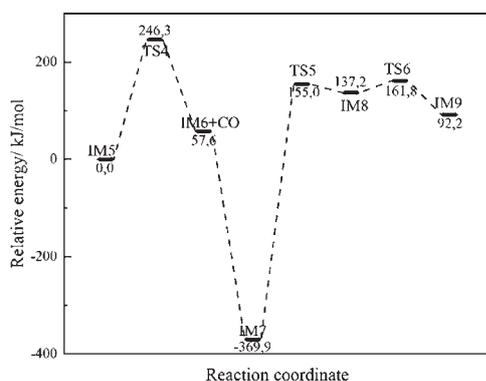
Figure 5 The Gibbs free energy of O* reduction by coke
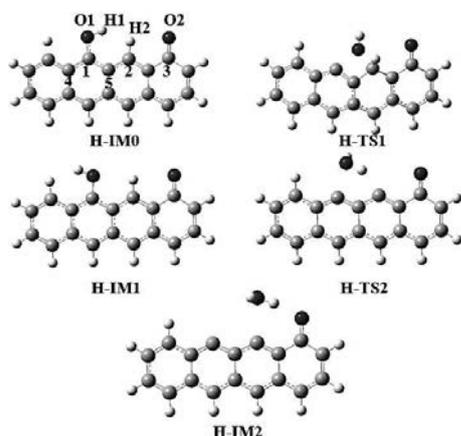
Figure 6 The geometries of intermediates and transition states during O* reduction by H_2
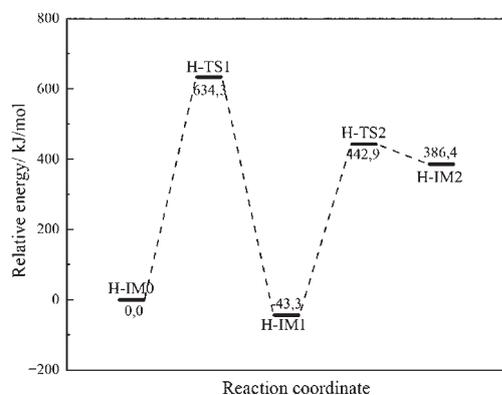
Figure 7 The Gibbs free energy of O* reduction by H_2

binds to another H atom, and the C(1)-O(1) bond length gradually increases and finally breaks. Also, the bond length of H(2)-C(2) also gradually increases, and finally H_2O is generated. It can be found that the rate-controlled step of O* reduction by H_2 is H-IM0→H-TS1, and the energy barrier needs to be overcome in this process is 634,3 kJ/mol. The overall reaction is endothermic and requires external energy of 386,4 kJ/mol.

Comparing Figure 5 and Figure 7, it can be seen that the energy barrier to be overcome by using coke to reduce O* is smaller than that to be overcome by using H_2 to reduce O*. Both reactions belong to endothermic reactions, but the use of coke to reduce O* requires less energy from the outside, and it is easier to occur from the perspective of thermodynamics. By comparing Figure 3

and Figure 5, it can be seen that the energy barrier that needs to be overcome for the NO reduction to N_2 by coke is smaller than that of O* reduced by coke. Due to the presence of a large amount of H_2, it is easy to competitive adsorption with NO, which may inhibit the NO reduction reaction. Comparing the results of this study with the results of Xu et al. [8], it was found that the activation energy required for coke-catalyzed NO reduction by CO (52,16 kJ/mol) is much smaller than that of the NO reduction by H_2. Although the use of hydrogen-rich blast furnaces can effectively solve the problem of carbon neutrality, it is necessary to reasonably control the H_2/CO ratio to reduce the harm of NOx to the environment.

CONCLUSIONS

In this study, density functional theory and classical transition state theory were used to study the microscopic mechanism of NO reduction in hydrogen-rich blast furnaces. NO can be reduced to N_2 on the coke surface, and the energy barrier to be overcome is 109,5 kJ/mol. However, the reactive oxygen species produced by NO decomposition remained on the surface of coke, which inhibited the NO reduction reaction. Both coke and H_2 can react with residual reactive oxygen species and re-release the active site, but the energy barrier to be overcome of reactive oxygen species reduction by H_2 is much higher than that to be overcome by coke. The conversion of hydrogen-rich blast furnace can effectively control the emission of CO_2, but it is necessary to pay attention to the ratio of H_2/CO to prevent the production of NO.

Supporting projects

Innovation and Entrepreneurship program of University of Science and Technology Liaoning

REFERENCES

[1] H. Liu, Formation mechanism and control analysis of nitrogen oxides in hot blast stove, Shandong Metallurgy 43 (2020)2, 28-30.

[2] J. Li, NO reduction by CO over a Fe-based catalyst in FCC regenerator conditions, Chemical Engineering Journal 225 (2014), 126-133.

[3] T. Yang, Research on deep treatment technology of air pollutants in iron and steel industry, Shandong Metallurgy 45 (2023)3, 56-59.

[4] X. Zhang, Development of amathematical model of raceway adiabatic flame temperature in hydrogen-rich blast furnace, Journal of Materials and Metallurgy 21 (2022), 31-36.

[5] X. Zhang, A thorough theoretical exploration of the effect mechanism of Fe on HCN heterogeneous formation from nitrogen-containing char, Fuel 280 (2020), 1118662.

[6] H. Zhang, DFT study on the C(N)-NO reaction with isolated and contiguous active sites, Fuel 2003 (2017), 715-724.

[7] X. Zhang, Microscopic effect mechanism of Ca on NO heterogeneous reduction by char: A DFT study, Journal of Fuel Chemistry and Technology 48 (2020)2, 163-171.

[8] Z. Xu, Reaction mechanism of NO reduction with CO catalyzed by char, Journal of Fuel Chemistry and Technology 48 (2020)3, 266-274.