Ni 物种形态对 Ni/AC 催化剂低温脱硫性能的影响

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摘要：采用过量浸渍法制备了 Ni/AC 催化剂, 考察了不同焙烧温度对 Ni/AC 脱硫活性的影响, 并通过 X 射线衍射和 X 射线光电子能谱对催化剂进行了表征, 研究了经不同温度焙烧后的催化剂上的 Ni 物种形态及其对催化剂性能的影响. 结果表明, 经400 °C 焙烧后的催化剂中 Ni 物种为 Ni_2O_3, 550 °C 焙烧后出现了 NiO 物种, 800 °C 焙烧后 Ni 物种变为 NiO 和 Ni 共存, 而 1 000 °C 焙烧后只存在单质 Ni. 这说明不同温度焙烧后的催化剂中 Ni 形成了不同的化学形态. 脱硫活性的测试结果表明, 经 550 °C 和 800 °C 焙烧后的催化剂表现出较好的脱硫活性, 而 400 °C 焙烧的催化剂脱硫活性最差. 这说明 Ni 在催化剂上的不同化学形态是造成脱硫效果差异的主要原因, 而 NiO 是 Ni/AC 催化剂脱硫的主要活性物相.

关键词：镍; 活性炭; 负载型催化剂; 化学形态; 脱硫; 氧化镍

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Influence of Ni Species of Ni/AC Catalyst on Its Desulfurization Performance at Low Temperature

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Abstract: A series of Ni/AC catalyst samples were prepared by excessive impregnation, and the desulfurization activity of Ni/AC calcined at different temperatures was investigated. The Ni species on the Ni/AC catalyst calcined at different temperatures were studied by X-ray diffraction and X-ray photoelectron spectroscopy. The characterization results showed that the Ni species on the catalyst calcined at 400 °C is Ni_2O_3. After calcination at 550 °C, NiO species is formed on the activated carbon. NiO and Ni coexist on the Ni/AC catalyst calcined at 800 °C, and only pure Ni species is observed after calcination at 1 000 °C. This suggested that Ni can form different chemical states on the Ni/AC catalyst calcined at different temperatures. The desulfurization test results showed that the catalysts calcined at 550 and 800 °C exhibit good desulfurization activity, whereas the catalyst calcined at 400 °C has poor activity, indicating that different chemical states of Ni on the Ni/AC catalyst show different desulfurization performance, and NiO is the main active phase of the Ni/AC catalyst.

Key words: nickel; activated carbon; supported catalyst; chemical state; desulfurization; nickel oxide

Coal burning is the main source of the atmospheric pollution in China, and SO_2 is one of the major pollutants. Controlling SO_2 emission from power plants has become a more urgent task. On the other hand, the emission limits of SO_2 are becoming more and more stringent. To resolve the problem, engineers and researchers have made efforts to improve the current technology of flue gas desulfurization (FGD) and developed novel FGD technologies with resourceful utilization, low costs, and high efficiency. Some of these technologies are based on catalytic processes, and catalysts like vanadium pentaoxide or bauxite are used for the conversion of SO_2 into sulphuric acid [1].

Activated carbon (AC) has high stability, large surface area, abundant micropore structure, and surface oxide species and can be used as a catalyst or carrier in gas-solid reactions. Considering these facts, AC may serve as a good support for SO_2 removal catalysts. For decades, the adsorption of SO_2 over AC has been proposed as a viable alternative because of its high SO_2 removal efficiency, cheap investment, and easy regeneration [2]. Several studies have reported that AC loaded with metal can significantly enhance the desulfurization activity of AC [3]. A granular Cu/AC catalyst has been investigated for desulfurization and exhibited high activity [4]. Liu et al. [5] also have studied the desulfurization activity of CuO/AC and found high desulfurization activity in the temperature range of 120–250 °C. Fe/AC that was prepared from AC-supported Fe_2O_3 has higher desulfurization activity than AC or Fe_2O_3 at 200 °C for flue gas SO_2 removal [6]. A lot of studies have reported the characteristics and behavior of Ni catalysts supported on AC in many industry processes such as hydrogenation, hydrogenolysis of hydrocarbons, and steam reforming [7–9]. Nickel supported on AC was used for adsorptive desulfurization of diesel by Selvavathi et al. [10]. It has been reported that the carrier can strongly influence the surface morphology and electronic structure of metal particles and directly affect the catalyst stability and catalytic activity [11]. The aim of this paper was to prepare a series of Ni/AC catalysts by excessive impregnation and evaluate their desulfurization performance. A hypothesis about the relation between chemical states of Ni on the catalyst and desulfurization activity was proposed.

1 Experimental

1.1 Catalyst preparation

The Ni/AC catalyst was prepared by the excessive impregnation method. A commercial AC (specific surface area 831 m^2/g, Lvye Co., Henan) was pretreated by strong nitric acid and then immersed into excessive nickel nitrate aqueous solution, followed by pouring out the excessive liquid and drying. The Ni content of the catalyst was 0.92% by inductively coupled plasma emission spectrometric (ICP) detection. The dried catalyst samples were calcined at 400, 550, 800, and 1 000 °C in pure nitrogen atmosphere. These catalyst samples were labeled Ni/AC-400, Ni/AC-550, Ni/AC-800, and Ni/AC-1000, respectively. The original activated carbon (AC) was used as a comparative sample.

1.2 Catalyst activity evaluation

The desulfurization activity of the Ni/AC catalyst was evaluated in a continuous flow multiple fixed-bed microreactor. The flow rate of the simulated flue gas mixture was controlled by a rotor flow meter before entering a blender. The flue gas mixture contained 0.3% SO_2, 9.1% O_2, 14% water vapor, and N_2 (balance). The gas space velocity (SV) was 2 000 h^{-1}. The test temperature was 90 °C.

1.3 Catalyst characterization

The crystal structure of the catalyst was determined by powder X-ray diffraction (XRD) on a DX-2000 diffractometer using Cu K_α radiation ($\lambda = 0.154\ 06$ nm) at 40 kV and 25 mA. The XRD data were recorded for 2θ values between 10° and 90° with an interval of 0.03°. The crystalline phases were identified by comparison with the reference data from the International Center for Diffraction Data (JCPDS).

X-ray photoelectron spectroscopy (XPS) was carried out on an XSAM-800 spectrometer (KRATOS) with Al K_α radiation under ultra-high vacuum (UHV) at 12 kV and 12 mA. Energy calibration was done by recording the core level spectra of Au $4f_{7/2}$ (84.0 eV) and Ag $3d_{5/2}$ (368.3 eV).

2 Results and discussion

2.1 Desulfurization performance of the Ni/AC catalyst

The desulfurization performance of the Ni/AC catalyst calcined at different temperatures is presented in Fig. 1, expressed as the relation between SO_2 removal rate and reaction time. The sulfur capacity (the total amount of SO_2 in the removal rate range of 90%−100%) and its corresponding reaction time are listed in Table 1. It can be seen that the samples calcined at different temperatures have different desulfurization performance. Compared with AC, the Ni/AC catalyst exhibits good desulfurization activity and high sulfur capacity, showing that the Ni component
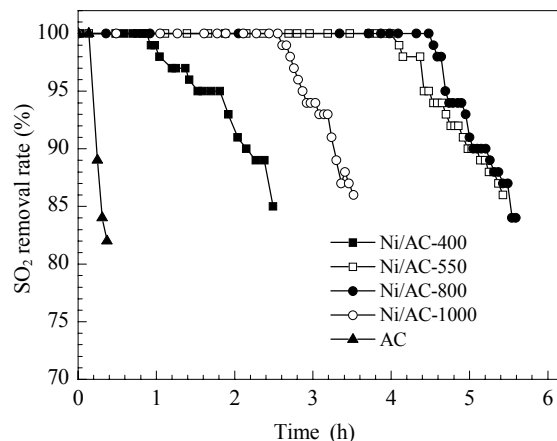

Fig. 1. Relations between SO_2 removal rate and reaction time over the Ni/AC catalyst samples.

Catalyst	Sulfur capacity (mg/g)	Time (h)
Ni/AC-400	81	2.15
Ni/AC-550	198	5.09
Ni/AC-800	203	5.21
Ni/AC-1000	135	3.24

can significantly change the desulfurization activity of AC. Under the same experimental conditions, the SO_2 removal rate over the Ni/AC-400 catalyst rapidly decreases to 90% in a short time (2.15 h), while the Ni/AC-800 catalyst can last longer (5.21 h). Their sulfur capacities are 81 and 203 mg/g, respectively, showing that the catalyst samples calcined at different temperatures have different catalytic activity. According to the results, the desulfurization activity of the catalyst samples from poor to excellent activity is in the order AC < Ni/AC-400 < Ni/AC-1000 < Ni/AC-550 < Ni/AC-800, which could be due to different Ni species on AC.

2.2 XRD and XPS results

Figure 2 shows the XRD patterns of the Ni/AC catalyst samples calcined at different temperatures. It is noticed that the Ni/AC catalyst calcined at 400 ℃ has very broad diffraction peaks, and no obvious NiO and/or pure Ni peaks are observed. The diffraction peaks of Ni_2O_3 cannot be detected because of a very low degree of crystallinity of Ni_2O_3 [12]. Ni_2O_3 normally forms during low temperature calcination [13], suggesting that decomposition of nickel nitrate in pure N_2 atmosphere at 400 ℃ could form Ni_2O_3, which can be proved by XPS. Small characteristic peaks of NiO at 2θ
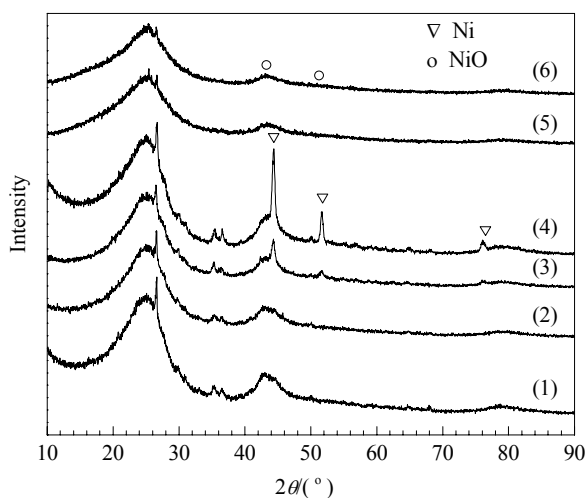

Fig. 2. XRD patterns of Ni/AC-400 (1), Ni/AC-550 (2), Ni/AC-800 (3), Ni/AC-1000 (4), Ni/AC-550 after desulfurization (5), and Ni/AC-800 after desulfurization (6).

= 43.29° and 51.26° (JCPDS 78-0643) are detected for the Ni/AC catalyst calcined at 550 ℃, indicating that nickel nitrate decomposition on AC begins to form crystalline NiO species. Minor characteristic peaks of NiO at 2θ = 43.29° and 51.26° and major characteristic peaks of Ni at 2θ = 44.5°, 51.8°, and 76.5° (JCPDS 04-0850) are observed for the Ni/AC-800 catalyst, showing that nickel nitrate on AC can form pure Ni at 800 ℃ but most of crystalline NiO are formed. Only pure Ni is detected on Ni/AC-1000. It can be concluded that different Ni species can be formed on the Ni/AC catalyst calcined at different temperatures.

In order to further clarify the valence state of Ni species on AC, all Ni/AC samples were characterized by XPS. The states of Ni species in the catalyst samples were evaluated by deconvolution of the Ni $2p$ region spectra using multiple Gaussian fitting functions, as shown in Fig. 3. The main peaks around 854.50−855.16 eV and satellite peaks at 860.98–861.56 eV are the spin-orbit split lines of Ni $2p_{3/2}$. The main peaks in the range 872.03–873.20 eV and accompanying satellite peaks at 878.39–879.97 eV correspond to the spin-orbit split lines of Ni $2p_{1/2}$. It was reported that the Ni $2p_{3/2}$ binding energy of Ni^0 appears at 852.6 eV [14]. The main peaks of Ni $2p_{3/2}$ in the range 853.9–854.9 eV and an accompanying shake-up satellite peak at 860.8–862.8 eV were assigned to Ni^{2+} species [15,16] of NiO, while the Ni $2p_{3/2}$ binding energies of 855.7–856.9 eV and 860.1–864.5 eV were assigned to the Ni–O bond of Ni_2O_3 [17,18]. Zhao et al. [19] also assigned the binding energy 855.5 eV to Ni_2O_3 on $TiO_{2-x}B_x$. Under our experimental conditions, the Ni $2p_{3/2}$ peaks of the Ni/AC-400 catalyst appear at 855.16 and 861.56 eV, and the Ni $2p_{1/2}$ peaks appear at 872.70 and 879.29 eV, which belong to nickel oxide. Romero et al. [20] reported that Ni_2O_3 can be generated on the Ni/HZSM-5 catalyst calcined at 400 ℃ in air. It can be proposed that this nickel oxide on AC belongs to Ni_2O_3. That is because all supports have the same porosity and the catalysts are prepared using the same experimental procedure. The surface groups containing oxygen on the carbon support play a major role in the final metal dispersion, resulting in the formation of Ni_2O_3 species [21]. The appearance of peaks at binding energies of 855.45 and 862.18 eV for Ni $2p_{3/2}$ and 873.20 and 879.97 eV for Ni $2p_{1/2}$ together with the results of XRD proves the existence of Ni_2O_3 and NiO on Ni/AC-550 in accordance with Lemonidou et al. [16] and Trigwell et al. [17].

For Ni/AC-800, the Ni $2p_{3/2}$ binding energies of 854.50 and 860.98 eV and the Ni $2p_{1/2}$ binding energies of 872.03 and 878.91 eV are attributed to NiO and Ni^0, respectively, which is in agreement with the reference [22]. The Ni $2p_{3/2}$ binding energies of 854.65 and 861.16 eV and the Ni $2p_{1/2}$ binding energies of 872.12 and 878.39 eV fit very well with the results reported previously for zero valent metallic
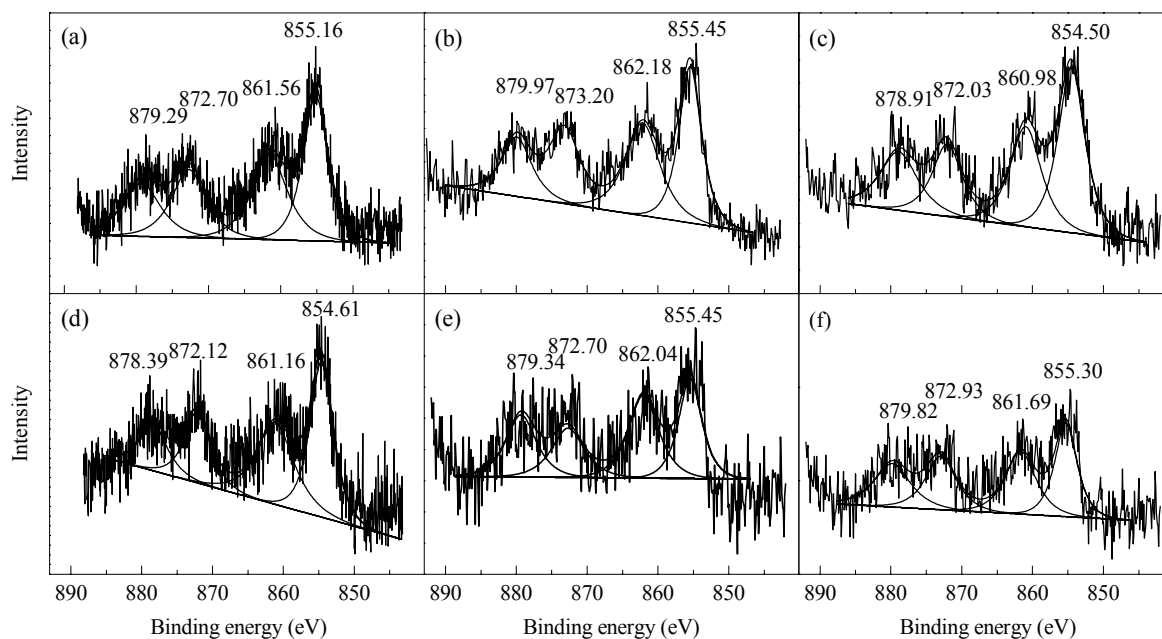
Fig. 3. Ni 3*d* XPS spectra of Ni/AC-400 (a), Ni/AC-550 (b), Ni/AC-800 (c), Ni/AC-1000 (d), Ni/AC-550 after desulfurization (e), and Ni/AC-800 after desulfurization (f).

nickel [23]. Therefore, based on the above analysis, it can be concluded that the Ni/AC catalyst calcined at 400 ℃ can form Ni_2O_3, NiO species are detected after Ni/AC calcination at 550 ℃, and pure Ni can be observed on the Ni/AC-800 catalyst. The Ni/AC calcined at 1 000 ℃ fully forms pure Ni. These changes could be due to the surface chemistry properties of AC, especially the oxygen-containing functional groups of AC, which can influence the Ni valence state.

Considering the results of desulfurization and different Ni chemical states, it is confirmed that the chemical states of Ni on AC can influence the desulfurization performance and NiO on AC possesses the best catalytic activity.

2.3 Ni species change before and after desulfurization

In order to further confirm the change of Ni species on the Ni/AC catalyst, the characterization by XRD and XPS for Ni/AC-550 and Ni/AC-800 after desulfurization was carried out. The results are shown in Fig. 2 and 3. It is interesting to note that both samples exhibit an amorphous state. Small characteristic peaks of NiO are detected at $2\theta =$ 43.29° and 51.26°, indicating that the chemical state of Ni species on Ni/AC-800 was changed after desulfurization. The results of XPS indicate that the Ni $2p_{3/2}$ peaks of Ni/AC-550 appear at 855.45 and 862.04 eV after desulfurization and the Ni $2p_{1/2}$ peaks appear at 872.70 and 879.34 eV, which is close to the findings for Ni/AC-550 before desulfurization, suggesting that the Ni chemical state of Ni/AC-550 does not change after desulfurization. In the case of Ni/AC-800, the Ni $2p_{3/2}$ peaks appear at 855.30 and 861.69 eV, and the Ni $2p_{1/2}$ peaks appear at 872.93 and 879.86 eV after desulfurization, which is in agreement with the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ binding energies of Ni_2O_3, indicating that the Ni chemical state changes after desulfurization. This could include the following chemical reactions:

$$Ni + H_2O \rightarrow NiO + H_2 \qquad (1)$$
$$Ni + 1/2O_2 \rightarrow NiO \qquad (2)$$
$$4NiO + O_2 \rightarrow Ni_2O_3 \qquad (3)$$
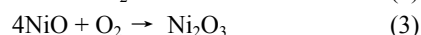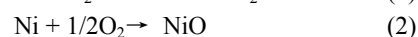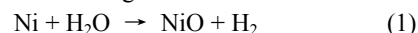
Reactions (1) and (2) are exothermic reactions [24], and Reaction (2) is a strong exothermic reaction. When water vapor is present in the feed gas mixture, Reaction (2) occurs. Water vapor containing oxygen can significantly enhance the reaction temperature and form more NiO, so that the catalyst at lower calcination temperature has a better desulfurization efficiency.

3 Conclusions

Ni/AC calcined at different temperatures has different chemical states (Ni_2O_3, NiO, and Ni), which can lead to different desulfurization performance. Ni/AC catalysts containing NiO exhibit good catalytic activity at low reaction temperature, which suggests that NiO on the Ni/AC catalyst is the best active species for the desulfurization. The Ni/AC catalyst can be potentially used to remove SO_2 from industrial flue gases.

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