

TiO₂-based Catalysts for SCR of NO_x with NH₃: State of the Art and Future Prospects

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Abstract

Selective catalytic reduction with NH₃ (NH₃-SCR) has been considered as the most successful denitration technology from stationary boilers and coal-fired plants. However, conventional commercial catalysts like V₂O₅-WO₃ (MoO₃)/TiO₂ show a series of drawbacks in practical applications, so developing novel catalytic is imperious. This paper begins by reviewing the latest TiO₂ based SCR catalysts. Then, it will go on to summarize three types of developed TiO₂ based catalysts, including pure TiO₂ as support catalysts, modification of TiO₂ as support catalysts and TiO₂ as active species catalysts. Firstly, although the species and content of interface-loaded active components are essential, the effect of interaction between species and supports on SCR reaction activity over TiO₂ supported has not been explored. Secondly, modification of TiO₂ as support catalysts mainly enhances a role of TiO₂ supported in activity and poisoning-resistant. However, the modification methods are limited to the doping of metal or nonmetal elements. Thirdly, titanium mainly regulates the strong oxidization of active species while its performance improvement on SCR is relatively limited. The challenges and opportunities for each type of catalysts are proposed while the effective strategies are summarized for developing novel TiO₂ based catalysts with high potential for industrial application. Some suggestions for future research are put forward, and TiO₂ based catalysts would be a fruitful area for further work. Hopefully, this review could make a little contribution to realize their commercial applications in the near future.

Keywords

Selective Catalytic Reduction; TiO₂ Based Catalysts; Acid Site; Redox Site; Dispersion.

1. Introduction

Reducing atmospheric pollution is a difficult global task. It is becoming increasingly serious as time goes by and as a result, many people have become involved in environmental awareness[1]. Emissions of nitrogen oxides (NO_x) from power stations, factories and cars are a major source of air pollution and a major cause of the greenhouse effects, acidic rain, photochemical smog and ozone depletion[2]. Therefore, it is necessary to remove nitrogen oxides. Several deNO_x technologies include adsorption method, pulse corona plasma, electron beam irradiation, selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) of NO_x with NH₃ (NH₃-SCR). Notably, SCR has been the most mature and widely used deNO_x technology with a higher deNO_x efficiency[1]. Catalysts are the heart of SCR technologies, providing effective and selective conversion of NO_x to N₂. At present, V₂O₅/TiO₂ with either WO₃ or MoO₃ as commercial catalysts have been used as industrial catalysts in stationary and mobile source NH₃-SCR deNO_x. Although the conventional vanadium-based catalyst shows high activity, it suffers from the narrow operating temperature window, the high SO₂ oxidation activity, the poor alkali-resistance, and the biological toxicity of V₂O₅[3].

Hence, novel catalysts should be developed for this issue. Currently, a great deal of work has been done on the development of SCR catalysts, including metal oxide catalyst, noble metal catalyst, carbon-based catalyst, molecular sieve catalysts and so on. Noble metals, transition metals, rare earth metals and other supported catalysts have shown their excellent performance in theoretical research and practical application. Support is one of indispensable components for the supported catalysts. The catalytic active species are mainly used to support the active components to make the catalyst have specific physical and chemical properties and they are doped is on the surface of the carrier. Alumina oxide, silica oxide, activated carbon, and titanium oxide are commonly used as carriers in the catalyst preparation process. Although titanium oxide carriers exist worse poison resistance, they have some excellent properties, like improving dispersion and SO₂ resistance. At present, titanium dioxide SCR catalyst research is very promising, while TiO₂-based catalysts have not been systematically reviewed. This paper provides an integrated overview of the core work on TiO₂-based catalysts targeting TiO₂ from three ways in recent years, and critical emphasis will be given on performance of catalysts and role of carriers as well as variation in the role of TiO₂. Furthermore, the author reviews the innovative TiO₂-based catalysts under three categories: TiO₂ supports catalysts, modified TiO₂ supports catalysts, and TiO₂ as active species catalysts. Subsequently, this paper provides an overview of the challenges and opportunities faced by various catalysts and makes some suggestions for future research directions.

2. TiO₂-based catalysts

2.1 TiO₂ supports catalysts

The CuSO₄/TiO₂ catalysts obtained by impregnated had better deNO_x performance than by mechanically mixed, and 20%-CuSO₄/TiO₂ catalysts showed the best performance, reaching >90% NO conversions at above 280°C. Besides, TiO₂ promoted the uniform dispersion of active component CuSO₄ [4]. H. Zhang et al. found that the pure carrier titanium dioxide is basically inactive, when it is loaded with cerium dioxide. While the CeO₂/TiO₂ activity gradually increases as the cerium dioxide content increases from 3% to 28% [5]. As illustrated in Figure 1, at a loading of 28% CeO₂, the cerium-titanium catalytic system achieved over 90% NO_x conversion at 350°C. In addition, the doping of CeO₂ can promote the formation of oxygen vacancies on the surface of TiO₂ and thus the generation of surface reactive oxygen species facilitates the SCR reaction (Figure 2).

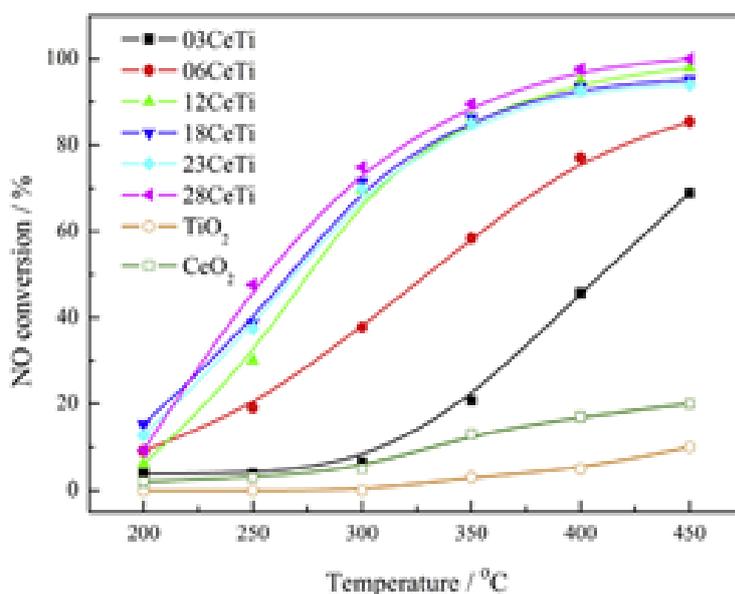


Figure 1. SCR performance of CeO₂/TiO₂ catalysts with various CeO₂ contents. Reproduced with permission.^[5] Copyright 2020, Zhang et al..

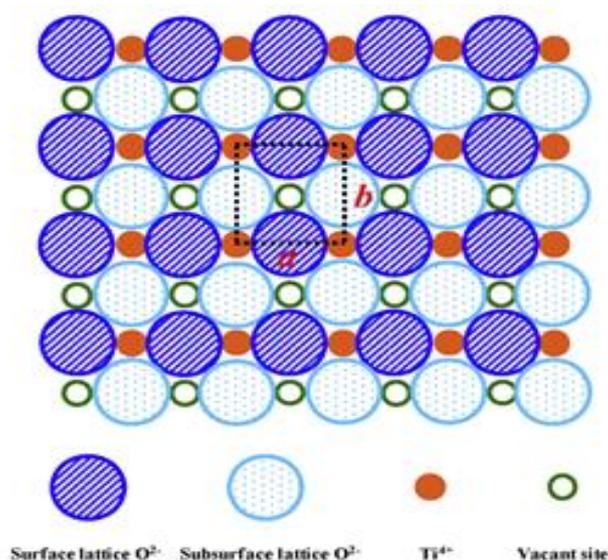


Figure 2. The schematic diagram of the (001) crystal plane of TiO_2 support. Reproduced with permission.^[5] Copyright 2020, Zhang et al..

In fact, none of the single component loaded catalysts perform extremely well, including the aforementioned CuSO_4 and CeO_2 , and although their NO_x conversions are above 90%, the active temperature window is not broad (280°C and 350°C respectively). In general, multi-component loaded catalysts are more commonly used. For examples, $\text{Mn-Ce-O}_x/\text{TiO}_2$ was studied by chao et al., and showed that the co-precipitated catalysts exhibited excellent low temperature activity (The NO_x conversion was 97% at 125°C and the N_2 selectivity was 97%). The co-precipitation method promoted the crystalline nucleation of the carrier, which led to an increase in the Mn^{4+} content of the TiO_2 surface and the content of surface adsorbed oxygen species, thus promoting SCR reactivity[6].

Du et al. explored the outcome of different precursor forms on the action of multi-component TiO_2 catalysts and exhibited that the catalysts synthesized from nitrate precursors in the $\text{Fe-Mn}/\text{TiO}_2$ system presented the most excellent activity, particularly at low temperatures. This was because the nitrate enabled the active component to be highly dispersed on the carrier surface and ensured that the TiO_2 still maintained a high BET area[7]. Furthermore three-component loaded catalysts, which are not particularly common, are also available. J. Wang et al. designed the MnCeV oxide simultaneously loaded onto the TiO_2 carrier surface exhibited high NO_x conversion and N_2 selectivity in the temperature range of 110 to 310°C (Figure 3). The doping of active elements significantly enhanced the BET area of the carrier TiO_2 and increased the pore fusion, providing more active sites for the activation process[8].

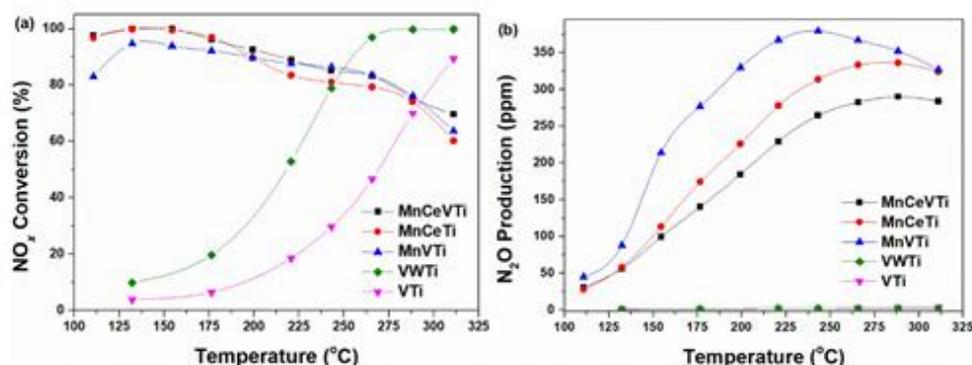


Figure 3. **a** NO_x conversion and **b** N_2O production of prepared samples measured at different temperatures with a gaseous mixture containing 500 ppm NO , 500 ppm NH_3 , 3% O_2 and N_2 balance. Reproduced with permission.^[8] Copyright 2020, J. Wang et al..

2.2 Modified TiO₂ supports catalysts

It can be seen from Figure 4 that H₂SO₄ pretreatment of the conventional P25 carrier effectively enhanced the high temperature reactivity of the CeO₂-TiO₂ catalyst (350-500°C), maintained the NO_x conversion at >90% and showed excellent resistance to alkali metal K toxicity (80% reactivity was maintained after K poisoning). At the same time, the catalytic system had excellent resistance to H₂O. The modification of TiO₂ effectively enhanced the medium to strong acidic sites on the surface of the carrier, thus providing a sacrificial site for coordination with alkali metal K and allowing the catalytic system to exhibit good stability[9].

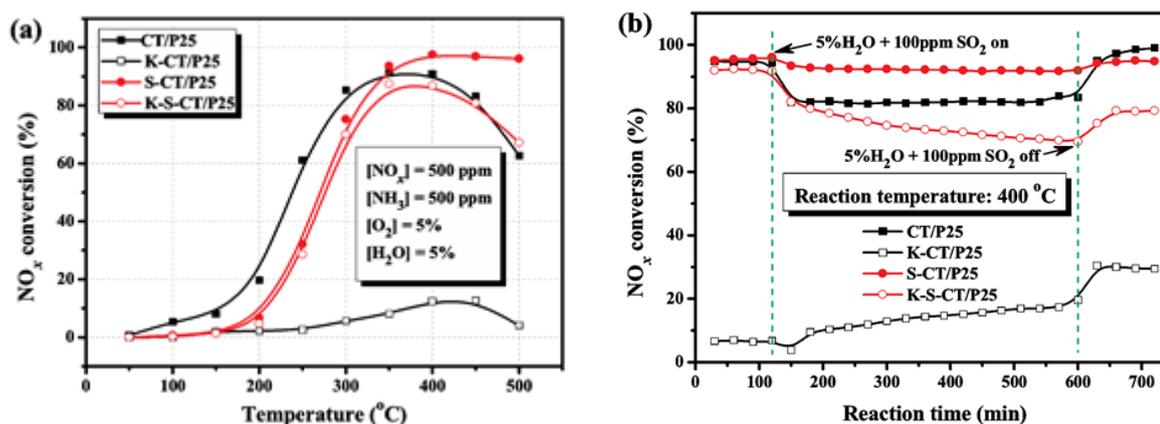


Figure 4. (a) NH₃-SCR catalytic activity and (b) resistance to H₂O+SO₂ over these fresh catalysts and K-poisoned catalysts. Reproduced with permission.^[9] Copyright 2020, Yao et al..

At the same time, the low temperature reduction activity of the MnO_x/TiO₂-S catalysts constructed on S-modified TiO₂ carriers was significantly increased (NO_x conversion increased from 42% to 79% at 150°C and maintained at over 90% at 200-325°C), and S doping also effectively promoted the N₂ selectivity of the system. S doping was achieved mainly through the substitution of S⁴⁺ by Ti⁴⁺ to form Ti-O-S bonds, increasing surface area and creating oxygen vacancies. Meanwhile, the S-modified TiO₂ enriched the Brønsted acid sites on the surface of the carrier, thus facilitating the activation process of ammonia and NO_x species adsorption by the reacting species. So, SCR reaction got triggered faster[10]. As figure 5, the S doping effectively promoted the L-H route on the catalyst surface.

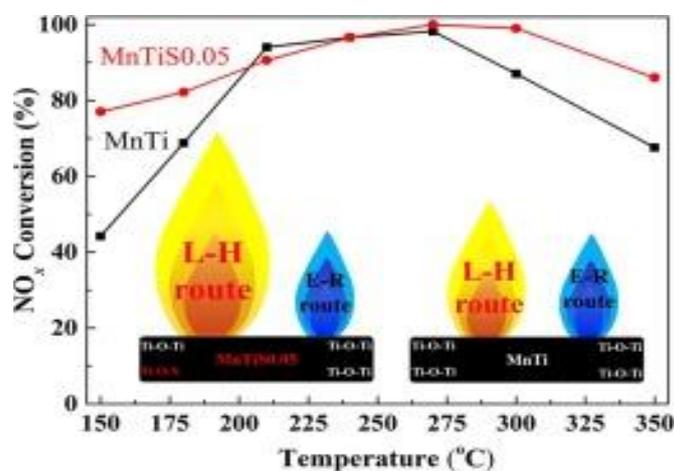


Figure 5. Graphical Abstract. Reproduced with permission.^[10] Copyright 2020, Liu et al..

Jiang et al. proposed that the doping modification of TiO₂ with Cl elements can efficiently strengthen the Lewis acidity of the carrier surface. When CeO₂ was loaded on TiO₂, it is capable of generating

more Ce^{3+} and surface active chemical oxygen species on its surface, also this reaction effectively promotes the low temperature reactivity of the ceria-titanium catalyst (90% NO_x conversion at 250-400 $^\circ\text{C}$) [11].

Besides, metal doping is also relatively common for TiO_2 modification. Wang et al. synthesized $\text{Cu}/\text{Ti}_2\text{NbO}_x$ catalyst by doping modification of TiO_2 carriers, using the metal element Nb (Figure 6). Among them, 0.8% $\text{Cu}/\text{Ti}_2\text{NbO}_x$ showed excellent resistance to alkali metal poisoning and hydrothermal stability, having a NO_x conversion efficiency of >90% and 97% N_2 selectivity at 275-425 $^\circ\text{C}$ (Figure 7). The acidic sites on the TiO_2 carrier surface were improved by the doping of Nb elements, thus creating an efficient synergistic catalytic mechanism between the acidic and redox sites in the catalytic system[12].

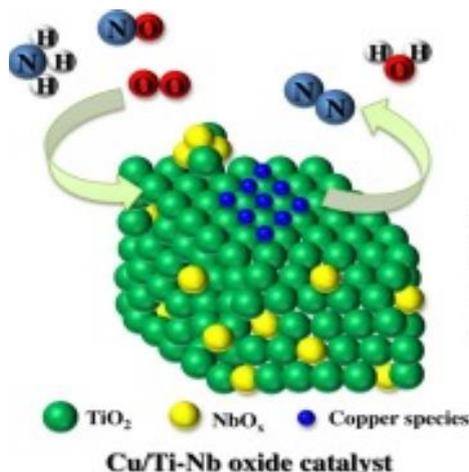


Figure 6. Graphical Abstract. Reproduced with permission.^[12] Copyright 2018, Wang et al..

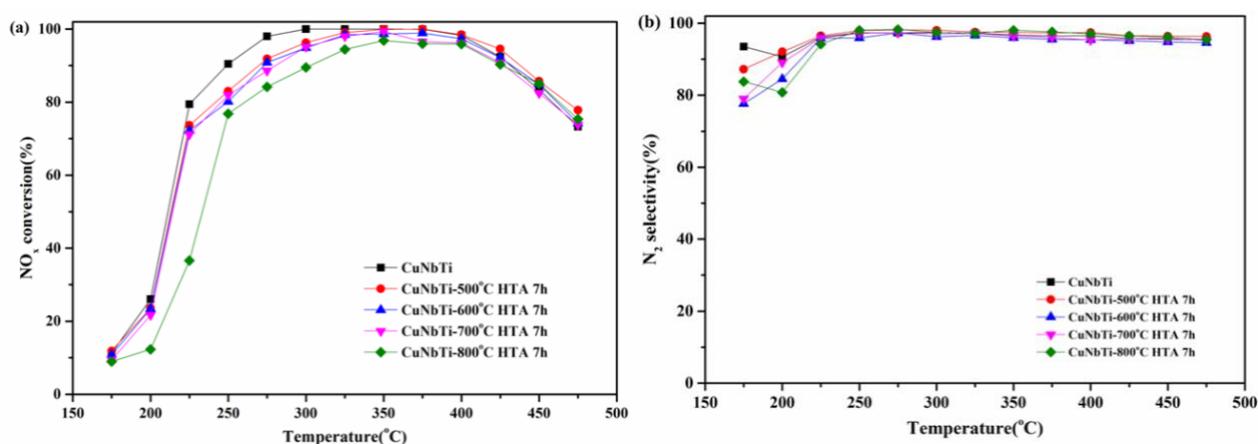


Figure 7. (a) NO_x conversion over different ratios of copper in CuNbTi . (b) N_2 selectivity over different ratios of copper in CuNbTi . Reproduced with permission.^[12] Copyright 2018, Wang et al..

When ZrO_2 and SO_4^{2-} were simultaneously doped with the modified carrier TiO_2 , the prepared $\text{CeO}_2/\text{TiO}_2\text{-ZrO}_2\text{-SO}_4^{2-}$ exhibited >90% NO_x conversion at 225-450 $^\circ\text{C}$. The two-element doping modification effectively optimized the carrier TiO_2 surface acid sites and thus promoted the shaping of active nitrate and -NH_2 intermediate species in synergy with the activated component CeO_2 , resulting in an excellent NO_x conversion[13].

For the efficient catalytic systems constructed by morphological modification of TiO_2 carriers, Huang et al. synthesized CeVTi -tube catalysts with multi-channel Ti -tube carriers doped with bimetallic elements, which exhibited NO_x conversion of not less than 90% and N_2 selectivity of not less than 95% at 225-425 $^\circ\text{C}$. In addition, the catalyst is highly effective against hydrothermal toxicity. The multi-channel Ti -tube promoted a high degree of homogeneous dispersion of the active species on its

surface and thus allowed more active intermediate species to be anchored in its walls, effectively boosting the SCR performance of the catalytic system[14]. Furthermore, Li et al. designed a V_2O_5/TiO_2 -R catalytic system for the loading of V_2O_5 on TiO_2 carriers after reduction modification. Compared to V_2O_5/TiO_2 , T90 of V_2O_5/TiO_2 -R was reduced from 300 to 270, while the catalyst demonstrated good resistance to hydrothermal toxicity. The TiO_2 reduction modification facilitates the shaping of surface oxygen vacancies and V^{4+} ions, and the reduced TiO_2 revealed larger specific area, thus effectively enhancing the SCR performance of the VTi catalyst[15]. Additionally, carbon nanotubes (CNT) modified TiO_2 for preparing VFe_3TiC_{10} catalyst, plus CNT served better SCR performance that NO_x conversion was 90% at 225 $^{\circ}C$ and N_2 selectivity was 90%. CNT was able to modulate the redox properties of the TiO_2 carrier surface, thus enhancing the system's low temperature reactivity and resistance to SO_2 toxicity[16].

2.3 TiO_2 as active species catalysts

It has been shown in several studies that TiO_2 can be used as an active component to improve the reactivity of catalytic systems. Zhao et al. found that the V_2O_5/TiO_2 catalyst achieved >90% NO_x conversion at 210-350 $^{\circ}C$ when the system contained 0.2 g Ti^{3+} by controlling the amount of Ti^{3+} species in the V_2O_5/TiO_2 catalyst. In this catalytic system, the formation of Ti^{3+} in the system was accompanied by the creation of oxygen vacancies on the catalyst surface, and both of them can react with each other to create more active oxygen species to promote NO oxidation to NO_2 , favoring the SCR reaction. Ti^{3+} as one of the most critical active sites had a decisive influence on the low-temperature reactivity of vanadium-titanium catalytic systems[17].

In the $FeTiSO_x$ system (Figure 8), the constitution of Fe-O-Ti sites greatly heightened the redox properties and inhibited the NH_3 strong oxidation, making this system reveal >97% NO_x conversion and >95% N_2 selectivity at 325-475 $^{\circ}C$ (Figure 9). This means that in this system, Ti was one of the essential active species as one of the components of the active site involved in the adsorption activation of the reaction and the reaction process[18].

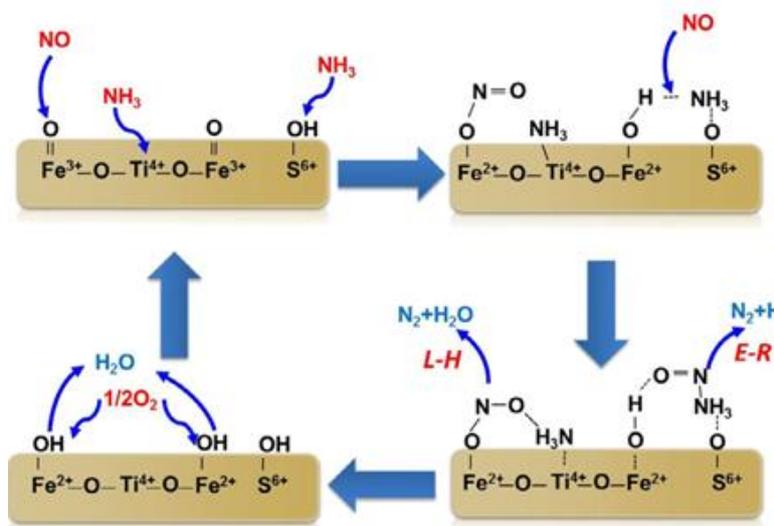


Figure 8. The proposed reaction route over the $FeTiSO_x$ catalysts. Reproduced with permission.^[18]
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TiO_2 as active species modified the MnO_x/CeO_2-ZrO_2 nanorod to modulate the redox ability of manganese and cerium species in the system, inhibiting the non-selective oxidation of ammonia and promoting enhanced surface acidity to enhance the SCR performance of the catalytic system. In this case, TiO_2 was not only an active species but also a modifier, which can effectively improve the activity of the system[19].

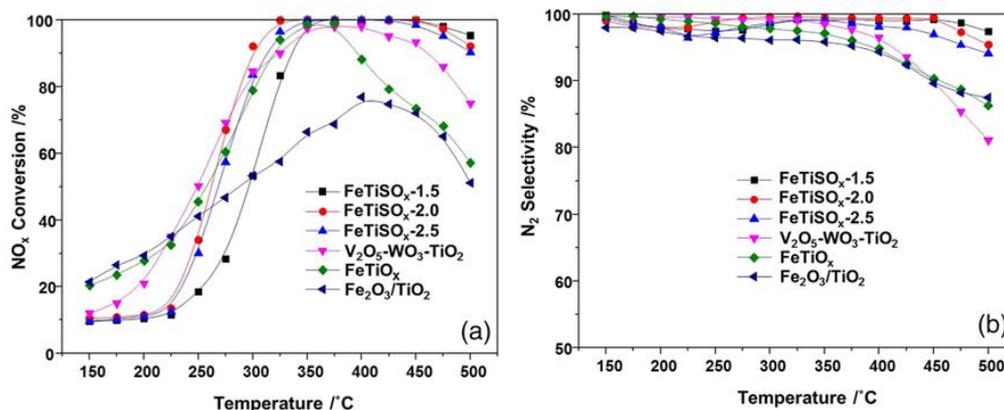


Figure 9. NH₃-SCR performance as a function of temperature. Reproduced with permission.^[18]
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Similarly, the core-shell WO₃/TiO₂@CeO₂ catalyst was synthesized by micro-tuning the catalyst structure, which has >90% NO_x conversion and N₂ selectivity at 225~500°C. The TiO₂ shell contributed to the efficient synergistic catalysis of the acidic and redox sites in the system, which is in favor of the excellent NH₃-SCR performance[20].

3. Summary and Future Perspectives

TiO₂-based catalyst remains a promising and investigative non-homogeneous SCR catalyst. Herein, the following conclusions are drawn from an analysis of existing research on TiO₂ based SCR catalyst:

(1) For pure TiO₂ as support catalysts, although the type and content of interfacially active components are two key factors for SCR catalysts affecting the wide temperature window of activity, the effect of species and carrier interactions on the activity of the TiO₂-based SCR reaction should be addressed. The introduction of the support improves the dispersion, surface acidity and redox properties of the catalyst, increasing the surface reactive oxygen species and ultimately reducing the activation energy of the NH₃-SCR reaction.

(2) To date, the research to simultaneously improve resistance to SO₂ water, alkalis and heavy metals is deficient. Due to the harsher environment of practical applications, it is pressing to develop catalysts that are resistant to a wide range of toxicities. Moreover, the modification of TiO₂ as support catalysts mainly improve the activity and anti-toxicity effect of the TiO₂-based, while the modification methods are limited to the doping of metallic or non-metallic elements. So, exploring innovative methods of modification may lead to surprises.

(3) TiO₂ as active species catalysts regulate the strong oxidation of active species and thus advance the SCR performance. Therefore, TiO₂ is not only an active component but also a modifier, whereas the biggest obstacle to restrict the pragmatic application of such catalysts is that too little improvement in SCR performance to be cost effectively.

TiO₂-based catalysts are promising low-temperature catalysts, so it is essential to carry out systematic modelling studies for boosting the industrial progress of deNO_x catalysts. With this review, the author could make little contribution to its commercialization in the near future.

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