

Preparation of (Ni/W)- γ -Al₂O₃ Microspheres and Their Application in Adsorption Desulfurization for Model Gasoline

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A kind of desulfurization adsorbent, (Ni/W)- γ -Al₂O₃ microsphere, was prepared by a new method of in situ chemical reduction. The adsorbent consists of active components (transition metals Ni and W) and a carrier (γ -Al₂O₃). Ni and W in γ -Al₂O₃ microspheres are fine in size and can be distributed homogeneously on the surface and inside of the γ -Al₂O₃ carrier. The desulfurization of the adsorbent made by the in situ chemical reduction method was carried out in model gasoline. Its desulfurization capacity increases 23% in comparison with that made by the conventional impregnation method. The composition and configuration of adsorbents were analyzed by scanning electron microscopy (SEM), electron energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). The in situ chemical reduction method offers a new and promising method for preparation of desulfurization adsorbents containing active components.

Keywords Adsorption desulfurization; Dibenzothiophene (DBT); Impregnation; In situ chemical reduction method; Ni; W; γ -Al₂O₃

Introduction

Adsorption is a simple and promising technique for fossil oil desulfurization (Ma et al., 2001; Mikhail et al., 2002). The key of adsorption desulfurization is to find effective adsorbents with high capacity and high selectivity for sulfur compounds. Because the loadings of transition metals (active components) can improve the selectivity and adsorptive capability of desulfurization adsorbents (Song and Reddy, 1999), a class of high-sulfur-selective and high-sulfur-capacity adsorbents has been reported by loading transition metals, such as Ag⁺, Cu⁺, Ni²⁺, and Co²⁺, on kinds of carriers (Yang et al., 2003), for example, zeolites X/Y, activated carbon, and clay (Takahashi et al., 2002). The adsorption mechanism of these adsorbents is π -complexation between the sorbent and sulphur compounds, which has been studied by a fluorescence technique (Shan et al., 2005). π -Complexation mainly depends on the type of metal components, among which both nickel (Ni) and tungsten (W) have

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a high capability for forming π -complexation (Sanchez et al., 2006). Thus, in this work, Ni and W were used as active components of adsorbents.

Conventionally, transition metals are loaded on carriers by impregnating (Bollinger and Vannice, 1996; Milenković et al., 2004), in which, however, the size and the amount of transition metals are complex and difficult to control. But the advantage of good dispersion and migration of transition metals in carriers can be used to prepare many new materials and adsorbents. For example, dispersion and migration of transition metals, such as Ni, Cu, and Co, in γ -Al₂O₃ carrier have been applied for the preparation of ceramic materials (Tuan and Brook, 1990; Li et al., 2002). The transition metals were dispersed uniformly on the surface and inside of carriers without congregation. This technique is defined as in situ chemical reduction technology. According to the migration mechanism of transition metals, new adsorbents in which transition metals are nano-dispersed may also be prepared by the adjustment of metalline content.

In this study, two kinds of adsorbents were prepared by the in situ chemical reduction method and the conventional impregnating method, respectively, and the performance of both was compared. Both kinds of adsorbents consist of active components (Ni and W) and a carrier (γ -Al₂O₃). Adsorbents were analyzed by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, and X-ray diffraction (XRD), which exhibit the characteristics and distribution of Ni and W on the surface and inside of the γ -Al₂O₃ carrier. The comparison of their desulfurization capacity was conducted by high-performance liquid chromatography (HPLC).

Materials and Methods

Materials

Dibenzothiophene (DBT, 99%) was purchased from Acros Organics. Methanol was HPLC grade, octane was chemical grade, and nickel chloride, ammonium tungstate, aluminium chloride, aluminium foil, hexamethylenetetramine, and ethanol were analytical reagent grade. Sulfonated kerosene was purchased from China Petroleum & Chemical Corporation.

Preparation of Aluminate Colloid

Aluminate colloid was prepared by the following process: 240 g AlCl₃·6H₂O was dissolved in 1800 mL deionized water, then 132.3 g aluminium foil with a slice shape was added into the system. The system was heated at 90°–95°C for about 50 h, and aluminate colloid was made.

Preparation of Desulfurization Adsorbents

Two kinds of adsorbents were made. The one prepared by the in situ chemical reduction method was called Adsorbent I, and the one prepared by the impregnation method as control was called Adsorbent II.

Adsorbent I was prepared by the following process: 100 mL of aluminate colloid containing 0.2 mol/L of NiCl₂ and 0.01 mol/L of ammonium tungstate was mixed with 95 mL of hexamethylenetetramine (120 g/L). The mixture was dispersed in sulfonated kerosene and formed a system of water-in-oil (W/O) micro-emulsions.

Then the system was heated at 85°–90°C for 2 h. The micro-emulsions were separated from the oil by spontaneously settling and the precursor of adsorbent I was obtained. Then the precursor was sintered at 650°C for 2 h. After that, the product was in situ reduced by hydrogen at 200°C for 2 h at normal pressure to yield Adsorbent I.

Adsorbent II was prepared by two steps. The first step was to mix 100 mL of aluminate colloid with 95 mL of hexamethylenetetramine (120 g/L). The mixture was dispersed in sulfonated kerosene and formed a system of W/O micro-emulsions. Then the system was heated at 85°–90°C for 2 h. Finally, the micro-emulsions were separated from the oil by spontaneously settling, and the precursor of Adsorbent II was obtained. The precursor was then sintered at 650°C for 2 h to obtain γ -Al₂O₃ carrier. The second step was to impregnate the carrier about 48 h with the aqueous solution containing 0.2 mol/L of NiCl₂ and 0.01 mol/L of ammonium tungstate. The impregnated product was then washed with deionized water and dried for 24 h at 120°C. After that, the product was reduced by hydrogen at 200°C for 2 h at normal pressure to obtain Adsorbent II.

Adsorptive Desulfurization for Model Oil

The adsorption desulfurization was performed at room temperature and normal pressure. The model oil consisted of DBT and octane. To compare the maximal adsorptive amount of the two adsorbents for desulfurization, the concentrations of DBT in octane were changed from 1 to 18 mM.

The adsorptive amount of the adsorbent was calculated by the following formula:

$$A = \frac{(C_0 - C_e) \times V}{M}$$

where M is the amount of adsorbents used, V is the volume of model oil, C₀ is the initial concentration of DBT in model oil, C_e is the final concentration of DBT in model oil after being adsorbed, and A is the adsorptive amount of the adsorbent.

Analysis

The desulfurization adsorbents were analyzed by a JSM-840 scanning electron microscope (Japan) with an EDX detector and XRD. XRD analysis was performed by D/Max-2400 Rigaku X-ray powder diffractometer operated in the reflection mode with Cu K α ($\lambda = 0.154$ nm) radiation and equipped with a graphite back monochromator. The scanning rate was 6°·min⁻¹.

The DBT concentrations in model oil before and after being adsorbed were analyzed by HPLC (Agilent 1100 with diode array detector (DAD)). The HPLC separation column was Zorbax SB-C18 (4.6 mm \times 25 cm). The flow phase used contained 90% methanol and 10% water. The flow rate was 1 mL·min⁻¹.

Results

Characteristics of Adsorbents

The desulfurization adsorbents were analysed by SEM and XRD. Figures 1 and 2 are SEM images of Adsorbents I and II, respectively. Comparing Figure 1 with

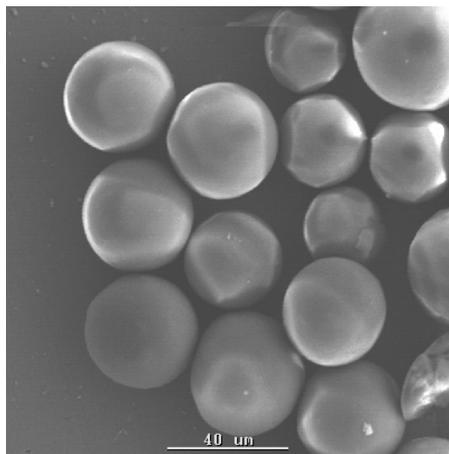


Figure 1. SEM image of adsorbent I.

Figure 2, the surface of the adsorbents prepared by in situ chemical reduction method is glazed, while that prepared by the conventional impregnation is coarse. The size of both Adsorbents I and II are about 20–80 μm .

According to the preparation procedure, Adsorbent I mainly consists of Al, Ni, and W elements. An EDX detector was used simultaneously to determine all the elements in the adsorbent. Figure 3 presents second electronic images of Adsorbent I obtained by scanning the slice with an EDX detector. It shows that Ni/W components can disperse uniformly and be homogeneous on the surface and inside of the carrier without congregation. Furthermore, the EDX detector can quantitatively analyze the element composition of adsorbents. Table I shows the element compositions of Adsorbents I and II.

Figure 4 is the XRD pattern of Adsorbent I. It shows that the crystal structure of Al₂O₃ is γ form, and the Ni/W is amorphous because no peak that represents the crystal structure of Ni and W is found.

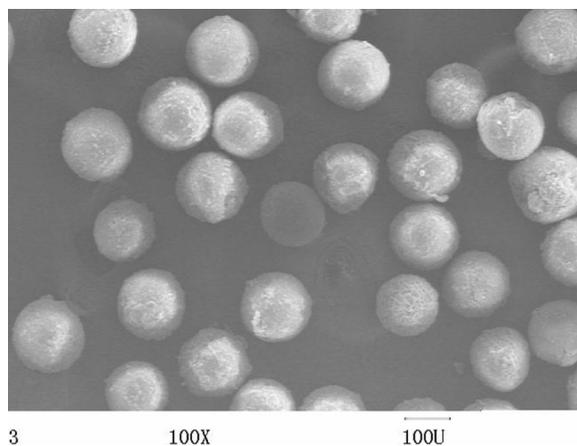


Figure 2. SEM image of adsorbent II.

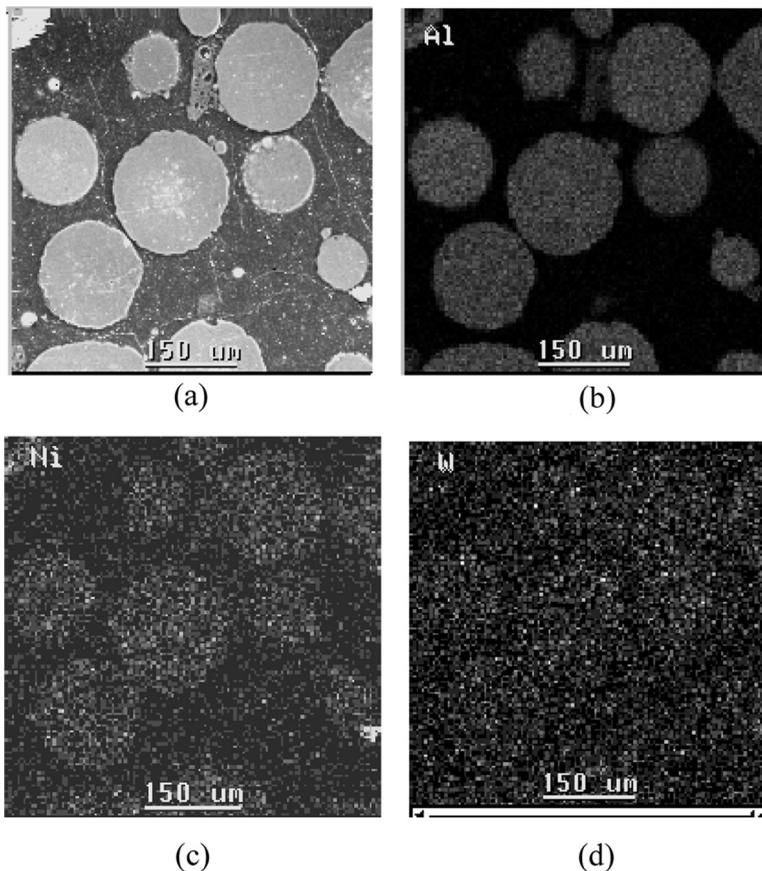


Figure 3. Second electronic images of adsorbent I.

Adsorptive Desulfurization

Figure 5 shows the changes of adsorptive capacity of the two kinds of adsorbents as a function of the concentration of DBT. It demonstrates that the adsorptive amounts increase with the concentration of DBT. The maximal adsorptive amount of Adsorbents I and II were 0.326 and 0.265 mmol (DBT)·g⁻¹, respectively. The maximal adsorptive amount of the adsorbent made by the in situ chemical reduction method increases 23% over that made by the conventional impregnation method.

Table I. Chemical composition of adsorbents

	Adsorbent I		Adsorbent II	
	Mass percent (%)	Error (wt%)	Mass percent (%)	Error (wt%)
Al	80.07	+/- 0.42	81.07	+/- 0.51
Ni	6.49	+/- 0.40	5.97	+/- 0.37
W	13.44	+/- 0.55	12.96	+/- 0.65
Total	100		100	

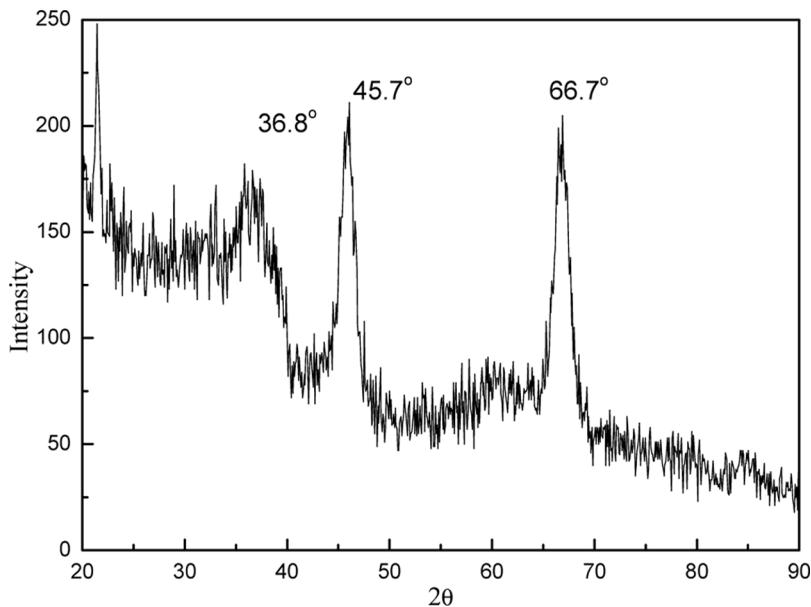


Figure 4. XRD pattern of adsorbent I.

Discussion

The key of adsorption desulfurization is to obtain effective adsorbents. In general, a desulfurization adsorbent consists of a carrier and some active components. γ -Al₂O₃ is one of the widely used carriers due to its porosity, large specific area, and dispersibility (Shan et al., 2004). Generally, transition metals are used as active components. Shan et al. (2005) in our group have proved that transition metals increase the adsorption capacity of adsorbents because of π -complexation between transition metals and sulfuric compounds in oil. Chevron Research and Technology Company

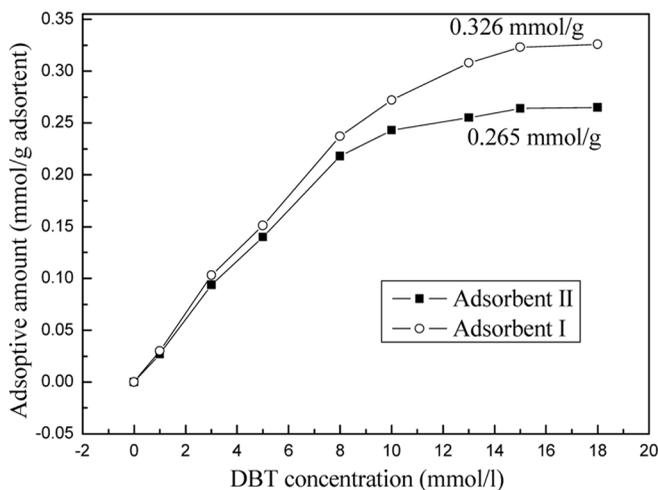


Figure 5. Desulfurization curves of adsorbents I and II.

(Robinson et al., 1993) has obtained a desulfurization adsorbent by impregnating Cu and Ni components on the γ -Al₂O₃ carrier. However, the conventional impregnation method needs two steps, while the in situ chemical reduction method can be done by only one step. And more importantly, as Figure 5 shows, the desulfurization capability of adsorbents prepared by the in situ chemical reduction method increases 23% over that prepared by the impregnation method. This is because, during the high temperature and the existence of H₂, transition metals are active and migrated in the γ -Al₂O₃, similar to melting. Transition metal transfers from the high concentration region of metal elements to the low concentration region of metal elements. As a result, the distribution of transition metal on the surface and inside of the γ -Al₂O₃ carrier is homogeneous and equal. N and W in carriers form amorphous structures more and more easily as their sizes become smaller, and their capabilities of adsorption are larger and larger due to their amorphous structures. Homogeneous distribution of active components on the surface and inside of carriers makes their sizes fine and thus can improve the adsorption capability of adsorbents. As a result, the adsorbent prepared by in the situ chemical reduction method has better desulfurization capability than that prepared by the impregnation method, as Figure 5 shows. Thus, the in situ chemical reduction method is more promising for preparation of desulfurization adsorbents than the impregnation method.

Conclusion

A kind of desulfurization adsorbent was first prepared by an in situ chemical reduction method. The adsorbent consists of active components (transition metals Ni and W), and a carrier (γ -Al₂O₃). By comparing with the control adsorbent prepared by the conventional impregnation method, it was found that Ni and W in the new adsorbents are very fine in size and can be distributed homogeneously on the surface and inside of γ -Al₂O₃ carrier. The adsorbent prepared by the in situ chemical reduction method performed better in adsorptive desulfurization for model oil than that prepared by the conventional impregnation method. Thus, the in situ chemical reduction method offers a new and promising method for preparation of desulfurization adsorbents.

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