Review

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Review

The Application of MnO_x/TiO_2 Catalyst in SCR-NH_3 Reaction

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Abstract: This article systematically reviews the research achievements on the MnO_x/TiO_2 catalyst doped with transition metals or rare earth metals for the catalytic selective catalytic reduction of NH_3 (SCR-NH_3) reaction. The Methodi Ordinatio systematic literature analysis method was employed to rank relevant articles based on journal impact factors, publication years, and citation counts. The ranking data shows that the undoped MnO_x/TiO_2 catalysts exhibit a catalytic efficiency of up to approximately 90% for NO_x reduction, while the doped MnO_x/TiO_2 catalysts with transition metals or rare earth metals can achieve a maximum reduction efficiency of 100%. Among all the doped metals, the catalyst doped with nickel demonstrates the best NO_x reduction performance. The comprehensive literature research concludes that MnO_x/TiO_2-based SCR catalysts, especially those doped with transition metals or rare earth metals, have significant catalytic efficiency and development potential in reducing NO_x emissions in SCR reactions.

Keywords: selective catalytic reduction; nitrogen oxides; ammonia; MnO_x/TiO_2 catalyst

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1. Introduction

Selective catalytic reduction (SCR) is a method that effectively treats nitrogen oxides (NO_x) in industrial flue gas and exhaust from commercial vehicles. It is widely applied in many countries in Asia, Africa and Europe [1–3]. In commercial industrial flue gas treatment systems, ammonia (NH_3) is one of the reducing agents with high reductive efficiency. Utilizing NH_3 to reduce NO_x to N_2 is a thermodynamically spontaneous reaction at low temperatures, but the kinetic process is too slow, hence the need for metal oxide catalysts to enhance the reaction rate [4–6].

Currently, commercially available metal oxide SCR catalysts mainly consist of V_2O_5-WO_3 (or MoO_3)/TiO_2 as the main components [7–9]. However, these catalysts require high operating temperatures (573K-673K), which means that the SCR denitration unit must be placed before the desulfurization unit [10]. At the same time, the presence of SO_2 and particulate matter in the flue gas can easily lead to rapid catalyst poisoning, increasing the frequency of catalyst replacement and resulting in significantly higher operating costs. On the other hand, low-temperature SCR technology operates at lower temperatures and can be placed after the desulfurization and dust removal processes, reducing the chances of catalyst poisoning and effectively reducing operating costs [8–12].

Commercial vehicles are also a significant source of NO_x emissions. According to the "Statistical Bulletin on the Development of the Transportation Industry in 2022" released by the Ministry of Transport of China, there were 11.666 million commercial vehicles in the country. Among them, there were 3.8769 million ordinary trucks, 0.6343 million special-purpose trucks, 3.5418 million tractor units, and 3.6136 million trailers, with the majority of them being diesel vehicles. A similar situation exists in the African continent [13,14]. This transportation scenario is directly related to the increase in atmospheric pollutant emissions [6,15,16]. The NO_x emissions from commercial vehicle exhaust can be reduced through SCR technology, thereby achieving emissions compliance [17,18].

Manganese oxide (MnO_x) can serve as the catalytically active component in low-temperature selective catalytic reduction (SCR). MnO_x exists in various oxidation states, and the interconversion between these states enables the catalytic oxidation-reduction reactions to take place. Among the different forms of MnO_x, amorphous MnO_x is considered to exhibit strong catalytic activity in SCR systems, while crystalline MnO_x is believed to have limited catalytic effects [19,20]. Research by Kapteijn et al. [21] demonstrated that MnO_x achieves the highest NO_x removal efficiency of up to 90% in SCR-NH_3 reactions at 450K. Studies by Xie et al. [22] have shown that MnO_x/TiO_2 catalysts hold promising prospects for SCR-NH3 reactions. MnO_x/TiO_2 catalysts are known for their good thermal stability, high mechanical strength, and high resistance to sulfur[23].

2. Research Methods

This paper provides a comprehensive summary of the recent progress in using MnO_x/TiO_2 catalysts containing transition metals or rare earth metals for the selective catalytic reduction of NO_x in SCR-NH_3 reactions. SCR plays a significant role in mitigating air pollution caused by NO_x emissions. In conducting this research, the following keywords were utilized during literature search: "SCR", "NO_x", "NO", and "Mn/TiO_2". The evaluation of the literature was performed using the Methodi Ordinatio methodology proposed by Pagani et al. [24], which takes into account factors such as the impact factor, citation count, and publication year to assess its quality. The categorization and classification of the literature were accomplished using the InOrdinatio formula described below.

$$\text{InOrdinatio} = IF + (10 * (10 - (A' - A''))) \quad (1)$$

IF：Impact Factor

A′：Year of the research

A′′：Year of publication

C_i：Number of citations

This study utilized two software tools, "Excel" and "Mendeley," to organize and sort articles based on factors such as impact factor, citation count, and publication year, in order to identify the most relevant articles related to the research topic. The literature search for articles was conducted on Science Direct (www.sciencedirect.com) from May to July 2023. Initially, without setting a specific time range for the database search, the initial literature search results covered articles published between 1996 and 2022. From the search results, book chapters were first excluded, followed by conference abstracts, and only research articles were selected. For the research articles, the titles were read as the first round of screening, then the abstracts were read and associated with the keyword "NH_3" for the second round of screening. Finally, the articles were downloaded and thoroughly read as the third round of screening to confirm their complete relevance to the research topic. Following the guidelines of the "Methodi Ordinatio" methodology [24], a subset of relevant research articles published between 2007 and 2022 was identified for presentation and discussion.

3. Results and Discussion

3.1. Search Results Based on the "Methodi Ordinatio" Approach

A total of 285 articles were retrieved from the Science Direct database based on the aforementioned keywords, among which 194 were research articles. The detailed results are shown in Table 1. During the selection process of research articles, the initial screening was conducted based on the article titles, followed by the second round of screening based on the association between the article abstracts and "NH_3". Subsequently, 77 full-text articles were downloaded and read in the third round of screening. Lastly, only articles related to SCR-NH_3 and NO_x were selected, and 19 of them were chosen as references for this literature review. The results of the descending ranking using the InOrdinatio score are shown in Table 2.

Table 1. Search results for SCR, NO_x, NO, and Mn/TiO_2 in the ScienceDirect database.

The types of articles	Number
Review articles	16
Research articles	194
Chapters of books	8
Conference abstracts	24
Discussions	1
Short communications	11
Others	31
Total	285

Table 2. Ranking of selected scientific papers.

Author and Title	Impact Factor	Number of citations	Year of publication	InOrdinatio
Thirupathi B & Smirniotis P G. Nickel-doped Mn/TiO_2 as an efficient catalyst for the low-temperature SCR of NO with NH_3: Catalytic evaluation and characterizations.	7.3	408	2012	405
Thirupathi B, Smirniotis P G. Co-doping a metal (Cr, Fe, Co, Ni, Cu, Zn, Ce, and Zr) on Mn/TiO_2 catalyst and its effect on the selective reduction of NO with NH_3 at low-temperatures.	22.1	379	2011	381
Xie S, Li L, Jin L, et al. Low temperature high activity of M (M= Ce, Fe, Co, Ni) doped M-Mn/TiO_2 catalysts for NH_3-SCR and in situ DRIFTS for investigating the reaction mechanism.	6.7	118	2020	195
Gao C, Shi J W, Fan Z, et al. " Fast SCR" reaction over Sm-modified MnO_x-TiO_2 for promoting reduction of NO_x with NH_3.	5.5	122	2018	178
Li J, Chen J, Ke R, et al. Effects of precursors on the surface Mn species and the activities for NO reduction over MnO_x/TiO_2 catalysts.	3.7	220	2007	164
Li Q, Li X, Li W, et al. Effect of preferential exposure of anatase TiO_2 {0 0 1} facets on the performance of Mn-Ce/TiO_2 catalysts for low-temperature selective catalytic reduction of NO_x with NH_3.	15.1	75	2019	150
Li W, Guo R, Wang S, et al. The enhanced Zn resistance of Mn/TiO_2 catalyst for NH_3-SCR reaction by the modification with Nb.	7.5	102	2016	140
Niu C, Wang B, Xing Y, et al. Thulium modified MnO_x/TiO_2 catalyst for the low-temperature selective catalytic reduction of NO with ammonia	11.1	45	2021	136
Ye B, Lee M, Jeong B, et al. Partially reduced graphene oxide as a support of Mn-Ce/TiO_2 catalyst for selective catalytic reduction of NO_x with NH_3.	5.3	67	2019	132
Kim Y J, Kwon H J, Nam I S, et al. High deNO_x performance of Mn/TiO_2 catalyst by NH_3.	5.3	143	2010	118
Huang J, Huang H, Jiang H, et al. The promotional role of Nd on Mn/TiO_2 catalyst for the low-temperature NH_3-SCR of NO_x.	5.3	45	2019	110

Hao C, Zhang C, Zhang J, et al. An efficient strategy to screen an effective catalyst for NO_x-SCR by deducing surface species using DRIFTS.	9.9	8	2022	108
Sun X, Guo R, Liu J, et al. The enhanced SCR performance of Mn/TiO_2 catalyst by Mo modification: Identification of the promotion mechanism.	7.2	51	2018	108
Jia B, Guo J, Luo H, et al. Study of NO removal and resistance to SO_2 and H_2O of MnO_x/TiO_2, MnO_x/ZrO_2 and MnO_x/ZrO_2–TiO_2.	5.5	42	2018	98
Wei L, Cui S, Guo H, et al. The effect of alkali metal over Mn/TiO_2 for low-temperature SCR of NO with NH_3 through DRIFT and DFT	3.3	44	2018	97
Fang D, Li D, He F, et al. Experimental and DFT study of the adsorption and activation of NH_3 and NO on Mn-based spinels supported on TiO_2 catalysts for SCR of NO_x.	3.3	33	2019	96
Jiang B, Lin B, Li Z, et al. Mn/TiO_2 catalysts prepared by ultrasonic spray pyrolysis method for NO_x removal in low-temperature SCR reaction.	5.2	21	2020	96
Huang C, Guo R, Pan W, et al. SCR of NO_x by NH_3 over $MnFeO_x$@ TiO_2 catalyst with a core-shell structure: The improved K resistance.	5.7	25	2019	91
Shi J, Zhang Z, Chen M, et al. Promotion effect of tungsten and iron co-addition on the catalytic performance of MnO_x/TiO_2 for NH_3-SCR of NO_x.	7.4	38	2017	85

3.2. Application of MnO_x/TiO_2 Catalysts in the SCR-NH_3 Reaction

Based on the ranking order of the InOrdinatio scores as reported in Table 2, this section presents the application of MnO_x/TiO_2 catalysts in the selective catalytic reduction of NH_3 (SCR-NH_3) reaction in a comprehensive and comprehensible manner.

Thirupathi and Smirniotis [25] used a wet impregnation co-doping method to incorporate transition metals such as chromium (Cr), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), zirconium (Zr), and cerium (Ce) into Mn/TiO_2-based catalysts. The results showed that the Mn/Ni-TiO_2 catalyst exhibited higher NO_x reduction efficiency in the SCR-NH_3 reaction, indicating that Ni is a promising metal additive. H_2-TPR and XPS analyses revealed that MnO_2 was the main phase in the Mn-Ni/TiO_2 catalyst with an atomic ratio of 0.4, and the increased reducibility of Mn led to higher NO_x reduction efficiency. The NO_x reduction efficiency of the Mn-Ni/TiO_2 catalyst with an atomic ratio of 0.4 could reach approximately 100% at around 200 °C. Moreover, the addition of Ni significantly improved the thermal stability of the catalyst, which still achieved 76% NO_x reduction efficiency at 300 °C.

Thirupathi and Smirniotis [26] further employed the wet impregnation co-doping method to incorporate nickel (Ni) atoms into modified Mn/TiO_2 catalysts. They evaluated the catalytic performance of these catalysts in the SCR-NH_3 reaction under different Ni/Mn ratios (0.0, 0.2, 0.4, 0.6, and 0.8). The results showed that the addition of Ni to the Mn/TiO_2 catalyst significantly enhanced its NO_x reduction efficiency and selectivity towards N_2 production. The Mn/TiO_2 catalyst with a Ni/Mn atomic ratio of 0.4 exhibited 100% NO_x conversion and high selectivity towards N_2 generation at 200 °C. Furthermore, the Mn/TiO_2 catalyst with a Ni/Mn atomic ratio of 0.4 demonstrated excellent stability, maintaining complete NO_x conversion over a reaction time of 240 hours.

Li et al. [27] utilized the wet impregnation method to synthesize MnO_x/TiO_2 catalysts using different precursors. In the experiments, a gas mixture containing 500 ppm of NO, 500 ppm of NH_3, 3% of O_2, and balanced with N_2 was employed. The evaluation was carried out using 500 mg of catalyst at a gas flow rate of 300 ml per minute. The experimental results indicated that the use of manganese nitrates (MN) and manganese acetate (MA) as precursors led to different oxidation states of manganese in the MnO_x catalysts prepared for the SCR reaction. According to the results, the MA-MnO_x/TiO_2 catalyst exhibited approximately 70% NO reduction efficiency at a lower temperature (50 °C), reaching 100% NO reduction efficiency at 150 °C. In contrast, the NO reduction efficiency of MN-MnO_x/TiO_2 catalyst increased more slowly with temperature, reaching a maximum conversion rate of only 96% at 200 °C. Manganese acetate, as a precursor for the catalyst, exhibited higher catalytic activity due to the formation of highly dispersed Mn_2O_3 surfaces, while manganese nitrates mainly resulted in less active MnO_2 surfaces.

Li et al. [28] incorporated niobium (Nb) into Mn/TiO_2 catalysts to prepare modified Mn/TiO_2 catalysts and evaluated their resistance to zinc (Zn) in the SCR-NH_3 reaction. In this study, two different catalyst formulations were employed. Firstly, catalyst samples without zinc were synthesized, with one formulation being Mn/TiO_2 at a molar ratio of 0.2:1, and the other formulation being Mn-Nb/TiO_2 at a molar ratio of 0.15:0.05:1. Additionally, catalyst samples containing zinc were prepared, with Zn/Mn or Zn/(Mn+Nb) molar ratios of 1:8. The evaluation tests of these catalysts were conducted using a gas mixture containing 600 ppm of NO, 600 ppm of NH_3, 5% of O_2, and balanced with argon (Ar) as the carrier gas, at a GHSV of 108,000 h^{-1}. The results revealed that for the Mn/TiO_2 catalyst without zinc, the maximum NO reduction efficiency was 95% at 200 °C, whereas in the presence of zinc poisoning, the NO reduction efficiency of the Mn/TiO_2 catalyst at 200 °C dropped to only 20%. On the other hand, the modified catalyst with Nb exhibited improved stability, maintaining a sustained NO reduction efficiency of 95% from 150 °C to 350 °C. Even in the presence of zinc poisoning, the Nb-doped Mn/TiO_2 catalyst still achieved an NO reduction efficiency of 80%. The authors suggested that the addition of Nb could lower crystallinity, promote the formation of Mn^{4+} and adsorbed oxygen, enhance catalytic efficiency, and improve resistance to zinc, thereby facilitating the reduction reaction between NO and NH_3.

According to the study conducted by Gao et al. [29], rare earth metals such as samarium (Sm) can also enhance the catalytic efficiency when incorporated into catalysts in the SCR reaction. This is attributed to their partially filled 4f and 5d orbitals. Gao et al. employed a reverse co-precipitation method to introduce compounds with different Sm/Mn molar ratios (0.1, 0.3, and 0.5) into MnO_x/TiO_2 catalysts and evaluated their performance in the SCR-NH_3 reaction. The evaluation tests were carried out using a gas mixture containing 500 ppm of NO, 500 ppm of NH_3, 5% of O_2, and balanced with N_2 as the carrier gas. The catalyst loading was 600 mg, and the tests were conducted at a GHSV of 36,000 h^{-1}. The results demonstrated that the catalyst with a Sm/Mn molar ratio of 0.3 achieved a NO reduction efficiency of approximately 100% within the temperature range of 210 °C to 360 °C. Furthermore, the catalyst with a Sm/Mn molar ratio of 0.3 exhibited a selectivity of 100% towards N_2 formation within the temperature range of 120 °C to 390 °C.

Xie et al. [22] conducted a study on the effects of incorporating various transition metals into MnO_x/TiO_2 catalysts. The molar ratio of the transition metal (M) to manganese (Mn) and titanium (Ti) in the catalysts was 0.05:0.3:1 (M = Ce, Fe, Co, and Ni), and the transition metals were introduced into MnO_x/TiO_2 through a wet impregnation method. The evaluation tests were carried out using a gas mixture containing 500 ppm of NO, 500 ppm of NH_3, 5% of O_2, and balanced with argon (Ar) as the carrier gas. The tests were conducted under two GHSV conditions, namely 120,000 $ml \cdot g^{-1} \cdot h^{-1}$ and 60,000 $ml \cdot g^{-1} \cdot h^{-1}$. The results demonstrated that the Ni-Mn/TiO_2 catalyst exhibited better performance than the other materials within the temperature range of 150 °C to 200 °C, achieving over 90% NO conversion rates under both gas flow rates. Additionally, the authors emphasized the importance of GHSV, which can affect the catalytic activity. Increasing the GHSV from 60,000 $ml \cdot g^{-1} \cdot h^{-1}$ to 120,000 $ml \cdot g^{-1} \cdot h^{-1}$ had an adverse effect on the reduction efficiency under preset conditions, especially at 100 °C. At the same reaction temperature, the reduction efficiency for NO was approximately 70% when the GHSV was 120,000 $ml \cdot g^{-1} \cdot h^{-1}$, but exceeded 80% when the GHSV was 60,000 $ml \cdot g^{-1} \cdot h^{-1}$, indicating that increasing the GHSV would lead to decreased catalytic activity for the Ni-Mn/TiO_2 catalyst.

The commonly used methods for preparing Mn/TiO_2 catalysts are sol-gel and impregnation methods. Kim et al. [18] demonstrated in their study that the catalytic reduction activity of this type of catalyst towards NO_x may be directly influenced by the synthesis method of the catalyst. Kim et al. prepared Mn/TiO_2 catalysts with different Mn contents (mass ratios ranging from 12% to 30%) using both sol-gel and impregnation methods. The evaluation tests were conducted using a gas mixture containing 500 ppm of NO_x, 500 ppm of NH_3, 5% of O_2, 10% of H_2O, and balanced with N_2 as the carrier gas. The tests were performed at a GHSV of 100,000 h^{-1} using 1g of the catalyst. The research results showed that the catalytic activity of the Mn/TiO_2 catalysts prepared by the impregnation method significantly decreased as the Mn content increased from 13% to 28% (mass ratio). In contrast, Mn/TiO_2 catalysts prepared by the sol-gel method exhibited strong catalytic ability at a Mn content of 30% (mass ratio), achieving 90% catalytic efficiency for NO_x reduction at 250 °C. On the other hand, the Mn/TiO_2 catalyst prepared by the impregnation method (with the optimal Mn content of 13%) only reached a conversion rate of 65% under the same conditions. Catalysts synthesized by the sol-gel method demonstrated superior performance because they could disperse MnO_2 more effectively, thereby enhancing the catalytic efficiency of the catalyst.

Ye et al. [30] prepared $Mn-Ce/TiO_2$ catalysts with dispersed metal oxide nanoparticles on graphene oxide (GO), reduced graphene oxide (rGO), and partially reduced graphene oxide (prGO) using a wet impregnation method. The performance of the catalyst in the selective catalytic reduction of NH_3 with SCR-NH_3 reaction was investigated in the temperature range of 100 °C to 300 °C. The experiments were conducted using a gas mixture containing 500 ppm of NO_x, 5% of O_2, 500 ppm of NH_3, and N_2 as the balance gas, with a GHSV of 100,000 $ml \cdot g^{-1} \cdot h^{-1}$.The results showed that the Mn-Ce/TiO_2 catalyst supported on partially reduced graphene oxide exhibited the highest NO_x reduction efficiency, reaching up to 99% in the temperature range of 150 °C to 250 °C. This high catalytic activity may be attributed to the excellent thermal conductivity of graphene oxide and its physical properties such as high dispersion, large surface area, and high thermal stability.

According to the study by Hao et al. [31], using TiO_2 as a catalyst support offers numerous advantages. TiO_2 possesses high thermal stability and is resistant to SO_2 poisoning. Additionally, TiO_2 provides adsorption sites for NH_3, including Lewis acid and Bronsted acid sites, which are beneficial for the SCR-NH_3 reaction to occur.

Li et al. [32] investigated the catalytic performance of $Mn-Ce/TiO_2$ catalysts supported on {0 0 1}-faceted titanium nanosheets, prepared via a wet impregnation method, in the SCR-NH_3 reaction. The experiments were conducted using a gas flow containing 0.08% NO, 0.08% NH_3, 5% O_2, and N_2 as the balance gas, with a GHSV of 10,000 h^{-1}. The results showed that the $Mn-Ce/TiO_2$ catalyst supported on {0 0 1}-faceted titanium nanosheets exhibited a catalytic NO_x reduction efficiency of 90% at 160 °C, while the $Mn-Ce/TiO_2$ catalyst supported on {1 0 1}-faceted anatase showed a much lower NO_x reduction efficiency of only 61.4% at the same temperature. The authors attributed the higher catalytic activity of the $Mn-Ce/TiO_2$ catalyst supported on {0 0 1}-faceted titanium nanosheets to the increased surface area and promotion of the SCR-NH_3 reaction facilitated by the {0 0 1}-faceted nanosheets.

Niu et al. [33] prepared modified MnO_x/TiO_2 catalysts by incorporating thulium (Tm) using a wet impregnation method and studied their catalytic performance. The experiments were conducted using a gas flow containing 500 ppm of NO, 500 ppm of NH_3, 5% O_2, and N_2 as the balance gas, with 180 mg of catalyst used for evaluation.The results showed that the catalysts modified with Tm exhibited a 100% NO reduction efficiency between 150 °C and 270 °C at a GHSV of 36,000 h^{-1}. In contrast, the unmodified catalysts achieved an approximate 90% NO reduction efficiency at around 240 °C under the same conditions but with a higher GHSV of 180,000 h^{-1}. However, the introduction of Tm into the catalysts at the same conditions improved the NO reduction efficiency to 95%.

Huang et al. [12] demonstrated that doping transition metals such as Cr, Mn, Fe, and Cu, as well as rare earth metals, can enhance the catalytic activity of Mn/TiO_2 catalysts. The authors synthesized a series of doped rare earth metal catalysts, $Mn-RE/TiO_2$, using a wet impregnation method. The RE metals used were Ce, Sm, Neodymium(Nd), Erbium(Er), and Gadolinium(Y), with a mass ratio of 3% for RE/TiO_2 and 30% for Mn/TiO_2.The experiments were conducted using a gas flow containing 600 ppm of NO, 600 ppm of NH_3, 3% O_2, and N_2 as the balance gas. The results showed that among these catalysts, Nd had the most significant impact on the reduction efficiency of NO_x in the SCR-NH_3 reaction. At 100 °C, the catalyst doped with Nd achieved a maximum catalytic reduction efficiency of 100%. The authors attributed the higher catalytic activity of the Nd-doped material to its

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larger specific surface area, smaller average pore size, and the improved dispersibility of MnO_x facilitated by Nd.

Sun et al. [34] investigated the application of $MnMo/TiO_2$, Mo/TiO_2, and Mn/TiO_2 catalysts synthesized via co-precipitation method in the SCR-NH_3 reaction. The experimental conditions consisted of NO (600 ppm), NH_3 (600 ppm), O_2 (5%), H_2O (5%), SO_2 (100 ppm), with Ar as the balance gas and a GHSV of 108,000 h^{-1}.The research findings indicated that the Mo/TiO_2 catalyst exhibited a reduction catalytic efficiency for NO below 35% within the temperature range of 50 °C to 400 °C. On the other hand, the Mn/TiO_2 catalyst achieved a reduction catalytic efficiency for NO of up to 90% in the temperature range of 219 °C to 319 °C. In comparison, the $MnMo/TiO_2$ composite catalyst with a Mn/Mo molar ratio of 0.04 demonstrated over 95% reduction catalytic efficiency within the temperature range of 200 °C to 300 °C. The NOx reduction catalytic efficiency of $MnMo/TiO_2$ catalyst was approximately twice that of the pure Mn/TiO_2 catalyst.

Jiang et al. [35] synthesized a series of Mn/TiO_2 catalysts using ultrasonic spray pyrolysis method, with Mn/Ti molar ratios ranging from 0.1 to 0.6. Within the temperature range of 120 °C to 240 °C, these Mn/TiO_2 catalysts exhibited high catalytic reduction efficiency for NO. Among them, the Mn(0.5)/TiO_2 catalyst achieved a catalytic reduction efficiency for NO of approximately 97% at a GHSV of 30,000 h^{-1}.

Jia et al. [36] synthesized MnO_x/TiO_2, MnO_x/ZrO_2, and MnO_x/ZrO_2-TiO_2 catalysts and studied their application in SCR-NH_3. The experimental setup involved a gas stream containing 500 ppm of NO, 500 ppm of NH_3, 10% of H_2O, 4% of O_2, and N_2 as the balance gas. A catalyst loading of 550 mg was used for the evaluation experiments.The results showed that among this series of catalysts, the MnO_x/TiO_2 catalyst achieved a 100% reduction catalytic efficiency for NO_x between 240 °C and 360 °C. Additionally, the MnO_x/ZrO_2-TiO_2 catalyst exhibited better resistance to H_2O and SO_2 under the same activity conditions.

Wei et al. [37] synthesized Mn/TiO_2 catalysts using a co-precipitation method with an atomic ratio of Mn/Ti of 0.4, and investigated the influence of potassium (K) poisoning on the catalyst performance. The experimental gas composition consisted of a 1:1 mixture of NO and NH_3 (1000 ppm), along with 3% O_2, and N_2 was used as the balance gas. The experiments were conducted at a GHSV of 40000 h^{-1}.The pristine Mn/TiO_2 catalyst exhibited a NO reduction catalytic efficiency exceeding 85% between 150 °C and 270 °C. However, the catalytic activity of the material affected by K poisoning significantly decreased within the same temperature range, remaining below 75%. The authors suggested that the catalyst experienced deactivation after being exposed to K poisoning, primarily due to the deposition of potassium leading to a reduction in surface area and pore volume of the catalyst.

Fang et al. [38] evaluated the catalytic efficiency of Mn/TiO_2 catalysts containing Ni and Cu. The molar ratio of Mn/Ti was 0.4, and the molar ratios of Mn/Cu and Mn/Ni were both 2. The experimental conditions included 720 ppm NO, 800 ppm NH_3, and 3% O_2, with N_2 as the balance gas at a total flow rate of 1120 ml·min^{-1}.The results showed that at 179 °C, the Ni-Mn/TiO_2 catalyst exhibited a NO_x reduction catalytic efficiency exceeding 87%. However, the Cu-Mn/TiO_2 catalyst demonstrated an even higher reduction catalytic efficiency at the same temperature, reaching 93%.

Huang et al. [39] synthesized a core-shell catalyst called $MnFeO_x@TiO_2$ using the impregnation method. The aim was to enhance the catalyst's resistance to potassium (K) poisoning in the selective catalytic reduction of NH_3 (SCR-NH_3) reaction. A comparison experiment was conducted with supported $MnFeO_x/TiO_2$ catalysts. The experimental conditions included a gas flow with 600 ppm NO, 600 ppm NH_3, 5% O_2, and Ar as the balance gas, under a gas hourly space velocity of 108,000 h^{-1}. The study results demonstrated that compared to the supported $MnFeO_x/TiO_2$ catalysts, the core-shell $MnFeO_x@TiO_2$ catalysts exhibited good NO_x reduction catalytic efficiency within the temperature range of 250 °C to 400 °C, even with a cumulative K poison amount of approximately 60%.

Shi et al. [40] conducted a study on the co-doping of tungsten (W) and iron (Fe) in MnO_x/TiO_2 catalysts. These catalysts were prepared by a wet impregnation method and evaluated under the following conditions: 600 ppm NO, 600 ppm NH_3, 15% O_2, with N_2 as the balance gas, and a gas hourly space velocity of 240,000 h^{-1}.The results showed that compared to MnO_x/TiO_2 catalysts, the $FeMnO_x/TiO_2$ catalysts exhibited a 27% improvement in the reduction catalytic efficiency for NO_x. The lower temperature window for catalytic activity was shifted from 200 °C to 150 °C. However, the reduction catalytic efficiency for NO_x decreased at 400 °C. On the other hand, the catalyst doped with tungsten ($WMnO_x/TiO_2$) showed a 40% increase in reduction efficiency for NO_x compared to MnO_x/TiO_2 catalysts at 400 °C.

4. Conclusion

With the development of our society, utilizing the SCR-NH_3 reaction for the degradation of NO_x has become an effective solution to reduce industrial and mobile source emissions. Consequently, the development of highly active and selective SCR-NH_3 catalysts has gained increasing attention in the field of environmental catalysis. MnO_x/TiO_2-based catalysts have attracted significant interest due to their excellent reduction catalytic performance and relatively low cost. In this study, we employed the Methodi Ordinatio systematic literature analysis method to summarize the latest progress in MnO_x/TiO_2-based catalysts doped with transition metals or rare earth metals for catalyzing the SCR-NH_3 reaction. These doped catalysts exhibited remarkably high catalytic efficiency. For instance, doping Ni, Nd, Tm, and other elements into MnO_x/TiO_2-based catalysts can enhance the reduction catalytic efficiency to around 95%, while MnO_x/TiO_2 catalysts doped with Ni can even achieve nearly 100% reduction catalytic efficiency. Doping transition metals or rare earth metals effectively increased the dispersion of MnO_x, enhanced the adsorption sites of NH_3 Lewis acid and Bronsted acid, and increased the surface area and pore volume of MnO_x/TiO_2-based catalysts. These improvements enhanced the catalytic activity and resistance to poisoning of the catalysts in the SCR-NH_3 reaction, leading to a lower optimal reaction temperature. Consequently, commercialization of low-temperature SCR systems becomes feasible. In conclusion, MnO_x/TiO_2-based catalysts doped with transition metals or rare earth metals have demonstrated great potential in enhancing the catalytic performance and selectivity of the SCR-NH_3 reaction. Their utilization can pave the way for significant advancements in emission control technologies.

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