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Article

Performance enhancement mechanism of Mn-based catalysts prepared under N₂ for NO_x removal: Evidence of the poor crystallization and oxidation of MnO_x

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ABSTRACT

Among multitudinous metal-oxide catalysts for the selective catalytic reduction of NO_x with NH₃ (NH₃-SCR), Mn-based catalysts have become very popular and developed rapidly in recent years because of its superior low-temperature denitrification activity, mainly originating from multi-valence of Mn. Most studies suggest that the catalytic activity of multi-component oxides is superior to that of single-component catalysts owing to the synergistic effect among the metallic elements in such materials, of which more attentions have been given to Ce as an additive owing to its powerful oxygen storage capacity, redox ability and its ready availability. As the core of SCR technology, the research points in catalyst development at the present stage of all researchers in countries mainly centralize on the optimization of active components, carriers, calcination temperature, calcination time and temperature-raising procedure, giving little thought to the effects of the calcination atmosphere. In the present work, Ce-modified Mn-based catalysts were prepared by a simple impregnation method. The effects of the calcination atmosphere (N₂, air or O₂) on the performance of the resulting materials during NH₃-SCR and its causes of the differences were subsequently investigated and characterized using various analytical methods. Data obtained from X-ray diffraction, thermogravimetry and temperature-programmed reduction with hydrogen show that calcination under N₂ reduces both the degree of oxidation and crystallization of the MnO_x. Scanning electron microscopy also demonstrates that the use of N₂ inhibits the growth of grains and increases the dispersion of the catalysts. In addition, the results of temperature-programmed desorption with ammonia indicate that catalysts calcined under N₂ exhibit a greater quantity of acid sites. Finally, X-ray photoelectron spectrometry and activity results demonstrate that MnO_x in the lower valence states is more favorable for NH₃-SCR reactions. In conclusion, catalysts calcined under N₂ show superior performance during NH₃-SCR for NO_x removal, allowing NO conversions up to 94% at 473 K.

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1. Introduction

Selective catalytic reduction with ammonia (NH₃-SCR) is

one of the most mature, reliable and efficient low-temperature NO_x removal processes, and has been studied as a means of flue gas denitrification [1]. Manganese oxides (MnO_x) have been

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extensively researched as low-temperature SCR catalysts due to their multivalence, low cost and excellent performance below 473 K [2–4]. Numerous studies have shown that the catalytic activity of multi-component oxides is superior to that of single-component catalysts owing to the synergistic effect among the metallic elements in such materials. To date, many transition metals (including Fe [5–7], Cu [5,8–10], Ni [5,11–12] and Cr [5,7,9]) have been found to act as modifiers to enhance the catalytic performance of $\text{MnO}_x/\text{TiO}_2$. More recently, catalysts with rare-earth elements as additives have received much attention, with research focusing on CeO_2 doping owing to the superior oxygen storage capacity and redox ability of this oxide, along with its ready availability [13–16]. Wu et al. [17] and Sheng et al. [18] have reported that Ce-modified $\text{MnO}_x/\text{TiO}_2$ catalysts exhibit superior NO conversion during NH_3 -SCR when using CeO_x as a promoter. As well, ceria-based solid solutions were synthesized and used as supports to prepare Mn/CeTi for the reduction of NO by NH_3 -SCR, with NO conversions greater than 90% [19]. Recently, Li et al. [20], Liu et al. [21] and Andreoli et al. [22] have synthesized Mn-Ce mixed oxides using different preparation methods and found that these materials yield high activity during NO conversion in the temperature range of 373 to 473 K. Moreover, Mn-Ce-Ti mixed oxide catalysts were reported to be suitable for practical applications in controlling NO_x emissions by Liu et al. [23]. Ce doping has been shown to enhance the surface area of these materials, as well as to improve catalyst dispersion and redox cycles [17–26]. Presently, the development of novel catalysts, which is crucial to the advancement of SCR, is largely focused on the optimization of active components, calcination temperature and calcination time [14–16], thus emphasizing the significance of the calcination process. Nevertheless, research regarding the effects of the calcination atmosphere has been relatively scarce, even though many reports [27–32] suggest that the calcination atmosphere could make a significant difference in terms of the particle sizes, defect concentrations, valence states and phase structures of catalysts, giving rise to variations in catalytic properties. In addition, previous studies conducted by our own group have determined that the calcination atmosphere greatly affects the catalytic activity of $\text{MnO}_x/\text{TiO}_2$ catalysts for low-temperature SCR [33,34].

In the present work, therefore, various characterization methods were adopted to obtain insights into the mechanism by which the performance of Mn-based catalysts is enhanced upon preparation in N_2 . On the basis of previous research, MnO_x and CeO_x were chosen as the active components, and Ce-Mn/ TiO_2 catalysts were prepared by a simple impregnation method. Analyses by X-ray diffraction (XRD), H_2 -temperature programmed reduction (TPR), thermogravimetry (TG), scanning electron microscopy (SEM), NH_3 -temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) were used to systematically investigate the phase structures and physicochemical properties of catalysts calcined under different atmospheres (N_2 , air or O_2). Most importantly, a N_2 atmosphere was found to contribute to the reduction of the degree of oxidation and crystallization of catalysts, especially in the case of the MnO_x , thus promoting the NH_3 -SCR reactions.

2. Experimental

2.1. Catalyst preparation

Ce-modified Mn-based catalysts were prepared by the impregnation method. In this process, precursor salts, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (4.9096 g, 0.02 mol) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (4.3422 g, 0.01 mol), were dissolved in distilled water (200 mL) to produce a homogeneous solution. Commercial TiO_2 (P25, Degussa, 80% anatase and 20% rutile, 4.000 g, 0.05 mol) was subsequently added to the mixture, followed by vigorous stirring at room temperature for 2 h. The resulting solutions were dried in air at 383 K overnight, after which the obtained catalysts were crushed and sieved (60–100 mesh). These samples were calcined under different atmospheres (N_2 , O_2 or air) for 3 h and then pressed into tablets in preparation for activity tests. A calcination temperature of 773 K was selected based on our previous work [34]. The catalysts are denoted herein as 0.20Ce-Mn/ TiO_2 - N_2 /air/ O_2 , where 0.20 represents the optimal Ce:Ti molar ratio, as previously determined by Fang [35].

2.2. Catalyst characterization

XRD patterns were recorded on a Bruker D8 Advance diffractometer equipped with a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.15418$ nm), over the scanning range of 10° – 80° . The microscopic structures of the catalysts were characterized by SEM (JSM-5610LV, Japan). TG (Discovery, USA) was performed at a heating rate of 10 K/min in N_2 from 303 to 1273 K. The surface states of catalysts were analyzed by XPS (ESCALAB 250Xi, USA), calibrated with respect to the C 1s level (284.6 eV) of contaminant carbon.

The H_2 -TPR and NH_3 -TPD experiments were conducted using an automated apparatus (TPDRO-1100, USA) equipped with a thermal conductivity detector. Prior to the TPR and TPD measurements, approximately 50 or 150 mg of the sample powder was purged with He at 473 or 773 K, respectively, for 1.5 h to remove physisorbed water and impurities. During H_2 -TPR, the catalyst powders were reduced under a 5% H_2 -95% N_2 flow while being heated from room temperature to 1073 K at a heating rate of 20 K/min. NH_3 -TPD data were acquired by saturating samples in pure NH_3 for 30 min, followed by flushing with pure He for 1.5 h at 373 K to remove weakly adsorbed NH_3 . The NH_3 -TPD profiles were collected from 373 to 773 K at a heating rate of 5 K/min in a He atmosphere.

2.3. NH_3 -SCR performance

The catalytic activities of the test specimens were evaluated in a fixed-bed catalysis system of our own design, equipped with a temperature-programming controller, as shown in Fig. 1. Catalyst powders (2000 mg) were introduced into a specialized quartz reactor (i.d. 20 mm) in which a simulated gas mixture was able to flow throughout the sample. The typical reactant gas contained 715×10^{-6} NO, 800×10^{-6} NH_3 , and 3 vol% O_2 , with N_2 as the balance, at a total flow rate of 1120 mL/min. Data collection was performed while the sample temperature

Fig. 1. The catalysis test apparatus and feed gas system.

was held constant for 30 min until a steady state (that is, equilibrium) was achieved. The effluent from the reactor was monitored online using an off-gas analyzer (Gasboard-3800 P). The NO conversion was calculated as the difference in the NO concentration at the inlet and outlet, divided by the initial NO concentration.

3. Results and discussion

3.1. NH_3 -SCR data

The NH_3 -SCR performance of catalysts calcined under different atmospheres (N_2 , air or O_2) and of used $0.20\text{Ce-Mn/TiO}_2\text{-N}_2$ as well as the catalytic stability of $0.20\text{Ce-Mn/TiO}_2\text{-N}_2$ and $0.20\text{Ce-Mn/TiO}_2\text{-O}_2$ at 453 K is shown in Fig. 2. It is evident that the $0.20\text{Ce-Mn/TiO}_2\text{-N}_2$ exhibited the highest NO removal, giving 94% NO conversion at 473 K, with excellent stability at a time-on-stream of 16 h. The high conversion was maintained for approximately 10 h, after which a slight decrease in activity is observed (ca. 2% over the next 6

Fig. 2. Effect of calcination atmosphere on the performance of the 0.20Ce-Mn/TiO_2 catalyst and variations in stability with time-on-stream over $0.20\text{Ce-Mn/TiO}_2\text{-N}_2$ and $0.20\text{Ce-Mn/TiO}_2\text{-O}_2$.

h), primarily as a result of the accumulation of reaction by-products on the catalyst surface, blocking the active centers. Furthermore, no significant differences were found between the fresh and used $0.20\text{Ce-Mn/TiO}_2\text{-N}_2$. The latter shows similar stability at a time-on-stream of 16 h at 453 K, indicating that these Ce-Mn/TiO_2 catalysts are sufficiently stable to allow prolonged use. In comparison, both the $0.20\text{Ce-Mn/TiO}_2\text{-air}$ and the $0.20\text{Ce-Mn/TiO}_2\text{-O}_2$ exhibit much poorer performance.

3.2. Phase identification

The contribution of phase composition to the above phenomena was examined by acquiring XRD, TG and H_2 -TPR data, as presented in Figs. 3 to 5. Fig. 3 shows the XRD patterns of the as-prepared 0.20Ce-Mn/TiO_2 powders treated under different atmospheres. Characteristic diffraction peaks corresponding to anatase TiO_2 (PDF No. 86-1157), rutile TiO_2 (PDF No. 73-1765), Mn_3O_4 (PDF No. 65-2776), Mn_2O_3 (PDF No. 65-1798) and CeO_2 (PDF No. 65-2975) can be clearly identified. The more intense diffraction peaks in the case of the samples treated under higher oxygen atmospheres suggest that such conditions promote a higher degree of crystallinity. Therefore, it can also be inferred that calcination under N_2 is advantageous in terms of producing powders with a low degree of crystallization. In addition, no significant variations were found in the XRD patterns of the $0.20\text{Ce-Mn/TiO}_2\text{-N}_2$ before and after a time-on-stream of 16 h. These results demonstrate that there were no significant changes in the catalyst composition during use, verifying the superior stability of this material.

TG measurements were conducted for further analysis of phase composition and thermal stability. Each specimen exhibited a mass loss in the vicinity of 323, 893 and 1050 K, attributed to the removal of physisorbed water/dehydration of surface hydroxyls, transition of MnO_2 to Mn_2O_3 and transition of Mn_2O_3 to Mn_3O_4 , respectively [36]. Interestingly, the presence of MnO_2 can also be inferred from these TG curves, even though MnO_2 was not detected in the XRD patterns, potentially

Fig. 3. XRD patterns of (a) $0.20\text{Ce-Mn/TiO}_2\text{-N}_2$, (b) $0.20\text{Ce-Mn/TiO}_2\text{-air}$, (c) $0.20\text{Ce-Mn/TiO}_2\text{-O}_2$, and (d) $0.20\text{Ce-Mn/TiO}_2\text{-N}_2$ following a time-on-stream of 16 h.

Fig. 4. TG-DTG profiles of (a) 0.20Ce-Mn/TiO₂-N₂, (b) 0.20Ce-Mn/TiO₂-air, and (c) 0.20Ce-Mn/TiO₂-O₂.

because this compound was present at very low levels. However, highly intense XRD peaks corresponding to Mn₂O₃ and Mn₃O₄ were clearly generated. It is probable that the majority of the originally formed MnO₂ was poorly crystallized or in a highly dispersed state on the TiO₂ support [37]. Consequently, the material showed a much low decomposition temperature (<773 K). Oddly, the temperatures associated with the transformation of MnO₂ to Mn₂O₃ and Mn₃O₄ in the TG curves are much higher than 773 K. This can be explained by noting that the calcination process spanned 3 h, during which the samples were maintained at 773 K. As a result, there was sufficient time and energy for further transformation, such that Mn₂O₃ was detected in the XRD and TG data. Because the TG measurements were performed at a heating rate of 10 K/min, there was likely a lag between the catalyst transformation and the temperature increase. Therefore, the presence of MnO₂ in the TG curves could be ascribed to a very small amount of MnO₂ that remained intact during the catalyst preparation. What is most deserving of attention is the observation that the temperatures for the transition of Mn₂O₃ to Mn₃O₄ following calcination in O₂, air and N₂ decreased successively, while the proportional mass losses increased. This suggests more highly amorphous catalysts and an inclination to the formation of Mn₂O₃ in oxy-

gen-depleted environments.

Fig. 5 presents the H₂-TPR profiles of catalysts calcined under different atmospheres. Two hydrogen-consumption peaks, centered around 554 and 702 K, are evident, corresponding to fractional reductions of MnO_x [8,38]. The ratios of the former reduction peak area to the latter are 0.72, 0.75 and 0.87, respectively. Based on the theoretical oxygen loss in each step (Equation (1)), the area ratios should be 0.5 if only Mn₂O₃ was present in the catalysts and 1 for the reduction of MnO₂ (MnO₂ → Mn₂O₃ → MnO). Hence, we propose that Mn₂O₃ was the main phase and that some small amount of MnO₂ was also present in the catalysts, which is in good agreement with the TG results. The first peak is attributed to overlapped peaks associated with the reductions of MnO₂ to Mn₂O₃ and Mn₂O₃ to Mn₃O₄, while the other is due to the reduction of Mn₃O₄ to MnO. As expected, changes in the calcination atmosphere led to variations in both the areas and locations of the reduction peaks. In particular, the light-off temperatures moved to lower values as the amount of oxygen in the calcination atmosphere was lowered. This result confirmed the significantly enhanced redox properties of catalysts calcined under N₂. An oxygen-deprived atmosphere may lead to the formation of more oxygen vacancies and crystal lattice defects (Equation (2)), thereby promoting the adsorption of reactants and the transition of Ti⁴⁺ to Ti³⁺ [39] and Ce⁴⁺ to Ce³⁺ [40]. In addition, the lower crystallinity identified by XRD also contributed to the lower reduction temperatures. Another distinct difference is the presence of less intense reduction peaks, especially at lower temperatures, in the N₂ sample data compared with the samples treated under O₂ or air. These data demonstrate a sequential decrease in average degree of oxidation of the MnO_x. It therefore appears that lower oxidation states of MnO_x tend to favor the SCR reactions.

Based on the XRD, TG and TPR data, the as-prepared catalysts primarily consisted of Mn₂O₃ with small amounts of amorphous MnO₂ and crystalline Mn₃O₄. Similar conclusions have also been reported by previous studies [33,38,41].

3.3. Surface analysis

The morphologies of the catalyst powders were observed by SEM, as shown in Fig. 6. Both well-dispersed and much smaller particles are evident in the materials calcined under N₂ or air. NH₃-TPD was employed to study the surface acidity of the 0.20Ce-Mn/TiO₂ catalysts prepared under different atmospheres, and the results are provided in Fig. 7. The continuous desorptions of ammonia species resulting from NH₃ adsorption on weak acid sites (433 and 513 K) and moderate acid sites (573 K), both of which are of vital importance to low-temperature catalytic activities throughout the entire range of testing temperatures, were observed [42]. Comparing the integrated areas of the NH₃ adsorption peaks (indicated under each curve), the highest NH₃ adsorption capacity and therefore greatest acidity was found in the case of those catalysts calcined under N₂. This result is in accordance with the SEM image, which shows that catalysts without agglomeration

Fig. 5. H₂-TPR profiles of (a) 0.20Ce-Mn/TiO₂-N₂, (b) 0.20Ce-Mn/TiO₂-air, and (c) 0.20Ce-Mn/TiO₂-O₂.

Fig. 6. SEM images of (a) 0.20Ce-Mn/TiO₂-N₂, (b) 0.20Ce-Mn/TiO₂-air, and (c) 0.20Ce-Mn/TiO₂-O₂.

Fig. 7. NH₃-TPD profiles of (a) 0.20Ce-Mn/TiO₂-N₂, (b) 0.20Ce-Mn/TiO₂-air, and (c) 0.20Ce-Mn/TiO₂-O₂.

can provide more active sites. In particular, a greater quantity of moderate acid sites can provide many more active sites for the adsorption and activation of NH₃, both of which are crucial factors determining the catalytic activity of NH₃-SCR [43–45].

With the aid of XPS, changes in the oxidation states of surface metals and oxygen species were determined, as shown in Fig. 8 (which has been processed by peak-fitting). Fig. 8(a) shows the characteristic Mn 2p_{1/2} and Mn 2p_{3/2} peaks, with the Mn 2p_{3/2} peak split into three: 640.0–640.3 eV for Mn²⁺, 641.0–641.3 eV for Mn³⁺ and 643.2–643.8 eV for Mn⁴⁺ [8,27].

Complex Ce 3d spectra are presented in Fig. 8(b), separated into eight components. Here, the peaks labeled as u and v correspond to 3d_{3/2} and 3d_{5/2} with the peaks denoted by u, u'', u''', v, v'' and v''' originating from Ce⁴⁺ and the u' and v' peaks relating to Ce³⁺ [46]. Fig. 8(c) shows the O 1s spectra with two fitted peaks for lattice oxygen (O_β) adsorption, centered at 528.7–529.0 eV, and chemical oxygen (O_α) adsorption, centered at 530–530.6 eV [47].

As can be seen in Figs. 8(a) and (b), the positions of the characteristic Mn and Ce peaks are shifted to the right, indicating lower binding energies. Significantly, the intensities of the Ce³⁺ (u', v') peaks are increased, thus increasing the Ce³⁺/(Ce³⁺ + Ce⁴⁺) ratio in O₂, air and N₂. These data demonstrate that Mn and Ce metal oxides with lower valences, which are believed to promote electron transfer and so to facilitate the redox cycles in the SCR process, are obtained via calcination under air or N₂ atmospheres. The results discussed above can also be ascribed to increases in the concentrations of oxygen vacancies induced by low-oxygen calcination conditions, on the basis of the electroneutrality principle evident in Equation (2). This effect further favors the adsorption and activation of reactant gases on the catalyst surface. More detailed information derived from peak-fitting of the XPS data are provided in Table 1. When the treatment atmosphere is changed from O₂ to air and then to N₂, the Mn⁴⁺/(Mn³⁺ + Mn²⁺) ratio evidently decreases, while the O_α/(O_α + O_β) ratio increases. This result confirms the lower degree of oxidation of MnO_x and the facilitated formation of oxygen vacancies under N₂. It has been reported that the formation of oxygen species (O_α) is due to the presence of surface

Fig. 8. (a) Mn 2p, (b) Ce 3d, and (c) O 1s XPS spectra of (1) 0.20Ce-Mn/TiO₂-N₂, (2) 0.20Ce-Mn/TiO₂-air, and (3) 0.20Ce-Mn/TiO₂-O₂.

Table 1

The effects of calcination atmosphere on the distributions of Mn and O species.

Catalyst	Mn ⁴⁺	Mn ³⁺	Mn ²⁺	Mn ⁴⁺ /(Mn ³⁺ + Mn ²⁺)	O _α /(O _α + O _β) ^a
0.20Ce-Mn/TiO ₂ -N ₂	0.228	0.719	0.053	0.295	0.568
0.20Ce-Mn/TiO ₂ -air	0.271	0.704	0.025	0.372	0.488
0.20Ce-Mn/TiO ₂ -O ₂	0.336	0.638	0.026	0.506	0.478

$$\text{Mn}^{x+} = A_{\text{Mn}^{x+}} / (A_{\text{Mn}^{4+}} + A_{\text{Mn}^{3+}} + A_{\text{Mn}^{2+}}).$$

$$^a \text{O}_\alpha / (\text{O}_\alpha + \text{O}_\beta) = A_{\text{O}_\alpha} / (A_{\text{O}_\alpha} + A_{\text{O}_\beta}).$$

oxygen vacancies [48]. In the present study, we believe that oxygen adspecies were located at the surface oxygen vacancies of MnO_x, CeO_x or TiO_x. This result is in good agreement with the O 1s XPS investigations. Chemisorbed oxygen (O_α) has been reported to be the most active oxygen species and to play a critical role in redox cycles [49]. Therefore, catalysts calcined under N₂ possess a greater ability to oxidize NO to produce NO₂, thereby promoting the “fast SCR” reaction [50,51]. Moreover, NO₂ is considered to be a highly reactive intermediate in NH₃-SCR [52–54]. The analyses in this work suggest that a N₂ atmosphere is advantageous to the formation of species helpful to the SCR reactions, which once again is in good agreement with the observed activities of Ce-Mn/TiO₂ specimens prepared in N₂, air and O₂.

4. Conclusions

The NO conversion efficiencies over 0.20Ce-Mn/TiO₂ samples calcined under different atmospheres varied significantly, decreasing in the order N₂ (94%) > air (85.6%) > O₂ (75.6%). Thus, the 0.20Ce-Mn/TiO₂-N₂ showed the highest catalytic ability. The two main active components required for the NH₃-SCR reactions, Mn₂O₃ and Mn₃O₄, were detected in this material. More importantly, the enhanced surface acidity, increased active oxygen (O_α) content and higher particle dispersion of the 0.20Ce-Mn/TiO₂-N₂ were also found to contribute to its superior performance. This work demonstrates that catalysts with metals in low valence states and well-distributed active components will more readily adsorb NH₃ and NO_x on their surfaces, thereby promoting NO conversions. In general, catalysts calcined under N₂ are evidently more active with regard to catalyzing the NH₃-SCR of NO_x.

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Graphical Abstract

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Performance enhancement mechanism of Mn-based catalysts prepared under N₂ for NO_x removal: Evidence of the poor crystallization and oxidation of MnO_xKai Qi, Junlin Xie*, De Fang, Fengxiang Li, Feng He*
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Ce-Mn/TiO₂ catalysts calcined under N₂ exhibit superior activity during NO removal, owing to a greater degree of particle dispersion, less agglomeration of particles, and a low degree of MnO_x crystallization together with low valence states, all of which favor the NH₃-SCR reactions.

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N₂气氛下焙烧制备的Mn基催化剂催化NO_x脱除性能的提升机理： 低MnO_x结晶度与氧化度

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摘要: 在众多的氧化物类NH₃-SCR催化剂体系中, Mn基氧化物催化剂因具有极高的低温(≤ 473 K)脱硝性能而备受关注。

其主要原因可能是Mn物种具有丰富的可变价态,作为活性组分的 MnO_x 能够提供自由电子.大量研究发现,由于不同金属元素间协同作用的存在,复合金属氧化物的催化脱硝活性普遍优于单金属氧化物类催化剂.为了抑制 MnO_x 在煅烧过程中的烧结,提高 MnO_x 的催化活性,一系列过渡金属氧化物,如Fe, Cu, Ni和Cr等的氧化物,被用来作为改性剂加入到 MnO_x 催化剂中.近年来,很多研究者将稀土元素作为改性剂加入到 MnO_x 催化剂中,并发现稀土金属氧化物的添加可以改善催化剂的活性、选择性、热稳定性及抗毒性能,是良好的添加助剂,其中对Ce的关注度颇高.而储氧性能是 CeO_2 最重要的性质, CeO_2 对氧气的存储和释放可以通过 Ce^{4+} 和 Ce^{3+} 两种价态之间的变化实现.文献研究表明,将 CeO_2 加入到锰氧化物材料中,能够提高锰氧化物在程序升温脱附过程中氧的脱附量,并且在低温条件下能够为锰氧化物提供氧,从而对锰氧化物的氧化态产生影响.此外,我国拥有丰厚的稀土Ce资源储备,使得锰铈复合氧化物在吸附脱除 NO_x 方面得到广泛应用.

催化剂作为选择性催化还原(SCR)工艺的核心,现阶段的研究重点主要集中于新型低温高活性催化剂的研究,如活性组分、载体组分、焙烧温度、焙烧时间及焙烧升温程序等,这表明焙烧过程对于催化剂性能的重要性.然而,在催化脱硝领域,对焙烧气氛的研究极少,但借鉴其他领域对焙烧气氛的研究,确有研究者证实焙烧气氛对材料的颗粒大小、缺陷浓度、价态及物相组成等有着显著的影响,进而影响材料的活性.我们课题组曾研究了焙烧气氛对 $\text{MnO}_x/\text{TiO}_2$ 脱硝性能的影响,并发现惰性气氛中焙烧的催化剂表现出最佳活性,然而对于催化剂催化性能增强的原因并未深入探究.在前期研究基础上,以 MnO_x 和 CeO_x 为活性组分,采用浸渍法制备得到Ce-Mn/ TiO_2 催化剂,通过X射线衍射(XRD)、氢气程序升温还原(H_2 -TPR)、热重(TG)、扫描电子显微镜(SEM)、氨气程序升温脱附(NH_3 -TPD)和X射线光电子能谱(XPS)等表征手段系统地研究了 MnO_x 和 CeO_x 负载于 TiO_2 表面制成的催化剂在不同气氛(N_2 , 空气和 O_2)中焙烧后的催化性能和物相结构.

XRD, TG和 H_2 -TPR测试结果表明,在 N_2 气氛中焙烧有利于催化剂氧化度与结晶度的降低,催化剂中主要存在两种主要活性成分:大量的 Mn_2O_3 和少量的 Mn_3O_4 .SEM图揭示了在 N_2 气氛下焙烧能够有效抑制晶粒长大,促进颗粒分散. NH_3 -TPD结果表明, N_2 气氛下焙烧的催化剂拥有更多的表面酸性位点,从而有利于反应气在催化剂表面的吸附和活化.结合XPS分析结果与脱硝活性测试结果,较低价态的 MnO_x 以及较高的表面活性氧浓度(O_a)更有利于 NH_3 -SCR反应的进行.不同焙烧气氛下0.20Ce-Mn/ TiO_2 催化剂(Ce:Ti摩尔比为0.20)上NO转化率顺序如下: N_2 (94%) > 空气(85.6%) > O_2 (75.6%).以上结果清晰地表明 N_2 焙烧气氛显著提升了催化剂的脱硝活性.

关键词: 锰基催化剂; 选择性催化还原; 焙烧气氛; 锰物种; 氧化度; 结晶度

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