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Article

V₂O₅/hematite catalyst for low temperature selective catalytic reduction of NO_x with NH₃

Ping Zhang, Tianhu Chen*, Xuehua Zou, Chengzhu Zhu, Dong Chen, Haibo Liu

Laboratory of Nano Mineral and Environmental Material, School of Resource and Environmental Engineering, Hefei University of Technology, Hefei 230009, Anhui, China

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ABSTRACT

A series of V₂O₅/hematite (V/H) catalysts were prepared by impregnation of goethite with NH₄VO₃ solution and used in the selective catalytic reduction (SCR) of NO with NH₃. The catalysts were characterized by X-ray diffraction, transmission electron microscopy, N₂ adsorption, H₂ temperature-programmed reduction, and NH₃ temperature-programmed desorption. The effects of V₂O₅ loading and calcination temperature on the SCR activity were investigated. The NO conversion over 3% V/H catalysts calcined at 300 °C exceeded 95% at 250–300 °C. Neither H₂O nor SO₂ (0.01%) had any adverse impact on the activity, but a decrease of SCR activity was observed after high concentrations (0.03% and 0.05%) of SO₂ were introduced. Cutting off the SO₂ supply resulted in activity restoration. The simultaneous addition of 5% H₂O and 0.03% SO₂ led to a synergistic poisoning effect, but when these gases were switched off, the activity was recovered. SO₂ adsorption on the catalyst surface led to the decrease in SCR activity.

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1. Introduction

Fossil fuel combustion in thermal power plants, cement kilns, and automobiles generates nitrogen oxides (NO_x), which have adverse effects, including photochemical smog, acid rain, greenhouse effects, ozone depletion, and causing respiratory diseases. The selective catalytic reduction of NO_x with ammonia (NH₃-SCR) is a key technology widely used to remove NO_x [1]. Due to their high NO_x conversion, high selectivity, and stable performance, V₂O₅/TiO₂ and V₂O₅-WO₃/TiO₂ are the most common commercial catalysts [2]. However, the high reaction temperature, narrow reaction window of 300–400 °C, the catalysts that mainly have to be imported, and the barriers to use due to intellectual property rights are problems that have to be solved in China. There is a need to develop new SCR catalysts

with excellent low temperature performance and wide reaction windows [3,4].

Iron-based catalysts have attracted interest in flue gas denitration. Fe-ZSM has received much attention in recent years [5–7]. Brandenberger et al. [8] investigated the different iron species coexisting on Fe-ZSM-5 during NH₃-SCR, such as isolated Fe³⁺ species, oligomeric Fe_xO_y clusters, and Fe₂O₃ particles, and proposed that below 300 °C, monomeric iron is the most active site for the SCR reaction while at higher temperatures, the contribution of dimeric iron species, oligomeric species, and Fe₂O₃ particles become important. Qi et al. [9] prepared a Pt/Fe-ZSM-5 catalyst and found that the noble metal improved the activity, as well as its tolerance for H₂O and SO₂. Other research has focused on iron oxides. Liu et al. [10] studied a Fe_xTiO_y catalyst prepared by co-precipitation and ob-

*Corresponding author. Tel: +86-551-62903990; E-mail: chentianhu@hfut.edu.cn

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served excellent activity, selectivity, and $\text{SO}_2/\text{H}_2\text{O}$ tolerance in the medium temperature range (200–400 °C). Yang et al. [11] synthesized $\alpha\text{-Fe}_2\text{O}_3$ samples with nanocube and nanorod morphology by a simple hydrothermal route. The results showed that the nanorods with exposed high energy faces had a much higher activity for $\text{NH}_3\text{-SCR}$ than the nanocube with exposed low energy faces. Apostolescu et al. [12] explored the effects of the Fe/W ratio in $\text{Fe}_2\text{O}_3\text{-WO}_3/\text{ZrO}_2$ catalyst and found that 1.4Fe/7.0W/Zr gave the best $\text{NH}_3\text{-SCR}$ performance and N_2 selectivity.

Goethite is one of the most widespread iron oxide (hydroxide) in the soil [13], and it is found in concentrated form in ore deposits [14]. The ore reserves of pyrite associated with goethite in Xinqiao, Tongling, China, exceed 100 million tons [15]. Thus, due to the abundant resources and low cost, goethite is an attractive candidate for potential catalyst use. After dehydration at 225 °C, goethite transforms into hematite, which has more crystallization and a smaller nano-phase. Higher specific surface areas can be obtained with the proper dehydration condition [16–18]. Due to their particular nanopore structure and high specific surface areas, a series of $\text{V}_2\text{O}_5/\text{hematite}$ (V/H) catalysts were prepared to investigate the effect of V_2O_5 loading and calcination temperature on SCR activity and $\text{H}_2\text{O}/\text{SO}_2$ tolerance.

2. Experimental

2.1. Preparation of V/H catalysts

Catalysts were prepared by the impregnation of goethite (G, synthesized by the hydrothermal method, Zhenjiang Fine Chemicals Factory) with a solution of ammonium metavanadate (NH_4VO_3 , Tianjin Guangfu Fine Chemicals Research Institute) and oxalic acid. All chemicals were analytical grade. The details are as follows. NH_4VO_3 (0.232 g) was dissolved in 20 ml oxalic acid (0.48 mol/L). Then the solution was added into a 100 ml beaker containing 10 g of goethite with stirring for 30 min. The mixture was aged for one night before being dried at 105 °C. The sample was ground and sieved to 40–60 mesh. After the powder has cooled to air temperature, it was calcined at 300 °C for 2 h in air to get the 1%V/H(300) sample, where the 1% means the mass ratio of V/support in the catalyst, and the 300 means the calcination temperature. Other V/H samples with different V/support mass ratios and calcination temperatures were synthesized using the same procedure.

2.2. Characterization of the catalysts

X-ray diffraction (XRD) patterns were recorded between 15° and 80° (2 θ) at steps of 4°/min using a Rigaku D/max diffractometer with Cu $K\alpha$ radiation (50 kV and 100 mA). A JEM-2100 high resolution transmission electron microscope (TEM) was used to observe the morphology and pore structure of the catalysts. The BET specific surface area and pore volume of the catalysts were measured by N_2 adsorption at liquid nitrogen temperature using a Quantachrome NOVA3000e analyzer. The samples were first degassed at 110 °C for 24 h.

Temperature-programmed reduction with H_2 ($\text{H}_2\text{-TPR}$) measurement was carried out with a quartz tube ($d = 10$ mm) containing 0.05 g catalyst. A 5% H_2 -95% Ar mixture with a flow rate of 50 ml/min was fed to the sample, which was heated from room temperature to 800 °C at a heating rate of 10 °C/min. The H_2 content of the effluent gas was analyzed by an online mass spectrometer (MS, Hiden QIC-20).

Temperature-programmed desorption of NH_3 ($\text{NH}_3\text{-TPD}$) measurement used a quadrupole mass spectrometer (Hiden QIC-20). Catalyst (0.1 g) was heated at its calcination temperature for 2 h under Ar flow of 50 ml/min and then cooled to 50 °C. A 0.5% NH_3 -99.5% Ar mixture was fed in at 50 °C until saturation, after which the catalyst was swept with Ar and heated at an increasing temperature up to 700 °C at a heating rate of 10 °C/min. The $m/e = 15$ fragment was chosen as the NH_3 signal to avoid the interference of H_2O .

2.3. Catalytic activity of the catalysts

Catalyst activity tests for the SCR reaction were conducted in a homemade fixed-bed reactor. The gas flow rate was controlled using mass flow controllers (Sevenstar D08, Beijing). A feed gas consisting of 0.1% NO , 0.1% NH_3 , and 3% O_2 with Ar as the balance at a total flow rate of 300 ml/min and gas hourly space velocity (GHSV) of 18000 h^{-1} was used. In the SO_2 tolerance test, SO_2/Ar was added into the model gas feed. In the H_2O tolerance test, Ar was bubbled through distilled water to obtain water vapor. The NO concentrations were continuously monitored by a flue gas analyzer (Kane KM9106). The data for each test temperature was recorded after 1 h to avoid the effect of adsorption. NO conversion was used to evaluate catalytic activity.

3. Results and discussion

3.1. Characterization results

The XRD patterns of catalysts with different V_2O_5 contents and prepared with different calcination temperatures are shown in Fig. 1. In Fig. 1(a), the peaks of hematite decreased with increasing V_2O_5 loading. This was due to absorption of the diffracted ray, which decreased the peak intensity, with the increase of the coverage and thickness of V_2O_5 highly dispersed on the surface of hematite. In Fig. 1(b), the peak intensity of the sample increased, which was mainly due to the improvement of the crystallinity degree of the catalyst, after calcination at higher temperatures. This agreed with the result reported by Zou et al. [18] on the structural and chromatic evolution of goethite with thermal treatment. Furthermore, there was no peak related to V_2O_5 in the XRD patterns, suggesting that V_2O_5 was highly dispersed. This was accordance with the TEM results.

The TEM images are shown in Fig. 2. The morphology and pore structure of 0%V/H(300) are shown in Fig. 2(a). In combination with the XRD analysis, we can see that although it has transformed into hematite, the acicular structure of goethite was preserved. Numerous nanopores were observed due to slit-shaped nanopores existing between polycrystalline hema-

Fig. 1. XRD patterns of V/H catalysts with different V_2O_5 loadings calcined at 300 °C (a) and 3%V/H catalysts calcined at different temperatures (b).

tite formed from the dehydroxylation of goethite. Figure 2(b) shows the morphology and pore structure of 0%V/H(500). Compared with 0%V/H(300), there still remained some goethite, but the slit-shaped micropores between hematite crystallites were due to the bigger hematite crystallites. Figure 2(c) shows the morphology and pore structure of 3%V/H(300). Despite the similarity with Fig. 2(a) and (b), the surface of hematite had small vanadium oxide patches dispersed uniformly on it. The inset in Fig. 2(c) shows the components of 3%V/H(300) detected by the energy dispersive spectrometer (EDS). The V content of the catalyst basically agreed with the nominal value. This indicated that V_2O_5 was dispersed well on the surface of hematite.

Fig. 2. TEM images of goethite calcined at 300 °C (a), goethite calcined at 500 °C (b), and 3%V/H(300) (c). The inset in (c) is EDS spectrum of 3%V/H(300).

Table 1

BET specific surface area and pore volume of the V/H catalysts with different calcination temperatures.

Catalyst	BET surface area (m^2/g)			Total pore volume (cm^3/g)		
	300 °C	400 °C	500 °C	300 °C	400 °C	500 °C
0%V/H	92.8	52.8	21.5	0.072	0.063	0.049
1%V/H	108.4	72.0	28.5	0.074	0.066	0.048
3%V/H	88.9	61.1	51.0	0.067	0.059	0.057
5%V/H	70.0	58.5	18.1	0.058	0.062	0.032
7%V/H	24.7	28.6	11.6	0.042	0.043	0.028

Table 1 shows the specific surface area and pore volume of the V/H catalysts. Without any V loading, the BET surface area and pore volume of 0%V/H(300) and 0%V/H(500) were 92.8 m^2/g , 0.072 cm^3/g and 21.5 m^2/g , 0.049 cm^3/g , respectively. Both surface area and pore volume decreased with increasing calcination temperature. In addition, the pore size distribution showed that most of the pores of 0%V/H(300) were micropores, and only a small amount were mesopores, while 0%V/H(500) had the opposite distribution. Furthermore, the amount of micropores decreased and mesopores increased with increasing temperature. After V loading, the 1%V/H catalyst has the largest surface area. With increasing V loading, the surface area decreased dramatically, which was ascribed to the blockage of pores caused by V_2O_5 particles of nano-size. In the catalytic test, 1%V/H(300) with the largest surface area showed low activity, which means that the surface area was not the key factor for de NO_x performance. The improvement of catalytic activity was probably due to the decrease of V_2O_5 dispersity and the increase of V_2O_5 clusters.

H_2 -TPR profiles of the different catalysts are presented in Fig. 3. Three main reduction peaks of 0%V/H(300) at 330, 535, and 660 °C were present due to the reduction of the iron oxides: $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$. The main reduction peaks of V_2O_5 were at 536 and 700 °C. After V_2O_5 loading, both the temperature and reduction peaks area increased. It can be concluded that the iron oxides were easier to oxidize and the quantity of reducible species on the catalyst increased after loading V_2O_5 , which was good for SCR activity.

NH_3 adsorption has a large impact on SCR activity. The NH_3 -TPD profiles are shown in Fig. 4. Both catalysts showed two obvious peaks corresponding to two acid sites. For 0%V/H(300), the area of the second peak (390 °C) was much

Fig. 3. H₂-TPR profiles of 0%V/H(300), 3%V/H(300), and V₂O₅.

Fig. 4. NH₃-TPD profiles of 0%V/H(300) and 3%V/H(300).

larger than the first one (235 °C), meaning that there were more acid sites. After doping with V₂O₅, the area of the two peaks increased significantly, showing that there were more acid sites. The intensity of the first peak became higher. The overlap of the two peaks led to a broadened peak between 200 and 500 °C. This was in accord with the better performance of the V/H catalysts.

3.2. Effect of V₂O₅ loading and calcination temperature on catalytic performance

Figure 5(a) shows the SCR activity of the catalysts calcined at 300 °C. It can be seen that the support alone (0%V/H(300)) has some catalytic performance. With increasing temperature, the NO conversion increased first and then decreased. With the support, the highest conversion reached 83.6% at 300 °C, and it exceeded 80% in the range of 250–300 °C, but the reaction window was quite narrow. With the addition of V₂O₅, the catalytic activity improved significantly, and the reaction window was enlarged too. Meanwhile, the increasing V loading had a significant promotion on the catalysts, e.g., the NO conversion of all the catalysts was > 95% at 250 °C, and excellent activity was obtained in the temperature range of 200–300 °C.

The SCR activity of catalysts with different V loading calcined at 400 and 500 °C is shown in Fig. 5(b) and (c), respec-

Fig. 5. NO conversion over V/H catalysts calcined at 300 °C (a), 400 °C (b), and 500 °C (c).

tively. The trends of the curves in Fig. 5(a), (b), and (c) were similar. In Fig. 5(b), catalytic activity increased with the increase of V loading before 350 °C. In the range of 100–250 °C, the NO conversion over the catalysts calcined at 500 °C with the same V loading was slightly lower than in Fig. 5(a) and (b) except for the 7%V/H(500), which indicated that when the temperature reached 400 °C, some NO was generated. The V/H catalysts calcined at 300 and 400 °C had better catalytic performance than that calcined at 500 °C. By considering both the preparation and the activity, the 3%V/H(300) sample was judged to have the best catalytic performance in the low temperature window (250–400 °C).

3.3. SO₂ and H₂O tolerance test

Because a combustion exhaust usually contains SO₂ and H₂O

Fig. 6. Effect of H₂O and SO₂ on SCR activity.

vapor, the 3%V/H(300) catalyst was further studied at 300 °C to investigate its SO₂/H₂O tolerance. As shown in Fig. 6, H₂O was added to the feed gases after 1 h of steady reaction. The addition of H₂O did not cause any obvious effect, which might be due to the high dispersion, large surface area, and special pore structure of the catalyst. The effect of SO₂ on SCR activity was related to SO₂ concentration. When 0.01% SO₂ was added to the reaction gas, NO conversion was still maintained at 99.6%. As the concentration of SO₂ was increased to 0.03% and 0.05%, the NO conversion decreased to 92% and 90%, respectively. Cutting off the SO₂ supply resulted in an instantaneous recovery of the original level. The NO conversion decreased to 83% in the presence of H₂O and 0.03% SO₂, and after cutting off the addition of H₂O and SO₂, the activity was restored quickly to its original level. As can be seen in Fig. 6, the coexistence of H₂O and SO₂ led to more catalyst deactivation than the addition of a single gas, indicating that they had synergistic inhibition on SCR performance.

The decreased activity with high SO₂ concentration may be due to three reasons [19–21]: (1) formation of iron sulfate; (2) ammonium bisulfate or ammonium sulfate on the catalyst surface; (3) adsorbed SO₂ on the active site of the catalyst. Alt-

hough iron sulfate decomposes at 480 °C, which is higher than the test temperature 300 °C, however, no diffraction line of the sulfate was observed in the XRD pattern of the sample, and reason (1) can be excluded, which agrees with Tang et al. [20]. If SO₂ was oxidized to SO₃ and this eventually formed (NH₄)₂SO₄ by reacting with NH₃ and H₂O, the (NH₄)₂SO₄ would decompose because the reaction temperature was higher than its decomposition temperature. Therefore, deposition would not occur on the catalyst and reason (2) can be excluded too. As a consequence, reason (3) was probably the cause of the deactivation, which was due to SO₂ adsorption competing with NH₃ and NO. The occupation of active sites by SO₂ would decrease SCR activity. This effect would disappear when SO₂ was removed, as was observed.

4. Conclusions

A series of V₂O₅/hematite (V/H) catalysts were prepared by impregnation. They exhibited excellent low temperature SCR performance. Vanadium oxide was highly dispersed on the surface of the support. The NO conversion over the 3%V/H(300) catalyst exceeded 95% between 250 and 300 °C. Neither the presence of H₂O nor SO₂ (0.01%) had an adverse effect on the activity, while SCR activity decreased when a high SO₂ concentration (0.03% and 0.05%) was introduced into the system. Cutting off the SO₂ supply resulted in a restoration of activity. The simultaneous introduction of 5% H₂O and 0.03% SO₂ led to a synergistic poisoning effect; when they were switched off, the activity was recovered. The mechanism of deNO_x and the effects caused by some other experiment parameter need further study.

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Graphical Abstract

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V₂O₅/hematite catalysts for low temperature selective catalytic reduction of NO_x with NH₃

Ping Zhang, Tianhu Chen*, Xuehua Zou, Chengzhu Zhu, Dong Chen, Haibo Liu
Hefei University of Technology

A series of highly dispersed V₂O₅/hematite (V/H) catalysts were prepared by the impregnation of V₂O₅ on goethite, which were highly efficient for the selective catalytic reduction of NO with NH₃.

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V₂O₅/赤铁矿催化剂结构及其NH₃选择性催化还原NO_x性能

张 萍, 陈天虎*, 邹雪华, 朱承驻, 陈 冬, 刘海波

合肥工业大学资源与环境工程学院纳米矿物与环境材料实验室, 安徽合肥230009

摘要: 以水热合成针铁矿为前驱体浸渍偏钒酸铵, 分别于300、400和500 °C空气中焙烧, 制备了不同活性组分负载量的V₂O₅/赤铁矿(V/H)催化剂, 用于氨选择性催化还原(SCR)脱硝。采用X射线衍射、透射电子显微镜、比表面积分析仪、程序升温还原及程序升温脱附等方法对催化剂结构进行了表征, 并用标气配制模拟烟气进行了脱硝实验。结果表明, 300 °C煅烧3% V/H催化剂当烟气温度为250–300 °C时NO转化率均可达95%以上; 当配气中单独加入水蒸气或低浓度SO₂ (0.01%)时, V/H催化脱硝的活性不受影响; 当系统加入高浓度的SO₂ (0.03%与0.05%)或同时添加H₂O与SO₂时, SCR脱硝效率下降, 其机制可能是SO₂在催化剂表面竞争吸附所致, 停止添加后, 催化活性迅速恢复。

关键词: 铁氧化物; 氧化钒; 氮氧化物; 选择性催化还原

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*通讯联系人. 电话: (0551)62903990; 电子信箱: chentianhu@hfut.edu.cn

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1. 前言

工业生产如火力电厂和水泥窑炉以及机动车辆在燃料燃烧过程中可产生大量氮氧化物(NO_x), 会引起光化学烟雾、酸雨、温室效应及臭氧层破坏等重大环境问题, 严重危害环境及人类健康, 是现今主要大气污染源之一。在目前的脱硝方法中, 选择性催化还原(SCR)是应用最广泛的烟气脱硝技术^[1]; 其中应用最多的是V₂O₅/TiO₂和V₂O₅-WO₃/TiO₂催化剂。此类催化剂具有脱硝效率高、选择性好及运行稳定等特点^[2]; 但其催化反应温度较高、温度窗口较窄(350–400 °C), 价格昂贵, 且大多依赖国外进口, 使用时存在一定知识产权壁垒, 因此急需自主开发性能良好的NH₃-SCR催化剂^[3,4]。

由于具有过渡金属的特殊性质, 近年来铁基催化剂在烟气脱硝研究中受到广泛关注。有学者研究了铁离子

交换分子筛催化剂(Fe-ZSM)^[5–7], Brandenberger等^[8]研究了Fe/ZSM-5脱硝催化剂上铁的三种形态, 即孤立Fe³⁺物种、低聚铁氧化物团簇以及Fe₂O₃颗粒, 认为低于300 °C时主要是孤立Fe³⁺发挥催化活性, 当温度升高时低聚铁氧化物团簇和Fe₂O₃颗粒对活性贡献增大。Qi等^[9]制备了添加Pt的Fe/ZSM-5催化剂, 发现Pt的引入明显提高了低温脱硝性能, 同时也提高了抗水及抗SO₂性能。另有一些铁基催化剂研究集中在铁氧化物上, Liu等^[10]用共沉淀法制备了Fe_xTiO_y催化剂, 其在较宽温度窗口(200–400 °C)有较高SCR活性与N₂选择性, 即使有H₂O与SO₂存在时NO转化率仍可接近100%。杨兴业等^[11]用水热合成法制备了α-Fe₂O₃纳米棒和纳米立方体, 前者由于暴露高表面能的活性面而具有比后者更高的催化活性。Apostolescu等^[12]制备了以ZrO₂为载体, 以WO₃为助剂的铁氧化物催化剂, 发现1.4Fe/7.0W/Zr具有最佳SCR催化

活性与 N_2 选择性.

针铁矿是土壤中分布最广的结晶铁(氢)氧化物之一^[13],大量聚集形成矿床^[14],仅铜陵新桥硫铁矿伴生针铁矿探明储量即超过1亿吨^[15],具有资源丰富和价格低廉的特点.针铁矿属于含水的铁氢氧化物,在225 °C受热脱水相变成赤铁矿,可以进一步多晶化,产生更小的纳米物相,在适当条件下脱水相变,比表面积可以进一步提高^[16–18].基于铁氧化物具有SCR催化活性和针铁矿热分解相变产物具有纳米孔结构及大比表面积的特点,本文直接以针铁矿为前驱体负载 V_2O_5 ,制备了 V_2O_5 /赤铁矿SCR脱硝催化剂,考察了其 NH_3 -SCR催化活性与钒负载量、烟气温度的关系及其抗水抗 SO_2 性能.

2. 实验部分

2.1. 催化剂制备

所用偏钒酸铵(NH_4VO_3)购自天津市光复精细化工研究所,针铁矿(G)为水热合成法生产针铁矿,购自镇江精细化工厂.催化剂采用等体积浸渍法制备,称取0.232 g NH_4VO_3 溶解于20 ml草酸溶液(0.48 mol/L)中,再将此混合溶液加入到100 ml装有10 g针铁矿粉末的烧杯中,用玻璃棒不断搅动30 min后,室温下陈化过夜,于105 °C下烘干,冷却至室温后压碎过筛,把获得的40–60目颗粒在300 °C空气中焙烧2 h,冷却至室温备用.所得V/赤铁矿催化剂记为1%V/H(300),其中1%为催化剂中钒与载体的质量比,300为焙烧温度(°C).同样方法制得400和500 °C焙烧的不同钒负载量系列催化剂.

2.2. 催化剂表征

X射线粉末衍射(XRD)在日本理学D/max-rB型X射线衍射仪上测定,Cu K_α 射线,管电压50 kV,管电流100 mA,扫描速率4°/min,扫描范围 $2\theta = 15^\circ\text{--}80^\circ$.催化剂形貌与孔结构观察使用日本电子JEM-2100F型场发射透射电子显微镜(TEM)完成.催化剂的BET比表面积和总孔体积用美国Quantachrome NOVA3000e型比表面积分析仪测定.

H_2 程序升温还原(H_2 -TPR)在石英管中进行.取0.05 g催化剂放入直径为10 mm石英管中,通入流量为50 ml/min的5% H_2 -95%Ar混合气至基线稳定后,以10 °C/min的速率升至800 °C,通过在线质谱仪(Hiden QIC-20型)监测尾气中 H_2 含量.

NH_3 吸附-脱附实验通过在线质谱仪(Hiden QIC-20型)监测尾气.取0.1 g催化剂放入直径为10 mm石英管中,先在催化剂焙烧温度下通入流量为50 ml/min的Ar气

预处理2 h,降至50 °C且质谱基线稳定后,将气体切换成0.5% NH_3 -99.5% Ar混合气进行 NH_3 吸附,吸附平衡后再切回Ar吹扫1 h至基线稳定,最后以10 °C/min的速率升至700 °C.为避免 H_2O 信号的影响,以 $m/e = 15$ 作为 NH_3 的检测信号.

2.3. 催化剂评价

催化剂活性评价在自制固定床气固相催化反应装置上进行.模拟烟气采用 NH_3/Ar , O_2/Ar , NO/Ar 标准气体及Ar气混合配制.各路气体流量均由D08系列质量流量计(北京七星华创)控制.模拟气体组成(体积分数)为0.1% NO , 0.1% NH_3 , 3% O_2 , Ar为载气;总流量300 ml/min,反应空速(GHSV)18000 h^{-1} .考察 SO_2 对催化剂活性影响时,另外混入 SO_2/Ar 标准气体.考察水蒸气的影响时,将载气氮气鼓泡进入恒定温度的纯水实现气体增湿.反应进出口气体NO浓度由Kane KM9106型烟气分析仪在线检测,为确保活性表征数据不受吸附的影响,在每个测试点稳定1 h后再进行数据记录,催化剂活性以NO转化率衡量.

3. 结果与讨论

3.1. 催化剂表征结果

图1(a)与(b)分别是300 °C焙烧针铁矿负载不同钒含量催化剂与不同温度下焙烧3%钒负载量催化剂的XRD谱.由图可见,所有催化剂都仅出现赤铁矿的系列衍射峰,未出现明显的钒氧化物衍射峰.图1(b)中低温焙烧催化剂中赤铁矿的衍射峰强度随温度升高而增强,这说明低温下赤铁矿的结晶度低,随着焙烧温度升高,赤铁矿结晶度增大,这与邹雪华等^[18]热处理针铁矿结构演化的结果一致.XRD图谱中没有出现钒氧化物的特征衍射峰,说明催化剂中钒氧化物的结晶度较低,在催化剂载体赤铁矿上均匀分散,下面的TEM分析结果也证实了这一点.图1(a)中可观察到,随钒负载量增加赤铁矿特征衍射峰逐渐减弱,这归结于高度分散的钒氧化物在赤铁矿表面均匀覆盖率增大和增厚导致对赤铁矿衍射线吸收增强,衍射强度减弱.

图2为催化剂的TEM照片.图2(a)为未负载钒的针铁矿在300 °C焙烧后的形貌和孔结构特征.结合XRD分析可知,针铁矿300 °C焙烧后转变为赤铁矿,但是仍保留针铁矿原有的针状形貌特征;图中可看到密集的纳米孔隙,这是由于针铁矿脱水相变为多晶赤铁矿,赤铁矿颗粒之间存在纳米空隙.图2(b)为未负载钒的针铁矿500 °C焙烧后形貌和孔结构特征,与300 °C焙烧产物相

比,形貌没有明显的变化,仍保持针铁矿的假象形态,但是由于焙烧温度升高,赤铁矿晶体变大,赤铁矿晶间空隙变大.图2(c)为负载钒的针铁矿300 °C焙烧后产物V/H催化剂的形貌特征,可见颗粒形貌仍保持针铁矿假象特征,与图2(a)和(b)中焙烧针铁矿形貌特征相近,同样具有大量纳米孔隙,同时可看出针铁矿假象颗粒表面有分散均匀、颗粒细小的钒氧化物.对催化剂不同颗粒进行了能谱分析(EDS),结果表明(图3(c)插图)钒的含量都比较接近,基本与制备催化剂时配比一致,这说明所制备的催化剂中 V_2O_5 具有很好的分散性.

表1给出了不同钒负载量催化剂的比表面积与孔体积.未负载钒时,300 °C焙烧针铁矿的比表面积为 $92.8\text{ m}^2/\text{g}$,孔体积 $0.072\text{ cm}^3/\text{g}$;随焙烧温度升高,产物的比表面积与孔体积均明显下降;500 °C焙烧产物比表面积与孔体积分别为 $21.5\text{ m}^2/\text{g}$ 和 $0.049\text{ cm}^3/\text{g}$.孔径分布显示,300 °C焙烧催化剂多为微孔,少量介孔;随温度升高,微孔减少,介孔增加;500 °C焙烧催化剂多为介孔,仅少量微孔.负载量为1%的催化剂比表面积最高,随着钒负载量提高,比表面积大幅度降低,可能是由于钒负载量提高,粒径只有几个纳米的 V_2O_5 覆盖针铁矿假象颗粒表面,阻塞了颗粒表面开放空隙.结合下面的活性实验发现,比表面积较大的1%V催化剂在低温(300 °C)下SCR脱硝活性却较低,这说明对于V/H系列催化剂,比表面积并非是决定催化剂脱硝活性的关键因素.这可能是由于随 V_2O_5 含量增加,其分散度降低,聚合态的钒氧化物含量增加,从而提高了催化剂的活性.

图3给出了不同催化剂的 H_2 -TPR曲线.由图可见,0%V/H(300)有三个还原峰,分别位于330,535和660 °C,对应着铁氧化物的逐步还原过程: $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$.而 V_2O_5 还原峰主要位于536与700 °C.由图中对比可知,负载氧化钒后,赤铁矿的三个还原峰温度均略有升高,且还原峰面积显著增大,该结果表明,钒氧化物的负载增加了催化剂的可还原物种量,提高了铁氧化物表面的氧化能力,有利于SCR反应的进行.

催化剂对 NH_3 的吸附能力是影响其SCR脱硝活性的关键因素, NH_3 -TPD实验结果示于图4.由图可知,两种催化剂均有二个明显的脱附峰,对应于两个酸位,其中0%V/H(300)第一个峰在235 °C左右,峰形较窄;第二个峰在390 °C左右,峰形较宽,且峰面积明显大于第一个峰,说明其酸位较多.负载钒后同样有两个主峰,两峰面积均显著增加,对应酸位有较大增加,且第一个峰强度变大,两峰有所叠加,使脱附峰(200–500 °C)较宽.这与

加入钒后催化剂低温段脱硝活性的显著提高一致.

3.2. 钒负载量和焙烧温度对催化剂活性的影响

图5(a)为针铁矿负载不同钒量300 °C焙烧得到的催化剂上SCR反应中的NO转化率.由图可以看出,焙烧针铁矿本身具有一定催化活性,其催化活性随着温度的升高呈先增后减的趋势,当反应温度为300 °C时NO转化率达到最高值83.6%,在250–350 °C可达80%以上,但是反应温度窗口较窄.催化剂负载钒后,催化活性显著提升,反应温度窗口增大,且随着钒负载量的增加,催化活性逐渐增强,250 °C的NO转化率均可达到95%以上,在200–300 °C效果较好.

图5(b)与(c)分别为400 °C与500 °C焙烧不同钒负载量的V/H催化剂上SCR反应中的NO转化率,活性趋势与图5(a)中大体相似.在图5(b)中,350 °C之前随负载量增加催化剂活性也提高;在图5(c)中,低温段100–250 °C除7%V/H(500)上NO转化率有所增加外,其他相同负载量500 °C焙烧催化剂在各反应温度NO转化率均较300 °C与400 °C焙烧的略降低,当反应温度增加到400 °C时,尾气中NO浓度反而略微增加,说明此时NO略有生成.比较而言,经300与400 °C焙烧的 V_2O_5 /H催化剂比经500 °C焙烧 V_2O_5 /H催化剂具有更高的催化活性.综合考虑催化剂制备消耗与催化效果,300 °C焙烧3%V/H催化剂具有在中低温区(250–400 °C)SCR脱除烟气中NO的最优性能.

3.3. 烟气中 H_2O 和 SO_2 对催化剂活性的影响

使用300 °C焙烧的3%V/H催化剂进行耐 H_2O 和抗 SO_2 性能评价.首先在无硫无硫的模拟气体下运行稳定反应1 h后开始进行 H_2O 影响实验.如图6所示, H_2O 的加入并未对反应造成影响,这可能归因于催化剂高分散度、大比表面积与特殊的孔结构.相同的反应条件下配入 SO_2 /Ar气体进行 SO_2 影响实验.如图6所示,加入 SO_2 后对NO转化率的影响与其浓度有关,当 SO_2 浓度为0.01%时,NO转化率不受影响,仍保持在99.6%;但当 SO_2 浓度继续增大到0.03%与0.05%时,NO转化率迅速下降,90 min时逐渐稳定,分别为92%与90%左右,当停止加入 SO_2 后,NO转化率迅速恢复至初始水平.当同时添加 H_2O 与0.03% SO_2 时,NO转化率迅速下降,然后稳定在83%左右;停止添加后,活性仍可恢复.由图6可知,当 H_2O 与 SO_2 同时存在时对催化剂活性的影响大于单独引入任一种气体的影响,说明此时 H_2O 与 SO_2 对催化剂活性的抑制有叠加作用.

高浓度 SO_2 引起催化活性的降低可能有以下三种原

因^[19–21]：一是生成硫酸铁盐覆盖表面，二是生成硫酸氢铵或硫酸铵覆盖表面，三是SO₂吸附在催化剂表面活性位点。硫酸铁盐的分解温度为480 °C，而该实验温度(300 °C)低于此温度，对抗硫反应后样品进行的XRD分析表明，仅出现赤铁矿峰，并无硫酸盐特征衍射峰出现，因此可以排除原因一。这与唐晓龙等^[20]的研究结果一致。抗硫性能实验过程中即使SO₂在V₂O₅催化作用下氧化生成SO₃，与反应物中的NH₃和生成物中的H₂O发生反应生成硫酸氢铵，但催化床层反应温度保持在300 °C，生成的硫酸氢铵在该温度下会分解，并不会沉积在催化剂表面上影响催化反应，因此也可排除原因二。由此可知，添加SO₂导致活性降低可能是原因三所引起的，即SO₂吸附在催化剂表面的活性位点，与反应物之间存在

竞争吸附，因此降低了催化活性，但不会完全毒化催化剂，停止加SO₂后不利影响能够完全消失。

4. 结论

以水热合成的针铁矿为前驱体，采用浸渍法制备的负载V/H SCR催化剂具有良好的中低温催化脱硝活性。活性组分钒氧化物在载体表面呈高度分散状态，其中300 °C焙烧的3% V/H催化剂在中低温区(250–300 °C) SCR脱除烟气中的NO转化率达95%以上。向反应体系中单独添加H₂O或低浓度SO₂ (0.01%)对催化剂活性无影响；添加高浓度SO₂ (0.03%与0.05%)对催化剂活性有影响，但停止添加后，活性可随即恢复；同时添加H₂O与SO₂时对催化剂活性抑制有叠加作用。