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Article

Low-temperature activity and mechanism of WO₃-modified CeO₂-TiO₂ catalyst under NH₃-NO/NO₂ SCR conditions

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ARTICLE INFO

Article history:

Received 5 May 2018

Accepted 22 June 2018

Published 5 November 2018

Keywords:

NH₃-NO/NO₂ selective catalytic reduction

CeWTi catalyst

Surface acidity

NH₄NO₃

Reaction mechanism

ABSTRACT

The CeO₂-TiO₂ (CeTi) and CeO₂/WO₃-TiO₂ (CeWTi) catalysts were prepared by a sol-gel precipitation method and their NH₃-NO/NO₂ selective catalytic reduction (SCR) performance was studied. N₂O formation and effect of oxygen concentration on SCR performance over CeWTi catalyst were also investigated while varying the NO₂/NO_x ratio. Results indicate that fast SCR behavior of CeWTi catalyst has the best NH₃-NO/NO₂ SCR performance due to the catalyst reoxidation rate by NO₂ higher than by O₂. Compared with CeTi catalyst, CeWTi catalyst exhibits higher de-NO_x performance under NH₃-NO/NO₂ SCR conditions. As the CeTi and CeWTi catalysts exhibit similar redox property, addition of WO₃ provides more acid sites which accelerate the reaction between NH₄NO₃ and NO to get a superior low-temperature activity. Amount of N₂O formation shows a peak at 250 °C mainly derived from NH₄NO₃ decomposition.

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1. Introduction

Nitrogen oxides NO_x (NO and NO₂) produced from mobile and stationary sources are major sources cause of photochemical and smog acid rain [1–3]. Selective catalytic reduction (SCR) by ammonia is one of the most efficient methods used for removal of NO_x [4,5]. It is widely used in power plants and other industrial settings [6–8]. The ratio of NO to NO₂ from exhaust gas entering the SCR catalytic converter affects the catalytic activity of the main reactions. NH₃-SCR generally occurs via three types of reaction paths, which are standard SCR (Eq. (1)), fast SCR (Eq. (2)), and NO₂ SCR (Eqs. (3)–(5)) [9–12].

Reaction (1) shows the standard SCR reaction. As the fraction of NO₂ increases, Reaction (2) occurs. When the mole ratio of NO₂ to NO is 1:1, the reaction rate is faster than standard SCR reaction [13]. Reaction (2) so called fast SCR does not involve oxygen [14]. If the NH₃:NO₂ mole ratio is increased up to 2.0, the reaction follows Reaction (3) and its reaction rate is very slow. When the reaction temperature is below 180 °C, as shown in Reaction (4), ammonium nitrate salt is formed, which may deactivate the catalyst. Reaction (5) occurs at temperatures above 300 °C [15]. It is known that NO₂ SCR Reactions (3)–(5) are much slower than the fast SCR Reaction (2). In addition, byproduct (nitrous oxide) is detected in a certain temperature range, which is a characteristic of NO₂ SCR. The proportion of NO₂ might facilitate or inhibit the SCR reaction. Therefore, NO₂ has an important effect on the reaction between NO, O₂, and

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This work was supported by the National Natural Science Foundation of China (51775296, 51375253).

DOI: 10.1016/S1872-2067(18)63129-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 11, November 2018

NH₃.

The comparative researches of standard, fast and NO₂ SCR mechanisms have been studied. Several papers have addressed the effect of the NO₂/NO_x ratio on SCR activity, such as V₂O₅-WO₃/TiO₂ [16,17], Fe-ZSM-5 [18,19] and Cu-zeolite [11,20]. In addition, CeO₂ based catalysts have attracted much attention in the NH₃-SCR field, due to its superior ability to store/release oxygen and nontoxicity [21–23]. CeO₂/WO₃-TiO₂ (CeWTi) catalyst as a typical deNO_x catalyst has been widely reported. Chen et al. [24] found the standard SCR activity of the CeO₂/TiO₂ catalyst was enhanced by the addition of WO₃. Because CeWTi catalyst provided more adsorbed NO_x and NH₃ species, and simultaneously enhanced the activity of both species resulting in the improvement of SCR activity. Zhang et al. [25] reported that WO₃ could interact with CeO₂ to improve the electron gaining capability of CeO₂ species and acted as electron donating groups to transfer the electrons to CeO₂ species. But these works did not research the difference of reaction route and mechanism between CeO₂-TiO₂ (CeTi) and CeWTi catalyst, especially under NH₃-NO/NO₂ SCR conditions. In addition, a few researches have reported the effect of NO/NO₂ ratios on the NO_x conversion over the CeO₂ based catalyst. However, there is few quantitative data describing detailed relationships among the NH₃-NO/NO₂ SCR reactions over CeO₂ based catalyst despite the fact that this information helps us understand activity data associated with a catalytic converter. Furthermore, the oxygen supply capacity of cerium based catalysts needs to be investigated.

Our previous work compared the standard and fast SCR by (TRA) and diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) method and analyzed adsorption and desorption steps of NO₂ [26]. In this work, we investigated the effect of WO₃ modified CeTi catalysts on NH₃-NO/NO₂ SCR reactions. The NO_x reduction activity over CeWTi catalyst occurs by changing the NO₂/NO_x ratio (0–100%) and oxygen concentration (0–10%) in small increments. We discussed the contributions from three SCR reactions based on the results and established the general chemistry of NH₃-SCR useful for the practical development of catalysts.

2. Experimental

2.1. Catalyst preparation

The CeWTi mixed oxide catalyst was prepared by a sol-gel method. Cerium nitrate hexahydrate (AR, Aladdin), ammonium paratungstate (AR, Beijing Chem. Plant) and commercial TiO₂ powders (DT-51, Millennium Chemicals, France) were mixed in deionized water according to a mass ratio of CeO₂: WO₃: TiO₂ = 5:5:90. And then citric acid (AR, Aladdin) and nitric acid (AR, Beijing Chem. Plant) were added. The solution was sufficiently stirred in a water bath and heated at 80 °C until a porous gel was formed. The gel was dried at 110 °C in an oven overnight. The resulting product was subsequently subjected to decomposition at 300 °C for 1 h and calcination at 600 °C for 3 h in a muffle. Finally, the samples were crushed and sieved to 40–60 mesh for catalytic activity measurements. The reference cata-

lyst CeTi was prepared by the same method.

In order to investigate the reaction behavior of NH₄NO₃ over different catalysts, a series of reference samples were prepared as follows. CeTi and CeWTi powder were mixed with 10 wt% NH₄NO₃ powder in a ball mill (QM-3SP04, China) for 3 h and the obtained samples were sieved to 40–60 mesh size for temperature-programmed surface reaction (TPSR) experiment.

2.2. Activity measurement

The measurement of NH₃-SCR activity was carried out in a fixed-bed quartz tube from 100 to 500 °C with an interval of 50 °C. 200 mg catalyst was sieved to a 40–60 mesh size and loaded into the reactor with a gas hourly space velocity (GHSV) of 150000 h⁻¹. The SCR feed stream consisted of 1000 ppm NH₃, 1000 ppm NO_x (NO and NO₂), O₂ (0–10%), 2% H₂O and N₂ in balance. The outlet gas was monitored by a Nicolet 380 FTIR spectrometer (Thermo Fisher Scientific, USA) at 150 °C. The NO_x conversion was calculated as follows.

$$\text{NO}_x \text{ conversion (\%)} = \left(1 - \frac{[\text{NO}]_{\text{out}} + [\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NO}_2]_{\text{in}}}\right) \times 100\% \quad (6)$$

2.3. Catalyst characterization

The NH₃ or NO oxidation activity at 200–500 °C was measured in a fixed bed reactor with 200 mg powder catalyst (40–60 mesh) and detected by a Nicolet 380 FTIR spectrometer (Thermo Fisher Scientific, USA). The gas mixture included 500 ppm NH₃ or NO, 5% O₂, 2% H₂O and N₂ in balance, and the GHSV was 150000 h⁻¹. The NH₃ or NO conversion was calculated as follows:

$$\text{NH}_3 \text{ conversion (\%)} = \frac{[\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}}{[\text{NH}_3]_{\text{in}}} \times 100 \quad (7)$$

$$\text{NO conversion (\%)} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\% \quad (8)$$

H₂ temperature-programmed reduction (H₂-TPR) experiments were conducted on a Micromeritics Autochem II 2920 chemisorption analyzer using 50 mg of the CeTi or CeWTi samples. The samples were preheated at 500 °C for 30 min in He flow. The temperature was increased from 50 to 1000 °C at a heating rate of 10 °C min⁻¹ with 10% H₂/Ar gases. The H₂ consumption was recorded continuously.

Temperature-programmed desorption of ammonia (NH₃-TPD) experiments were performed on a Nicolet 380 infrared (IR) spectrometer (Thermo Fisher, USA). Prior to the experiment, 200 mg sample was pretreated at 200 °C in a gas flow of 5% O₂/N₂ for 30 min. Then the samples were cooled down to 100 °C and purged with NH₃ until saturation, followed by flushing with N₂ to avoid the physisorption of NH₃. Afterwards, the NH₃-saturated samples were ramped to 500 °C at a rate of 10 °C min⁻¹ in N₂.

DRIFT spectra of adsorbed species arising from NH₃ adsorption at various temperatures, were recorded in the range of 4000–650 cm⁻¹ using a Thermo Nicolet 6700 FTIR spectrometer. The sample in a diffuse reflectance IR cell was purged by N₂

(100 mL min⁻¹) at 500 °C for 30 min to remove traces of organic residues. Then the sample was cooled down to 25 °C, exposed to 1000 ppm NH₃/N₂ (100 mL min⁻¹) for 1 h, and subsequently flushed with N₂. Afterwards, the DRIFT spectra of catalysts were collected at various temperatures.

Thermogravimetric (TG) analyses were carried out on a Mettler STA instrument to investigate the thermal decomposition of ammonium nitrate over the CeTi and CeWTi catalysts. For each experiment, the weight ratio of NH₄NO₃ and catalyst is 1:1. The mixed powders were analyzed from 30 to 900 °C at a heat rate of 10 °C min⁻¹ in N₂.

The reactivity of deposited ammonia nitrate on the catalysts was measured using TPSR with NO. Prior to the measurement, 200 mg catalyst was sufficiently mixed with 20 mg NH₄NO₃ powder using the above-mentioned method in Section 2.1. Subsequently, 20 mg NH₄NO₃ powder or the above samples were exposed to a stream consisting of 1000 ppm NO, 5% O₂, and N₂ as balance at a total flow rate of 500 mL min⁻¹. The temperature was ramped from 100 to 300 °C at a heating rate of 10 °C min⁻¹ with the outlet NO concentrations real-time monitored by the Thermo Nicolet 380 FTIR spectrometer.

3. Results and discussion

3.1. Catalyst activities on CeTi and CeWTi catalysts

Fig. 1 shows the NH₃-NO/NO₂ SCR performance of CeTi and CeWTi catalysts under standard, fast and NO₂ SCR conditions. For Standard SCR, the catalytic activity of CeWTi catalyst is much higher than that of CeTi catalyst in low temperature range below 250 °C. For fast SCR, which have the best catalytic activity in NH₃-NO/NO₂ SCR, the catalytic activity of CeWTi catalyst is also better in low temperature. For NO₂ SCR, the catalytic activity is much worse than fast SCR and standard SCR due to high production of N₂O; this will be discussed later. Generally speaking, the CeWTi catalyst has better SCR performance under the three SCR conditions in the temperature range of 100–250 °C. It is noted that addition of tungsten oxide promotes the low-temperature NH₃-NO/NO₂ SCR activities. In previous studies, the superior performance of tungsten oxide modified CeTi catalyst could be attributed to more Ce³⁺ state which was beneficial for redox performance in the SCR reaction [25]. Furthermore, the addition of tungsten brought more active NH₃ adsorbed species, which is believed to be the signifi-

cantly beneficial for SCR reaction. However, the main factor needs to be identified and the role of immediate species NH₄NO₃ which formed on catalyst surface at low-temperature should be investigated.

3.2. Catalyst oxidation activities on CeTi and CeWTi catalysts

The results of NH₃ and NO temperature programmed oxidation (TPO) experiments are shown in Fig. 2. For NH₃ oxidation reaction, the NH₃ conversion of both CeTi and CeWTi catalysts is negligible below 300 °C. As temperature increases, NH₃ oxidation activity increases sharply for both of CeTi and CeWTi catalysts and NH₃ was fully oxidized in the temperature above 450 °C. In the meantime, CeWTi catalyst show lower oxidation catalytic activity in temperature range of 300–450 °C. Moreover, CeWTi catalyst generates less byproduct (N₂O and NO₂) and owns high N₂ selectivity at 200–500 °C. For NO oxidation reaction, the sole production of NO oxidation is NO₂ in an oxygen-rich condition. CeWTi showed lower NO oxidation activity in the whole temperature range, as shown in Fig. 2(b). It is found that the CeWTi catalyst exhibits a poor activity for NO oxidation at low temperatures (<200 °C). The NO conversion at 200 °C is insignificant, which implies the limited contribution of NO₂ via fast SCR reaction to the low temperature activity under standard SCR conditions.

3.3. Redox property

H₂-TPR is an effective technique in the study of the redox properties of the catalysts. The H₂-TPR profiles of the CeTi and CeWTi catalysts are shown in Fig. 3. The reduction peaks at 508–525 °C appear in both catalysts, attributing to the surface/subsurface oxygen reduction of ceria [27,28]. It can be seen that the peak area of the CeWTi catalyst is smaller than that of CeTi, which implies that the introduction of tungsten oxide results in less reducible subsurface oxygen in the tri-component catalysts. The reduction peaks ranged from 550–700 and 700–900 °C for CeWTi catalyst, which are ascribed to the reduction of WO₃ to WO_{2.9} and WO_{2.9} to WO₂, respectively [29]. Results indicated that redox property of CeTi catalyst was higher than that of CeWTi catalyst, consistent with NH₃ and NO TPO.

Fig. 1. Catalytic activities of CeTi and CeWTi catalysts under standard, fast and NO₂ SCR conditions. Reaction conditions: 1000 ppm NH₃/1000 ppm NO_x (NO + NO₂)/5% O₂/N₂, GHSV = 150000 h⁻¹.

Fig. 2. NH₃ oxidation (a) and NO oxidation (b) activity of CeTi and CeWTi catalyst as a function of temperature. Reaction conditions: 500 ppm NH₃ or 500 ppm NO/5% O₂/N₂, GHSV = 150000 h⁻¹.

3.4. Surface acidity on CeTi and CeWTi catalysts

3.4.1. IR spectra of NH₃ adsorption

DRIFT spectra over CeTi and CeWTi catalysts arising from contact of NH₃ at different temperatures are shown in Fig. 4. The ammonia adsorption species are similar over CeTi and CeWTi catalysts. The bands at 1598 and 1170–1220 cm⁻¹ could be assigned to the σ_{as} NH₃ and σ_s NH₃ on Lewis acid sites, respectively [26,30]. The bands at 1680 and 1440 cm⁻¹ could be attributed to the σ_s NH₄⁺ and σ_{as} NH₄⁺ on Brønsted acid sites [30–32]. In addition, the band at 1325 cm⁻¹ is ascribed to the Brønsted acid sites of sulfates species on DT-51(TiO₂) materials [33]. As the temperature increases, the bands of ammonia derived species decrease in intensity except 1325 cm⁻¹ band. It may be attributed to the decomposition of ammonium sulfates at high temperature [34]. The addition of WO₃ on CeTi catalyst does not induce new band site because sulfates species on TiO₂ materials provide most of surface acidity.

3.4.2. NH₃-TPD

The results of ammonia DRIFTS show that the modification

Fig. 3. H₂-TPR profiles of the CeTi and CeWTi catalysts.

of WO₃ does not lead to new acid site. So it is necessary to measure the amounts and strengths of acid sites of the catalysts by NH₃-TPD experiments, and the results are shown in Fig. 5. The desorption temperature of CeTi and CeWTi catalysts is similar, which reach a peak at around 210 °C. While the intensity of NH₃ desorption peak over CeWTi catalyst is higher than that over CeTi catalyst, which implies the amount of NH₃ desorption is significant higher over CeWTi catalyst. Results imply that the addition of tungsten oxide has brought more NH₃ adsorption sites which are beneficial for the SCR reaction [28,29,35,36].

3.5. Behavior of NH₄NO₃ on SCR reaction

3.5.1. Decomposition activity of NH₄NO₃

As previous analysts [37,38], the decomposition of intermediate NH₄NO₃ is important for the low temperature NH₃-NO/NO₂ SCR activities. TGA is applied to study the effect of CeTi and CeWTi catalysts in the decomposition of NH₄NO₃. As shown in Fig. 6, the pure NH₄NO₃ starts to decompose at around 200 °C and finishes decomposing at 292 °C. Both of the initial temperature of weight loss and fully decomposition temperature lowered when mixed with CeTi or CeWTi catalysts, especially for the fully decomposition temperature decrease from 292 to 270 °C. It is indicated that the addition of catalysts could promote the decomposition of NH₄NO₃ in small extent. Furthermore, the decomposition curve of CeTi or CeWTi mixed with NH₄NO₃ almost coincides. It is suggested that the decomposition of ammonium nitrate is not main factor to affect SCR activity.

3.5.2. Reaction between NH₄NO₃ and NO

Our previous work has reported that the reaction between NH₄NO₃ and NO is the key step in SCR reaction at low temperatures [26,39]. Therefore, it is necessary to investigate the reaction activity between NH₄NO₃ and NO. Fig. 7 shows the TPSR profiles between NO and NH₄NO₃ in the pure state or deposited on different catalysts. The pure NH₄NO₃ sample starts to decrease at round 300 °C, which mean that pure NH₄NO₃ is im-

Fig. 4. DRIFT spectra of CeTi (a) and CeWTi (b) pretreated in 1000 ppm NH_3/N_2 at room temperature for 1 h and then purged by N_2 from 50 to 450 °C at a heating rate of 10 °C min^{-1} .

possible to participate in the reaction with NO below 250 °C. The reaction activities between NO and NH_4NO_3 are highly improved when ammonium nitrate mixes with the catalysts. For NH_4NO_3 mixed with CeWTi catalyst, NO starts to react with NH_4NO_3 at around 150 °C. The reaction activity improves sharply with the increase of temperature; over 30% of NO par-

ticipates in the reaction at 170 °C, the melting temperature of NH_4NO_3 . For NH_4NO_3 mixed with CeTi catalyst, NO start to react with NH_4NO_3 at much higher temperature around 225 °C. The reaction activity also increases sharply as the temperature increases. The reaction activity between NO and NH_4NO_3 is highly consistent with the $\text{NH}_3\text{-NO}/\text{NO}_2$ SCR activities. It has been reported that the acid and transition metal ions may accelerate the reduction of ammonium nitrate [37]. Results indicate the addition of WO_3 increases the surface acidity so that the CeWTi catalyst promotes the reaction between NO and NH_4NO_3 [29,39].

3.6. Low-temperature behavior and mechanism (<200 °C) of standard, fast and NO_2 SCR

3.6.1. Activity mapping of $\text{NH}_3\text{-NO}/\text{NO}_2$ SCR

Fig. 8 shows the map of $\text{NH}_3\text{-NO}/\text{NO}_2$ SCR activities as the NO_2/NO_x ratio and temperature varied. Results indicate that NO_x conversion depends strongly on the NO_2/NO_x ratio at low temperatures. The best activity occurs under fast SCR condition when the NO_2/NO_x ratio is 50%. The NO_x conversion is up to 100% at 200 °C under fast SCR and gradually decreased with

Fig. 5. NH_3 -TPD profiles of CeTi (a) and CeWTi (b) catalysts.

Fig. 6. The TGA curves of neat NH_4NO_3 and NH_4NO_3 mixed with CeWTi catalysts.

Fig. 7. The reaction activities between NH_4NO_3 and NO with or without the CeTi or CeWTi catalysts.

Fig. 8. Map of NO_x conversion vs. different temperatures and NO_2/NO_x ratios on CeWTi catalyst. Reaction conditions: 1000 ppm NH_3 /1000 ppm NO_x (NO and NO_2)/5% O_2 /2% $\text{H}_2\text{O}/\text{N}_2$, GHSV = 150000 h^{-1} .

increase of NO_2/NO_x ratio. Also, the maximum NO_x conversion for NO_2 SCR conditions is around 75%, which is much lower than standard SCR conditions. Moreover, the ratio of NO_2/NO_x has a little effect on NO_x conversion at high temperatures. In previous studies, ammonium nitrate has been reported thermally stable at low temperatures, which blocks the active sites and decreases the de NO_x performance. However, ammonium nitrate is easily decomposed at high temperatures so that NO_2 has a little influence on NO_x conversion at high temperatures [40]. In addition, the operation temperature window extends wide with increase of NO_2/NO_x ratio less than 50% and reaches widest under fast SCR conditions, and then the operation temperature window gets narrowed with the NO_2/NO_x ratio increase. As the NO_x conversion is linear with the NO_2 ratio from 0% to 50% and 50% to 100%, indicating that the NO and NO_2 preferential to participate in the SCR reaction with the ratio of 1:1, the rest NO or NO_2 could be participate NO or NO_2 SCR separately without affect the activities. Therefore, the SCR reactions in terms of NO_x conversion are ranked: fast SCR > standard SCR > NO_2 SCR.

3.6.2. N_2O production mapping against NO_2/NO_x ratio and temperature

N_2O is a important byproduct for SCR reaction at high temperatures, which decreases the NO_x conversions. On the other hand, N_2O is an immediate species which could react with NH_3 to produce N_2 and H_2O [10]. It indicated that the N_2O production was a significant reaction during NO_x conversion, especially in the higher NO_2/NO_x region. Fig. 9 shows the concentration of N_2O produced as a function of temperatures and NO_2/NO_x ratio. A small amount of N_2O is observed when $\text{NO}_2/\text{NO}_x < 50\%$, whereas N_2O is increased sharply as NO_2 ratio increases. So there is a relationship between N_2O formation and NO_2 SCR reaction. Furthermore, the N_2O concentration was the highest at 250 °C, suggesting that the N_2O production is highly temperature depended.

According to literature [20], there are two routes of N_2O formation on SCR catalysts: NH_4NO_3 decomposition and NH_3 oxidation (Eq. (9)) [4,41]. As shown in Fig. 2(a), the NH_3 oxida-

Fig. 9. Map of N_2O formation vs different temperatures and NO_2/NO_x ratio on CeWTi catalyst. Reaction conditions: 1000 ppm NH_3 /1000 ppm NO_x (NO and NO_2)/5% O_2 /2% $\text{H}_2\text{O}/\text{N}_2$, GHSV = 150000 h^{-1} .

tion of CeWTi catalyst starts at around 300 °C and owns high N_2 selectivity, which means the N_2O formation from NH_3 oxidation is trivial. N_2O formation is mainly due to the NH_4NO_3 decomposition.

Based on the previous reports [18,42,43], the adsorption of NO_2 may lead to nitrites and nitrates formation which reacts with ammonia forming NH_4NO_3 and NH_4NO_2 . NH_4NO_2 decomposed readily to N_2 and H_2O on catalyst surface, which is the main route to de- NO_x at low temperatures (Eq. (10)). NH_4NO_3 formed may deposit as a solid on the catalyst surface [44]. Above 250 °C there is a rapid exothermic decomposition to N_2O and H_2O (Eq. (11)) [38]. This decomposition will be accelerated by acids and transition metal cations [37]. It is reported that the amount of medium strong acid sites significantly increases with WO_3 serving as Brønsted acid sites, resulting in changing of effective decomposition temperature [38].

It is known that raising the temperature accelerates Reaction (12). For NO_2 SCR, NH_4NO_3 decomposition (Eq. (11)) plays a dominate role at temperature below 250 °C [12], and the amount of N_2O formation reaches a peak at 250 °C. As temperature increases above 250 °C, the reduction of N_2O by NH_3 (Eq. (12)) will be prevailed [45,46].

In summary, increased N_2O production rate is attributed to an increase in the rate of Reaction (11). The decreasing N_2O production rate above 250 °C (Fig. 3) results from an increase in the rate of Reaction (12) [47]. Reduction of N_2O by NH_3 becomes significant at $T > 300$ °C [46]. Combining reactions (4), (11) and (12) yields the NO_2 SCR Reaction (5). Thus, it is suggested that Reaction (5) progresses sequentially via N_2O formation step (Eq. (11)) and N_2O reduction step (Eq. (12)).

3.6.3. Effect of O_2 on SCR reactions

The redox property of catalysts in response to oxygen is one of the most important factors in standard SCR reaction. Fast and NO_2 SCR reactions do not involve oxygen but they show remarkable activities. It is necessary to evaluate the relative

Fig. 10. (a) Decline of NO_x conversion with time after shut-off O₂ over CeWTi catalyst on SCR conditions. (b) Effect of O₂ concentration on NO_x conversion over CeWTi catalyst under standard SCR condition.

contributions of the three different SCR reactions under different oxygen concentrations (0–10 vol%). Fig. 10(a) shows the results of O₂ on-off experiments under different SCR conditions for CeWTi catalyst at 200 °C. 5% O₂ was added to the inlet gas and stopped when the reaction reached a steady state. After stopping supply of 5% oxygen the activity was significantly decreased under NO SCR conditions. Meanwhile, at the steady state even if the supply of oxygen did not affect the activities of the fast and NO₂ SCR. The reoxidation of the active sites is the rate-determining step in SCR reaction at temperatures below 300 °C [48]. According to Ref. [49], the catalyst reoxidation rate by NO₂ was higher than by O₂. The fast SCR reaction rate is higher than standard SCR reaction rate due to efficient oxidizer role of NO₂. Therefore, the standard SCR activity is inhibited by the lack of reoxidation species (NO₂ or O₂).

Fig. 10(b) shows the effect of the concentration of O₂ on the catalytic activities over CeWTi catalyst under standard SCR condition. CeWTi catalyst shows poor catalytic activities in the temperature range of 200–500 °C in the absence of oxygen. Effect of oxygen concentration is more pronounced at low temperature. With the increase of temperature, the ability of catalytic materials to supplement lattice oxygen of catalytic materials is enhanced by gas phase O₂. As a result, the catalytic materials still maintain high catalytic activity at high temperature with low O₂ concentration. Based on the previous reports [13], the NO could react with NH₃, forming N₂ and H₂O on the catalyst (Eq. (13)). However, the reaction rate is lower than standard SCR reaction rate so that it will not occur in presence of O₂. It is illustrated that CeWTi catalyst still maintains a certain activity without oxygen.

3.7. Mechanism of CeWTi catalyst on low-temperature SCR reactions

In the standard SCR reaction, surface nitrites/nitrates form via NO oxidative adsorption. Oxidative adsorption of NO to nitrates/nitrites (standard SCR) is harder and slower than NO₂ disproportionation reaction (fast SCR). In addition, the catalyst

reoxidation rate by NO₂ was higher than by O₂ (Fig. 10(a)). Therefore, catalytic activity of standard SCR is lower than that of fast SCR.

However, the fast SCR conversion is poor below 180 °C which is near the melting point of ammonium nitrate [37]. It has been presented that ammonium nitrate accumulates on the catalyst surface with decreasing temperature. According to our previous study [26], the drastic decrease in the de-NO_x conversion of fast SCR results from the inhibition of rate-determining step by a thermal stable NH₄NO₃ formation. It is interesting to find that the CeTi and CeWTi catalysts own a similar SCR activity under fast SCR conditions. Compared with standard SCR condition, surface nitrites are produced by NO₂ disproportionation, which is more efficient. So that the main route to N₂ is easier under fast SCR condition. In this case, the difference of SCR catalytic activity between CeTi and CeWTi catalysts is small.

In the NO₂ SCR chemistry, reaction between NH₃ and NO₂ leads to NH₄NO₃ formation (Eq. (4)) [50,51]. The NH₄NO₃ deposits on the catalyst surface and blocks active sites because of the lack of NO in the atmosphere below 180 °C. The NH₄NO₃ start to be decomposed into N₂O and H₂O above 170 °C (Eq. (11)). At high temperatures above 250 °C, NO₂ SCR mainly involves a NH₃/NO₂ conversion ratio of 4/3 (Eq. (5)). Therefore, the NO_x conversions at high temperature region would be limited by the ammonia deficiency. The NO_x conversions (75% at 350 °C) correlates well the values in theoretical calculation.

At low temperatures, the main route to N₂ relies on the effortless decomposition of NH₄NO₂ (Eq. (14)) [39,40]. According to our previous research, there are two ways to produce ammonium nitrite that is reaction between adsorbed ammonia and surface nitrite as well as reduction of ammonium nitrate by NO (Eq. (15)). The latter route is the key step of the SCR reaction at low temperature under standard and fast SCR conditions [30,37]. According to literature [37], the acid species may accelerate the reduction of ammonium nitrate. The CeTi and CeWTi catalysts exhibit a similar redox property (Fig. 2). However, the addition of WO₃ provides more acid sites which accelerates the reaction between NH₄NO₃ and NO (Fig. 7). Therefore,

Fig. 11. $\text{NH}_3\text{-NO/NO}_2$ SCR reaction routes on CeTi and CeWTi catalysts. the CeWTi catalyst shows a higher NO_x conversion due to its more surface acidity.

4. Conclusions

$\text{NH}_3\text{-NO/NO}_2$ SCR behavior of CeTi and CeWTi catalyst was studied to understand effect of redox property and surface acidity on the SCR mechanism. N_2O formation and effect of oxygen concentration of CeWTi catalyst were also investigated. The CeWTi catalyst exhibits better $\text{NH}_3\text{-NO/NO}_2$ SCR activity than CeTi catalyst. Fast SCR behavior of CeWTi catalyst has the best $\text{NH}_3\text{-NO/NO}_2$ SCR performance due to the catalyst reoxidation rate by NO_2 higher than by O_2 . The key role of NO is to reduce NH_4NO_3 to NH_4NO_2 , which is the rate-determining step of standard and fast SCR at low-temperatures. As the CeTi and CeWTi catalysts exhibit similar redox property, addition of WO_3 provides more acid sites which accelerate the reaction between NH_4NO_3 and NO to get a superior low-temperature activity.

Under NO_2 SCR condition, the reaction involves a NH_3/NO_2 conversion ratio of 1/1 and leads to ammonium nitrate deposition at low temperature. The rapid exothermic decomposition of NH_4NO_3 leads to N_2O formation with a peak temperature of 250 °C. Furthermore, the lack of NO causes the declines of NO_x conversion because the reaction between ammonium nitrate and NO could not occur. At high temperatures, NO_2 SCR mainly involves a NH_3/NO_2 conversion ratio of 4/3. The stoichiometry of NH_3/NO_2 limits the NO_x conversions at high temperature region.

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Graphical Abstract

Chin. J. Catal., 2018, 39: 1804–1813 doi: 10.1016/S1872-2067(18)63129-8

Low-temperature activity and mechanism of WO_3 -modified CeO_2 - TiO_2 catalyst under NH_3 - NO/NO_2 SCR conditions

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NH_3 - NO/NO_2 SCR reaction routes on CeTi and CeWTi catalysts. Addition of WO_3 provides more acid sites which accelerate the reaction between NH_4NO_3 and NO to get a superior low-temperature activity.

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WO_3 改性 CeO_2 - TiO_2 催化剂的低温 NH_3 - NO/NO_2 SCR活性和机理研究

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摘要: 在铈钛基 NH_3 -SCR催化材料中, 改性元素对催化材料的酸性位和氧化还原性能的影响较大。本文采用过量浸渍法分别制备了 CeO_2 - TiO_2 (CeTi)和 CeO_2/WO_3 - TiO_2 (CeWTi)催化剂, 研究了CeWTi催化材料结构、酸性位及氧化还原性能对 NH_3 - NO/NO_2 SCR反应性能的影响。结果发现, CeTi和CeWTi样品均有较优异的 NH_3 - NO/NO_2 SCR催化性能, 后者略高。 WO_3 的加入增加了催化材料的表面酸性, 对其氧化还原性能影响不大。通过对反应中间物种 NH_4NO_3 的研究, 发现 NH_4NO_3 的分解主要与氧化还原性能相关, 而NO还原 NH_4NO_3 的反应需要氧化还原能力和酸性位共同作用, 即在氧化还原性能差异不大的条件下, 酸性对该反应起到重要作用。而该反应也是 NH_3 - NO/NO_2 SCR的限速步骤, 这是CeWTi催化材料活性高于CeTi催化材料的原因。

同时, 为了获得 NH_3 - NO/NO_2 SCR反应的高活性, NO_2 : NO 比例宜为1:1。然而实际情况中, 预氧化催化材料的氧化活性、 NO_x 浓度、温度等变量使得准确控制 NO_2 的比例较难, 因此, 深入了解 NO_2 浓度对 NH_3 - NO/NO_2 SCR反应的影响至关重要。本文探讨 NO_2 : NO 的比例、 O_2 浓度等对 NH_3 - NO/NO_2 SCR反应性能的影响; 并研究了不同 NO_2 含量条件下 NH_3 - NO/NO_2 SCR反应网络。通过分析CeWTi材料上 NH_3 - NO/NO_2 SCR反应网络可知, 当NO与 NO_2 比例为1:1时, NH_3 -SCR催化活性最高, 并以快速SCR形式进行; 当NO与 NO_2 比例为1:1消耗完全之后, 剩余的NO或 NO_2 各自独立以标准或慢速SCR进行, 不影响其本来的反应活性。催化材料的标准SCR、快速SCR和慢速SCR均取决于材料表面酸度和氧化还原性能, 但快速SCR和慢速SCR对材料这两方面性能的要求相对较低。同时 O_2 并不参与快速和慢速SCR, 而 NO_2 可以取代 O_2 作为SCR反应中主要的氧

化剂, 氧化 Ce^{4+} 为 Ce^{3+} , 甚至比 O_2 和 NO 再氧化活性位的能力更强, 保持催化材料的高催化活性. 低温条件时, 慢速SCR和快速SCR反应均在材料表面生成硝酸铵中间物种, 但由于慢速SCR气氛中缺乏 NO 将硝酸铵还原, 进而引发快速SCR反应, 因此材料表面快速SCR的 NO_x 转化率要高于慢速SCR反应; 高温条件下, 由于硝酸铵容易热分解, 导致硝酸铵的抑制效应不太明显. NH_4NO_3 分解是 NO_2 含量升高后 N_2O 的形成的重要途径.

关键词: NH_3 - NO/NO_2 选择催化还原; CeWTi催化剂; 表面酸性; NH_4NO_3 ; 反应机理

收稿日期: 2018-05-05. 接受日期: 2018-06-22. 出版日期: 2018-11-05.

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基金来源: 国家自然科学基金(51775296, 51375253).

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