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In situ IR studies of selective catalytic reduction of NO with NH₃ on Ce-Ti amorphous oxides

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ABSTRACT

A series of in situ infrared (IR) studies of the selective catalytic reduction (SCR) of NO_x with NH₃ on the short-range ordered structure Ce–O–Ti sites in amorphous Ce–Ti mixed oxides were performed. Under the reaction conditions, the catalyst surface was mainly covered by NH₃ ad-species and no NO_x ad-species were detected. The reaction order of 0.5–0.6 with respect to NO confirmed a hybrid Langmuir–Hinshelwood and Eley–Rideal mechanism. A possible route may involve the reaction of NH₃ ad-species and weakly adsorbed NO_x to form an active intermediate, NH₃NO₃ ($\gamma = 0-4$); this was confirmed by GAUSSIAN calculations and the in situ IR results. The Ce–O–Ti structure, with Ce–Ti interactions on the atomic scale, enhanced the redox properties in the active temperature window of the SCR reactions.

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1. Introduction

Selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with NH₃ is not only an important heterogeneous catalytic reaction, but also has immediate practical significance for the control of NO_x, an atmospheric pollutant that contributes to acid rain, photochemical smog, and the depletion of tropospheric ozone [1]. The commercial V₂O₅–WO₃(MoO₃)/TiO₂ (VWTiO₂) catalyst causes problems, because of the toxicity of vanadium, high activity in the oxidation of SO₂ to SO₃, and a relatively narrow temperature window of 300–400 °C [2]. Con-

tinuing efforts are therefore being made to develop new catalytic systems.

A comprehensive overview of the NH₃–SCR reaction mechanism shows that both surface acidity and redox properties are necessary [1,3]. This strategy has been used to develop many new catalysts [4–9]. Recently, Ce-based catalysts, particularly Ce–Ti mixed oxides, have been receiving much attention [10–18]. However, little has been reported on the reaction mechanism and kinetics.

The SCR reaction mechanism is often studied using in situ infrared (IR) spectroscopy. Regardless of the catalyst used, the

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rate constant for evaluating the activity is often assigned based on the hypothesis that the SCR reaction is approximately first order with respect to NO [8,19]. Kinetic data need to be obtained to determine the validity of this assumption.

In VWTiO₂ systems, the active acid sites (V–OH) and redox sites (V=O) are separate on the catalyst surface [3]. However, if they are combined, synergism provides more efficient catalysis. Previously, we proposed that the short-range ordered structures in the amorphous phase could be good candidates for this. In our previous work, this was achieved by forming Ce–O–Ti species with Ce–Ti interactions on the atomic scale [20]. In the present work, further mechanistic aspects are investigated using in situ IR absorption/reaction spectra and kinetic data.

2. Experimental

2.1. Catalyst preparation

A series of Ce–Ti mixed oxides with different molar ratios of Ce and Ti were prepared using a co-precipitation method [20]; these are denoted by Ce_aTiO_x, where *a* represents the Ce/Ti atomic ratio and equals 0.3, 0.5, or 0.7. For comparison, CeO₂ and TiO₂ were also prepared.

2.2. Catalyst test

A fixed-bed U-shaped quartz reactor (ID = 6 mm) with a thermocouple placed inside the catalyst was used for kinetic reaction measurements under atmospheric conditions. A model flue gas consisting of 0.05% NO, 0.05% NH₃, and 5.3 vol% O₂ in He at 300 mL min^{−1}, and a gas hourly space velocity (GHSV) of 100000 h^{−1} was used. In order to ensure that only the intrinsic SCR reactions are in the kinetic regime, a series of experiments were performed to exclude internal and external diffusion and heat transfer effects. We found that there were no intraparticle mass transport limitations when the diameter was below 100–200 mesh. For a total flow rate of 300 mL min^{−1}, no external mass transport limitations were detected. When the conversion of NO_x was lower than 20%, there was no increase in the temperature of the catalyst bed. The concentrations of NO and NO₂ were monitored using a chemiluminescence NO_x analyzer (42i-HL, Thermo). N₂O and NH₃ were detected using a Fourier-transform IR spectrometer (Tensor 27, Bruker) with a gas cell with a 2.4 m optical path.

2.3. Catalyst characterization

In situ X-ray diffraction (XRD) patterns were collected at the XRD station of the Beijing Synchrotron Radiation Facility, using a curved image plate detector with an angle accuracy of 0.01° and an X-ray wavelength of 1.38 Å, in transmission mode. Temperature-programmed reduction with H₂ (H₂-TPR) experiments were performed in a quartz reactor with a thermal conductivity detector to monitor the H₂ consumed. A 50 mg sample was pretreated in situ at 500 °C for 1 h in a flow of O₂, and cooled to room temperature in the presence of O₂. H₂-TPR

experiments were conducted at 10 °C min^{−1} up to 900 °C in a 30 mL min^{−1} flow of 5 vol% H₂ in N₂. To quantify the total amount of H₂ consumed, CuO was used as a calibration reference. The temperature-programmed desorption of NH₃ (NH₃-TPD) experiments were performed in a quartz reactor using 50 mg catalyst. NH₃ was monitored using quadrupole mass spectrometer (MS; OmniStar 200, Balzers) with *m/z* = 16. Prior to the experiments, the samples were pretreated at 500 °C for 30 min in 10 vol% O₂/He (50 mL min^{−1}) and cooled to 100 °C. NH₃ adsorption was operated in 0.4% NH₃ (50 mL min^{−1}) until the outlet NH₃ concentration was stable. Then, the samples were purged with He to remove any weakly absorbed NH₃. Finally, the samples were heated to 700 °C at a ramping rate of 10 °C min^{−1}.

In situ IR spectra were recorded using a Bruker Tensor 27 spectrometer over the range 400–4000 cm^{−1}, with 16 scans, at a resolution of 4 cm^{−1}. Self-supporting wafers were pretreated in the IR cell at 500 °C in a flow of He for 30 min to remove any adsorbed species. After cooling to 100 °C, the background spectrum was recorded. Adsorption/reaction spectra were then recorded at the desired temperatures, as indicated in the figure captions. Because Ce_{0.7}TiO_x was difficult to mold, an approximately double-mass sample, compared to Ce_{0.3}TiO_x and Ce_{0.5}TiO_x, was pelletized and then used in the in situ IR experiments. In some cases, the effluents from the in situ IR cell were also monitored, using a quadrupole mass spectrometer (MS; OmniStar 200, Balzers) with *m/z* values of 28 for N₂, 17 for NH₃, 30 for NO, and 46 for NO₂.

2.4. Theoretical calculation

The GAUSSIAN 09 program was used to optimize the structures and calculate the vibrational wavenumbers for the N_xH_yO_z intermediate on Ce_aTiO_x. The 6–311++G** basis set was used to perform the DFT-B3PW91 calculations (Becke's three-parameter functional with the non-local correlation provided by the Perdew 91 expression).

3. Results and discussion

Our previous work [20] and in situ synchrotron-radiation XRD patterns (Fig. 1) show an amorphous structure and the presence of possible short-range ordered structures of Ce–O–Ti and Ti–O–Ti in Ce_{0.3}TiO_x, Ce–O–Ti in Ce_{0.5}TiO_x, and Ce–O–Ti and Ce–O–Ce in Ce_{0.7}TiO_x calcined at 500 °C, in accordance with the fact that the Ce/Ti atomic ratios are less than, equal to, and more than the stoichiometry of CeTi₂O₆.

Fig. 2 shows NH₃-TPD curves on TiO₂, CeO₂, and Ce_aTiO_x adsorbed at 100 °C after purging with He, and the corresponding IR spectra are shown in Fig. 3. NH₃ desorption on CeO₂ is negligible. However, TiO₂ and Ce_aTiO_x show broad NH₃ desorption peaks between about 100 and 500 °C. NH₃ adsorption species on Brønsted acid sites derived from residual sulfate from the precursor Ti(SO₄)₂ were not observed [18,21]. TiO₂ has only surface Lewis acid sites [22], and no NH₄⁺ species can be formed on CeO₂ [23], therefore the common bands at 1440 and 1670 cm^{−1} for Ce_aTiO_x can be assigned to NH₄⁺ on Ce–O–Ti

Fig. 1. In situ heating XRD patterns for Ce_aTiO_x . (a) $\text{Ce}_{0.3}\text{TiO}_x$; (b) $\text{Ce}_{0.5}\text{TiO}_x$; (c) $\text{Ce}_{0.7}\text{TiO}_x$.

Fig. 2. NH_3 -TPD curves of TiO_2 , CeO_2 , and Ce_aTiO_x .

Brönsted acid sites, and the bands at 1310, 1292, and 1297 cm^{-1} arise from coordinated NH_3 on Ce–O–Ti Lewis acid sites (Table 1). The bands at 1600 and 1176 cm^{-1} were only observed for $\text{Ce}_{0.3}\text{TiO}_x$ and TiO_2 , and are assigned to coordinated NH_3 on Ti–O–Ti Lewis acid sites. The present results indicate that there were more Brönsted acid sites than Lewis acid sites on the Ce–O–Ti structure at 100 °C. With increasing tempera-

ture, the band at 1440 cm^{-1} gradually weakened and eventually disappeared at 250, 350, and 400 °C for $\text{Ce}_{0.3}\text{TiO}_x$, $\text{Ce}_{0.5}\text{TiO}_x$, and $\text{Ce}_{0.7}\text{TiO}_x$, respectively. Simultaneously, the bands for Lewis acid sites shifted to higher wavenumbers, eventually reaching 1350 cm^{-1} at 450 °C for all Ce_aTiO_x samples.

Figure 4 shows a series of IR spectra of $\text{NO} + \text{O}_2$ adsorbed on Ce_aTiO_x at different temperatures. At 100 °C, strong IR bands were observed at 1617, 1555, and either 1235, 1285, or 1297 cm^{-1} . The first band is attributed to an NO_2 ad-species (nitro group or adsorbed NO_2 molecule) on Ce–O–Ti sites, because it did not disappear after purging with He for 30 min (Fig. 5), the second corresponds to bidentate nitrate, and the last three correspond to bridge-bound nitrites/nitrates on Ce–O–Ti sites. The band at 1576 cm^{-1} was only observed for $\text{Ce}_{0.3}\text{TiO}_x$ and is assigned to bidentate nitrate on Ti–O–Ti sites. With increasing temperature, these bands vanished and a new band at about 1360 cm^{-1} was formed at 450 °C for all Ce_aTiO_x samples.

Figure 6 shows IR spectra of the reaction between $\text{NO} + \text{O}_2$ and NH_3 ad-species at 100 °C. For $\text{Ce}_{0.3}\text{TiO}_x$, both NH_4^+ and coordinated NH_3 species disappeared from the surface after $\text{NO} + \text{O}_2$ was passed over the sample for 15 min (Fig. 6(a)). In addition, the disappearance of coordinated NH_3 on Ti–O–Ti

Fig. 3. In situ IR spectra of NH_3 adsorbed on Ce_aTiO_x as a function of temperature.

Table 1

IR bands and assignments.

IR bands (cm ⁻¹)	Assignments	References
1440 (1420), 1665 (1670, 1680)	Asymmetric and symmetric bending vibrations of NH ₄ ⁺ on Brönsted acid sites	[3]
1600 (1593), 1176 (1168, 1150, 1200)	Asymmetric and symmetric bending of the NH bonds in coordinated NH ₃ on Ti–O–Ti Lewis acid sites	[24]
1310 (1300, 1297), 1260 (1250)	Coordinated NH ₃ on Ce–O–Ti Lewis acid sites	[24]
1166, 1090, 1020	Monodentate nitrite (ν(NO))	[25]
3667, 3670, 3645	The hydroxyl consumption through interaction with NH ₃ to form NH ₄ ⁺	
3150–3400	NH stretching vibration	[26]
1350 (1352, 1353)	Partially oxidized NH ₃ ad-species (monodentate nitrite species or nitro compounds) on Ce–O–Ti sites, for instance, N _x H _y O _z	[26,27]
1906, 1850	Gaseous or weakly adsorbed NO	[26]
1617, 1630	NO ₂ ad-species	[24,26]
1270 (1280, 1290)	Monodentate nitrate	[28]
1576, 1555 (1550, 1540)	Bidentate nitrate	[27]
1513, 1525	–NH ₂	[29]

Fig. 4. In situ IR spectra of NO + O₂ adsorbed on Ce_xTiO_x as a function of temperature.

Lewis acid sites (1176 and 1600 cm⁻¹) indicates that the Ti–O–Ti structure (TiO₂) is capable of carrying out the reduction of NO by NH₃; however, this is not a catalytic reaction, because TiO₂ does not show any catalytic activity at this temperature [20,30]. For Ce_{0.5}TiO_x, the reaction between NO + O₂ and NH₃ ad-species requires about 45 min (Fig. 6(b)). However, this

Fig. 5. In situ IR spectra of NO + O₂ adsorption on Ce_xTiO_x at 100 °C for 30 min, followed by purging with He for 30 min.

reaction was incomplete even after 70 min for Ce_{0.7}TiO_x. These results suggest that (1) NH₄⁺ ions and coordinated NH₃ on the Ce–O–Ti structure are both active in SCR reactions and (2) the activity order is Ce_{0.3}TiO_x > Ce_{0.5}TiO_x > Ce_{0.7}TiO_x.

Figure 7 shows IR spectra of the reaction between NH₃ and NO + O₂ ad-species at 100 °C. After NH₃ introduction into the cell for 2–3 min, the intensities of the IR bands from NO₂ ad-species at 1617 cm⁻¹ and nitrate species quickly decreased, corresponding to the formation of N₂, as observed by on-line MS. This indicated that NO_x ad-species had reacted with NH₃. IR bands attributed to NH₄⁺ ions and coordinated NH₃ on the Ce–O–Ti structure were formed.

Figure 8 shows IR spectra of Ce_xTiO_x in a flow of NO + NH₃ + O₂. At 100 °C, the surface was covered mainly by NH₄⁺ ions in comparison with those in Fig. 5. Raising the temperature resulted in a decrease in the intensity of the peak from NH₄⁺ ions, which finally vanished at 250, 350, and 400 °C for Ce_{0.3}TiO_x, Ce_{0.5}TiO_x, and Ce_{0.7}TiO_x, respectively. For coordinated NH₃ species, the IR bands shifted gradually to about 1350 cm⁻¹ at 450 °C, similar to those obtained in Fig. 3 and those obtained in the adsorption of NO + O₂, which are always in the range 1355–1361 cm⁻¹ from a low temperature to 450 °C (Fig. 4). This suggests that the coordinated NH₃ species are similar to the monodentate nitrite species or nitro compounds on

Fig. 7. In situ IR spectra of surface reactions on Ce_aTiO_x between pre-adsorbed $\text{NO} + \text{O}_2$ and NH_3 .

As shown in our previous work, the order of catalytic activ-

ity in NO_x conversion is Ce_{0.3}TiO_x > Ce_{0.5}TiO_x > Ce_{0.7}TiO_x [20], which is the same as that for the decrease in $T_{\max}$ (the peak temperature for H₂ consumption) in H₂-TPR ($T_{\max}$ and the amount of H₂ consumed for Ce_{0.7}TiO_x are 710 °C and 906 μmol g⁻¹, respectively). This confirms the indispensable role of the catalyst redox properties, which catalyze NO oxidation to NO_x ad-species. As can be seen from Fig. 4, the oxidation activity follows the same order as the NO_x conversion and H₂-TPR properties. This has been confirmed to be derived from the

Fig. 8. In situ IR spectra of NO + NH₃ + O₂ reactions on Ce_aTiO_x. 0.05% NO + 0.05% NH₃ + 5.3 vol% O₂ + He, total flow 120 mL min⁻¹.

formation of Ce–O–Ti short-range ordered structures with Ce–Ti interaction on the atomic scale. The reducibility plays a key role in NH₃ activation and NO oxidation [31,32].

Steady-state kinetic studies were performed to determine the reaction mechanism. A large excess of O₂ was used, therefore the reaction order with respect to O₂ is assumed to be 1. The strong adsorption of NH₃ (Fig. 8) indicates a zero-order reaction with respect to NH₃. The kinetic reaction rate of NO_x conversion as a function of reactant concentrations can be ex-

Fig. 9. Reaction orders with respect to NO for Ce_aTiO_x. Reaction conditions: 0.02–0.1% NO + 0.1% NH₃ + 5.3 vol% O₂ + He, total flow 300 mL min⁻¹, GHSV 100000 h⁻¹, reaction temperature 160 °C.

pressed as $r_{\text{NO conv.}} = k[\text{NO}]^x$. The reaction orders with respect to NO were calculated to be 0.67, 0.58, and 0.67 for Ce_{0.3}TiO_x, Ce_{0.5}TiO_x, and Ce_{0.7}TiO_x, respectively (Fig. 9). All of these values are less than 1, suggesting that the SCR reaction involves both the Langmuir–Hinshelwood (LH) and ER pathways [33]. This is commonly observed for low-temperature SCR oxide catalysts [19]. However, as shown in Fig. 8, no NO_x ad-species were detected. The IR spectra were very similar to the NH₃ adsorption curves, even though NO_x adsorption did take place in the NO + O₂ flow without NH₃ (Fig. 4). This strongly suggests that the activity of the reaction between NH₃ and NO_x ad-species is much higher than that between NO + O₂ and NH₃ ad-species; this is confirmed by the IR spectra of the two reactions (Fig. 6 vs Fig. 7). The pathway possibly involves the reaction of NH₃ ad-species and weakly adsorbed NO_x. A similar mechanism on CeO₂/TiO₂ and its W-doped analog has been observed [26].

Possible structures of N_xH_yO_z were determined using the GAUSSIAN program [34]. As shown in Table 2, the calculated NO stretching frequency is 1359 cm⁻¹, which is close to the experimental data in Fig. 3 (1352, 1353, and 1346 cm⁻¹), Fig. 4

Table 2

Structure and calculated vibrational frequencies and intensities of N_xH_yO_z.

Formula	Structure	NO stretching vibration frequency ^a (cm ⁻¹)
N ₂ HO ₃		1342 (170)
N ₃ H ₂ O ₃		1360 (231)
N ₃ HO ₄		1353 (523)
N ₂ H ₄ O ₃ (NH ₄ NO ₃)		1359 (390); 1535 ^b (358)

^a Data in parentheses represent intensity (km mol⁻¹).

^b NH₄⁺ bending vibration.

Graphical Abstract

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In situ IR studies of selective catalytic reduction of NO with NH₃ on Ce-Ti amorphous oxides

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The selective catalytic reduction of NO_x with NH₃ on a short-range ordered Ce–O–Ti structure was confirmed to involve the reaction of NH₃ ad-species, and weakly adsorbed NO_x to form an intermediate, NH_yNO₃ ($y = 0-4$).

(1356, 1361, and 1357 cm⁻¹), and Fig. 8 (1352, 1353, and 1350 cm⁻¹). A specific compound, NH₄NO₃, has been identified as an intermediate by many researchers [35]. Furthermore, the NH₃ bending vibration at 1535 cm⁻¹ is close to those observed in Fig. 6 (1522 cm⁻¹), Fig. 7 (1520 cm⁻¹), and Fig. 8 (1535 cm⁻¹). It is deduced that NH_yNO₃ is one of the most probable intermediates in the present case. As shown in Figs. 3 and 8, below temperatures at which NH₄⁺ species (1440 cm⁻¹) existed (~250, ~350, and ~400 °C for Ce_{0.3}TiO_x, Ce_{0.5}TiO_x, and Ce_{0.7}TiO_x, respectively), $y \leq 4$. With increasing temperature, y gradually decreases, even reaching 0, because no NH₃ can be desorbed above ~450°C (Fig. 2), i.e., the oxidation of NH₃ to nitrites/nitrate species is predominant (Figs. 3 and 4). This corresponds to a decrease in NO_x conversion to N₂.

4. Conclusions

On Ce-Ti amorphous oxides, Ce–O–Ti short-range ordered structures with Ce–Ti interactions on the atomic scale enhanced NO oxidation and NH₃ activation. Under these reaction conditions, the catalyst surface was mainly covered by NH₃ ad-species, and no NO_x ad-species were detected. The reaction order with respect to NO was calculated to be 0.5–0.6, supporting a hybrid LH and ER mechanism. A possible route involves the reaction of NH₃ ad-species and weakly adsorbed NO_x to form an active intermediate, NH_yNO₃ ($y = 0-4$); this was confirmed by GAUSSIAN calculations and in situ IR data.

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非晶Ce-Ti氧化物用于NH₃选择性催化还原NO的原位红外研究

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摘要: 采用原位红外光谱研究了在具有短程有序Ce-O-Ti结构的非晶Ce-Ti氧化物上NH₃选择性催化还原(SCR) NO_x反应. 在反应条件下, 催化剂表面主要被NH₃吸附物种覆盖, 而检测不到NO_x吸附物种. 经测定, NO的反应级数为0.5–0.6, 表明Langmuir-Hinshelwood机理和Eley-Rideal机理同时存在. 可能的机理是NH₃吸附物种和弱吸附的NO_x反应, 生成NH₃NO₃ ($\gamma = 0-4$)活性中间物种, 并通过GAUSSIAN计算和原位红外结果证实了它们的存在. Ce-O-Ti结构中Ce与Ti之间表现出原子尺度的相互作用, 所以在SCR反应的活性温度窗口下, 催化剂的氧化还原活性提高.

关键词: 选择性催化还原; 一氧化氮; 氨气; 非晶Ce-Ti氧化物; 原位红外; 机理

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1. 前言

氮氧化物(NO_x)的危害很大, 可产生酸雨、光化学烟雾和臭氧层空洞等, 氨气选择性催化还原(NH₃-SCR)技术是有效控制NO_x的重要手段^[1]. 商用V₂O₅-WO₃(MoO₃)/TiO₂(VWTiO₂)催化剂中的钒具有毒性, 其催化氧化SO₂为SO₃的活性过高, 活性温度窗口也比较窄(300–400 °C)^[2]. 因此, 需要努力开发新型催化剂体系.

NH₃-SCR反应机理研究表明催化剂的表面酸性和氧化还原性对反应性能影响很大^[1,3]. 据此开发了许多新型催化剂^[4–9]. 最近, Ce基催化剂, 尤其是Ce-Ti复合氧化物受到极大关注^[10–18]. 但对反应机理和动力学的报道相对较少.

文献中通常采用原位红外(in situ IR)技术来研究SCR的反应机理. 但是, 不论选用何种催化剂, 用于评价活性的速率常数都是基于SCR反应对NO的级数接近于1的假设^[8,19]. 因此, 需要提供动力学数据来证实这种假设.

对于VWTiO₂体系, 催化剂上的活性酸性位(V-OH)和氧化还原位(V=O)是独立的^[3]. 但是如果能将它们统一到一起, 协同效应将会更加显著. 我们曾通过形成Ce-O-Ti物种, 使得Ce与Ti之间存在原子尺度的相互作用, 从而在非晶相中形成短程有序结构, 可导致上述效应增强^[20]. 本文采用in situ IR吸附/反应光谱和动力学数据进一步对反应机理进行了研究.

2. 实验部分

2.1. 催化剂制备

采用共沉淀法制备了一系列不同Ce/Ti摩尔比的铈钛复合氧化物^[20], 将它们标记为Ce_aTiO_x, 其中 a 表示Ce/Ti原子比, 分别为0.3, 0.5和0.7. 为了比较, 同法制备了CeO₂和TiO₂.

2.2. 催化剂测试

动力学反应测试在常压固定床U形石英管反应器上进行. 催化剂置于内径为6 mm的反应管中, 并插入热电偶测量催化剂温度. 模拟烟气总流量为300 mL min⁻¹, 其中含有0.05% NO, 0.05% NH₃, 5.3 vol% O₂, He为平衡气, 体积空速(GHSV)为100000 h⁻¹. 为了确保SCR本征反应在动力学模式下进行, 我们进行了一系列的实验以排除内扩散、外扩散和传热因素的影响. 发现当催化剂粒径低于100–200目时, 颗粒内部质量传递不受限制. 反应气流量达到300 mL min⁻¹时, 外部的质量传递不受限制. 当NO_x的转化率低于20%时, 催化剂床层温度没有明显的升高. NO和NO₂的浓度通过化学发光NO_x分析仪(42i-HL, Thermo)检测. N₂O和NH₃通过傅里叶变换红外(FTIR)光谱仪(Tensor 27, Bruker)进行检测, 其中气体池的光路长度为2.4 m.

2.3. 催化剂表征

原位XRD测试在北京同步辐射装置的XRD站上进行, 采用弯曲的图像板检测器, 测角精度为0.01°, X射线波长为1.38 Å, 测试在透射模式下进行. 氢气程序升温还原(H₂-TPR)实验在石英管反应器中进行, TCD检测氢

气消耗. 样品用量为50 mg, 在O₂气氛下500 °C原位预处理1 h, 然后在O₂气氛下降至室温. 然后切换为5% H₂/N₂混合气(30 mL min⁻¹), 以10 °C min⁻¹升至900 °C. 采用CuO为标准样对样品的耗氢量进行定量计算. 氨气程序升温脱附实验(NH₃-TPD)在石英管反应器中进行, 催化剂用量为50 mg. 利用瑞士BALZERS公司生产的Omnistar质谱仪检测NH₃的浓度, 核质比采用16. 实验前, 将样品在10 vol% O₂/He (50 mL min⁻¹)中500 °C预处理30 min. 预处理结束后, 降温至100 °C, 通入0.4%的NH₃ (50 mL min⁻¹)进行吸附. 待吸附饱和后, 通入高纯氦气吹扫至质谱信号稳定. 最后, 以10 °C min⁻¹升至700 °C进行脱附.

In situ IR实验在美国Bruker公司Tensor 27红外光谱仪上进行, 扫描范围为400–4000 cm⁻¹, 扫描次数为16次, 分辨率为4 cm⁻¹. 自支撑片在红外池中500 °C下He气氛下预处理30 min以除去吸附物种. 然后降至100 °C并录背景谱, 在给定温度下记录吸附/反应光谱. 由于Ce_{0.7}TiO_x难以压片, 因而其用量约为Ce_{0.3}TiO_x或Ce_{0.5}TiO_x的两倍. 某些情况下, 原位红外池中排出的气体也通过四极质谱(MS, OmniStar 200, Balzers)进行检测, 其中N₂, NH₃, NO和NO₂的*m/z*分别为28, 17, 30和46.

2.4. 理论计算

使用GAUSSIAN 09程序优化Ce_aTiO_x中N_xH_yO_z中间物种的结构, 并计算其振动波数. 采用密度泛函理论B3PW91方法(Becke三参数混合泛函, 非局域相关泛函由Perdew 91提供), 6-311++G**基组进行计算.

3. 结果与讨论

前期工作^[20]和原位同步辐射XRD (图1)结果表明: 500 °C焙烧时, 催化剂为非晶结构, 其中可能含有短程有序的结构, Ce_{0.3}TiO_x中为Ce–O–Ti和Ti–O–Ti, Ce_{0.5}TiO_x中为Ce–O–Ti, Ce_{0.7}TiO_x中为Ce–O–Ti和Ce–O–Ce. 这与样品中的Ce/Ti原子比是一致的, 三种样品的Ce/Ti原子比分别小于、等于和大于CeTi₂O₆的化学计量比.

图2为TiO₂, CeO₂和Ce_aTiO_x上100 °C吸附NH₃并用He吹扫后的程序升温脱附(TPD)谱图, 相应的随温度变化的NH₃的IR谱见图3. 可以看出, CeO₂上几无NH₃的脱附, 而TiO₂和Ce_aTiO_x在100–500 °C范围内出现一个宽的NH₃脱附峰. 实验中并没有观察到可能由于制备过程中Ti(SO₄)₂前驱体残留的硫酸盐而导致的Brönsted酸性位上的NH₃吸附物种^[18,21]. 由于TiO₂仅

含有表面Lewis酸性位^[22], CeO₂上也没有生成NH₄⁺物种^[23], 所以可将Ce_aTiO_x上的1440和1670 cm⁻¹的峰归属于Ce–O–Ti中Brönsted酸性位上的NH₄⁺物种, 而1310, 1292和1297 cm⁻¹的峰归属于Ce–O–Ti中Lewis酸性位上的配位态NH₃物种(表1). 仅在Ce_{0.3}TiO_x和TiO₂样品上观测到了1600和1176 cm⁻¹的峰, 将其归属于Ti–O–Ti中Lewis酸性位上的配位态NH₃物种. 结果表明: 在Ce–O–Ti结构中, 100 °C时Brönsted酸性位比Lewis酸性位更多. Ce_{0.3}TiO_x, Ce_{0.5}TiO_x和Ce_{0.7}TiO_x样品上, 随着温度的升高, 1440 cm⁻¹处的峰逐渐弱化, 并分别于250, 350和400 °C时最终消失. 同时对于所有的Ce_aTiO_x样品, Lewis酸性位上的峰逐渐向高波数移动, 450 °C时最终移动至1350 cm⁻¹处.

图4给出了Ce_aTiO_x在不同温度下吸附NO + O₂的IR谱. 100 °C时, 观测到了1617, 1555和1235/1285/1297 cm⁻¹处的强峰. 第一个峰在He气氛下吹扫30 min后仍不消失(图5), 将其归属于Ce–O–Ti位上的NO₂吸附物种(硝基或吸附态NO₂分子), 第二个峰对应着双齿硝酸盐, 最后三个峰归属于Ce–O–Ti位上的桥式键合的亚硝酸盐或硝酸盐物种. 在Ce_{0.3}TiO_x上仅观测到了1576 cm⁻¹处的峰, 将其归属于Ti–O–Ti位上的双齿硝酸盐. 对于所有的Ce_aTiO_x样品, 随着温度的升高, 这些峰都逐渐消失, 并在450 °C时于1360 cm⁻¹处出现了一个新峰.

图6为NO + O₂与NH₃吸附物种在100 °C下反应的IR谱. 对于Ce_{0.3}TiO_x, NO + O₂通入后15 min, 表面上的NH₄⁺物种和配位态的NH₃物种均消失(图6(a)). 另外, Ti–O–Ti中Lewis酸性位上配位态NH₃物种(1176和1600 cm⁻¹)消失, 表明Ti–O–Ti结构(TiO₂)上NH₃可以还原NO. 但是, TiO₂在此温度下没有催化活性^[20,30], 所以认为该过程并不是催化过程. 对于Ce_{0.5}TiO_x, NO + O₂与NH₃吸附物种的反应需要大约45 min (图6(b)). 但是对于Ce_{0.7}TiO_x, 反应进行70 min后仍未结束. 这些结果表明: (1)在SCR反应过程中, Ce–O–Ti结构上的NH₄⁺离子和配位态的NH₃均具有活性; (2)活性顺序为Ce_{0.3}TiO_x > Ce_{0.5}TiO_x > Ce_{0.7}TiO_x.

图7为100 °C下NH₃与NO + O₂吸附物种反应的IR谱. NH₃通入红外池2–3 min后, NO₂吸附物种(1617 cm⁻¹)和硝酸盐物种的红外峰迅速减弱, 同时对应着N₂的生成(通过在线质谱检测). 这表明NO_x吸附物种与NH₃进行了反应. 同时, Ce–O–Ti结构上出现了属于NH₄⁺离子和配位态NH₃的红外峰.

图8为Ce_aTiO_x上NO + NH₃ + O₂气氛下的IR谱.

100 °C时, 与图5相比, 发现 Ce_aTiO_x 表面主要被 NH_4^+ 离子覆盖; 提高温度导致该离子峰强度降低, 在 $\text{Ce}_{0.3}\text{TiO}_x$, $\text{Ce}_{0.5}\text{TiO}_x$ 和 $\text{Ce}_{0.7}\text{TiO}_x$ 上, 此峰分别于250, 350和400 °C时最终消失. 对于配位态 NH_3 物种, 红外峰逐渐移至约 1350 cm^{-1} 处(450 °C), 与 NH_3 -TPD结果类似(图3), 也与图4的 $\text{NO} + \text{O}_2$ 吸附实验中总会在 $1355\text{--}1361\text{ cm}^{-1}$ 范围内出现红外峰的结果类似. 这表明配位态的 NH_3 物种与 $\text{Ce}\text{--O}\text{--Ti}$ 位上的单齿亚硝酸盐物种或硝基化合物(如 $\text{N}_x\text{H}_y\text{O}_z$)^[26]具有一定的相似性. 在反应过程中的整个温度区间内, 除了在 1906 和 1850 cm^{-1} 处有两个不可分辨的IR峰以外(可以归属为气相或弱吸附的 NO_x 物种), 并没有观测到 NO_x 吸附物种的红外峰, 这是通过ER机制进行的SCR反应的典型特点^[21,24]. 由此可见在SCR反应条件下, NH_3 的吸附是最主要的(图7).

前期研究发现, 各催化剂上 NO_x 转化率的顺序为: $\text{Ce}_{0.3}\text{TiO}_x > \text{Ce}_{0.5}\text{TiO}_x > \text{Ce}_{0.7}\text{TiO}_x$ ^[20], 这与 H_2 -TPR实验中 T_{max} (耗氢峰顶温度)降低的顺序是一致的($\text{Ce}_{0.7}\text{TiO}_x$ 样品的 T_{max} 与耗氢量分别为 710 °C 和 $906\text{ }\mu\text{mol g}^{-1}$). 这表明催化剂的氧化还原特性起着不可或缺的作用, 可能表现为 NO 氧化为 NO_x 吸附物种的能力. 如图4所示, 氧化活性同 NO_x 转化率和 H_2 -TPR特性的顺序一致. 这可由 $\text{Ce}\text{--O}\text{--Ti}$ 短程有序结构的生成(Ce 与 Ti 存在原子尺度的相互作用)得到证实. 催化剂的可还原性在 NH_3 活化和 NO 氧化过程中起着关键的作用^[31,32].

为了确认反应机理, 我们进行了稳态动力学研究. 由于反应过程中 O_2 是大大过量的, 所以反应对 O_2 的级数可以认为是1. 同时, 由于 NH_3 存在强吸附(图8), 其反应级数可以认为是0. NO_x 转化的动力学反应速率与反应物浓度的函数关系可以表示为: $r_{\text{NO conv.}} = k[\text{NO}]^x$. 通过计算, $\text{Ce}_{0.3}\text{TiO}_x$, $\text{Ce}_{0.5}\text{TiO}_x$ 和 $\text{Ce}_{0.7}\text{TiO}_x$ 上 NO 的反应级数分别为0.67, 0.58和0.67(图9). 所有的数值均小于1, 表明SCR反应同时包含LH和ER路径^[33]. 这是低温SCR氧化物催化剂常见的特性^[19]. 但是, 图8中没有检测到 NO_x 吸附物种. 即便在无 NH_3 的

$\text{NO} + \text{O}_2$ 气氛中(图4)催化剂上的确发生了 NO_x 的吸附, 但图8中的红外光谱与 NH_3 的吸附光谱是非常相似的. 这充分表明, NH_3 与 NO_x 吸附物种的反应活性远远高于 $\text{NO} + \text{O}_2$ 与 NH_3 吸附物种的, 这也可以从两种反应的IR谱得到证实(图6和图7). 因此, 反应路径可能包含 NH_3 吸附物种与弱吸附 NO_x 的反应. 在 $\text{CeO}_2/\text{TiO}_2$ 和W掺杂的催化剂上也证实存在类似的机理^[26].

使用GAUSSIAN程序计算了 $\text{N}_x\text{H}_y\text{O}_z$ 的可能结构^[34]. 如表2所示, 算得 NO 伸缩振动频率为 1359 cm^{-1} , 这与图3(1352 , 1353 和 1346 cm^{-1})、图4(1356 , 1361 和 1357 cm^{-1})和图8(1352 , 1353 和 1350 cm^{-1})中的实验数据非常接近. 许多研究者认为, NH_4NO_3 是反应的中间物种^[35]. 另外, 1535 cm^{-1} 处 NH_8 弯曲振动峰与图6(1522 cm^{-1})、图7(1520 cm^{-1})和图8(1535 cm^{-1})中的位置是很接近的. 因此可以推断, NH_4NO_3 是本文反应中可能性最大的中间物种之一. 如图3和图8所示, 低于 NH_4^+ 物种(1440 cm^{-1})存在的温度时($\text{Ce}_{0.3}\text{TiO}_x$, $\text{Ce}_{0.5}\text{TiO}_x$ 和 $\text{Ce}_{0.7}\text{TiO}_x$ 分别为 ~ 250 , ~ 350 和 $\sim 400\text{ °C}$), y 等于4或者更小. 随着温度的升高, y 逐渐降低甚至降为0(如图2所示高于 $\sim 450\text{ °C}$ 时没有 NH_3 脱附). 也就是说, 这种情况下 NH_3 氧化为亚硝酸盐/硝酸盐物种是占主导作用的(图3和图4); 相应地, NO_x 生成 N_2 的转化率下降.

4. 结论

在 $\text{Ce}\text{--Ti}$ 非晶氧化物上, $\text{Ce}\text{--O}\text{--Ti}$ 短程有序结构中 Ce 与 Ti 存在原子尺度的相互作用, 可以促进 NO 的氧化和 NH_3 的活化. 反应条件下, 催化剂表面主要被 NH_3 吸附物种覆盖而没有检测到 NO_x 吸附物种. 经计算得到反应对 NO 的级数为0.5–0.6, 表明Langmuir-Hinshelwood和Eley-Rideal机理共存. 反应路径可能包含 NH_3 吸附物种与弱吸附的 NO_x 反应生成 NH_yNO_3 ($y = 0\text{--}4$)活性中间物种, 此推论可为GAUSSIAN计算和原位红外结果所证实.