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Article

Preparation and characterization of Ni-Ti-O mixed oxide for selective catalytic reduction of NO under lean-burn conditions

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ABSTRACT

A novel Ni-Ti-O mixed-oxide catalyst was prepared by a homogeneous coprecipitation method and tested in the selective catalytic reduction of NO by propene (C_3H_6 -SCR) in the presence of excess O_2 . Catalysts with different molar ratios of Ni-Ti were characterized using X-ray diffraction, N_2 adsorption-desorption, pyridine adsorption, temperature-programmed desorption, and in-situ Fourier-transform infrared spectroscopy. The $Ni_{1.1}Ti_1$ catalyst showed good activity in C_3H_6 -SCR at 430 °C and the NO_x conversion achieved 68%. This catalyst displayed an anatase structure and had a high surface area ($149 \text{ m}^2/\text{g}$), which is helpful to enhance the catalyst activity. Lewis acid sites were beneficial for adsorbing nitrate, which was the main intermediate produced during the SCR of NO by C_3H_6 .

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1. Introduction

With the fast development of the automobile industry and the rapid increase in the number of automobiles, increasing attention is being paid to pollution by nitrogen oxides (NO_x) from vehicle exhaust gases. High-efficiency lean-burn engines can significantly reduce energy consumption and have good potential for applications [1]. However, the exhaust of a lean-burn engine contains a large quantity of O_2 , which can reduce the activities of traditional three-way catalysts [2]. The development of new catalysts that can effectively remove NO_x under conditions of excess O_2 is therefore of great theoretical and practical significance.

The selective catalytic reduction (SCR) of NO by hydrocarbons is considered to be one of the most effective methods of controlling NO emissions by motor vehicles [3]. Moreover, this method does not need the addition of any exogenous reducing agents, so it has great potential in development and applica-

tions. Previous research has shown that Ni-based catalysts have activities for SCR of NO by hydrocarbons, and Ni is used as an active component of catalytic systems [4]. Titanium dioxide (TiO_2) has been widely used as a catalyst supporting material for SCR of NO because of its competitive cost and low toxicity [5]. Combining the virtues of Ni-based catalysts and TiO_2 , we prepared a Ni-Ti-O mixed-oxide catalyst using a urea homogeneous coprecipitation method and tested it in SCR of NO by C_3H_6 in the presence of excess O_2 and explored the relationship between catalyst structure and catalytic performance.

2. Experimental

2.1. Catalyst preparation

The Ni-Ti-O mixed-oxide catalysts were prepared by homogeneous coprecipitation. $Ni(NO_3)_2 \cdot 6H_2O$ and $Ti(SO_4)_2$ were mixed with deionized water to obtain salt solutions with ionic

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ratios of Ni/Ti = 0.5, 1, 2, and 3, which were denoted as Ni₁Ti₂, Ni₁Ti₁, Ni₂Ti₁ and Ni₃Ti₁. The salt solution and a urea solution (salt ions/urea = 3.3) were added to a beaker and stirred at 90 °C for 48 h. All the precipitates were centrifuged, washed, and dried at 70 °C for 24 h. The resulting precursors were calcined at 450 °C for 6 h to give the Ni-Ti-O mixed-oxide catalysts.

2.2. Catalyst tests

C₃H₆-SCR activity tests over the catalysts were carried out in a fixed-bed quartz reactor with an inner diameter of 6 mm, containing 0.2 g of catalyst. The feed gas compositions were 0.1% NO, 0.1% C₃H₆, and 10% O₂ in balance He. The total flow rate was 100 ml/min. The N₂ and C₃H₆ in the off-gas were detected by gas chromatography (Techcomp 7980II). The concentration of N₂ was analyzed using a 5A zeolite column with a thermal conductivity detector, and C₃H₆ was analyzed using a 6DX-104 column with a flame ionization detector. The concentrations of NO and NO₂ were determined using a Testo 350 gas analyzer. The N₂O yield was calculated as the NO conversion minus the N₂ and NO₂ yields.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns of the samples were obtained using a LabX-6000 X-ray powder diffractometer (Shimadzu) with a Cu K α radiation source (λ = 0.154056 nm) and 2 θ scan rate of 5°/min from 10°–80°. The Brunauer-Emmett-Teller (BET) surface areas and the Barrett-Joyner-Halenda pore diameters of the catalysts were determined using a NOVA 4200 automated gas sorption analyzer (Quantachrome) through the N₂ adsorption equilibria at –198 °C. The acidities of the catalysts were determined from chemisorbed pyridine using a Bruker VERTEX 70 Fourier-transform infrared (FTIR) spectrometer. The catalysts (0.02 g) were pressed into wafers and heated in a vacuum at 400 °C for 1 h. After the system had cooled to room temperature, the catalysts were saturated with pyridine vapor for 20 min and then stabilized for 30 min. The desorption of pyridine was carried out by evacuation at 200 °C, and FTIR spectra were recorded.

2.4. Temperature-programmed desorption (TPD) and in-situ FTIR

(NO + O₂)-TPD experiments were carried out in a fixed-bed reactor, and the effluent gases were detected using an on-line quadrupole mass spectrometer (Ametek, LC-D200M). Prior to the experiments, the catalysts (0.1 g) were pretreated in He at 250 °C for 1 h. After cooling to room temperature, the catalysts were treated in a flow of 0.25% NO + 25% O₂/He at 25 °C for 1 h and flushed with He for 1 h to remove physically adsorbed molecules. Finally, the TPD process was carried out at a heating rate of 10 °C/min up to 650 °C.

In-situ FTIR experiments were conducted using a VERTEX 70-FTIR spectrometer. Before performing the experiments, the catalysts (0.02 g pressed into wafers) were treated in He at 400 °C for 1 h. The total flow rate was 40 ml/min.

3. Results and discussion

3.1. Catalyst activity

The Ni-Ti-O mixed-oxide catalysts were tested in C₃H₆-SCR under lean-burn conditions; the results are shown in Fig. 1. The NO_x conversion increased with increasing reaction temperature to a maximum and then decreased, whereas C₃H₆ conversion increased until oxidation was complete. The reaction temperature of the maximum NO_x conversion was close to that for complete consumption of C₃H₆, indicating that the drop in NO_x conversion with increasing temperature could be caused by lack of reductant. The Ni₁Ti₁ catalyst displayed the optimal catalytic activity, i.e., the highest NO_x conversion, the best selectivity for N₂, and the largest operating-temperature window.

3.2. Catalyst characterization results

The XRD patterns of the catalysts are shown in Fig. 2. For the Ni₁Ti₂ and Ni₁Ti₁ catalysts, diffraction peaks at 2 θ $\approx$ 25.28°, 37.80°, 48.05°, 55.06°, 62.69°, 68.76° and 75.03°, attributed to anatase were detected. With increasing Ni content to Ni₂Ti₁ and Ni₃Ti₁, two additional peaks at 37.24° and 43.36° appeared. These were ascribed to nickel oxide and nickel titanate, respectively. These results imply that the Ni₂Ti₁ and Ni₃Ti₁ catalysts consist mainly of anatase and small amounts of nickel oxide and nickel titanate. It is noteworthy that anatase is the major

Fig. 1. Catalytic performance of Ni-Ti-O mixed-oxide catalysts for C₃H₆-SCR. Reaction conditions: 0.1% NO, 0.1% C₃H₆, 10% O₂ in balance He.

Fig. 2. XRD patterns of Ni-Ti-O mixed-oxide catalysts.

structure in these Ni-Ti-O mixed-oxide catalysts with continuously increasing amounts of Ni. This might be the result of trapping Ni atoms inside the anatase lattices and the formation of amorphous nickel oxide on the crystallite surfaces.

The BET surface areas and textural properties of the Ni-Ti-O mixed-oxide catalysts were evaluated using N_2 adsorption/desorption measurements; the results are listed in Table 1. As the Ni content increases, the surface area of the catalyst first increases and then decreases. The BET surface area of the Ni_2Ti_1 catalyst is the highest, namely $182 \text{ m}^2/\text{g}$. The average pore diameters of the four catalysts are slightly different from each other, and all the catalysts are mesoporous materials. The surface areas of the Ni-Ti-O mixed-oxide catalysts with an anatase crystalline phase are higher than that of commercial anatase ($47 \text{ m}^2/\text{g}$) [6]. These catalysts could therefore supply more available active binding/sorption sites, which is beneficial to catalytic reactions.

According to previous studies [4–9], the Lewis acidity plays an important role in SCR by hydrocarbons. Chemisorption of pyridine followed by FTIR spectroscopy was used to probe the nature of the surface acid sites on the Ni-Ti-O mixed-oxide catalysts; the results are displayed in Fig. 3. The concentrations of Lewis acid sites, Brønsted acid sites, and total acid sites are proportional to the strengths of the bands at 1448, 1540–1550, and 1490 cm^{-1} , respectively [10]. With increasing Ni content, the concentration of Lewis acid sites first increased and then decreased, whereas the concentrations of Brønsted acid sites and total acid sites decreased significantly. The results show that the concentration of Lewis acid sites is in line with the catalytic performance. This observation and our previous results certify that the Lewis acid sites are the adsorption sites for NO in C_3H_6 -SCR and are beneficial in enhancing the catalytic

Fig. 3. FTIR spectra of pyridine adsorbed on Ni-Ti-O mixed-oxide catalysts.

performance [9]. Furthermore, the catalytic performance is not improved by increasing the concentration of Brønsted acid sites. It can therefore be concluded that Lewis acid sites are favorable for the catalytic performance in C_3H_6 -SCR, but the role of Brønsted acid sites is not clear.

3.3. TPD and in-situ FTIR

(NO + O_2)-TPD experiments were carried out to further analyze the adsorptive properties of the Ni-Ti-O mixed-oxide catalysts. Figure 4 shows the TPD profiles in He over the Ni_1Ti_1 and Ni_3Ti_1 catalysts; these display the highest and lowest catalytic performance, respectively. The desorption product detected below 150°C is the result of physical adsorption [11], whereas the desorption species above 150°C are ascribed to

Fig. 4. (NO + O_2)-TPD profiles of Ni_3Ti_1 (a) and Ni_1Ti_1 (b) catalysts.

Table 1

Surface areas, pore volumes, average pore diameters, Ni contents, and selectivities for N_2 of Ni-Ti-O mixed-oxide catalysts.

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)	Ni content (wt%)	Selectivity for N_2 (%)
Ni_1Ti_2	149	0.30	3.44	2.33	69.73
Ni_1Ti_1	154	0.24	3.43	5.68	82.76
Ni_2Ti_1	182	0.31	3.42	24.80	73.04
Ni_3Ti_1	171	0.27	3.82	30.79	70.93

chemical adsorption. The chemical adsorption of reactant is the basis and the prerequisite of catalytic reaction. NO is the main chemical desorption product for the two catalysts. They both exhibit a broad and high strength peak in the range 200–400 °C. Desorbed O₂ displays a peak centered at 390 °C over the two catalysts. However, the amount of desorbed N₂O over the Ni₁Ti₁ catalyst is larger than that over the Ni₃Ti₁ catalyst, and the temperature window is broader. For the two catalysts, it is noteworthy that the desorption peaks of NO and O₂, centered at 390 °C, have similar shapes, but the amounts of these species over the Ni₁Ti₁ catalyst are larger. This desorption temperature is the optimal reaction temperature for C₃H₆-SCR, and the catalytic activity of the Ni₁Ti₁ catalyst is higher than that of Ni₃Ti₁. These results suggest that an adsorbed species contributing to the desorption of NO and O₂ is the intermediate for C₃H₆-SCR. The simultaneous desorption of NO and O₂ is caused by the adsorption nitrate (NO₃⁻) [12], which acts as an important intermediate species for C₃H₆-SCR.

To elucidate if the nitrate is the important intermediate of the reactivity, in-situ FTIR experiments were conducted to determine the adsorbed species and key species during the reaction. Figure 5(a) shows the in-situ FTIR spectra for adsorbed NO and O₂ over the Ni₃Ti₁ catalyst. The characteristic peaks at

1905 and 1845 cm⁻¹ arise from surface NO⁻. The bands at 1629 and 1602 cm⁻¹ are assigned to bidentate bridging nitrate. The peak at 1581 cm⁻¹ is attributed to monodentate nitrate. The bands at 1360–1390 cm⁻¹ are ascribed to nitrate anions (NO₃⁻)₂ [13–16]. The monodentate nitrate product decomposes gradually with time on stream, indicating that monodentate nitrate is unstable under the reaction conditions. In the case of the Ni₁Ti₁ catalyst (Fig. 5(c)), the same products are formed during the coadsorption process, except for the absence of monodentate nitrate. These nitrates are Lewis bases, which are electron donors. The Lewis acid sites are coordinatively unsaturated cationic metal sites, which are electron acceptors. The nitrates can therefore be adsorbed on the Lewis acid sites [12].

Switching the feed gas to C₃H₆ resulted in disappearance of the nitrates (Fig. 5 (b) and (d)), and formate (1377 and 1505 cm⁻¹) and adsorbed C₃H₆ (1505 cm⁻¹) were detected over the two catalysts. Moreover, acetate (1578 cm⁻¹) appeared over the Ni₃Ti₁ catalyst [16,17]. According to a previous study [17], surface NO⁻ cannot be reacted with catalyst directly, therefore the disappearance of surface NO⁻ might be caused by reaction of NO⁻ and O₂. The in-situ FTIR results show that the nitrate species are intermediates in C₃H₆-SCR over the Ni-Ti-O

Fig. 5. In-situ FTIR spectra over Ni₃Ti₁ (a, b) and Ni₁Ti₁ (c, d) mixed-oxide catalysts without (a, c) and with (b, d) exposure to 0.1% NO + 10% O₂ after switching to a flow of 0.1% C₃H₆ + 10% O₂.

Graphical Abstract

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Preparation and characterization of Ni-Ti-O mixed oxide for selective catalytic reduction of NO under lean-burn conditions

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A novel Ni-Ti-O mixed-oxide catalyst was used in the selective catalytic reduction of NO by C₃H₆ under lean-burn conditions; the catalyst demonstrated good activity at 430 °C.

mixed-oxide catalysts and can react with C₃H₆. Monodentate nitrate was produced over the Ni₃Ti₁ catalyst, occupying the adsorption sites and being decomposed in the presence of excess O₂, and it was not involved in the reaction of C₃H₆-SCR, so it might be the reason that the catalytic performance of Ni₃Ti₁ was lower than that of Ni₁Ti₁. To sum up, both the TPD and FTIR results show that nitrate species are key intermediates for C₃H₆-SCR.

4. Conclusions

A series of environmentally friendly Ni-Ti-O mixed-oxide catalysts were prepared using a co-precipitation method. The catalyst with Ni/Ti molar ratio of 1 exhibited good catalytic performance in C₃H₆-SCR at 430 °C; the NO_x conversion reached 68%. The catalyst structure changed with increasing Ni content in the catalysts, from an anatase structure to a mainly anatase structure with minor nickel oxide and nickel titanate phases. The catalysts had high surface areas (149–182 m²/g). The TPD and in-situ FTIR results clarified the SCR reaction mechanism over the Ni-Ti-O mixed-oxide catalysts. Nitrate is an important intermediate in SCR, and high surface areas and Lewis acid sites are beneficial to nitrate adsorption. This study broadens research on non-noble-metal-oxide catalysts for SCR of NO_x in the presence of excess O₂ and provides a theoretical foundation for the development of environmentally friendly deNO_x catalysts.

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Ni-Ti-O混合氧化物的制备、表征及其富氧选择性催化还原NO

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摘要: 采用均匀共沉淀法制备了不同Ni/Ti摩尔比的Ni-Ti-O混合氧化物, 考察了它们在富氧条件下丙烯选择性催化还原NO反应中的催化性能, 并运用X射线衍射、N₂吸附-脱附、吡啶吸附、程序升温脱附和原位红外光谱对催化剂进行了表征. 结果表明, Ni/Ti摩尔比为1的催化剂表现出最佳催化活性, 430 °C时NO_x转化率达68%. 该催化剂具有锐钛矿结构, 比表面积较高(149 m²/g), 有利于提高催化活性; 其表面Lewis酸性位有利于硝酸盐物种的吸附, 而硝酸盐物种是该反应的重要中间体.

关键词: 镍钛混合氧化物; 选择性催化还原; 一氧化氮; 程序升温脱附

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1. 前言

随着汽车工业的快速发展和机动车保有量的逐年增加,其排放的氮氧化物(NO_x)污染引起了人们的高度重视.高效的贫燃发动机能显著减少能源的消耗,有着广阔的应用前景^[1];但是,其排放的尾气中含有大量的 O_2 ,使得传统三效催化剂的催化活性大大降低^[2].因此,开发能够在富氧条件下有效去除 NO_x 的催化剂具有重要的理论和现实意义.

碳氢化合物选择性催化还原(SCR)技术被认为是消除机动车尾气排放NO最有效的方法之一^[3];该法无需额外添加还原剂,具有巨大的应用潜力.研究表明,Ni基催化剂对富氧条件下碳氢化合物SCR-NO反应表现出一定的活性^[4]; TiO_2 因其廉价低毒而被广泛地用作SCR催化剂载体^[5].因此,本文采用尿素均匀共沉淀法制备了Ni-Ti混合氧化物催化剂,考察它在富氧条件下丙烯-SCR NO反应中的催化性能,并探讨了催化剂性能与结构之间的关系.

2. 实验部分

2.1. 催化剂的制备

将一定量的 $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 和 $\text{Ti}(\text{SO}_4)_2$ 加入到去离子水中,搅拌溶解,配制成混合盐溶液;再将尿素加入到去离子水中,搅拌溶解,配制成尿素溶液.然后,将盐溶液和尿素溶液混合(金属盐离子/尿素的摩尔比为3.3)、搅拌,加热至90℃持续反应48 h,将离心分离所得沉淀物水洗,于70℃干燥24 h,450℃焙烧6 h,即得Ni-Ti-O混合氧化物催化剂,分别记为 Ni_1Ti_2 , Ni_1Ti_1 , Ni_2Ti_1 和 Ni_3Ti_1 ,相应的Ni/Ti摩尔比分别为0.5, 1, 2, 3.

2.2. 催化剂的评价

C_3H_6 -SCR NO反应活性测试在固定床石英反应器(直径6 mm)上进行.催化剂用量0.2 g.反应气成分为0.1% NO + 0.1% C_3H_6 + 10% O_2 + He(平衡气),流量100 ml/min.尾气中 N_2 和 C_3H_6 采用天美7980II气相色谱在线分析;其中 N_2 的测定采用5A分子筛色谱柱和TCD检测器, C_3H_6 的测定采用6DX-104色谱柱和FID检测器.NO和 NO_2 浓度测定采用Testo 350型化学传感器多组分气体分析仪. N_2O 收率由NO转化率减去 N_2 和 NO_2 收率而得.

2.3. 催化剂的表征

催化剂的XRD谱采用LabX-6000型X射线粉末衍射仪(日本岛津公司)测得Cu K_α 射线($\lambda = 0.15406$ nm),扫描范围 $10^\circ \sim 80^\circ$,扫描速度 $5^\circ/\text{min}$.催化剂的 N_2 吸附-脱附在

NOVA 4200e型气体吸附分析仪(美国康塔仪器公司)上进行,实验温度 -198°C .

催化剂的表面酸性使用吡啶吸附红外光谱(FTIR)检测,使用布鲁克公司VERTEX 70红外光谱仪测定,取0.02 g催化剂压成圆片,真空加热至400℃预处理1 h,降至室温后吸附吡啶20 min至饱和,再稳定30 min.最后,在200℃真空脱附吡啶并采集图谱.

2.4. 程序升温脱附(TPD)和原位FTIR测试

TPD实验在固定床反应器上进行,尾气采用阿美特克公司LC-D200M型质谱仪检测.取0.1 g催化剂在He气中于250℃预处理1 h,冷至室温后,将入口气氛换为0.25% NO + 25% O_2 + He(平衡气),于室温下处理1 h,再用He吹扫1 h以去除表面物理吸附物种.最后,在He以 $10^\circ\text{C}/\text{min}$ 升至650℃.原位FTIR实验在布鲁克公司VERTEX 70型红外光谱仪上进行,取0.02 g样品压成圆片,于400℃用He气预处理1 h.入口气体流量40 ml/min.

3. 结果与讨论

3.1. 催化剂活性评价

图1为Ni-Ti-O混合氧化物催化剂在富氧条件下 C_3H_6 -SCR的催化性能.由图可见,随着反应温度的升高, NO_x 转化率先增加至最大值后下降; C_3H_6 的转化率逐渐增加至100%,此时 NO_x 转化率达最大值.可见 NO_x 转化率的下降是由缺少还原剂所致.其中 Ni_1Ti_1 催化剂上最大 NO_x 转化率略高于其它催化剂,操作温度窗口最宽,且最大转化率时 N_2 的选择性最高(见表1).

3.2. 催化剂的表征结果

图2为各Ni-Ti-O催化剂的XRD谱.由图可见,各催化剂均在 $2\theta = 25.28^\circ, 37.80^\circ, 48.05^\circ, 55.06^\circ, 62.69^\circ, 68.76^\circ$ 和 75.03° 处出现衍射峰,对应于锐钛矿结构.其中Ni含量较高的 Ni_2Ti_1 和 Ni_3Ti_1 催化剂还在 2θ 为 37.24° 和 43.36° 处出现衍射峰,分别对应于氧化镍和钛酸镍,说明它们为以锐钛矿结构为主,且含有少量钛酸镍和氧化镍的混合结构.随着催化剂中Ni含量的增加,Ni不断团聚生成钛酸镍和氧化镍,但是最终产物结构主要是锐钛矿.这可能是由于这种均匀沉淀法导致镍进入了锐钛矿晶格内,或者以无定形的形式分散在晶体表面.

表1为各Ni-Ti-O混合氧化物催化剂的比表面积、孔体积和孔径.由表可见,随着Ni含量的增加,催化剂的比表面积先增大后减小,其中以 Ni_2Ti_1 催化剂的最大,为 $182\text{ m}^2/\text{g}$;四种催化剂的孔径变化很小,均属于介孔材

料. 由于Ni-Ti-O混合氧化物催化剂的主要晶相是锐钛矿, 而商品锐钛矿 TiO_2 比表面积为 $47 \text{ m}^2/\text{g}$ ^[6], 可见, 本文所制Ni-Ti-O混合氧化物具有较大的比表面积, 可以提供更多的吸附位, 有利于催化反应的进行.

研究表明, 催化剂表面酸性在碳氢化合物SCR NO反应中起到了重要作用. 本文采用吡啶作为探针检测催化剂的表面酸性, 结果如图3所示. 位于 1448 cm^{-1} 处红外峰强度对应于Lewis酸含量, $1540\sim 1550 \text{ cm}^{-1}$ 处峰强度对应Brönsted酸含量, 1490 cm^{-1} 处峰则对应催化剂表面总酸含量^[10]. 由图可以看出, 随着Ni含量的增加, 催化剂表面的Lewis酸量先增大后减小, Brönsted酸含量明显减小, 因此总酸含量呈现出明显下降的趋势. 其中, Lewis酸性位是 C_3H_6 -SCR NO的吸附位, 其含量与催化活性呈正相关性^[9]; 而Brönsted酸含量明显增加时, 催化活性未见明显提高. 这再一次说明, Lewis酸在富氧 C_3H_6 -SCR反应中有着重要的作用, 而Brönsted酸的作用尚不清楚.

3.3. TPD和原位FTIR结果

为了进一步考察Ni-Ti-O混合氧化物催化剂的吸附性能, 图4给出了催化活性最高和最低的 Ni_1Ti_1 和 Ni_3Ti_1 催化剂上共吸附NO和 O_2 后在He中的TPD谱. 当温度低于 150°C 时, 脱附物可认为是由物理吸附所致^[11]; 高于 150°C 时的脱附物则被认为是由化学吸附引起的. 反应物的化学吸附是催化反应的基础和前提. 由图可见, 两种催化剂的主要化学吸附的脱附物种是NO, 且均在 $200\sim 400^\circ\text{C}$ 时出现一个强度低且宽的 N_2 脱附峰, 390°C 时出现 O_2 的脱附峰, 其中 Ni_1Ti_1 催化剂上 N_2O 的脱附峰强度更高, 且温度窗口更宽. 值得注意的是, 在脱附温度为 390°C 时, 两种催化剂上同时出现了明显的NO和 O_2 脱附峰, 峰形相似, 但 Ni_1Ti_1 催化剂上NO和 O_2 的脱附量更大. 结合图1发现, NO和 O_2 同时脱附的温度是催化反应的最佳温度, 且 Ni_1Ti_1 催化剂的催化活性高于 Ni_3Ti_1 催化剂. 由此可见, 引起NO和 O_2 同时脱附的物种是 C_3H_6 -SCR NO反应的重要中间体. 研究表明^[12], NO和 O_2 的同时脱附是由吸附的硝酸盐引起的^[12], 后者是 C_3H_6 -SCR NO反应的重要中间体.

为了验证吸附的硝酸盐是否为反应的重要中间体,

图5(a)给出了 Ni_3Ti_1 氧化物催化剂共吸附NO和 O_2 的FTIR谱. 图中 1905 和 1845 cm^{-1} 处峰可归属为NO的气态吸附(NO^-); 1629 和 1602 cm^{-1} 处峰归属于二齿桥式硝酸盐; 1581 cm^{-1} 处峰可归属于单齿硝酸盐; $1360\sim 1390 \text{ cm}^{-1}$ 处峰则对应于离子态的硝酸盐(NO_3^-)^[13~16]. 由图可见, 单齿硝酸盐随吸附时间的延长而逐渐分解, 表明单齿硝酸盐在反应条件下不稳定. Ni_1Ti_1 催化剂(图5(c))上共吸附NO和 O_2 的产物与 Ni_3Ti_1 催化剂类似, 只是并未检测到单齿硝酸盐. 这些硝酸盐属于Lewis碱, 是电子供体. Lewis酸是由配位体中心的金属原子引起的, 是电子受体. 因此, 这些硝酸盐可以被吸附在Lewis酸位上^[12].

当入口处气体改为 C_3H_6 (见图5(b)和(d)), 两种催化剂上硝酸盐的谱峰逐渐消失, 同时生成甲酸盐(1377 和 1505 cm^{-1})和吸附态 C_3H_6 (1505 cm^{-1}), 在 Ni_3Ti_1 催化剂上还检测到了乙酸盐(1578 cm^{-1})^[16,17]. 由于气态吸附的 NO^- 不能直接反应, NO^- 吸收峰的逐渐消失可能是 NO^- 与 O_2 反应所致. 上述结果表明, 在富氧条件下NO在Ni-Ti-O混合氧化物催化剂表面上生成了硝酸(二齿桥式和离子态硝酸盐), 它们是SCR反应的中间体, 可以和氧化的 C_3H_6 发生反应. 在 Ni_3Ti_1 催化剂上还生成了单齿硝酸盐, 此物种占据了催化剂的吸附位, 在富氧条件下会发生分解, 并未参与 C_3H_6 -SCR反应. 这也可能是 Ni_3Ti_1 催化活性低于 Ni_1Ti_1 的原因. TPD和原位FTIR结果均说明, 硝酸盐是 C_3H_6 -SCR反应的重要中间体.

4. 结论

采用均匀共沉淀法制备了一系列环境友好型的Ni-Ti-O氧化物催化剂. 其中 Ni_1Ti_1 催化剂在 430°C 表现出最佳的 C_3H_6 -SCR NO性能, NO_x 转化率达68%. 随着Ni含量的增加, 催化剂中除锐钛矿为主外, 还含有少量氧化镍和钛酸镍的混合结构, 这些催化剂表现出较高的比表面积. TPD和原位FTIR结果很好地说明了Ni-Ti-O氧化物催化剂上选择性催化还原的反应机理, 硝酸盐是反应的重要中间体, 高的比表面积和较多的表面Lewis酸位均有利于硝酸盐的吸附. 该结果拓宽了非贵金属氧化物催化剂用于富氧条件下尾气脱硝的思路, 为进一步开发高效的环境友好型脱硝催化剂提供了理论依据.