

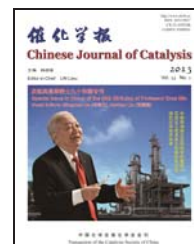


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Communication

Improvement of adsorptive desulfurization performance of Ni/ZnO adsorbent by doping with Mn additive

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ABSTRACT

The effect of Mn doping on the adsorptive desulfurization performance of 5%Ni/ZnO adsorbents was investigated in model gasoline, with thiophene as a sulfur-containing compound, using a fixed-bed reactor. The 5%Ni/MnO-ZnO adsorbents with different levels of Mn doping were prepared using an incipient wetness impregnation method and characterized by powder X-ray diffraction (XRD). It was found that the adsorption performances of the 5%Ni/MnO-ZnO adsorbents were considerably improved after Mn doping compared with that of 5%Ni/ZnO. Moreover, the 5%NiO/MnO-ZnO adsorbents showed high desulfurization activities after regeneration. Sulfur removal by a 5%NiO/8%MnO-ZnO adsorbent after three reaction-regeneration cycles was 4% higher than that by a 5%NiO/ZnO adsorbent without Mn doping. The excellent performance of the 5%NiO/8%MnO-ZnO adsorbent in desulfurization, and its regenerability, were attributed to formation of a new compound, ZnMnO₃, in the adsorbent; this compound was characterized using XRD.

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Sulfur-containing compounds in gasoline have been receiving increasing attention because they are the main precursors of acid rain and have severe negative effects in most gasoline-using systems, such as three-way catalysts for auto exhausts [1,2]. More stringent environmental regulations have been enacted worldwide for oil-refining industries. Since 2011, the sulfur content of gasoline has been required to be less than 50 mg/kg under the GB 17930-2011 emission limitation. New strategies for ultra-deep desulfurization have therefore been explored to meet the urgent need to produce cleaner gasoline [3–9]. Adsorptive desulfurization (ADS) is one of the most promising methods [10–14]. Among various adsorbents investigated, Ni-based adsorbents gave better performance in the removal of thiophenic sulfur compounds from liquid fuels [15,16]. The ConocoPhillips Petroleum Company developed the

S-Zorb process for the production of low-sulfur gasoline by reactive adsorption of sulfur compounds using a solid sorbent [17–22]. This process preserves the octane number well while effectively removing sulfur species. Bezverkhyy and coworkers carried out a series of ADS experiments on Ni-based adsorbents [23–26]. They found that the initial limiting step is thiophene decomposition on the metallic Ni of the Ni/ZnO adsorbent, whereas after partial sulfidation, thiophene diffusion becomes the rate-determining step. Zhang et al. [27] reported that Ni/ZnO adsorbents using ZnO with a large surface area and small crystal grains as the active component showed higher desulfurization activity and stability.

In our previous work, we systematically investigated the effect of ZnO particle size on the ADS performance of Ni/ZnO adsorbents [28]. The results showed that as the ZnO particle

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size decreased, both the desulfurization activities and sulfur capacities of the Ni/ZnO adsorbents were enhanced. When the ZnO particle size was less than 8 nm, a small amount of NiZn alloy formed, and the desulfurization performance improved significantly. However, nano-sized ZnO particles are easily agglomerated into larger grains in the subsequent regeneration stage at high temperatures, leading to a sharp decline in the desulfurization activities and sulfur capacities of the regenerated adsorbents. The aim of this work is to study methods for preventing agglomeration of ZnO particle in the regeneration stage at high temperatures through Mn doping of ZnO, and to maintain the ADS activities and sulfur capacities of adsorbents after multicycle regenerations.

Ni(NO₃)₂·6H₂O, Zn(CH₃COO)₂·2H₂O, Mn(CH₃COO)₂·4H₂O, oxalic acid, and ethanol (analytical grade) were purchased from Kernal. The adsorbents were prepared in two steps. First, Mn-doped ZnO samples were prepared. Mn-doped zinc oxalate was obtained by slow addition of oxalic acid (0.15 mol/L in ethanol) to mixtures of Zn(CH₃COO)₂·2H₂O (0.10 mol/L in ethanol) and Mn(CH₃COO)₂·4H₂O (0.0105 mol/L in ethanol), with vigorous stirring for 12 h at room temperature. The precipitate obtained was filtered, washed, and then dried at 120 °C. Mn-doped ZnO was obtained by calcining the Mn-doped zinc oxalate at 500 °C. Ni was supported on the Mn-doped ZnO by the incipient wetness impregnation method using Ni(NO₃)₂ solution as the Ni precursor. A 5%NiO/8%MnO-ZnO sample was prepared by calcination of Ni(NO₃)₂/8% MnO-ZnO at 500 °C. In addition, we prepared 5%NiO/MnO-ZnO samples containing 1%, 2%, 5%, and 12% MnO, using the same method. The NiO/MnO-ZnO system sorbents are denoted by 5N_xMZO-*T* (*x* is the amount of Mn doping and *T* is the calcination temperature) in the following discussion. The NiO/MnO-ZnO samples were reduced in situ to Ni/MnO-ZnO in a fixed-bed reactor before adsorption.

X-ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer with a Cu K_α radiation source operated at *V* = 40 kV and *I* = 200 mA. XRD patterns were collected from 20° to 75° at a speed of 5°/min.

Transmission electron microscopy (FEI Tecnai G2 spirit) was used to characterize the prepared 5N8MZO-500 adsorbent at an accelerating voltage of 120 kV.

The adsorption experiments were performed in a fixed-bed reactor at 300 °C under the following operating conditions: H₂ partial pressure 0.4 MPa, liquid hourly space velocity (LHSV) 6 h⁻¹, and H₂/oil ratio of 600. The model gasoline feedstock was thiophene-containing *n*-heptane, with a total sulfur concentration of 500 mg/L. The sulfur content was determined using an Antek 9000S total sulfur analyzer with a detection limit of 0.1 mg/L.

The sulfuration and regeneration processes were performed on the adsorbents in a tube furnace reactor, using the following conditions: sulfuration 10% (v/v) H₂S, 25–300 °C at room pressure; regeneration 10% (v/v) O₂, 25–500 °C at atmospheric pressure.

The sulfur removal and normalized cumulative effluent volume (effluent) are expressed by equations 1 and 2, respectively, where *c*₀ is the sulfur concentration in the feedstock

(mg-S/L), *c*_{*t*} is the transient effluent sulfur concentration (mg-S/L) at time *t* (min), *v* is the feedstock volumetric flow rate (ml/min), and *m*_{adsorbent} is the mass (g) of the adsorbent.

$$\text{Sulfur removal} = (1 - c_t/c_0) \times 100\% \quad (1)$$

$$\text{Effluent} = v \cdot t / m_{\text{adsorbent}} \quad (2)$$

Figure 1 shows powder XRD patterns of 5N_xMZO-500 samples, i.e., samples calcined at 500 °C with different amounts of Mn doping. The diffraction peaks for the Mn-doped Ni/ZnO samples are the same as those for the wurtzite phase of Ni/ZnO, demonstrating that the 5N_xMZO-500 adsorbents retain the ZnO wurtzite phase. However, as the amount of Mn doping increased, the diffraction peaks of ZnO broadened. This indicates that the ZnO particle size is modified by doping with Mn. In order to obtain quantitative information, based on the full-width at half-maximum of the highest-intensity peak of ZnO (101), the average particle sizes of the 5N_xMZO-500 samples were estimated using the Debye-Scherrer formula (Table 1). The calculated results show that the average particle size of ZnO was reduced from 30 to 11 nm by Mn doping. As shown in Table 1, the minimum ZnO particle size was obtained when the Mn-doping amount was increased to 8%, which implied that this was the optimum composition for the 5N_xMZO-500 adsorbents.

Figure 2 shows the impact of Mn doping on the desulfurization performance of NiO/ZnO. The 5NZO-500 adsorbent, i.e., without Mn doping, only gave a sulfur removal of 49.9% at an effluent of 60 ml. However, the 5N8MZO-500 adsorbent gave a sulfur removal of 82.4% at an effluent of 60 ml, which is 32.5% higher than the removal achieved by the undoped adsorbent.

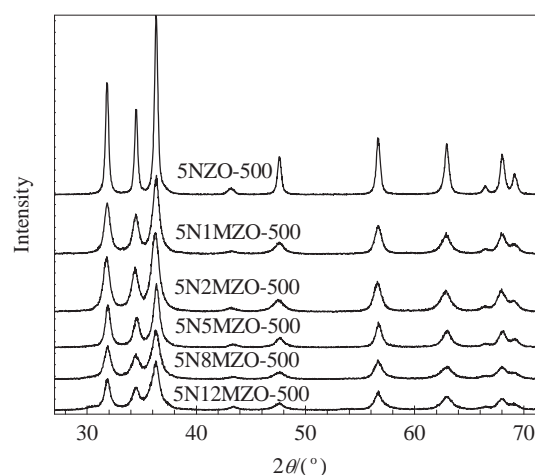


Fig. 1. Powder XRD patterns of 5N_xMZO samples with different amounts of MnO doping, calcined at 500 °C.

Table 1

Particle sizes estimated using the Debye-Scherrer formula for 5%NiO/*x*MnO-ZnO samples calcined at 500 °C.

Amount of MnO (<i>x</i> , %)	Particle size (nm)
0	30
1	26
2	20
5	15
8	11
12	11

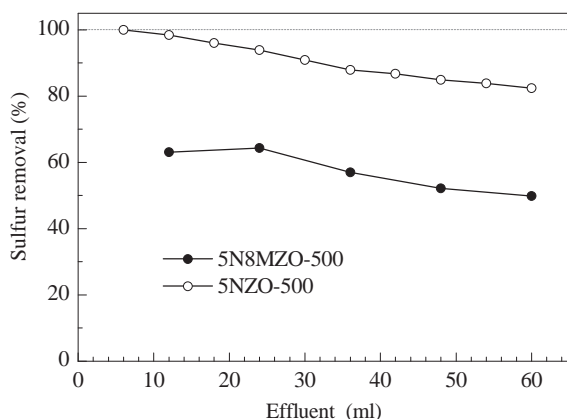


Fig. 2. Effect of Mn doping on desulfurization performance of Ni/ZnO adsorbents calcined at different temperatures. Adsorption conditions: H_2 partial pressure 0.4 MPa, LHSV 6 h^{-1} , H_2 /oil ratio 1/600, $300\text{ }^\circ\text{C}$.

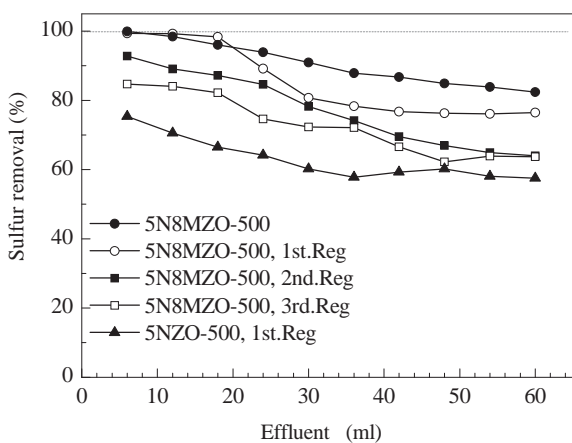


Fig. 3. Desulfurization performance of regenerated 5N8MZO-500 for model gasoline at $300\text{ }^\circ\text{C}$. Adsorption conditions: H_2 partial pressure 0.4 MPa, LHSV 6 h^{-1} , H_2 /oil ratio 1/600, and $300\text{ }^\circ\text{C}$.

This result clearly shows that Mn doping effectively increases the ADS activity.

The effect of Mn doping on the regeneration performance of the Ni/ZnO adsorbents is shown in Fig. 3. Although we used a very high sulfur content of 500 mg-S/L to evaluate the ADS activity of 5N8MZO-500, it can be seen that the sulfur removal by the 5N8MZO-500 adsorbent remained above 60% after three reaction–regeneration cycles. The 5N8MZO-500 adsorbent regenerated after one cycle gave a sulfur removal of over 76% at an effluent of 60 ml. The sulfur removal (63.7%) by the regenerated 5N8MZO-500 adsorbent after the third cycle was 4% higher than that by the 5NZO-500 adsorbent (59.5%) regenerated after only one cycle. The results show that the 5N8MZO-500 adsorbent had excellent regenerability in the desulfurization process. The excellent desulfurization and regeneration performance of 5N8MZO-500 could be explained by a change in the structure of the adsorbent. Figure 4 shows the XRD patterns of Ni/ZnO and Mn_5O_8 (ICDD-PDF 39-1218), which were prepared using the same method as that used to prepare the 5N8MZO adsorbent. The XRD pattern of the

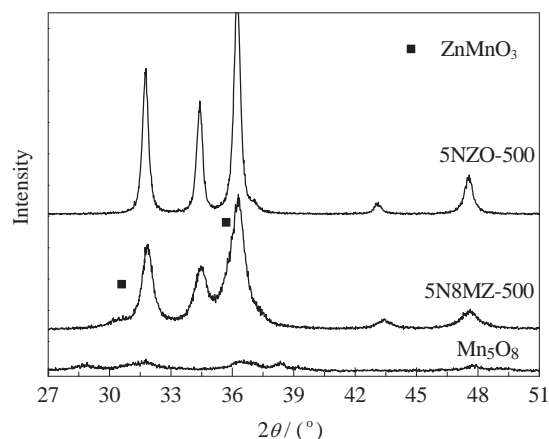


Fig. 4. Powder XRD patterns of 5NZO-500, 5N8MZO-500, and Mn_5O_8 .

5N8MZO adsorbent after Mn doping was complex. A weak diffraction peak ($2\theta = 30.3^\circ$) and a shoulder peak ($2\theta = 35.7^\circ$) appeared for the 5N8MZO-500 adsorbent. It is clear that the new peaks are different from those of ZnO or Mn_5O_8 , and can be attributed to $ZnMnO_3$ (ICDD-PDF 19-1461). This new structure may be the reason for the excellent desulfurization activity and regenerability.

In summary, the optimum Mn-doping amount for the Ni/MnO–ZnO adsorbents was 8%. The desulfurization performances of the adsorbents were improved significantly by Mn doping. Sulfur removal using the 5%NiO/8%MnO–ZnO adsorbent was 32.5% higher than that achieved using undoped 5%NiO/ZnO. Moreover, the 5%NiO/8%MnO–ZnO adsorbent showed high desulfurization activity after regeneration. Sulfur removal using the 5%NiO/8%MnO–ZnO adsorbent after three reaction–regeneration cycles was 4% higher than that obtained using the undoped 5%NiO/ZnO adsorbent. XRD characterization showed that $ZnMnO_3$ was formed in the adsorbent after Mn doping. The $ZnMnO_3$ could restrain growth of ZnO nanoparticles in the regeneration process at high temperatures.

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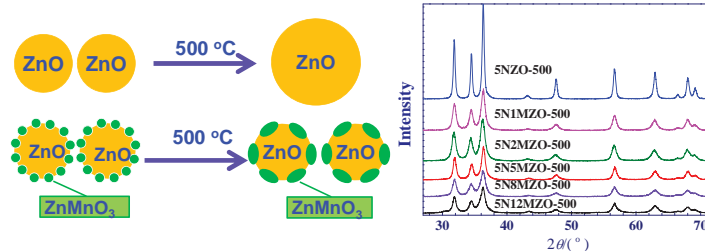
Graphical Abstract

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Improvement of adsorptive desulfurization performance of Ni/ZnO adsorbent by doping with Mn additive

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As a result of doping with Mn, the average particle size of ZnO was reduced by formation of ZnMnO₃ at high temperature. The desulfurization performance and regenerability of adsorbents were significantly improved by Mn doping.

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Mn掺杂对Ni/ZnO吸附剂脱硫性能的改进

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摘要: 合成了5%Ni/Mn-ZnO吸附剂体系,并在固定床上考察了Mn的掺杂对该吸附剂的吸附脱硫性能的影响。8%MnO掺杂的5%Ni/MnO-ZnO吸附剂抗烧结性能显著提高,并且吸附剂的脱硫活性和再生活性均有较大提高,三次再生后的脱硫率仍比一次再生的无Mn掺杂的5%Ni/ZnO吸附剂的脱硫率高出约4%。XRD表征显示掺杂后的吸附剂有ZnMnO₃生成。

关键词: 吸附脱硫; 镍; 锰; 氧化锌; 吸附剂; 再生

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由于汽油中的含硫化合物会造成酸雨、催化剂中毒(如三效催化剂失效)等影响,近年来已引起越来越多的重视,各国都制订了严格的法规来限制汽油中的硫含

量^[1,2],2011年制定的GB 17930-2011标准规定汽油中硫含量不能超过50 mg/kg. 因此,开发新的超深度脱硫方法来生产清洁汽油日趋重要^[3-9];而吸附脱硫是目前最

有前景的替代方法之一^[10-14]。其中,基于Ni的吸附剂在脱除噻吩类含硫化合物时显示出比较好的脱硫效果^[15,16]。美国康菲石油公司开发的S-Zorb技术利用Ni/ZnO体系的吸附剂通过流化床反应吸附进行脱硫,该工艺可以在比较好地保持辛烷值的情况下有效脱除含硫化合物^[17-22]。Bezverkhyy等^[23-26]对Ni/SiO₂和Ni/ZnO体系的吸附剂的吸附脱硫性能做了一系列的研究。他们发现Ni/ZnO吸附剂的脱硫活性在初始阶段受限于噻吩在金属镍上的分解速度,当ZnO被部分硫化以后,硫元素在ZnO中的扩散速度成为脱硫活性的决定因素。Zhang等^[27]发现ZnO的表面积越大,粒子越小,Ni/ZnO吸附剂的脱硫活性和稳定性越高。

我们的前期工作系统研究了ZnO粒子大小对Ni/ZnO吸附剂脱硫性能的影响^[28]。结果发现,随着ZnO粒子尺寸的减小,吸附剂的脱硫活性和硫容逐渐增大;当ZnO的粒子尺寸小于8 nm时,脱硫反应的表现活化能显著下降,吸附剂的脱硫性能大幅度提高,XRD表征表明这时Ni和ZnO生成了具有特殊的结构NiZnO组分。然而,在Ni/ZnO吸附剂吸附饱和之后的高温再生阶段中,ZnO纳米粒子容易聚结成大颗粒,造成再生后的Ni/ZnO吸附剂脱硫活性和硫容的急剧下降。本文通过在ZnO中掺杂Mn的方式抑制了ZnO在高温再生中的纳米粒子聚集,提高了吸附剂的反应吸附脱硫活性,且能够在多步再生循环中保持较高的脱硫活性。

本文所用药品皆是分析纯试剂,购自天津科纳公司。吸附剂通过两步制备。首先,制备Mn掺杂的ZnO载体。将0.15 mol/L的草酸乙醇溶液滴加到0.10 mol/L的醋酸锌和0.0105 mol/L的醋酸锰乙醇溶液中,室温下剧烈搅拌12 h。将沉淀过滤,洗涤,在120 °C干燥,制得锰掺杂的草酸锌,经500 °C煅烧后得到锰掺杂的氧化锌(8% MnO-ZnO)。第二步,用适量的Ni(NO₃)₂水溶液通过等体积浸渍法负载到8% MnO-ZnO载体上,将得到的Ni(NO₃)₂/8%MnO-ZnO样品在500 °C下煅烧制得5% NiO/8%MnO-ZnO吸附剂(Mn掺杂量按MnO计算)。此外,用同样的方法制备了MnO含量依次为1%,2%,5%和12%的5%NiO/MnO-ZnO系列吸附剂。在后面的研究中,5%NiO/MnO-ZnO系列样品命名为5N_xMZO-T吸附剂(x代表Mn的掺杂量,T代表煅烧温度)。NiO/MnO-ZnO样品在进行反应吸附脱硫前在固定床反应器中原位还原成Ni/MnO-ZnO吸附剂。

XRD表征采用Rigaku衍射仪,Cu K_α发射源,操作条件为40 kV电压和200 mA电流,扫描速率为5°/min,衍射

角度范围为20°~75°。TEM表征在荷兰FEI Tecnai G2 spirit型透射电子显微镜上进行,加速电压120 kV。

吸附脱硫实验在固定床反应器上进行,H₂分压为0.4 MPa,液体空速为6 h⁻¹,氢油比为600,反应温度为300 °C。进料为噻吩和正庚烷组成的模型汽油,硫含量为500 mg/L。硫含量通过检测限为0.1 mg/L的Antek 9000S总硫测定仪分析。

吸附剂的完全硫化和再生在管式炉中进行,硫化条件:H₂S含量为10% (v/v,N₂平衡),硫化温度为25~300 °C,常压进行。当完全硫化后,进行吸附剂再生,再生条件:O₂含量为5% (v/v,N₂平衡),温度为25~500 °C,常压进行。

脱硫率(Sulfur removal)和流出液体积(Effluent, ml)计算公式如下:

$$\text{Sulfur removal} = (1 - c_t/c_0) \times 100\% \quad (1)$$

$$\text{Effluent} = v \cdot t / m_{\text{adsorbent}} \quad (2)$$

其中,c₀为模型汽油硫含量(mg/L),c_t为在反应时间t (min)时流出液的硫含量(mg/L),v为液体进料速度(ml/min),m_{adsorbent}代表吸附剂的质量(g)。

不同Mn含量的5N_xMZO-500样品经500 °C煅烧后的XRD衍射图见图1。由图可见,掺杂Mn后的Ni/Mn-ZnO和Ni/ZnO样品中的纤锌矿衍射峰一致,说明5N_xMZO-500系列吸附剂中的ZnO保持了纤锌矿结构。然而,随着Mn掺杂量的增加,ZnO的衍射峰逐渐变宽,表明ZnO的粒子尺寸变小。为了定量比较ZnO的粒子变化,利用ZnO(101)衍射峰的半峰宽,通过Debye-Scherrer公式计算得到了不同Mn掺杂量的5N_xMZO-500样品的平均粒子尺寸(见表1)。由表1可见,与Ni/ZnO中ZnO的粒子尺寸为30 nm相比,随着Mn掺杂量由1%增加到12%,ZnO的粒子尺寸由26 nm减小到11 nm。另外,当Mn的掺杂量增加到8%时,ZnO粒子不再减小(11 nm),说明8%是一个比较合适的掺杂量。后面的吸附脱硫实验详细考察了5N8MZO-500吸附剂的脱硫性能。

图2是Mn的掺杂对NiO/ZnO吸附剂的脱硫性能的影响。不含Mn的5NZO-500吸附剂在流出液为60 ml时脱硫率仅为49.9%,但是,Mn掺杂的5N8MZO-500吸附剂在流出液为60 ml时的脱硫率达到82.4%,脱硫率提高了32.5%。这表明Mn的掺杂显著提高了吸附剂的吸附脱硫活性。

Mn的掺杂对Ni/ZnO吸附剂在再生循环中的脱硫性能的影响示于图3。尽管我们采用了一种硫含量高达500 mg/L的模型汽油来评价5N8MZO-500吸附剂,可以看出,5N8MZO-500吸附剂在三次反应-再生循环中脱硫率保

持在63%以上。第一次再生后的5N8MZO-500吸附剂在流出液为60 ml时的脱硫率为76.4%，比之新鲜吸附剂的脱硫率(82.4%)下降了约6%。第三次再生后的5N8MZO-500吸附剂的脱硫率(63.7%)仍然比仅仅一次再生后的无Mn掺杂的5NZO-500吸附剂脱硫率(59.5%)高了约4%。这表明Mn的掺杂能够大幅度提高吸附剂的脱硫活性，使5N8MZO-500吸附剂在脱硫实验中有良好的再生脱硫性能。5N8MZO-500吸附剂在脱硫活性和再生后脱硫活性上的有效提高可以通过吸附剂的结构变化来解释(图4)。图4中，与5N8MZO-500吸附剂采用相同方法制备的锰的氧化物由XRD表征确认为 Mn_5O_8 (ICDD-PDF 39-1218)。与5NZO-500和 Mn_5O_8 的XRD图相比，Mn掺杂后，5N8MZO-500吸附剂的XRD图变得较为复杂。首先，在 $2\theta = 30.3^\circ$ 出现一个较弱的衍射峰，其次在 $2\theta = 35.7^\circ$ 出现一个肩峰。显然，新出现的衍射峰不属于ZnO或者 Mn_5O_8 ，它们可归属于 $ZnMnO_3$ (ICDD-PDF 19-1461)。 $ZnMnO_3$ 有利于ZnO纳米粒子在高温煅烧中保持稳定，防止ZnO在再生步骤中聚集。所以，

5N8MZO-500吸附剂的脱硫活性和再生脱硫活性有显著提高。

综上所述，本文通过Mn的掺杂对Ni/Mn-ZnO吸附剂的脱硫性能进行改进，并且将Mn的掺杂量优化为8%。实验表明Mn的掺杂可以显著提高5N8MZO吸附剂的抗高温烧结性能，在500 °C煅烧后，吸附剂中ZnO纳米粒子的平均粒径由30 nm (不含Mn的吸附剂)降到11 nm。Mn的掺杂可以大幅度提高吸附剂的脱硫性能，5N8MZO-500吸附剂的脱硫率比5NZO-500提高了32.5%。此外，5N8MZO-500吸附剂还表现出优异的再生脱硫活性，一次再生后的5N8MZO-500吸附剂在处理了60 ml模型汽油(500 mg/L)时的脱硫率保持在76%以上，三次再生后的脱硫率仍比一次再生的无Mn掺杂的5NZO-500吸附剂的脱硫率高出约4%。XRD表征显示在Ni/ZnO吸附剂中加入Mn后生成一种新的化合物 $ZnMnO_3$ ，可以限制ZnO纳米粒子在高温煅烧过程中聚集长大，从而提高Ni/Mn-ZnO吸附剂的脱硫活性和再生脱硫活性。