

Strategy and Technical Progress of Recycling of Spent Vanadium–Titanium-Based Selective Catalytic Reduction Catalysts

Jianyong Zhao, Xiaoguang Zhang,* Feihua Yang, Yonghong Ai, Yousheng Chen, and Dean Pan*



Cite This: *ACS Omega* 2024, 9, 6036–6058



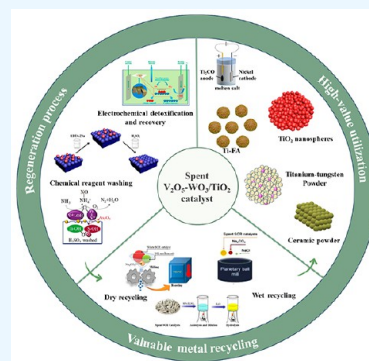
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: Selective catalytic reduction denitration technology, abbreviated as SCR, is essential for the removal of nitrogen oxide from the flue gas of coal-fired power stations and has been widely used. Due to the strong demand for energy and the requirements for environmental protection, a large amount of SCR catalyst waste is produced. The spent SCR catalyst contains high-grade valuable metals, and proper disposal or treatment of the SCR catalyst can protect the environment and realize resource recycling. This review focuses on the two main routes of regeneration and recycling of spent vanadium–titanium SCR catalysts that are currently most widely commercially used and summarizes in detail the technologies of recycling, high-efficiency recycling, and recycling of valuable components of spent vanadium–titanium SCR catalysts. This review also discusses in depth the future development direction of recycling spent vanadium–titanium SCR catalysts. It provides a reference for promoting recycling, which is crucial for resource recovery and green and low-carbon development.



1. INTRODUCTION

Globally, fossil fuels, such as natural gas, oil, and coal, are the primary energy source required by national industries. Nitrogen oxides (NO_x) emitted in significant quantities during the combustion of fossil fuels cause environmental pollution such as acid rain, the greenhouse effect, and photochemical smog and even harm human health.^{1–4} Figure 1(a) is a schematic diagram of the different pathways of NO_x pollution in the environmental system.⁵ Coal-fired power plants are considered one of the significant sources of anthropogenic NO_x emissions to the atmosphere.^{6,7} China is a sizable coal-consuming country. According to statistics, China's NO_x emissions have been more serious than those of the United States and European Union countries in recent years, as shown in Figure 1(b).⁸ To control the generation of NO_x , China included NO_x in the list of the total amount of air pollutants in the “Twelfth Five-Year Plan” and proposed that the overall NO_x emission of active and newly built coal-fired units should not exceed 100 mg/m^3 . Each thermal power plant has installed a flue gas denitrification device to achieve this goal. As a result, the flue gas denitrification market has grown rapidly.

Flue gas denitrification technology mainly includes selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR). SNCR technology does not employ any catalyst but reducing agents such as ammonia (NH_3), urea, and ammonium bicarbonate (NH_4HCO_3) to reduce NO_x in the temperature range of $850\text{--}1050 \text{ }^\circ\text{C}$. The nitrogen removal temperature range is extensive, and the nitrogen removal efficiency can only reach about 50%.¹⁰ In comparison, SCR is currently the mainstream technology for denitrification, accounting for about 96% of the

flue gas denitrification projects that have been built or planned in China.^{11,12} Figure 1(c) shows the overall structure and process flow of SCR technology in the out-of-stock device.⁹ This method has high deoxygenation efficiency (up to 80–90%) and high technology maturity. As the core of the technology, the SCR catalyst constitutes approximately 30–50% of the total de- NO_x system investment.^{13,14} Due to the complex flue gas environment, the SCR catalyst will be poisoned during long-term use, which results in a reduction in specific catalytic activity and affects its denitrification efficiency.^{15–17} Generally, the service life of denitration catalysts is three to five years, depending on the composition of the flue gas and the type of combustion system.¹⁸ The use of SCR technology is increasing, and the catalysts abandoned by denitration units have gradually become problematic. With the vigorous implementation of the carbon peaking and carbon neutrality goals and deepening people's understanding of sustainable development strategy, high efficiency, energy saving, emission reduction, and resource recycling have become the major concepts for the treatment and reduction of waste. Considering its environmental impact and economic value, the spent SCR catalyst with a complete structure can be chosen to enter a suitable recycling scheme.

Received: September 14, 2023

Revised: December 27, 2023

Accepted: December 28, 2023

Published: January 29, 2024



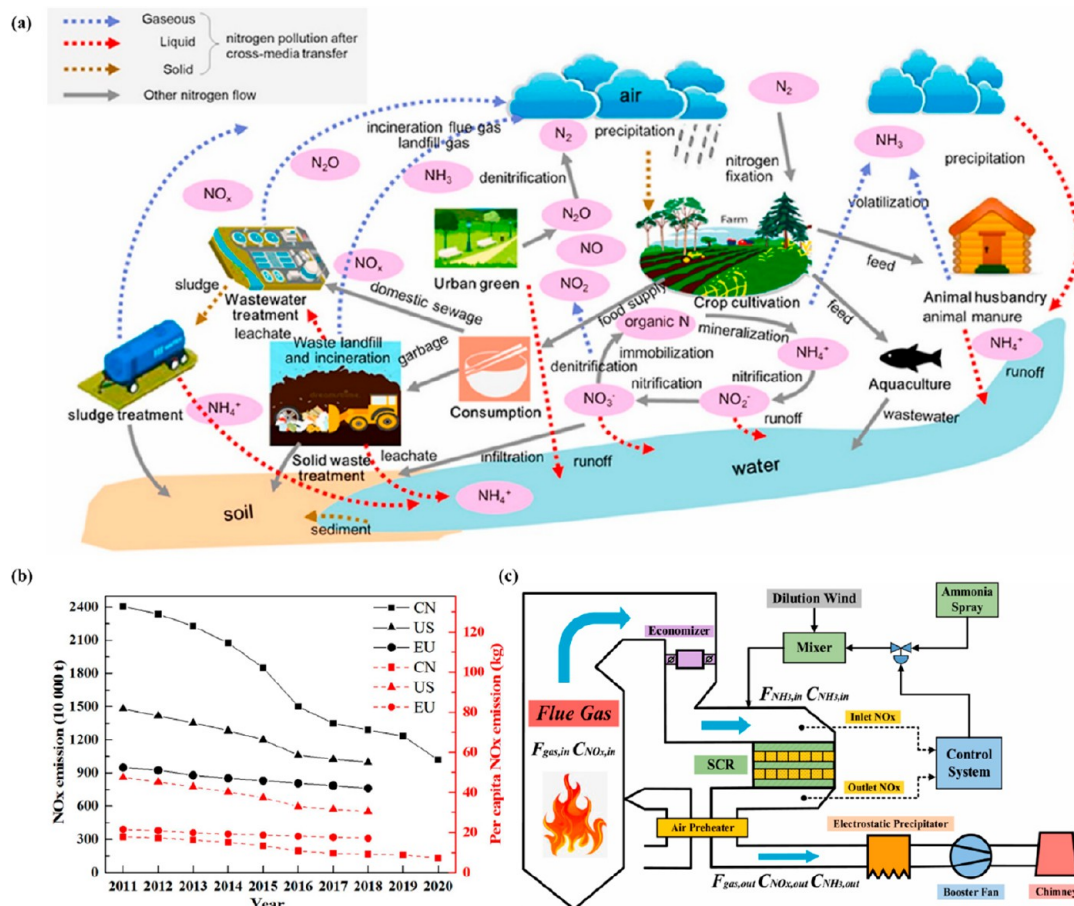


Figure 1. (a) Schematic diagram of the NO_x pollution pathway.⁵ Reproduced with permission from ref 5. Copyright 2023 Elsevier. (b) NO_x emissions from China, the US, and the EU over the past decade.⁸ Reproduced with permission from ref 8. Copyright 2023 Elsevier. (c) SCR technology denitration device structure and production process.⁹ Reproduced with permission from ref 9. Copyright 2023 Elsevier.

Table 1. Comparison of Three Types of Catalysts^{10,14}

Catalyst type	Structural manufacturing	Characteristics	Conditions of use	Market share
Honeycomb monolith-type	Load or uniform extrusion	Large specific surface area, good wear resistance, less fly ash blockage, good catalytic activity	For all conditions	60%–75%
Flat plate-type	Metal plate or mesh as a skeleton, surface loaded with active components	Low catalyst consumption, good flue gas evacuation capacity, high degree of production automation, easy disassembly and assembly, poor wear resistance	Cleaner flue gas	20%–30%
Corrugated plate-type	Carrier is corrugated glass fiber loaded with an active coating	Less active ingredient exposed, lighter mass, corrugated structure easily blocked by deposition	Mainly for low-dust conditions	Around 5%

Catalyst regeneration is limited, and the completely deactivated SCR catalyst has great recycling value because of its wide variety of valuable metals.¹⁴ Almost all SCR catalysts used in commercial flue gas treatment are vanadium–titanium catalysts, consisting of vanadia oxide (V₂O₅) and tungsten oxide (WO₃) or molybdenum oxide (MoO₃) on titania dioxide (TiO₂), denoted V₂O₅–WO₃(MoO₃)/TiO₂.¹⁹ Spent SCR catalysts are rich in heavy metals such as arsenic and mercury released from coal combustion, which are included in China’s “National Hazardous Waste List (2021 Edition)”. If discarded randomly, it will cause secondary pollution to the environmental system and also cause a waste of resources. Therefore, the current research hotspot has become how to effectively recover the valuable components of spent vanadium–titanium SCR catalysts and promote resource recycling.

This review summarizes the regeneration and recycling methods of spent vanadium–titanium-based SCR catalysts and outlines the procedures for extracting, separating, and purifying valuable metals from spent vanadium–titanium catalysts in recent years. Finally, the future recycling of spent vanadium–titanium catalysts has been explored from the perspective of the recycling pathway of practical component carriers. This review will reference the regeneration and recycling strategies of spent catalysts.

2. STATUS OF SPENT VANADIUM–TITANIUM SCR CATALYSTS

As the core of the denitration system, the SCR catalyst plays a vital role in the operation. The continuous optimization and improvement of the catalyst is the key factor in promoting the

Table 2. Main Compositions of Original and Spent Catalysts (wt %)

Catalyst	TiO ₂	V ₂ O ₅	WO ₃	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	K ₂ O	As ₂ O ₃	Na ₂ O	SO ₃	ref.
original	88.61	0.70 ^a	4.66	0.58 ^a	3.69	0.05 ^a	1.04 ^a	—	—	—	—	26
original	93.54 ^a	0.73 ^a	3.75 ^a	0.26 ^a	0.24 ^a	0.43 ^a	0.52 ^a	0.04 ^a	0.26 ^a	0.06 ^a	0.43	27
spent	88.72	0.37 ^a	3.78	0.85 ^a	3.96	0.07 ^a	1.50 ^a	0.20 ^a	—	0.09 ^a	—	26
spent	91.35 ^a	0.55 ^a	3.42 ^a	0.54 ^a	0.45 ^a	0.45 ^a	0.78 ^a	0.47 ^a	0.54 ^a	0.15 ^a	0.46	27
spent	80.819	0.319 ^a	4.834	1.786	1.345	0.609 ^a	2.867	0.095	—	0.266	—	28
spent	83.39	1.05	5.41	1.04	6.22	0.22	1.34	—	—	—	1.33	29
spent	81.78	1.19	4.20	1.75	6.83	0.285	2.06	0.061	—	0.096	0.18	30

^aData from ICP-OES and others from XRF.

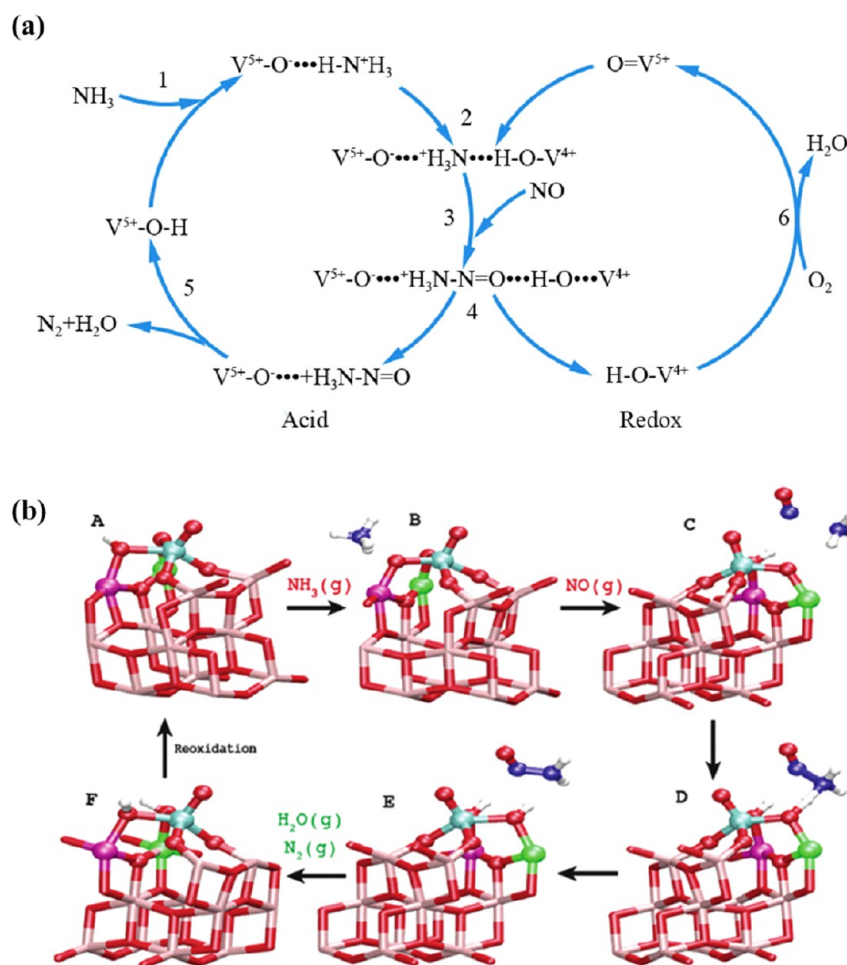


Figure 2. (a) Catalytic scheme for NO_x removal. (b) Mechanism of the catalytic reduction step of the monomeric VO₃H/TiO₂ (001) model.³¹ Reproduced with permission from ref 31. Copyright 2020 Elsevier.

denitrification catalytic system. In the 1970s, V₂O₅–WO₃/TiO₂ catalysts were extensively studied by Hitachi and Mitsubishi and gradually became the dominating commercial catalysts in the world.²⁰ With the continuous in-depth rectification of industrial waste pollution in China, the denitration market is slowly developing, and the demand for denitration catalysts is increasing. Currently, around one million tons of SCR catalysts are used in China. The average operating life of V₂O₅–WO₃/TiO₂ catalysts is about 24,000 h. According to statistics, China produces about 300,000 tons of SCR catalysts annually,²¹ and the treatment of spent V₂O₅–WO₃/TiO₂ catalysts has become an urgent and severe problem.

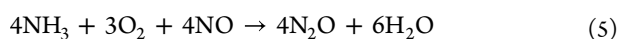
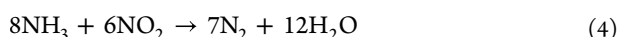
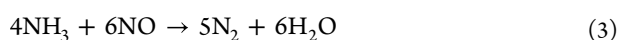
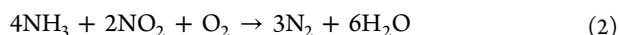
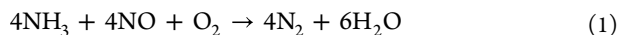
2.1. Overview of the Vanadium–Titanium SCR Catalyst. The V₂O₅–WO₃/TiO₂ catalyst is one of the best catalysts for SCR denitrification because of its high-temperature

catalytic activity, good sulfur dioxide (SO₂) resistance, and nitrogen (N₂) selectivity.²² V₂O₅–WO₃/TiO₂ catalysts are usually divided into three types according to their morphology: honeycomb monomer type, flat plate type, and corrugated plate type. Table 1 shows a comparison of the three different types of V₂O₅–WO₃/TiO₂ catalysts. The primary performance of the catalyst refers to the activity of NO_x removal, which is not much influenced by its structure. However, because of the high density of active substances, the honeycomb catalyst has a remarkable denitrification effect and a higher market share.⁸

2.1.1. Composition of the Vanadium–Titanium SCR Catalyst. The V₂O₅–WO₃/TiO₂ catalyst uses TiO₂ as the carrier, V₂O₅ as the active component, and WO₃ or MoO₃ as an additive. Its main characteristics are shown in Table 2. V₂O₅, the vibrant center of the catalytic reaction, creates an acidic catalyst

surface, which is conducive to capturing NH_3 . TiO_2 , as a catalyst carrier, stabilizes V_2O_5 to promote catalyst activity as well as extend service life.¹⁰ The active auxiliaries WO_3 and MoO_3 are the main forms of W and Mo present in the catalyst, deposited on the bases of TiO_2 , which can prevent the transformation of TiO_2 from anatase to rutile. The additives also block the adsorption of sulfur trioxide (SO_3) and avoid the sulfation of the carrier. MoO_3 reacts more easily with arsenic oxide As_2O_3 than WO_3 , protecting V_2O_5 from As poisoning.²³ Active auxiliaries also regulate catalyst activity and the catalyst temperature window and enhance catalytic selectivity. WO_3 mainly controls the catalyst activity in the high-temperature interval above 400 °C, and MoO_3 primarily compensates for the activity deficiency in the low-temperature interval below 300 °C. In addition, WO_3 can promote the formation of polyvanadate and increase the acidic site on the surface of the catalyst to enhance the effect of NO removal and improve the performance of the catalyst.²⁴ As observed by electron microscopy, Ti, W, and V appear mainly as irregular particles, while Al, Si, and Ca are primarily in the form of rod-shaped particles.²⁵ Compared with the original catalysts, the main valuable metal components of the spent catalysts (TiO_2 , WO_3 , V_2O_5) are little changed and have the potential and value for recycling.

2.1.2. Denitrification Mechanism of Vanadium–Titanium SCR Catalysts. The SCR mechanism uses the rich pore-like structure of the catalyst surface and its abundant active sites to selectively reduce NO_x to nontoxic substances such as N_2 and water (H_2O) with NH_3 or urea as the reducing agent at a controlled temperature range. Eqs 1–4 can express the reduction of NH_3 and NO_x in the presence of a catalyst, while excessive oxidation of NH_3 leading to the production of N_2O is described by eq 5.



Based on density functional theory (DFT), Zhao et al.³¹ summarized the chemical reactions on the surface of V_2O_5 – WO_3 /TiO₂ catalysts and basic structural models and pointed out that the denitrification mechanism of NH_3 in the response with NO to form N_2 and H_2O generally follows the Eley–Rideal (E-R) mechanism; i.e., the reductant NH_3 molecules are first adsorbed on the active sites on the catalyst surface and activated, and NH_2NO is an essential intermediate in the reaction. Specifically, NH_3 is first adsorbed on $\text{V}=\text{O}$ (Lewis acid site) to form coordinated NH_3 and on $\text{V}-\text{OH}$ (Brønsted acid site) to form protonated ammonium NH_4^+ , which then reacts with NO_x in the flue gas to form the intermediate species NH_2NO , which is then decomposed into N_2 and H_2O and desorbed from the catalyst, while oxygen O_2 from the flue gas diffuses onto the catalyst active site to regenerate the catalyst. Figure 2(a) shows the SCR reaction mechanism over a vanadium–titanium-based catalyst.^{19,32} Arnarson et al.³³ studied the reduction step of the SCR mechanism using the monomeric VO_3H /TiO₂(001) catalytic model, where NH_3 and NO react to form N_2 and H_2O as shown in Figure 2(b), and indicated that the reaction follows the E-R mechanism.

2.2. Causes of the Deactivation of Vanadium–Titanium SCR Catalysts. V_2O_5 – WO_3 /TiO₂ catalysts are medium- to high-temperature flue gas denitrification catalysts with an optimum reaction temperature range of 300–400 °C to maintain high activity.^{34–39} The catalysts are usually placed upstream of the dedusting equipment to meet the mentioned temperature requirements while avoiding the impact of flue gas particles on the catalyst.¹⁰ However, the complex flue gas environment can easily lead to catalyst deactivation. The reasons for the deactivation of V_2O_5 – WO_3 /TiO₂ catalysts can be ascribed to physical and chemical factors.

2.2.1. Physical Factors.

(2.2.1a) Catalyst blockage. There are two leading causes of blockage. First, the combustion of coal produces more fly ash, which is deposited on the surface of the catalyst, resulting in backup of the pore structure; second, ammonium salts and sulfate particles are generated under certain conditions due to the presence of ammonia and sulfur in the flue gas, which adhere to the catalyst surface, blocking the pore entrance of the catalyst and impeding the active sites on the inner surface of the catalyst, causing a decline in the catalytic performance of the catalyst.

(2.2.1b)

Catalyst wear. In practice, as the gas flow scours the catalyst surface over a long period, the mechanical strength of the catalyst gradually decreases under the loss of active material, resulting in a reduction in denitrification performance. The degree of wear is related to the mechanical strength of the catalyst and the gas flow rate.

2.2.2. Chemical Factors.

(2.2.2a) High-temperature sintering of the catalyst and volatilization of active components. As the temperature increases, the TiO_2 carrier changes its crystalline form from anatase to rutile, which reduces the pore volume and specific surface area of the catalyst, thus affecting the number of active sites and reducing denitrification activity. Furthermore, high temperatures can cause the active component to evaporate. Studies have shown that catalysts will be severely deactivated at temperatures above 500 °C.⁴⁰

(2.2.2b)

Chemical poisoning. The chemical components in coal are transformed into toxic components in the flue gas by diffusion into the SCR catalyst pores and binding closely to the active sites, participating in the catalytic reaction and thus causing the catalyst to deactivate. Chemical poisoning is currently the main cause of SCR catalyst deactivation in coal-fired power plants¹⁰ and is predominant in heavy oil-fired coal units. Substances that can cause chemical poisoning of V_2O_5 – WO_3 /TiO₂ catalysts include alkali metals, alkaline earth metals, acids (like SO_2 and hydrogen chloride (HCl)), water vapor, and heavy metals (like As and Pb).^{41,42} Table 3 summarizes the mechanisms and characteristics of the leading chemical poisons of SCR catalysts.

Table 3. Mechanisms and Characteristics of the Main Poisons for SCR Catalysts

Type of poison	Poisoning mechanisms	Characteristics
Alkali metals	Binding to the active acidic site of V_2O_5 (hydrogen bonding in V–OH is replaced), inhibiting NH_3 adsorption; Na^+ and K^+ cations attaching to functional O_2 on the catalyst surface; metal particles deposited on the catalyst surface causing blockage. ^{43–45}	The main ways in which catalyst deactivation is caused in coal-fired boilers and the intensity of poisoning is related to alkalinity: $Cs > Rb > K > Na > Li$. ⁴¹
Alkaline earth metals	The deactivation mechanism is similar to that of alkali metals, reducing the number of acidic sites and inhibiting NH_3 adsorption	Alkaline earth metals have a weaker poisoning effect on SCR catalysts than alkali metal oxides: $K > Na > Ca > Mg$. ⁴⁶
SO_2	Competitive adsorption with NO and NH_3 reactants; ⁴⁷ generation of ammonium sulfate-based substances with NH_3 to cover the active sites on the catalyst surface. ^{48,49}	SO_2 has a greater impact on low-temperature catalysts. ⁵⁰
HCl	In contact with HCl, the content of V of the more concentrated catalyst is reduced, resulting in lower activity	The presence of HCl promotes the production of new acidic sites but is less active compared to the original acid site, which does not restore the actual activity. ⁵¹
H_2O	Competition with NH_3 and NO for adsorption inhibits the ability of the catalyst to adsorb these reactants. ⁵²	Less toxic and reversible; high impact on denitrification at low temperatures (250 °C). ^{53,54}
As	As occupies the acidic active site on the catalyst surface, preventing the adsorption of NH_3 molecules to the active site on the catalyst surface; ⁵⁵ gaseous As blocks the catalyst micropores, preventing reactants from reaching the active site. ⁵⁶	Undergoes three stages of adhesion, permeation, and deactivation; ⁵⁷ low effect on specific surface area; ⁵⁸ MoO_3 replaces WO_3 to improve resistance to arsenic poisoning. ⁵⁹

3. RECYCLING OF SPENT VANADIUM–TITANIUM SCR CATALYSTS

For fully deactivated catalysts, landfill disposal is used in Europe and the USA, and partial landfill and partial metal recovery is used in Japan. Overall, few non-Chinese companies specialize in the large-scale industrial recycling of spent SCR catalysts. China, as a sizable coal-consuming country, cannot meet the demand for the disposal of large volumes of waste denitrification catalysts through landfills due to limited land resources. Since the large-scale installation of denitrification units from 2012 onward, the disposal and recycling of spent denitrification catalysts have gradually received attention but are still a new field. Recycling technology research by many institutions and enterprises is still in the laboratory or pilot stage on a small scale, and the recycling industry is hardly developed, lacking practical technology, and far from meeting market demand. Globally, the technology of SCR catalyst regeneration and recycling of spent vanadium–titanium systems is not yet mature and is still being explored as a research hotspot.

3.1. Regeneration Technology for Spent Vanadium–Titanium SCR Catalysts. The true effective deactivation level of a “deactivated catalyst” is 30% to 40% of the total activity. In other words, 60% to 70% of the basic activity is still retained in most cases. Therefore, regenerating deactivated catalysts for direct recycling is an ideal way to reduce costs and energy consumption and recycle resources. Whether a deactivated catalyst can be restored to its former activity by regeneration depends on the cause of the deactivation and the ease with which it can be regenerated. Therefore, before regenerating spent catalysts, analysis and diagnosis of the valuable component content, specific surface area, strength, and catalytic denitrification activity should be conducted to determine the value of the regeneration options. Deactivated catalysts with some potential for recovery can be regenerated using suitable and effective regeneration methods. Currently, there are mainly physical regeneration, chemical regeneration, and current new regeneration methods.

3.1.1. Physical Regeneration. **3.1.1a. Ultrasonic-Assisted Water Washing.** Water washing can remove floating dust, accumulated ash, impurities inside the blocked pore, and toxic substances such as soluble alkali metal salts from the surface of V_2O_5 – WO_3 /TiO₂ catalyst modules. The water-washing regeneration method is simple and convenient, with low regeneration costs and low equipment requirements. However, for severely poisoned catalysts, water-washing regeneration is limited, and ultrasonic-assisted washing can remove the more challenging adherents. Liu et al.²⁸ used ultrasonic-assisted water washing to remove iron deposited on the surface of spent SCR catalysts by ultrasonic cleaning. Figure 3 shows a comparison before and after ultrasonic cleaning. However, high-pressure rinsing can wash away some active ingredients, so subsequent soaking is often required to replenish the active ingredients.

3.1.1b. Active Component Loading. Yu et al.⁶⁰ used a combination of experiments and simulations to calculate the interaction of ammonium hydrogen sulfate NH_4HSO_4 with V_2O_5 – WO_3 /TiO₂ catalysts, showing that TiO₂-loaded NH_4HSO_4 dissociates to NH_4^+ and SO_4^{2-} during the reaction. V_2O_5 , WO_3 , and MoO_3 can form a protective layer to inhibit the adsorption of NH_4HSO_4 by TiO₂ and accelerate the response of NH_4^+ with NO. Because of the active components, such as V_2O_5 and WO_3 , the V_2O_5 – WO_3 /TiO₂ catalyst can achieve relatively regular operation. However, in the actual process, the

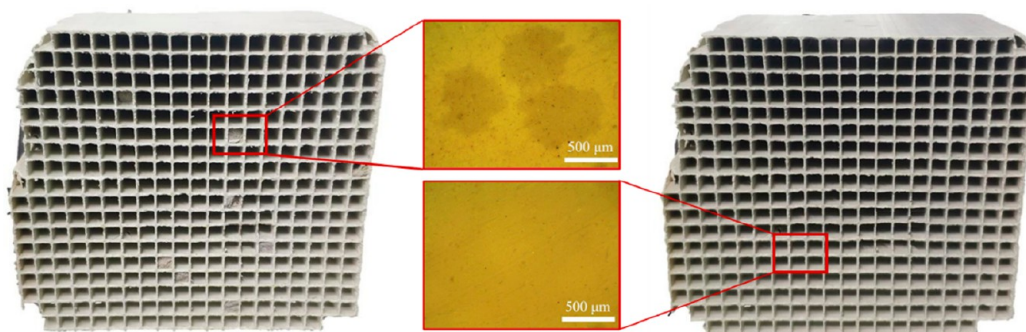


Figure 3. Images of spent SCR catalyst before and after ultrasonic water cleaning.²⁸ Reproduced with permission from ref 28. Copyright 2022 Elsevier.

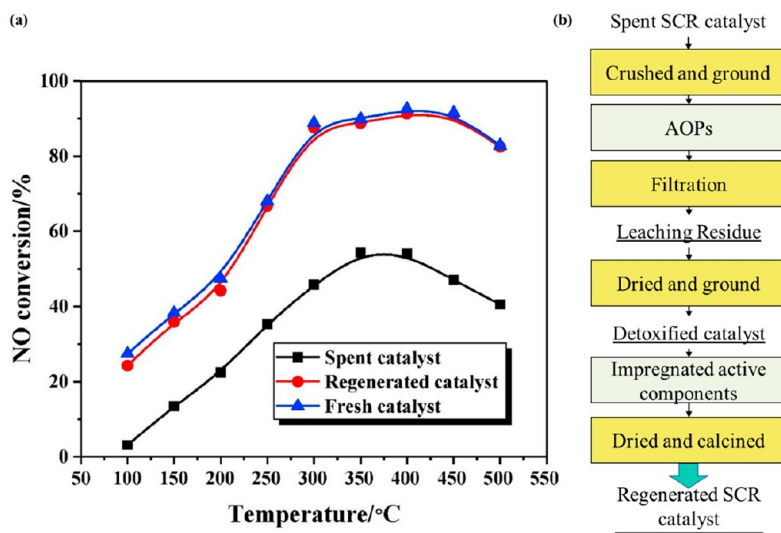


Figure 4. (a) Flowchart of the OABL treatment process for spent V₂O₅-WO₃/TiO₂ catalysts and (b) NO conversion of fresh catalyst, spent catalyst, and catalyst regenerated by the OABL process.²⁷ Reproduced with permission from ref 27. Copyright 2018 Elsevier.

denitrification performance of the catalyst decreases due to the loss of active components because of prolonged commissioning. Therefore, solutions containing, e.g., ammonium metavanadate, ammonium paratungstate, and ammonium paramolybdate can be used to impregnate deactivated V₂O₅-WO₃/TiO₂ catalysts for effective regeneration by replenishing them with active components such as V, W, and Mo. Qiu et al.⁶¹ used a microwave-heated mixture of ethanol and water to wash the spent catalyst, followed by impregnating the active component with a solution containing ammonium vanadate NH₄VO₃ and ammonium tungstate (NH₄)₂WO₄ for 2 h, then achieved efficient regeneration by rapid microwave drying and calcination. The results showed that the surface area of the catalyst could be increased by 123.2% over that of the deactivated catalyst when using a 20% ethanol content under microwave heating. By impregnating the active component, the V content increased by 62.2%, and the NO conversion of the catalyst increased from 39% to 90% at the temperature of 320 °C. The efficient green advanced oxidation process of the oxidative ammonium bicarbonate leaching (OABL) at medium temperature and atmospheric pressure proposed by Li et al. includes an active ingredient impregnation step ((Figure 4(a),(b)).²⁷ The results showed that the denitrification activity of the regenerated catalyst after loading the active component was close to that of the fresh SCR catalyst, achieving a NO conversion of 91% at 400 °C.

3.1.2. Chemical Regeneration. 3.1.2a. Heat Treatment Regeneration. Thermal treatment regeneration can be divided into thermal regeneration and thermal SO₂-acidification regeneration. Thermal regeneration refers to heating the spent catalyst at a certain rate, generally under an inert atmosphere, and maintaining it for a certain time at the final temperature before cooling to room temperature. The presence of an ambient gas prevents oxidation reactions, based on which reducing gases such as NH₃ or H₂ can be introduced to react with surface-deposited salts to decompose them. SO₂-acidification regeneration refers to the high-temperature calcination of the spent catalyst in an SO₂ atmosphere after water washing to increase its active acid level and achieve reusability. Xu et al.⁶² carried out simulations of in situ SO₂ poisoning of V₂O₅-WO₃/TiO₂ catalysts at 200 °C in an atmosphere of 500 ppm of NH₃, 500 ppm of SO₂, 5% H₂O, 5% O₂, and N₂. The results showed that SO₂ poisoning on 1% V-W-Ti was mainly due to the formation of adsorbed NH₄HSO₄, and its activity can be restored by decomposition at 400 °C. Kato et al.⁶³ thermally regenerated As-poisoned V₂O₅-WO₃/TiO₂ catalysts with methanolic steam. The authors identified the temperature range of 250–275 °C as optimal for thermal regeneration with methanol steam to achieve successful removal of As with low impact on catalyst activity. Thermal treatment techniques are generally effective in removing alkali metal and As from As-poisoned spent catalysts.

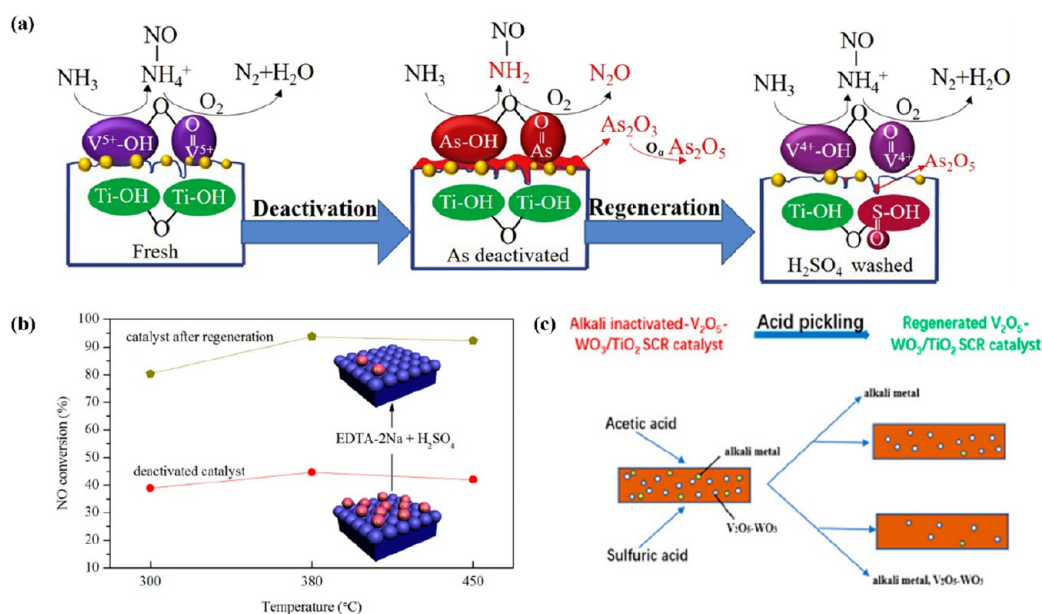


Figure 5. (a) Mechanism of deactivation of As-poisoned V₂O₅-WO₃/TiO₂ catalyst and regeneration by H₂SO₄ scrubbing.⁷² Reproduced with permission from ref 72. Copyright 2020 Elsevier. (b) Regeneration with EDTA-2Na in combination with H₂SO₄ solution.⁷¹ Reproduced with permission from ref 71. Copyright 2016 Elsevier. (c) Regeneration of alkali metal-poisoned spent V₂O₅-WO₃/TiO₂ catalyst by acetic acid and sulfuric acid pickling.⁷³

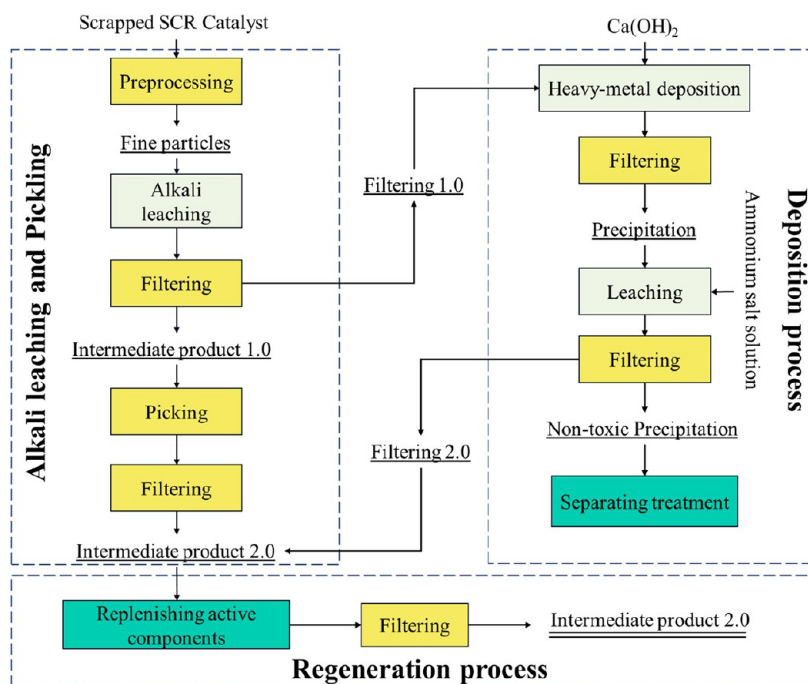


Figure 6. Process flow of stepwise alkali-acid leaching.⁷⁷ Reproduced with permission from ref 77. Copyright 2019 Elsevier.

3.1.2b. Chemical Cleaning and Regeneration. By ultrasonic water washing, the micropores of the catalyst surface are deeply cleaned from fly ash and the catalyst surface from adsorbed toxic elements. Still, the substances causing chemical poisoning of the catalyst, such as CaO, As₂O₃, PbO,^{64–66} and other harmful oxides, are not entirely removed from the catalyst surface. The removal of the oxides can be achieved by immersing the blown and water-washed V₂O₅-WO₃/TiO₂ catalyst in chemical reagents such as acidic and alkaline solutions and organic polyethers.

Acid Washing. An acid solution is used as a cleaning solution to clean and regenerate the replaced SCR catalyst. The acid-washing process generally involves soaking the deactivated catalyst in inorganic acids such as sulfuric acid (H₂SO₄), nitric acid (HNO₃), and hydrochloric acid (HCl)^{67–69} or organic acid solutions, such as oxalic acid and acetic acid,^{70,71} and then rinsing the catalyst with deionized water until neutral and finally drying and roasting to obtain the regenerated catalyst. Tian et al.⁷² regenerated commercial V₂O₅-WO₃/TiO₂ catalyst after As poisoning by washing with H₂SO₄ (Figure 5(a)). The results show that this method exposes acid sites and removes As oxides

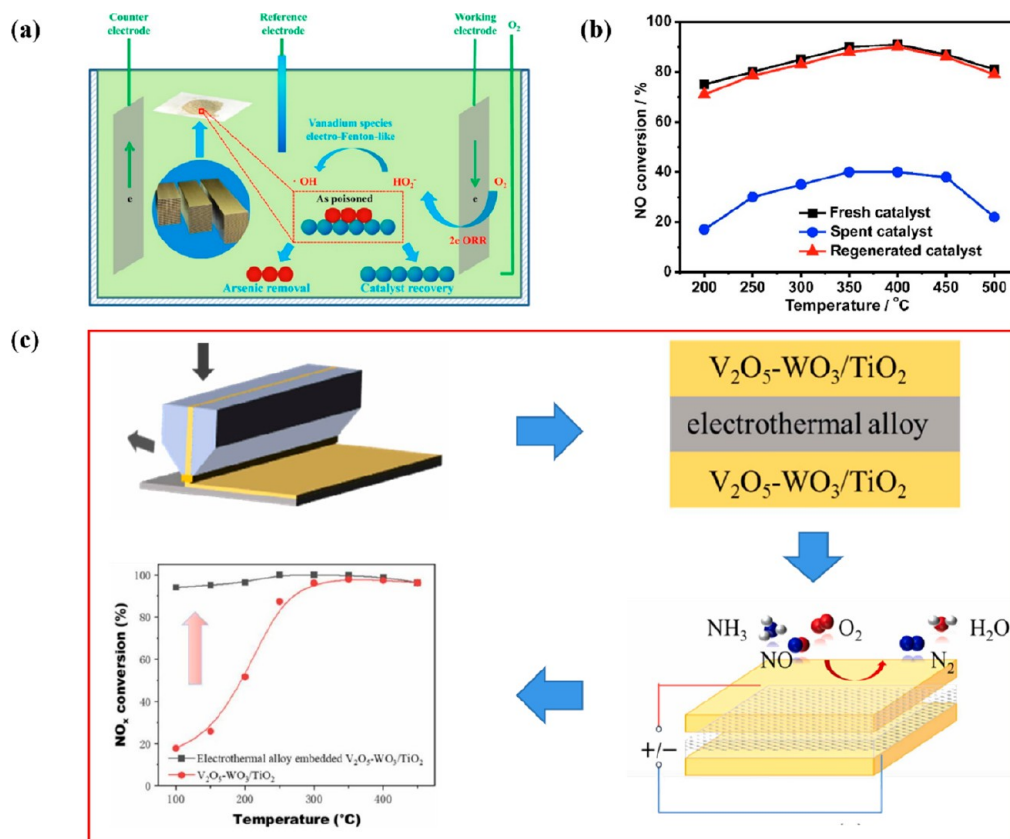


Figure 7. (a) Electrochemical detoxification and recovery of As-poisoned $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts.⁸² (b) Comparison of SCR performance of regenerated catalysts recovered by electrochemical detoxification with fresh and spent catalysts.⁸² Reproduced with permission from ref 82. Copyright 2017 Elsevier. (c) Schematic diagram of the preparation of electrothermal alloy-embedded $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts.⁸³ Reproduced with permission from ref 83. Copyright 2022 Elsevier.

from the catalyst surface, while chelated SO_4^{2-} generates new Brønsted acid sites and improves catalytic performance. However, H_2SO_4 cleaning also results in a certain loss of V so that the activity of the regenerated catalyst remains relatively low at 300–400 °C. Yu et al.⁷¹ removed impurities from Pb-poisoned deactivated catalysts by washing with ethylenediaminetetraacetic acid (EDTA), H_2SO_4 , acetic acid, oxalic acid, or HNO_3 , showing that single acid washing increased the specific surface area and Brønsted acid sites, leading to increase partial catalytic performance. The combination of EDTA-2Na and H_2SO_4 was found to be the most effective for the regeneration of the above acid washes, outweighing HNO_3 , EDTA, oxalic acid, H_2SO_4 , and acetic acid in that order (Figure 5(b)). Li et al.⁷³ regenerated the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2\text{-SiO}_2$ catalysts poisoned with Pb, As, and alkali metals by washing with acetic acid and H_2SO_4 (Figure 5(c)). The results showed that the removal of Pb, Na, As, and K reached 99.2, 99.9, 98.8, and 93.9%, respectively. Compared to the conventional H_2SO_4 -wash regeneration process, the acetate washing of alkali-deactivated catalysts can save the activation solution soaking step while ensuring the regeneration effect.

Alkaline Washing. Yu et al.⁷⁴ used a dilute sodium hydroxide (NaOH) solution to wash $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$ catalysts deactivated after a service life of approximately 37,000 h. The results showed that this method achieved the effect of removing impurities, increasing the specific surface area and porosity and restoring the V^{4+} content, with the relative activity increasing to 0.74 at 380 °C. However, this method partially dissolves active V, reducing its regeneration effectiveness. Qi et al.⁷⁵ investigated

the treatment of As-poisoned catalysts with deionized water, acetic acid, and alkaline sodium carbonate (Na_2CO_3) solutions and demonstrated that effective As removal and a NO_x conversion of 98.45% of the original efficiency could be achieved after this regeneration process. Jia et al.⁷⁶ treated the catalysts with 0.001 mol/L acetic acid and 0.0015 mol/L ammonia solution and achieved an activity recovery of the regenerated catalyst between 94.3% and 97.4% in the temperature range of 300–400 °C. Lou et al.⁷⁷ regenerated an end-of-life $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst with high As content using a stepwise alkali-acid leaching process, as shown in Figure 6. Under optimized conditions of 80 °C, a 1 mol/L alkaline solution, and a 3:1 liquid to solid ratio, the As content could be reduced from 1.92% to below the detection limit. The commercial catalyst standard could be achieved by acid washing and reimpregnating the active ingredient.

Organic Polyether Reagent Cleaning. Li et al.⁷⁸ treated CaO-poisoned $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts using the 1-hydroxyethyl-1,1-diphosphate (HEDP) solution impregnation method. The results showed that the denitrification performance of the HEDP-treated poisoned catalysts was significantly improved by achieving higher CaO removal and less loss of active ingredients. Li et al.⁷⁹ used alkylphenol polyoxyethylene ether 10 (OP-10) to clean and regenerate Ca-poisoned $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts, resulting in 78% removal of Ca and less than 15% removal of V, which was better than employing conventional H_2SO_4 as a cleaning solution, confirming that OP-10 could effectively restore the catalytic performance of the spent catalyst.

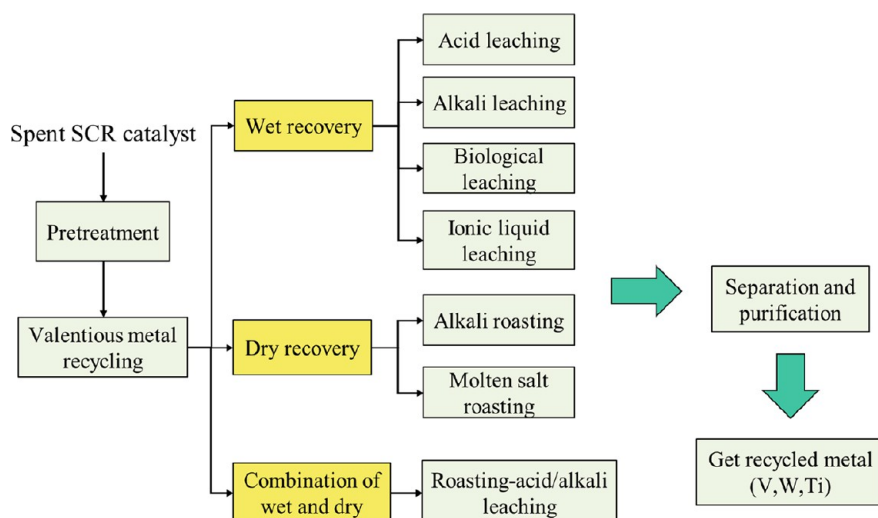


Figure 8. Spent SCR catalyst valuable metal recovery process.

Washing and regeneration of $V_2O_5-WO_3/TiO_2$ catalysts with acidic/alkaline solution are more effective than regeneration by water washing.⁸⁰ However, washing with acidic or alkaline solutions can cause equipment corrosion to a certain extent. Loss of active elements can occur during this washing method, decreasing the catalytic performance of $V_2O_5-WO_3/TiO_2$ catalysts.¹⁴ Some studies have shown that the regeneration effect of mixed acidic/alkaline washing (dilute NaOH- HNO_3 solution) is superior to single acid-base washing, which can effectively overcome the disadvantages of single acid washing, resulting in the loss of active elements, and single-base washing, resulting in poor contaminant removal and deposition of alkali metal ions.⁸¹ At the same time, chemical reagent washing should focus on the development of more environmentally clean process methods that can retain the active components to a greater extent by effectively removing the catalyst poisons.

3.1.3. New Regeneration Methods. In addition to physicochemical regeneration methods, there has been continuous research into the regeneration of spent catalysts in combination with novel techniques such as electrochemistry, bioleaching, and ammonium salt decomposition of deposits from the perspective of optimizing stepwise procedures.

Xue et al.⁸² proposed a process method for the electrochemical detoxification of spent SCR catalysts by in situ generation of active oxygen in alkaline media to recycle As-poisoned deactivated commercial $V_2O_5-WO_3/TiO_2$ catalysts, mainly through the step of crushing and sieving, magnetically stirred electrochemical advanced oxidation, filtration and separation, acid washing, active ingredient impregnation, and drying and calcination (Figure 7(a),(b)). It was found that the structure and original composition of the catalyst after electrochemical treatment on a TiO_2 carrier was well retained and could be utilized for recycling or further retreatment processes. The catalytic deoxygenation activity could reach its original levels after impregnating the active component on the detoxification catalyst. Li et al.⁸³ used an electrothermal alloy to heat the catalyst surface temperature to expand the working temperature window of the catalyst. At the same time, it was found that electrical heating could effectively regenerate the NH_4HSO_4 -poisoned catalyst and restore the NO_x conversion to the level of a fresh sample (Figure 7(c)). Niu et al.²¹ used an active bioleach solution from indirect bioleaching with *Acid-*

ithiobacillus thiooxidans for the deep removal of As from the recycled product. According to the results, the microbially secreted bioleach solution contained high levels of cysteine, which promoted As removal and had a strong activating effect on the product. Based on a mixture of acetic acid, oxalic acid, H_2SO_4 , and phosphoric acid as selective agents for the effective removal of contaminants from SCR catalyst surfaces, Kapkowski et al.⁸⁴ proposed an optimal three-step procedure of acidic cleaning in a mixture of acetic acid, H_2SO_4 , phosphoric acid, and oxalic acid, followed by an auxiliary treatment in an alkaline NaOH and hydrogen peroxide (H_2O_2) solution and the subsequent removal of residual alkali with acetic acid. This method ensures the recovery of catalyst efficiency to a level comparable to that of new catalysts and is equally suitable for high-volume treatment in industrial power stations. Zheng et al.⁸⁵ added ammonium nitrate (NH_4NO_3) to spent SCR catalysts with simulated NH_4HSO_4 deposition deactivation and found that the addition of NH_4NO_3 not only improved NO_x conversion at low temperatures but also accelerated the removal of NH_4HSO_4 on the catalyst surface and effectively prevented the new deposition of NH_4HSO_4 .

The regeneration of $V_2O_5-WO_3/TiO_2$ catalysts employs different treatment methods depending on the type of deactivation. Specifically, spent SCR catalysts, as hazardous wastes, are rich in As, Sn, and Pb hazardous components due to the perennial influence of flue gas from thermal power plants. Among them, poisoning is the leading cause of its deactivation. It is mainly deposited on the catalyst surface and internal channels in the form of As_2O_3 and As_2O_5 . Currently, the industry standard for the regeneration of spent catalysts has a limit of 200 mg/kg for As residual concentration, and the removal of this type of component is the focus of regeneration process research.²¹ Combined acid and alkali purification is the mainstream commercial method. It can remove As and alkali metals at the same time, increase acidic sites,⁷⁷ and remove As^{3+} and As^{5+} in deep channels to obtain regenerated products. However, the chemicals themselves are damaging to the substrate and do not guarantee the complete removal of As residues occupying the V_2O_5 active sites.⁸⁶ This still has an impact on the activity of the regenerated catalyst. Therefore, it is a common goal to explore milder regeneration reagents with deep purification of As residue carriers.

As industrial production continues to innovate and the flue gas environment becomes more complex, future treatment methods can be based on the effective retention of active ingredients, shortening the process flow, and improving recovery efficiency, combining the concept of environmental sustainability and exploring process method optimization techniques in different fields to achieve low-energy, efficient, and clean regeneration of catalysts. In particular, biological regeneration methods as environmentally friendly practices have potential and advantages, and further exploration of bacteria strains for efficient removal of toxic substances could be a point of interest.

3.2. Valuable Metal Recovery Methods for Spent Vanadium–Titanium SCR Catalysts. More than 20% of deactivated catalysts are not reusable due to structural damage and irreversible deactivation.⁸⁷ For these deactivated catalysts with low recovery potential, when regeneration is no longer able to achieve reuse value and meet reuse criteria, considering metal recovery is a favorable approach to reducing potential pollution hazards and fully utilizing the resources contained in the spent catalysts due to their richness in strategic metals such as V, W, and Ti. Typically, metals in deactivated catalysts are recovered in three significant stages: pretreatment, recovery of precious metals, and separation and purification. After pretreatment, the metal extraction process is further divided into wet recovery, dry recovery, and a combination of wet and dry methods, depending on the extraction method. Figure 8 shows the valuable metal recovery process of the spent SCR catalyst.

3.2.1. Wet Recovery. Wet recovery involves the use of leaching agents to break the bonds between V, W, and O in the catalyst, mainly affecting the bonding of V–O₂, W–O₄, and W–O₂,⁸⁸ thereby removing the components V₂O₅ and WO₃ from the carrier. Depending on the leaching agent, wet recovery can be divided into acid leaching, alkaline leaching, and new leaching methods adapted to the environment.

3.2.1a. Acid Leaching. The acid leaching method, which mainly uses acidic reagents to transfer the valuable metals in the catalyst into acidic solutions, is widely used for its low cost and effective recovery advantages. V₂O₅ in the catalyst is soluble in acids, while WO₃ is soluble in alkali. Consequently, in the acidic solution, W remains in the residue, which also contains TiO₂ since it reacts only weakly to acids and bases. Accordingly, acid leaching targets the extraction of V, and the current process mostly uses inorganic acids such as HCl, H₂SO₄, and HNO₃ but also organic acid reagents such as oxalic acid for leaching. Nie et al.⁸⁸ identified the leaching mechanisms of NaOH, H₂SO₄, HCl, and HNO₃ for V and W and compared to their leaching capacities using DFT calculations and experimental studies. The leaching experiment was carried out under the conditions of different inorganic acid solutions with a concentration of 5 mol/L, a solid–liquid ratio of 1:20 g/mL, a temperature of 80 °C, and a time of 8 h. The order of leaching capacity and leaching rate of inorganic acid solutions for V decrease in the order H₂SO₄ (69.0%) > HCl (52.5%) > HNO₃ (42.2%), and W was almost not leached under these conditions. Zhang et al.⁸⁷ investigated the reducing acid leaching system of H₂SO₄ and sodium sulfite (Na₂SO₃) to recover V: with an H₂SO₄ concentration of 5 wt %, a leaching temperature of 95 °C, a material–liquid ratio of 1:10 g/mL, a leaching time of 2 h, and adding 1 g of Na₂SO₃ to the mixture every 0.5 h, nearly 100% V removal rate can be achieved. By comparing with inorganic acids, Yao et al.⁸⁹ found that the leaching efficiency of W in oxalic acid could reach 70%, which was significantly higher than that achieved in HCl (16%) and

HNO₃ (19.5%). Wu et al.⁹⁰ studied the selective leaching of V with oxalic acid and the reaction mechanism, as shown in Figure 9. Under the optimized conditions of an oxalic acid

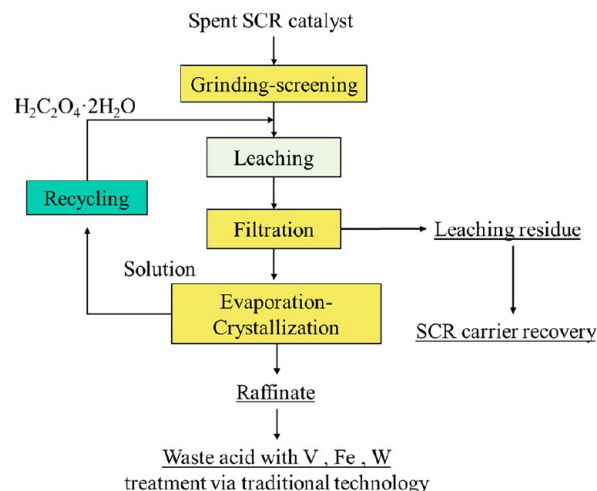


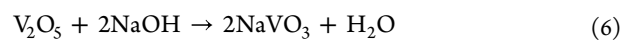
Figure 9. Selective leaching process of V and Fe with oxalic acid.⁹⁰ Reproduced with permission from ref 90. Copyright 2018 Elsevier.

concentration of 1.0 mol/L, a reaction temperature of 90 °C, a liquid–solid ratio of 20 mL/g, a particle size smaller than 75 μm, and a leaching time of 180 min, the leaching rate of V reached more than 84%.

For the direct acid leaching of Ti and W, Zhao et al.²⁶ considered that the increased content of K, Na, and Fe in the spent V₂O₅–WO₃/TiO₂ catalyst was not conducive to catalyst recovery, and Si, Al, and Ca were insoluble in the H₂SO₄ solution; therefore, their separation from Ti and W could be achieved during the acid digestion process. Therefore, the authors used hot concentrated H₂SO₄ as a leaching agent for the simultaneous leaching of W and Ti from the V₂O₅–WO₃/TiO₂ catalyst and shortened the process route as shown in Figure 10, obtaining as optimum conditions a temperature of 150 °C, a reaction time of 60 min, an H₂SO₄ concentration of 80%, a mass ratio of H₂SO₄ to TiO₂ of 3:1, and dilution to an H₂SO₄ concentration of 20% after the reaction. Under these conditions, the leaching efficiency of Ti and W reached 95.92% and 93.83%, respectively. After further hydrolysis and calcination steps, titania powder with low levels of impurities and reconstructed porosity properties was obtained.

The acid process recovers V products with high purity but, at the same time, leaches out other impurity metal components that are easily soluble in acid, which require the input of reducing agents for reduction. There is still relatively little direct leaching of Ti and W. Subsequent research can be conducted for the direct leaching of Ti and W in various aspects. In addition, acidic reagents have a corrosive effect on the equipment. Finding more environmentally friendly leaching reagents and process methods is still something that needs to be investigated.

3.2.1b. Alkali Leaching. Alkali is considered to be the best reagent for the simultaneous leaching of the valuable metals V and W from spent V₂O₅–WO₃/TiO₂ catalysts,⁹¹ with the advantages of lower costs and higher leaching efficiency. V and W can be transferred to the alkaline reagent solution by alkali leaching according to eqs 6–7), while TiO₂ is retained in the residue phase.



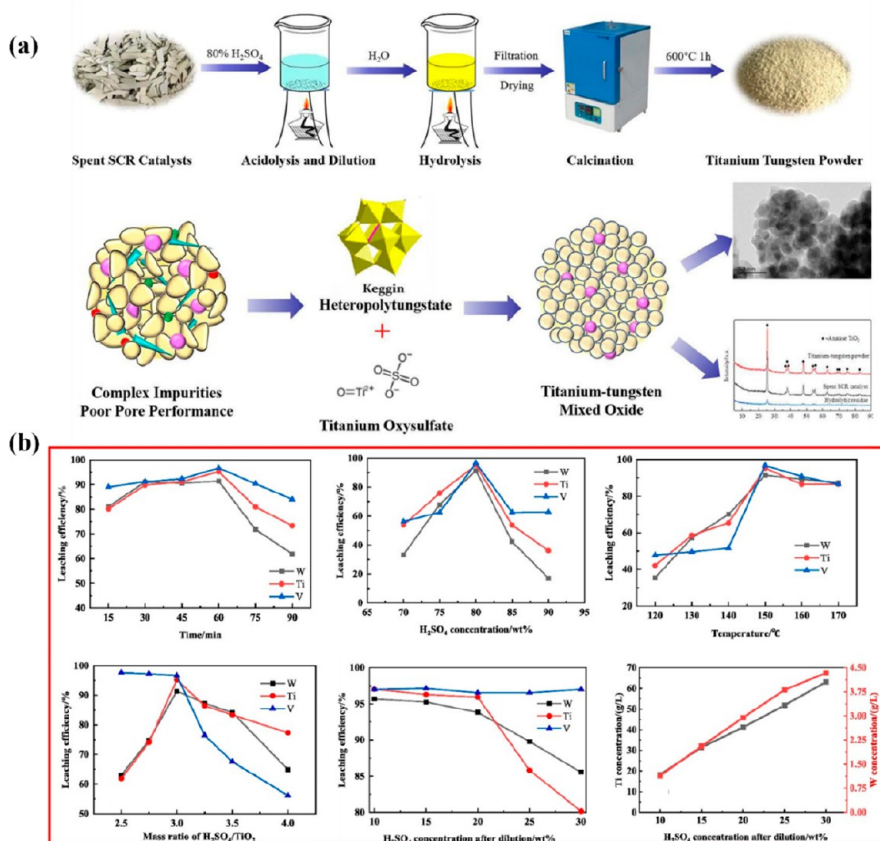
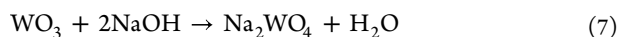


Figure 10. (a) Process flow of the simultaneous leaching of W and Ti with H₂SO₄ to reconstruct the pore properties. (b) Effect of acid digestion parameters (time, H₂SO₄ concentration, temperature, H₂SO₄/TiO₂ mass ratio, diluted H₂SO₄ concentration) on leaching efficiency and effect of diluted H₂SO₄ concentration on the leaching concentration of Ti and W.²⁶ Reproduced with permission from ref 26. Copyright 2023 Elsevier.



Commonly used alkaline leaching reagents include NaOH, H₂O₂, and (NH₄)₂CO₃. Wu et al.⁹² used the NaOH alkaline leaching method and achieved leaching rates of 87 wt % for V and 91 wt % for W at the optimum conditions of a NaOH concentration of 0.3 kg/kg catalyst, a pulp density of 3%, a leaching temperature of 70 °C, a particle size of less than 74 μm, and a leaching time of 30 min. Su et al.⁹¹ premixed NaOH with spent catalyst and obtained 68.3% V leaching and 50.1% W leaching at the optimum conditions of a leaching temperature of 100 °C, a NaOH/catalyst ratio of 0.9, a liquid to solid ratio of 15, a stirring speed of 900 rpm, and a leaching time of 240 min. Furthermore, premixing NaOH and catalyst significantly increased V and W leaching and reduced silicon leaching at 25 °C and atmospheric pressure. Cao et al.⁹³ investigated the effects of (NH₄)₂CO₃ concentration, H₂O₂ concentration, time, and temperature on the leaching efficiency and the leaching thermodynamics and kinetics of V and W, as shown in Figure 11. The optimum leaching conditions were obtained as 1.5 mol/L H₂O₂, 70 °C, 2.0 mol/L (NH₄)₂CO₃, a liquid to solid ratio of 25:1, and a leaching time of 30 min. The recovered products were V₂O₅ and ammonium paratungstate (APT), with recoveries of V and W equal to or exceeding 98% and 99%, respectively. The apparent activation energy after leaching was 64.18 kJ/mol for V and 58.95 kJ/mol for W. The leached residue crystals were identified as anatase TiO₂, which was structurally stable and could be used as a carrier for the remanufactured catalyst.

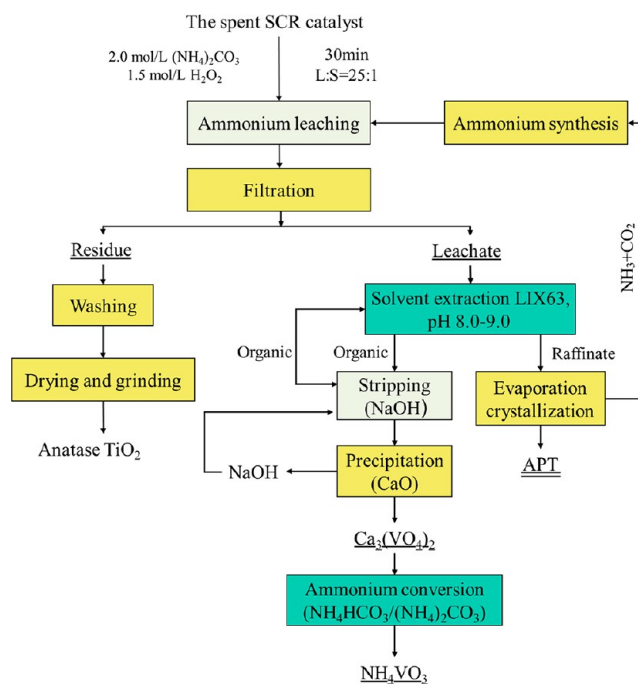


Figure 11. W and Ti recovery process using (NH₄)₂CO₃/H₂O₂ leaching.⁹³ Reproduced with permission from ref 93. Copyright 2021 Elsevier.

In contrast to leaching at atmospheric pressure, Kim et al.⁹⁴ proposed an alkaline leaching process with a solution of NaOH

and Na_2CO_3 under pressure and found that high V and W leaching efficiency could be achieved while reducing the concentration of NaOH. They mixed 2 mol/L NaOH and 0.2 mol/L Na_2CO_3 solutions to leach V and W from spent $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts under pressure and achieved leaching rates of 99.6% and 98.8% for V and W, respectively, at an optimum temperature of 300 °C, a leaching time of 120 min, a liquid to solid ratio of 20:1, and stirring speed of 1000 rpm. Choi et al.⁹⁵ used a steam-assisted high-pressure reaction in a sealed autoclave and found that the NaOH pressure leaching process was more effective in dissolving V and W from the spent $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst. Under leaching conditions of a NaOH concentration of 3 mol/L, a temperature of 250 °C, a solid-to-liquid ratio of 0.4, and a particle size below 150 μm , the leaching efficiencies of V and W were 91.5% and 87%, respectively.

Using alkaline reagents results in the coleaching of V and W. Hence, the separation of V and W needs further consideration in subsequent purification steps to obtain high recovery rates.

3.2.1c. New Environmentally Friendly Leaching. Compared to conventional acid–base leaching, the choice of milder and more effective reagents is the focus of current research into leaching processes in response to environmental protection and energy efficiency.

Microbial leaching is gentler and more environmentally friendly and avoids high energy consumption. Wang et al.⁹⁶ studied the leaching of V using a combination of five methods: depleted nutrient, eutrophic, S-mediated, Fe-mediated, and mixed S-mediated and Fe-mediated. The total W and V leaching rates by the S-mediated, mixed, depleted, eutrophic, and Fe-mediated methods were 90%, 35%, 33%, 20%, and 7%, respectively. Among them, the S-mediated method achieved the highest leaching rate, probably due to the action of *Acidithiobacillus* and *Sulfobacillus* that contributed to the leaching of V and W. However, the mechanism of bioleaching needs to be further clarified. The disadvantages of the microbial leaching process are too long leaching times and stringent leaching process conditions to culture the microorganisms.

To avoid the generation of large amounts of leaching wastewater and to reduce corrosion of equipment and environmental pollution, Liu et al.⁹⁷ selected nine different ionic liquids (ILs) for the extraction of V and W from spent catalysts. The results showed that V_2O_5 could be dissolved in basic ILs ([MEA]L, [TMG]L, N_{2222} [L-Pro], N_{2222} [Sar]) and not in neutral ILs ([BMIM][BF₄], [BMIM][PF₆], [TMG]-[BF₄]) at 45 °C–120 °C. The pH needs to be considered in the acidic case, and at pH = -0.43, V_2O_5 can be dissolved in [Hnmp]HSO₄. The order of leaching efficiency for vanadium is N_{2222} [L-Pro] > N_{2222} [Sar] and [Hnmp]HSO₄ > [MEA]L and [TMG]L, with leaching efficiencies of up to 70% at temperatures below 100 °C. The above five reagents were also effective for the leaching of tungsten with efficiencies of up to 77%. Ionic liquids, as new green solvents with the advantages of both high-temperature molten salts and organic reagents, are used for the leaching of valuable metals from spent SCR catalysts as a new and sustainable technology. Its leaching effect is comparable to that of acid–base leaching and holds some promise. However, the application is limited by a combination of cost and technology. With this approach, the continuous development of economical and efficient new ionic liquid leaching agents could be a subject for further research.

3.2.2. Dry Recycling. Dry recovery mainly involves the extraction of target metals from hard-to-decompose minerals and waste by roasting the oxidized metals at high temperatures,

here mainly divided into alkaline roasting and molten salt methods.

3.2.2a. Alkaline Roasting Method. The roasting process is a solid-phase reaction between reagents and spent SCR catalysts at high temperatures to form salts, with the main reagents being NaOH and Na_2CO_3 . Metals such as V, W, Si, and Al react with the molten alkali to form water-soluble sodium salts. In contrast, Ti reacts with the molten alkali to form water-insoluble sodium titanate.⁹⁸ The sodium roasting-water leaching process is an effective way to extract V and W from spent SCR catalysts. Cueva et al.⁹⁹ compared a standard roasting process using solid NaOH as the roasting agent with an innovative process using dissolved NaOH, concluding that roasting in NaOH solution was a more efficient method, reducing silicon leaching to nearly half while maximizing V and W leaching. The process is shown in Figure 12. Choi et al.¹⁰⁰ investigated the impact of the

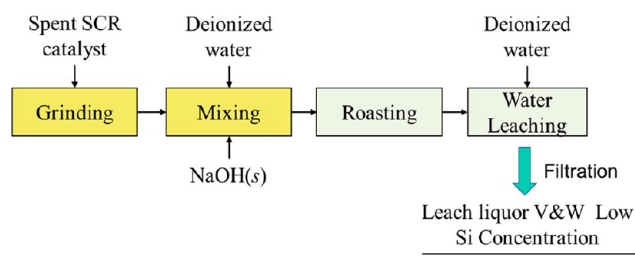


Figure 12. NaOH solution roasting leaching process.

parameters of Na_2CO_3 addition, temperature, and roasting time for V and W on the extraction efficiency. The results showed that the effect on W extraction when adding Na_2CO_3 to the roasting process of spent catalyst was significant, and the extraction efficiency of W increased significantly with the increase in Na_2CO_3 dosage, where excess Na_2CO_3 inhibited the formation of calcium tungstate (CaWO_4). The maximum extraction of W was 92% under the optimum reaction conditions with a Na_2CO_3 particle size of less than 106 μm and an equivalence ratio (the ratio of the amount of Na_2CO_3 added to the total content of W as Na_2WO_4 and V as NaVO_3 in 10g of raw material) of 10. Moon et al.¹⁰¹ investigated the water leaching and acid leaching of spent SCR catalysts after alkali melting with Na_2CO_3 . The reaction of the spent SCR catalyst with Na_2CO_3 , the water leaching process in a temperature range of 303–373 K, and liquid-to-solid ratios of 2–20% resulted in leaching efficiencies greater than 99.2% for both W and V. The HCl leaching efficiency of Ti was 98.3% after 3 h of leaching with 8 mol/L HCl at 353 K and a liquid-to-solid ratio of 10%.

3.2.2b. Compound Salt Melting. To reduce the roasting-leaching temperature and the amount of used Na_2CO_3 and to increase the leaching rate of V and W, a salt component is generally added to the alkali-based roasting step, thus lowering the roasting melting point and increasing the efficiency of the reaction. Song et al.²⁹ used a molten salt roasting-leaching method with $\text{Na}_2\text{CO}_3\text{-NaCl-KCl}$ to recover valuable metals from spent $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts, as shown in Figure 13(a), achieving optimal W and V leaching rates of 99.3% and 98.4% at roasting conditions of 12% $\text{Na}_2\text{CO}_3\text{-40% NaCl-KCl}$ and 750 °C. Yang et al.¹⁰² studied the extraction of W and V with $\text{Na}_2\text{CO}_3\text{-NaCl}$, as shown in Figure 13(b), achieving leaching rates of 94.9% and 95.5% for V and W, respectively, and recoveries of 93.4% and 96.2% at roasting conditions of 16% $\text{Na}_2\text{CO}_3\text{-8.8% NaCl}$ and 750 °C. The leaching residues of nano-TiO₂ and sodium titanate nanowires were also used as

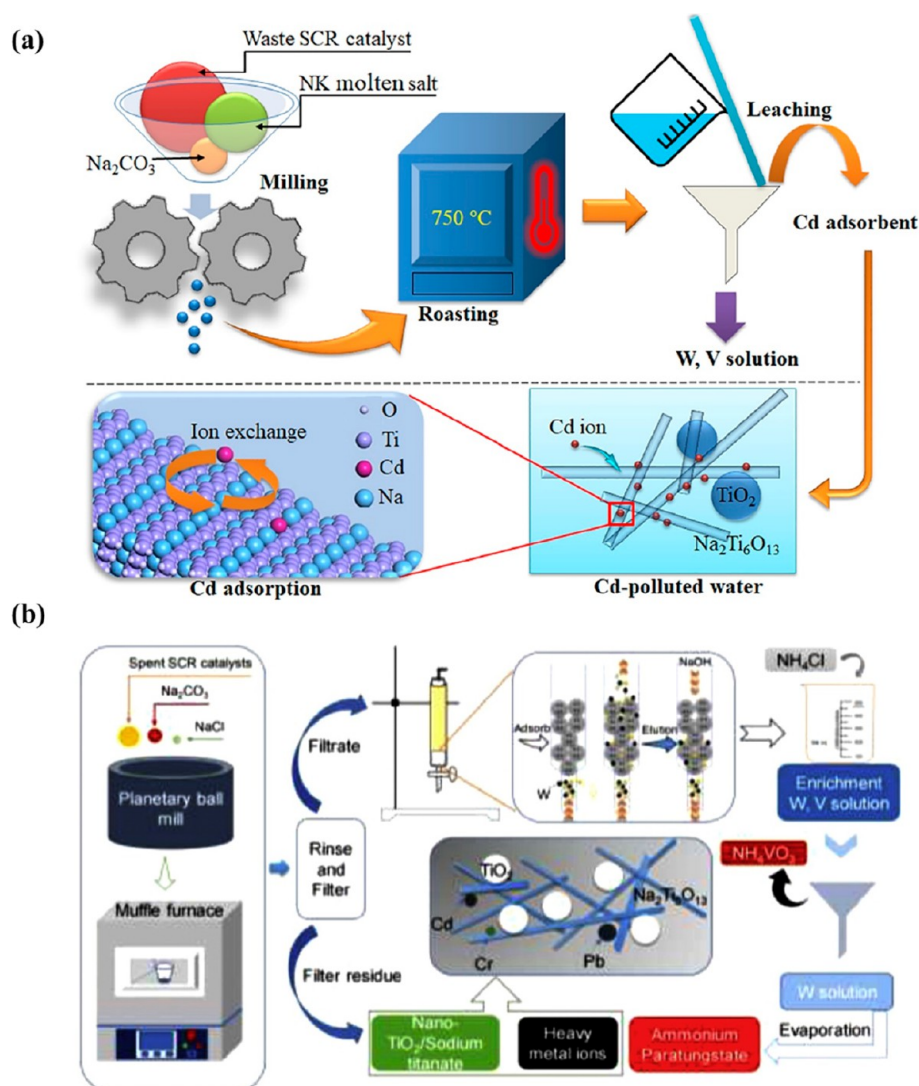


Figure 13. (a) Na_2CO_3 – NaCl – KCl molten salt roasting-leaching method to recover titanium dioxide and sodium titanate nanowires TiO_2 /STNWs from spent V_2O_5 – WO_3 /TiO₂ catalysts as Cd(II) adsorbent.²⁹ Reproduced with permission from ref 29. Copyright 2018 Elsevier. (b) Na_2CO_3 – NaCl Yungan roasting process to recover TiO_2 /STNWs from spent V_2O_5 – WO_3 /TiO₂ catalysts and extract and separate W and V.¹⁰² Reproduced with permission from ref 102. Copyright 2020 Elsevier.

heavy metal adsorbents. The addition of NaCl allowed decomposition-generated chlorine Cl_2 to act as a catalyst and oxidant to promote the oxidation of low-valent V, thus facilitating the leaching of V. Wang et al.¹⁰³ compared different types of sodium additives and found that the leaching efficiency of NaOH – NaCl roasting for V and W was up to 91.39% and 98.26% higher compared to acid and alkaline leaching, respectively. At the same time, the addition of low melting point NaOH promoted the reaction to a greater extent than the addition of sodium additives with different melting points. Under the optimum roasting conditions of $750\text{ }^\circ\text{C}$, a roasting time of 2.5 h, a sodium additive to catalyst mass ratio of 2.5, and a NaCl to NaOH mass ratio of 1.5, V and W leaching efficiencies were 93.25% and 99.17%, respectively.

The composite salt melting method in dry recovery can decrease the melting point, reduce the number of roasting reagents, and shorten the process compared to a single alkaline roasting way. It can achieve more effective leaching of V and W. However, the added chloride component may cause secondary contamination during the roasting process, and the impact on

the specific heavy metal adsorption application needs to be considered.

3.2.3. Combined Wet and Dry Method. As some catalyst components are not homogeneous, sometimes one method, wet or dry, does not achieve good recovery, and a combination of wet and dry methods addresses the shortfall and achieves the leaching target. Choi et al.¹⁰⁴ used a roasting– HCl decomposition– NaOH leaching-precipitation process to recover W from spent V_2O_5 – WO_3 /TiO₂ catalysts for the synthesis of CaWO_4 (Figure 14). According to the results, the addition of CaO during the roasting process could effectively improve the extraction efficiency of W. Using 4 mol/L HCl solution as the decomposition solution, the removal of V reached 92.5%, and the loss of W was negligible. The dissolution of H_2WO_4 with 1 mol/L NaOH solution gave W yields more significant than 99%. Calcium chloride (CaCl_2) was then added to the sodium tungstate (Na_2WO_4) solution for the synthesis of CaWO_4 , and the final product contained 96.1 wt % CaWO_4 , giving a total W recovery of 96.4% from the feedstock using this process.

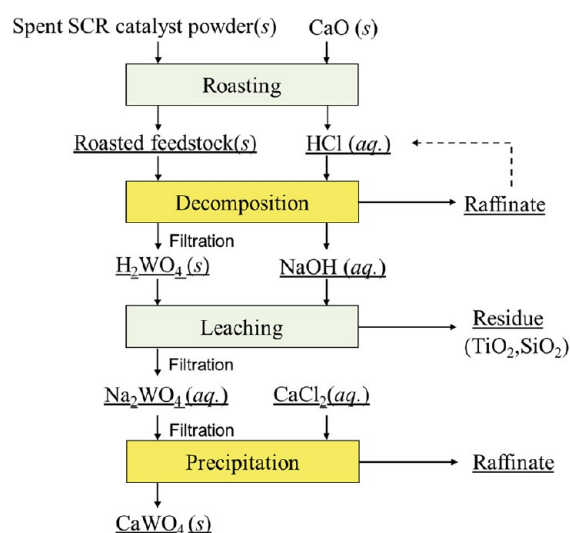
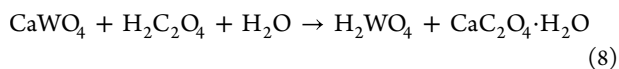


Figure 14. Recovery of W from spent V_2O_5 – WO_3 /TiO₂ catalyst by the roasting–HCl decomposition–NaOH leaching–precipitation process for the synthesis of $CaWO_4$.¹⁰⁴ Reproduced with permission from ref 104. Copyright 2018 Elsevier.

Yao et al.⁸⁹ used CaO– $H_2C_2O_4$ sequential calcination–oxalic acid leaching to recover W from spent V_2O_5 – WO_3 /TiO₂ catalysts and investigated the conversion mechanism of W during two calculations. The results showed that W partially reacted with Ca during the first calcination to form $CaWO_4$, which was converted to the soluble chelate compound $H_2[WO_3(C_2O_4)H_2O]$ after leaching by dilute oxalic acid, as shown in eqs 8–9:



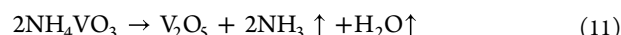
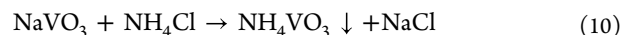
The filtrate was roasted twice; the W leaching rate reached up to 87%; and the purity of the resulting WO_3 was up to 91%. Teng et al.¹⁰⁵ used a combined wet and dry process to achieve efficient separation and leaching of Ti, V, and W elements from waste V_2O_5 – WO_3 /TiO₂ catalysts. The optimum process conditions for acid leaching–reduction leaching of V were a temperature of 140 °C and a liquid-to-solid ratio of 30:1. In comparison, the optimum process conditions for sodium roasting and leaching of W were a calcination temperature of 750 °C and a reactant to Na_2CO_3 mass ratio of 1:1.5. Under these conditions, the leaching rates of V and W reached 97.6% and 93.6%, respectively. The anatase TiO₂ obtained by H_2SO_4 leaching was roasted at 750 °C, and the recovery was 97.17% with a purity of 95.35%.

The above process can effectively leach the major valuable metals V, W, and Ti from the spent catalyst. Table 4 summarizes the corresponding methods. Exploring shorter processes and environmentally and economically viable extraction processes remains a direction for future research efforts.

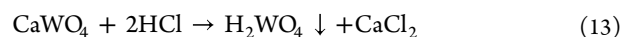
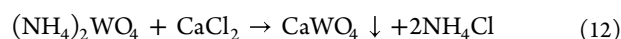
3.2.4. Separation and Purification of Vanadium and Tungsten. After the above leaching and extraction of the valuable metals from the spent V_2O_5 – WO_3 /TiO₂ catalyst, the V- and W-rich leach solution and the Ti-rich residue obtained by filtration need to be further processed, separated, and purified to achieve the separation and utilization of V, W, and Ti. For solutions containing V, W, and other valuable metal elements, further separation and treatment is required for the leachate,

depending on the differences in the nature of V and W ions, to achieve the separation and recovery of the two metals. The processes can be mainly categorized as chemical precipitation, ion exchange, and solvent extraction methods.

3.2.4a. Chemical Precipitation Method. The chemical precipitation method is mainly used to separate and purify V and W by adding precipitating agents to different compounds with different solubilities. The main precipitation methods currently used for the purification and separation of V- and W-containing leachates are ammonium precipitation for the recovery of V and calcium precipitation for the recovery of W. Ammonium salts are added to the leachate to obtain NH_4VO_3 sludge, which is calcined at high temperature to obtain V_2O_5 , according to eqs 10–11:



The filtrate is then added to Ca salt solution to obtain $CaWO_4$ precipitate, which is acid-washed and calcined to give WO_3 , reacting as in eqs 12–14):



Yang et al.¹⁰⁶ used Na_2CO_3 – $NaCl$ molten salt roasting and leaching to extract W and V from spent V_2O_5 – WO_3 /TiO₂ catalyst and obtained enriched W and V solutions by ion exchange and NaOH elution. The further separation involved ammonium precipitation, and the recoveries of V and W were up to 93.4% and 96.2%, respectively. Wang et al.³⁰ used H_2SO_4 –ascorbic acid to leach V and enrich V by pH adjustment. Then NH_4Cl was selected as the precipitant to obtain ammonium polyvanadate (APV), and the product V_2O_5 was obtained by roasting at 550 °C for 1 h. The chemical precipitation method is simple, inexpensive, and high-throughput. Still, the product purity is low, and this method is relatively suitable for purification and separation when high product purity is not required.

3.2.4b. Ion Exchange Method. The ion exchange method mainly uses ion exchange resins to separate and purify V and W ions based on their different selectivity for these ions. Kim et al.¹⁰⁷ adsorbed W and V on synthetic extraction resins and then desorbed them for recovery from the separated sodium silicate. According to the analysis of the adsorption mechanism of the synthetic resins, W followed an ion-exchange sorption mechanism, while V followed a physical sorption mechanism; the sorption of V was less than that of W because of the higher selectivity for WO_4^{2-} than for VO_3^- . The synthetic methylcellulose-grafted anion extraction resin was found to have 1.77 times and 1.39 times higher sorption performance for V and W than the standard resin, respectively. Wu et al.⁹² passed a strong base leaching solution through a strong base anion exchange resin (Amberlite IRA900) and investigated the effect of the leaching parameters of added NaOH amount, pulp density, leaching temperature, particle size, and time on the leaching of W and V (Figure 15). A selective loading of WO_4^{2-} was obtained at high pH, and the adsorbed W could be eluted with a mixture of 1 mol/L NaCl and 0.5 mol/L NaOH. The final W concentration of the solution was 8.4 g/L with a purity of 98%. The ion exchange method is generally not suitable for

Table 4. Summary of Recycling Leaching Methods Mentioned in the Article

Recycling type	Process methodology	Reaction medium	Leaching parameters	Leaching/recovery rate	Pros and cons	Ref
Wet recovery	Acid leaching	H ₂ SO ₄ + Na ₂ SO ₃	5 wt % H ₂ SO ₄ , 95 °C, a material–liquid ratio of 1:10 g/mL, 2 h	V close to 100%	Low cost, high leaching rate, simple operation, but a large amount of acid discharge waste liquid, corrosion to the equipment.	87
		H ₂ C ₂ O ₄	C(H ₂ C ₂ O ₄) = 1 mol/L, 90 °C, 20 mL/g, <75 μm, 180 min	V more than 84%; Fe 96%		
Alkali leaching		H ₂ SO ₄	150 °C, 60 min, concentration of 80%, <i>m</i> (H ₂ SO ₄): <i>m</i> (TiO ₂) = 3:1	Ti 95.92%; W 93.83%	The conditions are mild, the leaching rate is high, but there are many impurities, and the amount of alkaline waste liquid discharged is large.	26
		NaOH	0.3 kg/kg, pulp density 3%, 70 °C, 30 min, <74 μm	V 87 wt %; W 91 wt %		
		NaOH (NH ₄) ₂ CO ₃ + H ₂ O ₂	100 °C, the NaOH/catalyst ratio is 0.9, 5 mL/g, 900 rpm, 240 min	V 68.3%; W 50.1%		
Dry recovery	Roasting	NaOH + Na ₂ CO ₃	1.5 mol/L H ₂ O ₂ , 70 °C, 2.0 mol/L (NH ₄) ₂ CO ₃ , 2.5 mL/g, 30 min	Recovery rate V 98%, W 99%		93
		NaOH	2 mol/L NaOH, 0.2 mol/L Na ₂ CO ₃ , 300 °C, 120 min, a liquid to solid ratio of 20:1, 1000 rpm, pressure	V 99.6%; W 98.8%		
Biological leaching	Ionic liquids of leaching	NaOH	<i>c</i> (NaOH) = 3 mol/L, 250 °C, a solid to liquid ratio of 0.4, <150 mm, steam auxiliary high pressure	V 91.5%; W 87%	The leaching process has strict conditions, a long experimental cycle, and many experimental interference factors.	94
		S-mediated	Acidithiobacillus and sulfobacillus	V 90%		
Dry recovery	Roasting	Na ₂ CO ₃	0.1 g catalyst, 1 mL H ₂ O, 45–120 °C, 200 rpm, 5–60 min	V, N ₂₂₂₂ [L-pro] > N ₂₂₂₂ [Sar], [Hmmp]HSO ₄ > [MEA]L, [TMG]L up to about 70%, W, up to about 77%	The operation is simple, the cycle is short, and the energy consumption is low, but the extraction efficiency of metal is low.	97
		Na ₂ CO ₃ –NaCl–KCl	10 equiv ratio of Na ₂ CO ₃ , <106 μm, 1073 K, 120 min	W 92%		
Combination of wet and dry	Roasting–acid/alkali leaching	Na ₂ CO ₃ –NaCl	12% Na ₂ CO ₃ –40% NaCl–KCl, 750 °C	V 98.4%, W 99.3%	The leaching rate is high, but the cost is large, the energy consumption is high, the requirements for the equipment are high, and the amount of waste liquid is large.	101
		NaOH–NaCl	Na ₂ CO ₃ –8.8% NaCl, 750 °C	V 94.9%, W 95.5%; recovery rates are 93.4% and 96.2%, respectively		
Combination of wet and dry	Roasting–acid/alkali leaching	CaO roasting–HCl decomposition–NaOH leaching	750 °C, 2.5 h, <i>m</i> (Na): <i>m</i> (catalyst) = 2.5, <i>m</i> (NaCl): <i>m</i> (NaOH) = 1.5	V 93.25%; W 99.17%	The extraction efficiency is high and easy to scale, but the process temperature is high, the equipment needs to be resistant to high temperature and corrosion, and the cost is high.	102
		CaO calcination–H ₂ C ₂ O ₄ leaching	1123 K, 3 h, the amount of CaO added is 3 times that of CaO (weight %) in the raw material, <125 μm; 4 mol/L HCl, ambient temperature, S/L (w/v) ratio, 0.1, 2 h, 350 rpm; <i>c</i> (NaOH) = 1 mol/L	V 92.5%, W > 99%		
Combination of wet and dry	Roasting–acid/alkali leaching	Na ₂ CO ₃ , H ₂ SO ₄	1123 K, 4 h, further roasted at 1123 K for 4 h; 0.3 mol/L HCl	W 87%		89
		Na ₂ CO ₃ , H ₂ SO ₄	<i>m</i> (catalyst): <i>m</i> (Na ₂ CO ₃) = 1:1.5, V was acid-leached at 140 °C and 30:1, and W was extracted by roasting at 750 °C	V 97.6%; W 95.35%		

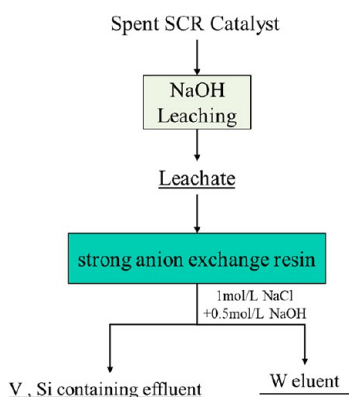


Figure 15. Strong base leaching of spent SCR catalyst followed by W extraction through a strong base anion exchange resin process.

large-scale industrial applications due to its small throughput, poor selectivity, and high cost for the limited use of the resin.

3.2.4c. Solvent Extraction Method. Solvent extraction is the use of extractants to purify or separate V and W components from the solution. The main extractants currently used for V or W extraction from leach solutions are Cyphos IL 104, primary amine N1923, diethylhydroxydodecanone oxime (LIX 63), trioctylphosphine oxide (TOPO), trioctylmethylammonium chloride (Aliquat 336), and bis(2-ethylhexyl)phosphoric acid (HDEHP).^{108–111} In particular, Xiao et al.¹⁰⁹ used acidified primary amine N1923 to extract V and W and V, Mo preferentially. W were separated by selective stripping of V and W with H₂SO₄ and ammonia solutions, respectively (Figure 16). At a pH of 6.7, compared to an O/A (oil phase/aqueous phase) of 1, a contact time of 4 min, and a primary amine N1923 concentration of 10%, 99.91% V and 96.86% W were extracted. In the presence of H₂SO₄ and ammonia, the vapor extraction of V and W reached 95.34% and 95.50%, respectively, and the organic phase remained recyclable. The solvent extraction

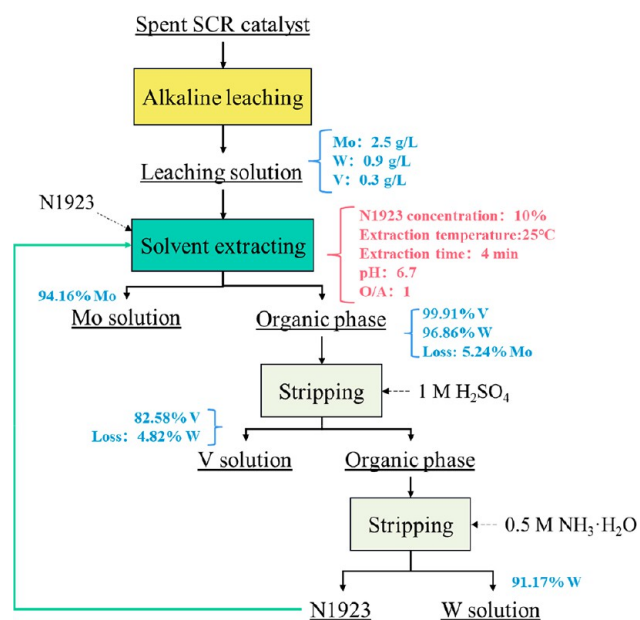


Figure 16. Separation processes of V, Mo, and W in alkaline leachate from spent SCR catalysts using acidified primary amine N1923 as extractant.¹⁰⁹ Reproduced with permission from ref 109. Copyright 2022 Elsevier.

method is characterized by high product purity, large throughput, and high recovery levels and is suitable for purification and separation when high product purity is required. However, the extractants are mostly volatile organic substances of low toxicity, and their use poses certain environmental risks.

At present, in addition to the process of achieving pure products, there is continuous research on the direct high-value utilization of V and W obtained after separation and purification for the preparation of photocatalytic materials like Zn₃(VO₄)₂/ZnWO₄¹¹² and for the synthetic assembly of VO₂ battery materials,¹¹³ and others. This is conducive to reducing process losses and improving the efficiency of V and W utilization. As a subsequent direction of V and W separation technology, it can be further considered to focus on value-added utilization on the basis of low-cost and effective recycling to reduce environmental pollution. At the same time, there is still a relatively complete technical evaluation system as to whether the products obtained from the SCR catalyst recovery process really meet the demand and are economically viable. It is necessary to use environmental evaluation methods for technical analysis and collocation.

3.3. Recycling of Spent Vanadium–Titanium SCR Catalyst Carriers. **3.3.1. Applications of Elemental Ti Products.** Ti is of great recovery value as the main carrier component of spent V₂O₅–WO₃/TiO₂ catalysts with a mass fraction of more than 80%. For the separation of titanium-rich slag by the alkaline leaching and roasting process, the insoluble titanate is usually acid-washed, filtered, and calcined to obtain TiO₂ powder. Ma et al.¹¹⁴ used Na₂CO₃ roasting to transform the TiO₂ in the spent SCR catalyst to sodium trititanate (Na₂Ti₃O₇) at a Na₂CO₃ to catalyst mass ratio of 3:1. Na₂Ti₃O₇ was leached out for 3 h at a temperature of 80 °C using 3.73 mol/L H₂SO₄ with an acid to catalyst mass ratio of 30:1. The leaching rate of Ti reached 97.5%. Then, the pH of the acid leach solution was adjusted to neutral with Na₂CO₃, and the filtrate was roasted at 600 °C for 3 h to obtain nanoanatase TiO₂ and a small amount of rutile TiO₂ with high purity. Zhang et al.¹¹⁵ used the NaOH molten salt method to efficiently (>98%) convert the Ti component to sodium metatitanate α-Na₂TiO₃ at the optimum conditions of a roasting temperature of 550 °C, a roasting time of 10 min, a mass ratio of NaOH to spent SCR catalyst of 1.8:1, and a NaOH concentration of 60–80 wt %. The α-Na₂TiO₃ was then subjected to water leaching, acid solubilization, hydrothermal treatment, and regeneration to produce a high-purity (>99.0%) TiO₂ photocatalyst with excellent performance, which can meet commercial requirements. The process is shown in Figure 17.

Due to the rich component and recovery value of spent V₂O₅–WO₃/TiO₂ catalysts, using them as a source of Ti is an effective and meaningful way to offer the potential for more value-added utilization. The purification of high-purity metal Ti elements or their use to prepare alloys and nanoultrafine powders has become a significant direction for the application of spent catalysts at present (Figure 18). Zhang et al.¹¹⁶ proposed an environmentally friendly and efficient method for the preparation of Ti₅Si₃ and Ti₅Si₄–TiAl₃ alloys using spent SCR catalysts, Ti-containing blast furnace slag, and aluminum (Al) alloy scrap. Ti and Si were extracted from the spent catalyst and Ti-containing blast furnace slag using Al alloy scrap as the reducing agent under simultaneous production of the Ti–Si–Al alloy. Finally, the Ti–Si–Al melt was separated by electromagnetic directional crystallization to obtain Ti₅Si₃ and Ti₅Si₄–TiAl₃ alloys, which is a method with lower energy consumption than in the conventional Ti metallurgy process. Chen et al.¹¹⁷

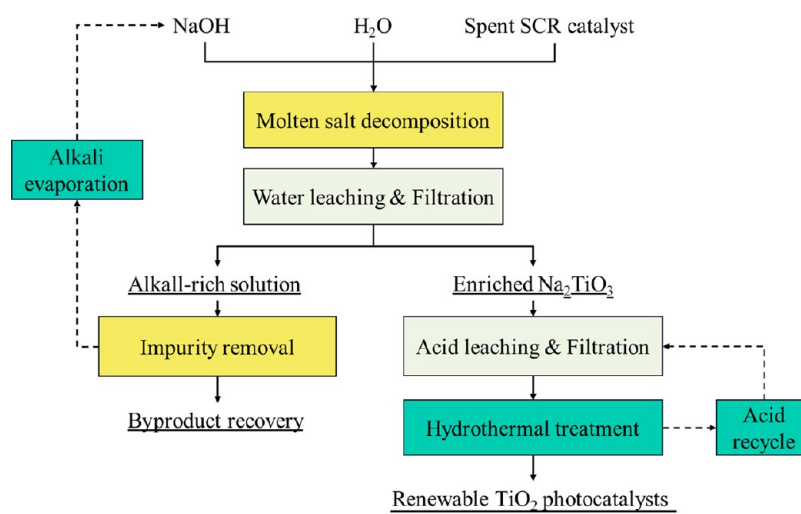


Figure 17. Process flow for the production of sustainable TiO₂ photocatalytic materials using Ti recycled from waste SCR catalysts.¹¹⁵

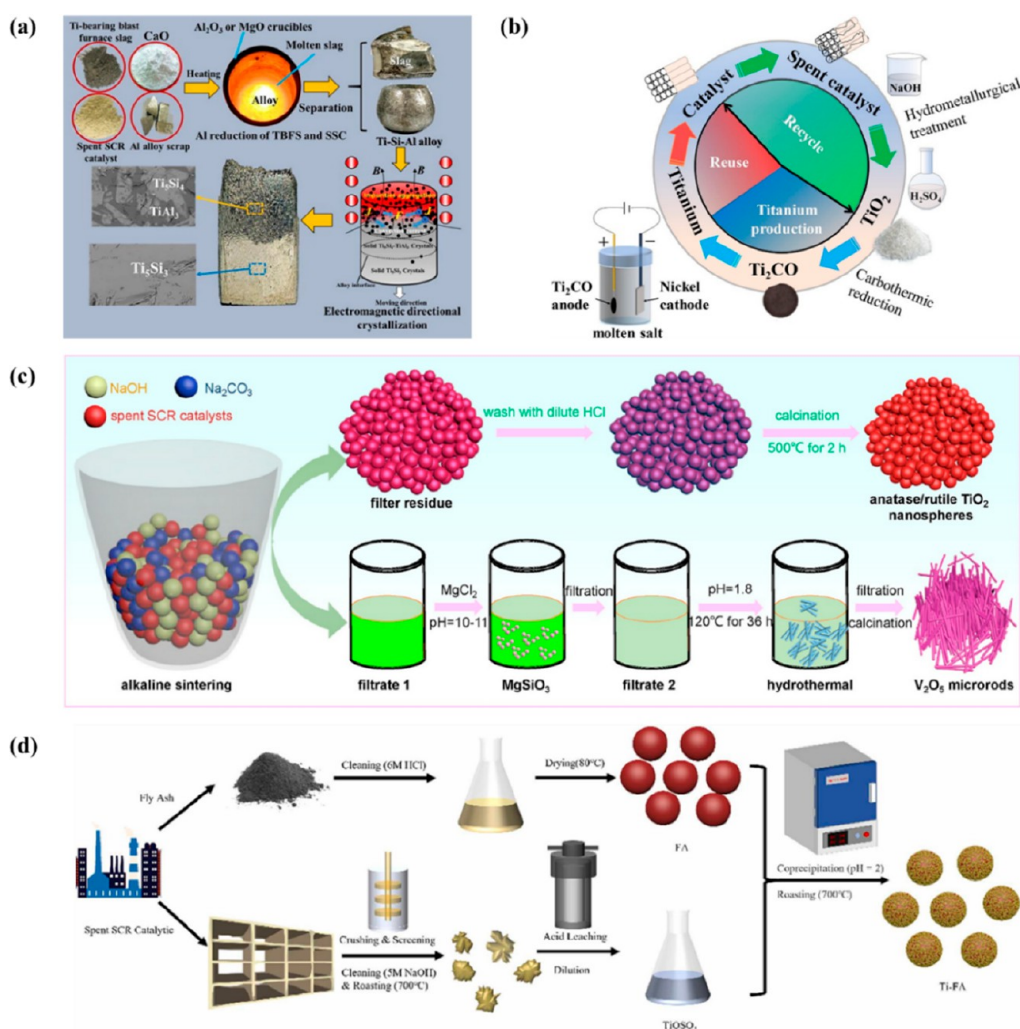


Figure 18. (a) Simultaneous treatment of spent V₂O₅-WO₃/TiO₂ catalysts, Ti-bearing blast furnace slag, and Al alloy scrap to prepare Ti₃Si₃ and Ti₃Si₄-TiAl₃ alloys.¹¹⁶ Reproduced with permission from ref 116. Copyright 2022 Elsevier. (b) Sustainable recycling of TiO₂ from spent V₂O₅-WO₃/TiO₂ catalysts by molten salt electrolysis.¹¹⁸ Reproduced with permission from ref 118. Copyright 2021 Elsevier. (c) Preparation of anatase/rutile TiO₂ nanospheres and V₂O₅ microrods from spent V₂O₅-WO₃/TiO₂ catalysts.¹¹⁷ Reproduced with permission from ref 117. Copyright 2021 Elsevier. (d) Preparation of Ti-FA photocatalysts from spent V₂O₅-WO₃/TiO₂ catalysts.¹¹⁰ Reproduced with permission from ref 110. Copyright 2022 Elsevier.

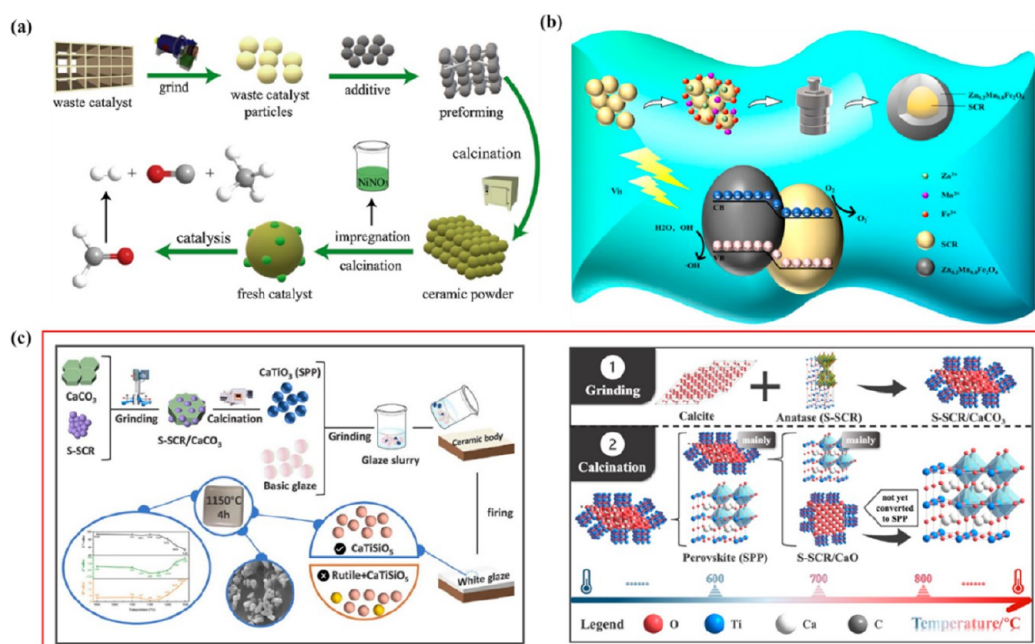


Figure 20. (a) Hydrogen reforming with a catalyst prepared from spent V_2O_5 – WO_3 /TiO₂.¹²³ Reproduced with permission from ref 123. Copyright 2020 Elsevier. (b) Schematic diagram of the degradation mechanism of methylene blue (MB) over ZMF@S10.¹²¹ Reproduced with permission from ref 121. Copyright 2022 Elsevier. (c) Solid phase synthesis process of perovskite powder using CaCO₃ and spent SCR catalyst as raw materials.¹²² Reproduced with permission from ref 122. Copyright 2022 Elsevier.

regenerated carrier up to the standard of the virgin denitrification titanium and tungsten powder to realize the solid waste recycling of spent environmental catalysts systematically.

3.3.3. Other Functionalized Applications. Spent V_2O_5 – WO_3 /TiO₂ catalysts contain oxides with catalytic activity, which are innovative as catalytic carriers for functional applications in different fields (Figure 20). Tian et al.¹²¹ synthesized magnetic composite photocatalysts (ZMF@S10) with a high photocatalytic performance by using waste zinc–manganese batteries as manganese–zinc ferrite and spent V_2O_5 – WO_3 /TiO₂ catalyst as raw material. Using the carrier properties of TiO₂ in waste SCR catalysts, it has become a hot research topic in recent years to prepare coated liquid or mixed ceramic products with metal oxides loaded with the corresponding components for the degradation of pollutants and the production of clean energy, following the principle of “treating waste with waste”. Zhang et al.¹²² used the solid phase method to mix waste V_2O_5 – WO_3 /TiO₂ catalyst and calcium carbonate CaCO₃ as raw materials in a TiO₂ to CaO molar ratio of 1:1 and calcined the material at 1000 °C. TiO₂ was converted to synthetic perovskite powder (SPP), inhibiting its dissociation and eliminating its high-temperature conversion to the rutile phase, which then acts as an opacifier that can eliminate ceramic yellowing of glazes and improve ceramic opacity. Jin et al.¹²³ fully exploited the catalytic properties of V_2O_5 and TiO₂ by grinding the spent SCR catalyst into powder, adding alumina (Al₂O₃), diatomaceous earth, and agglomerates, calcining at 1000 °C to obtain ceramics, and loading nickel oxide (NiO) to prepare NiO-based catalysts for the reforming of formaldehyde and hydrogen from water vapor, reaching selectivities of 100% for H₂, 31.9% for CO, and 53.2% for CO₂ with a formaldehyde conversion exceeding 93.0% at a reaction temperature of 500 °C.

TiO₂ has photocatalytic properties, and V and W can also form heterogeneous structures with TiO₂.^{110,124–127} It was

found that the combination of TiO₂ carriers with excellent photocatalytic properties from spent V_2O_5 – WO_3 /TiO₂ catalysts and the contained metals V and W can be used to produce porous ceramics for application in photocatalysis to solve environmental problems as an innovative solid-waste research direction for the reuse of spent V_2O_5 – WO_3 /TiO₂ catalyst.

4. SUMMARY AND OUTLOOK

Recycling spent V_2O_5 – WO_3 /TiO₂ catalysts is a hot topic of current research. The treatment by regeneration methods can restore the activity to a certain extent, and spent V_2O_5 – WO_3 /TiO₂ catalysts that are difficult to regenerate have great value for extraction and recycling due to their high content of valuable metals. This review summarizes the recycling strategies for spent V_2O_5 – WO_3 /TiO₂ catalysts in three categories, regeneration, recycling, and recycling of valuable components, and provides an outlook for future research directions. Furthermore, this review provides a summary of recovery strategies from the perspective of the regenerative treatment and recycling of valuable components of spent V_2O_5 – WO_3 /TiO₂ catalysts with an outlook on future research directions:

- (1) Future regeneration of spent V_2O_5 – WO_3 /TiO₂ catalysts can implement the concept of environmental sustainability from the perspective of effective retention of active ingredients, shortening the process flow and improving recovery efficiency, and explore process method optimization techniques in combination with different fields to achieve energy-saving, efficient, and clean regeneration methods. Among them, biological regeneration is environmentally friendly and economical, and physical strains with better removal effects than reagent cleaning can be further explored for different causes of poisoning.
- (2) For the recovery of the valuable metals V and W, on the basis of continuous optimization of the leaching process, more innovative ways of direct functional utilization can

be developed to reduce losses and waste in the process of product regeneration; TiO₂ carriers combined with the photocatalytic properties of V and W to prepare porous ceramics for applications in the field of photocatalysis to solve environmental problems can become an innovative direction for future research and development. In contrast, the leaching method of Ti can be optimized from the perspective of effective control of the crystal shape to avoid subsequent repeated processing.

- (3) Strengthen the research of high-throughput, deep learning, and artificial intelligence methods in the field of spent SCR catalysts recycling, build an intelligent screening system, and form intelligent identification and control of high-value utilization of valuable elements.
- (4) Expand the coprocessing scheme of spent SCR catalysts and other solid waste resources and build new synthesis methods for multiscale and multidimensional nanomaterials, such as tungsten oxide nanowires, nickel tungstate nanoparticles, etc.
- (5) At present, there is no complete technical evaluation system for the regeneration and recycling of spent SCR catalysts, and further clarification is needed as to whether the regenerated products are genuinely suitable for subsequent industrial application and whether they effectively reduce economic losses. In the future, from the perspective of economic applicability, different regeneration technology methods can be compared and evaluated in combination with simulation evaluation methods such as environmental input and output, life cycle assessment, and whole life cycle cost.

AUTHOR INFORMATION

Corresponding Authors

Xiaoguang Zhang – Institute of Circular Economy, Faculty of Materials and Manufacturing, Beijing University of Technology, Beijing 100124, PR China; orcid.org/0000-0003-3222-2743; Email: zhangxg@bjut.edu.cn

Dean Pan – Institute of Circular Economy, Faculty of Materials and Manufacturing, Beijing University of Technology, Beijing 100124, PR China; Email: 15801662924@139.com, pandean@bjut.edu.cn

Authors

Jiaying Zhao – Institute of Circular Economy, Faculty of Materials and Manufacturing, Beijing University of Technology, Beijing 100124, PR China

Feihua Yang – Solid Waste Reuse for Building Materials State Key Laboratory, Beijing Building Materials Academy of Science Research, Beijing 100038, PR China

Yonghong Ai – Jiangxi Minmetals Gao'an Non-ferrous Metal Co., Ltd., Gaoan 330800, PR China

Yousheng Chen – Jiangxi Minmetals Gao'an Non-ferrous Metal Co., Ltd., Gaoan 330800, PR China

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsomega.3c07019>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant No. 52002004) and Young Elite

Scientists Sponsorship Program by BAST (Grant No. BYESS2023070).

REFERENCES

- (1) Chen, X.; Geng, Y.; Shan, W.; Liu, F. Deactivation Effects of Potassium on a CeMoTiO_x Catalyst for the Selective Catalytic Reduction of NO_x with NH₃. *Ind. Eng. Chem. Res.* **2018**, *57*, 1399–1407.
- (2) Liu, Z.; Han, J.; Zhao, L.; Wu, Y.-w.; Wang, H.-x.; Pei, X.-q.; Xu, M.-x.; Lu, Q.; Yang, Y.-p. Effects of Se and SeO₂ on the denitrification performance of V₂O₅-WO₃/TiO₂ SCR catalyst. *Appl. Catal. A Gen.* **2019**, *587*, 117263.
- (3) Schill, L.; Fehrmann, R. Strategies of coping with deactivation of NH₃-SCR catalysts due to biomass firing. *Catalysts* **2018**, *8*, 135.
- (4) Zhu, L.; Zhong, Z.; Yang, H.; Wang, C. A comparative study of metal oxide and sulfate catalysts for selective catalytic reduction of NO with NH₃. *Environmental Technology (United Kingdom)* **2017**, *38*, 1285–1294.
- (5) Chen, C.; Wen, Z. Cross-media transfer of nitrogen pollution in the fast-urbanized Greater Bay Area of China: Trends and essential control paths. *J. Environ. Manage* **2023**, *326*, 116796.
- (6) Cao, Y.; Han, F.; Wang, M.; Han, L.; Zhang, C.; Wang, J.; Bao, W.; Chang, L. Regeneration of the Waste Selective Catalytic Reduction Denitrification Catalyst by Nitric Acid Washing. *ACS Omega*. **2019**, *4*, 16629–16637.
- (7) Zhang, Q.; Wu, Y.; Zuo, T. Green Recovery of Titanium and Effective Regeneration of TiO₂ Photocatalysts from Spent Selective Catalytic Reduction Catalysts. *ACS Sustain Chem. Eng.* **2018**, *6*, 3091–3101.
- (8) Ding, L.; Wang, Y.; Qian, L.; Qi, P.; Xie, M.; Long, H. Flue gas deNO_xing spent V₂O₅-WO₃/TiO₂ catalyst: A review of deactivation mechanisms and current disposal status. *Fuel* **2023**, *338*, 127268.
- (9) Wu, Z.; Zhang, Y.; Dong, Z. Prediction of NO_x emission concentration from coal-fired power plant based on joint knowledge and data driven. *Energy* **2023**, *271*, No. 127044.
- (10) Ferella, F. A review on management and recycling of spent selective catalytic reduction catalysts. *J. Clean Prod.* **2020**, *246*, 118990.
- (11) Ko, A.; Woo, Y.; Jang, J.; Jung, Y.; Pyo, Y.; Jo, H.; Lim, O.; Lee, Y. J. Availability of NH₃ adsorption in vanadium-based SCR for reducing NO_x emission and NH₃ slip. *Journal of Industrial and Engineering Chemistry* **2019**, *78*, 433–439.
- (12) Tan, L.; Guo, Y.; Liu, Z.; Feng, P.; Li, Z. An investigation on the catalytic characteristic of NO_x reduction in SCR systems. *J. Taiwan Inst Chem. Eng.* **2019**, *99*, 53–59.
- (13) Liu, C.; Wang, H.; Zhang, Z.; Liu, Q. The latest research progress of NH₃-SCR in the SO₂ resistance of the catalyst in low temperatures for selective catalytic reduction of NO_x. *Catalysts* **2020**, *10*, 1034.
- (14) Zhang, Q.; Wu, Y.; Yuan, H. Recycling strategies of spent V₂O₅-WO₃/TiO₂ catalyst: A review. *Resour Conserv Recycl* **2020**, *161*, 104983.
- (15) Qi, L.; Li, J.; Yao, Y.; Zhang, Y. Heavy metal poisoned and regeneration of selective catalytic reduction catalysts. *J. Hazard Mater.* **2019**, *366*, 492–500.
- (16) Zhao, L.; Zhang, Y.; Kang, M. Recent advances in heighten sulfur resistance of SCR catalysts: A review. *Environmental Engineering Research* **2022**, *27*, 200642–0.
- (17) Li, M.; Liu, B.; Wang, X.; Yu, X.; Zheng, S.; Du, H.; Dreisinger, D.; Zhang, Y. A promising approach to recover a spent SCR catalyst: Deactivation by arsenic and alkaline metals and catalyst regeneration. *Chem. Eng. J.* **2018**, *342*, 1–8.
- (18) Hong, Z.; Wang, Z.; Li, X. Catalytic oxidation of nitric oxide (NO) over different catalysts: An overview. *Catal. Sci. Technol.* **2017**, *7*, 3440–3452.
- (19) Han, L.; Cai, S.; Gao, M.; Hasegawa, J. Y.; Wang, P.; Zhang, J.; Shi, L.; Zhang, D. Selective Catalytic Reduction of NO_x with NH₃ by Using Novel Catalysts: State of the Art and Future Prospects. *Chem. Rev.* **2019**, *119*, 10916–10976.
- (20) Rezaei, F.; Rowanghi, A. A.; Monjezi, S.; Lively, R. P.; Jones, C. W. SO₂/NO_x Removal from Flue Gas Streams by Solid Adsorbents: A

Review of Current Challenges and Future Directions. *Energy Fuels* **2015**, *29*, 5467–5486.

(21) Niu, T.; Wang, J.; Chu, H.; Qian, C.; Duan, N.; Michael Gadd, G.; Shi, W.; Xin, B. Deep removal of arsenic from regenerated products of spent V_2O_5 - WO_3 /TiO₂ SCR catalysts and its concurrent activation by bioleaching through a novel mechanism. *Chem. Eng. J.* **2021**, *420*, 127722.

(22) Xiong, S.; Chen, J.; Liu, H.; Chen, X.; Si, W.; Gong, Z.; Peng, Y.; Li, J. Like Cures like: Detoxification Effect between Alkali Metals and Sulfur over the V_2O_5 /TiO₂ deNO_x Catalyst. *Environ. Sci. Technol.* **2022**, *56*, 3739–3747.

(23) Zhao, S.; Peng, J.; Ge, R.; Yang, K.; Wu, S.; Qian, Y.; Xu, T.; Gao, J.; Chen, Y.; Sun, Z. Poisoning and regeneration of commercial V_2O_5 - WO_3 /TiO₂ selective catalytic reduction (SCR) catalyst in coal-fired power plants. *Process Safety and Environmental Protection* **2022**, *168*, 971–992.

(24) Choo, S. T.; Yim, S. D.; Nam, I. S.; Ham, S. W.; Lee, J. B. Effect of promoters including WO₃ and BAO on the activity and durability of V_2O_5 /sulfated TiO₂ catalyst for NO reduction by NH₃. *Appl. Catal., B* **2003**, *44*, 237–252.

(25) Wu, W.; Wang, C.; Bao, W.; Li, H. Selective reduction leaching of vanadium and iron by oxalic acid from spent V_2O_5 - WO_3 /TiO₂ catalyst. *Hydrometallurgy* **2018**, *179*, 52–59.

(26) Zhao, C.; Wang, C.; Wang, X.; Li, H.; Chen, Y.; Wu, W. Recovery of tungsten and titanium from spent SCR catalyst by sulfuric acid leaching process. *Waste Management* **2023**, *155*, 338–347.

(27) Li, M.; Liu, B.; Wang, X.; Yu, X.; Zheng, S.; Du, H.; Dreisinger, D.; Zhang, Y. A promising approach to recover a spent SCR catalyst: Deactivation by arsenic and alkaline metals and catalyst regeneration. *Chem. Eng. J.* **2018**, *342*, 1–8.

(28) Liu, J.; Wang, C.; Wang, X.; Li, H.; Zhao, C. Iron removal and titanium dioxide support recovery from spent V_2O_5 - WO_3 /TiO₂ catalyst. *Sep Purif Technol.* **2022**, *301*, 121934.

(29) Song, C.; Zhou, D.; Yang, L.; Zhou, J.; Liu, C.; Chen, Z. G. Recovery TiO₂ and sodium titanate nanowires as Cd(II) adsorbent from waste V_2O_5 - WO_3 /TiO₂ selective catalytic reduction catalysts by Na₂CO₃-NaCl-KCl molten salt roasting method. *J. Taiwan Inst Chem. Eng.* **2018**, *88*, 226–233.

(30) Wang, B.; Yang, Q. Recovery of V_2O_5 from spent SCR catalyst by H₂SO₄-ascorbic acid leaching and chemical precipitation. *J. Environ. Chem. Eng.* **2022**, *10*, 108719.

(31) Zhao, Z.; Li, E.; Qin, Y.; Liu, X.; Zou, Y.; Wu, H.; Zhu, T. Density functional theory (DFT) studies of vanadium-titanium based selective catalytic reduction (SCR) catalysts. *J. Environ. Sci. (China)* **2020**, *90*, 119–137.

(32) Topsoe, N. Y.; Dumesic, J. A.; Topsoe, H. Vanadia-Titania Catalysts for Selective Catalytic Reduction of Nitric-Oxide by Ammonia: II. Studies of Active Sites and Formulation of Catalytic Cycles. *J. Catal.* **1995**, *151*, 241–252.

(33) Arnarson, L.; Falsig, H.; Rasmussen, S. B.; Lauritsen, J. v.; Moses, P. G. The reaction mechanism for the SCR process on monomer V⁵⁺ sites and the effect of modified Brønsted acidity. *Phys. Chem. Chem. Phys.* **2016**, *18*, 17071–17080.

(34) Zhang, X.; Diao, Q.; Hu, X.; Wu, X.; Xiao, K.; Wang, J. Modification of V_2O_5 - WO_3 /TiO₂ catalyst by loading of MnO_x for enhanced low-temperature NH₃-SCR performance. *Nanomaterials* **2020**, *10*, 1900.

(35) Guo, Y.; Luo, L.; Zheng, Y.; Wang, J.; Zhu, T. Low-medium temperature application of selective catalytic reduction denitration in cement flue gas through a pilot plant. *Chemosphere* **2021**, *276*, 130182.

(36) Liang, Q.; Li, J.; He, H.; Yue, T.; Tong, L. Effects of SO₂ and H₂O on low-temperature NO conversion over F- V_2O_5 - WO_3 /TiO₂ catalysts. *J. Environ. Sci. (China)* **2020**, *90*, 253–261.

(37) Zhang, Y. S.; Li, C.; Wang, C.; Yu, J.; Xu, G.; Zhang, Z. G.; Yang, Y. Pilot-Scale Test of a V_2O_5 - WO_3 /TiO₂-Coated Type of Honeycomb DeNO_x Catalyst and Its Deactivation Mechanism. *Ind. Eng. Chem. Res.* **2019**, *58*, 828–835.

(38) Shang, X.; Hu, G.; He, C.; Zhao, J.; Zhang, F.; Xu, Y.; Zhang, Y.; Li, J.; Chen, J. Regeneration of full-scale commercial honeycomb

monolith catalyst (V_2O_5 - WO_3 /TiO₂) used in coal-fired power plant. *Journal of Industrial and Engineering Chemistry* **2012**, *18*, 513–519.

(39) Liu, X.; Yang, Q. Research on the deactivation mechanism of a denitration catalyst WO_3 - V_2O_5 /TiO₂ at a coal-fired power plant. *RSC Adv.* **2020**, *10*, 44025–44033.

(40) Reiche, M.A.; Ortelli, E.; Baiker, A. Vanadia grafted on TiO₂-SiO₂, TiO₂ and SiO₂ aerogels Structural properties and catalytic behaviour in selective reduction of NO by NH₃. *Appl. Catal. B: Environmental* **1999**, *23*, 187.

(41) Du, X.; Yang, G.; Chen, Y.; Ran, J.; Zhang, L. The different poisoning behaviors of various alkali metal containing compounds on SCR catalyst. *Appl. Surf. Sci.* **2017**, *392*, 162–168.

(42) Yu, Y.; Wang, J.; Chen, J.; He, X.; Wang, Y.; Song, K.; Xie, Z. Regeneration of commercial selective catalyst reduction catalysts deactivated by Pb and other inorganic elements. *J. Environ. Sci. (China)* **2016**, *47*, 100–108.

(43) Xiang, J.; Du, X.; Wan, Y.; Chen, Y.; Ran, J.; Zhang, L. Alkali-driven active site shift of fast SCR with NH₃ on V_2O_5 - WO_3 /TiO₂ catalyst via a novel Eley–Rideal mechanism. *Catal. Sci. Technol.* **2019**, *9*, 6085–6091.

(44) Xiao, H.; Chen, Y.; Qi, C.; Ru, Y. Effect of Na poisoning catalyst (V_2O_5 - WO_3 /TiO₂) on denitration process and SO₃ formation. *Appl. Surf. Sci.* **2018**, *433*, 341–348.

(45) Peng, Y.; Li, J.; Si, W.; Luo, J.; Wang, Y.; Fu, J.; Li, X.; Crittenden, J.; Hao, J. Deactivation and regeneration of a commercial SCR catalyst: Comparison with alkali metals and arsenic. *Appl. Catal., B* **2015**, *168*–*169*, 195–202.

(46) Chen, L.; Li, J.; Ge, M. The poisoning effect of alkali metals doping over nano V_2O_5 - WO_3 /TiO₂ catalysts on selective catalytic reduction of NO_x by NH₃. *Chem. Eng. J.* **2011**, *170*, 531–537.

(47) Wang, Y.; Yi, W.; Yu, J.; Zeng, J.; Chang, H. Novel Methods for Assessing the SO₂ Poisoning Effect and Thermal Regeneration Possibility of MO_x- WO_3 /TiO₂ (M = Fe, Mn, Cu, and V) Catalysts for NH₃-SCR. *Environmental Science & Technology* **2020**, *54*, 12612–12620.

(48) Wang, X.; Du, X.; Zhang, L.; Chen, Y.; Yang, G.; Ran, J. Promotion of NH₄HSO₄ decomposition in NO/NO₂ contained atmosphere at low temperature over V_2O_5 - WO_3 /TiO₂ catalyst for NO reduction. *Appl. Catal. A Gen.* **2018**, *559*, 112–121.

(49) Yu, J.; Zhang, E.; Wang, L.; Song, Z.; Kong, F.; Ma, Y.; Zhao, H.; Sun, L. The Interaction of NH₄HSO₄ with Vanadium–Titanium Catalysts Modified with Molybdenum and Tungsten. *Energy & Fuels* **2020**, *34*, 2107–2116.

(50) Fan, A.; Jing, Y.; Guo, J.; Shi, X.; Yuan, S.; Li, J. Investigation of Mn doped perovskite La-Mn oxides for NH₃-SCR activity and SO₂/H₂O resistance. *Fuel* **2022**, *310*, 122237.

(51) Lisi, L.; Lasorella, G.; Malloggi, S.; Russo, G. Single and combined deactivating effect of alkali metals and HCl on commercial SCR catalysts. *Appl. Catal., B* **2004**, *50*, 251–258.

(52) Amiridis, M.D.; Wachs, I.E.; Deo, G.; Jehng, J.-M.; Kim, D.S. Reactivity of V_2O_5 Catalysts for the Selective Catalytic Reduction of NO by NH₃: Influence of Vanadia Loading, H₂O, and SO₂. *Journal of Catalysis* **1996**, *161*, 247–253.

(53) Shi, Y.; Zhang, P.; Fang, T.; Gao, E.; Xi, F.; Shou, T.; Tao, M.; Wu, S.; Bernards, M. T.; He, Y.; Pan, H. In situ regeneration of commercial NH₃-SCR catalysts with high-temperature water vapor. *Catal. Commun.* **2018**, *116*, 57–61.

(54) Magnusson, M.; Fridell, E.; Ingelsten, H. H. The influence of sulfur dioxide and water on the performance of a marine SCR catalyst. *Appl. Catal., B* **2012**, *111*–*112*, 20–26.

(55) Zhang, H.; Kong, M.; Cai, Z.; Liu, Q.; Zeng, J.; Duan, M.; Yang, J.; Ren, S.; Li, J. Comparative Studies of Effects of Vapor- and Liquid-Phase As₂O₃ on Catalytic Behaviors of V_2O_5 - WO_3 /TiO₂ Catalysts for NH₃-SCR. *ACS Omega* **2020**, *5*, 24195–24203.

(56) Kong, M.; Liu, Q.; Wang, X.; Ren, S.; Yang, J.; Zhao, D.; Xi, W.; Yao, L. Performance impact and poisoning mechanism of arsenic over commercial V_2O_5 - WO_3 /TiO₂ SCR catalyst. *Catal. Commun.* **2015**, *72*, 121–126.

- (57) Chen, G.; Xiong, S.; Chen, X.; Chu, X.; Yin, R.; Liu, C.; Chen, J.; Li, J. Penetration of Arsenic and Deactivation of a Honeycomb V_2O_5 - WO_3/TiO_2 Catalyst in a Glass Furnace. *Environmental Science & Technology* **2021**, *55*, 11368–11374.
- (58) Hu, W.; Gao, X.; Deng, Y.; Qu, R.; Zheng, C.; Zhu, X.; Cen, K. Deactivation mechanism of arsenic and resistance effect of SO_4^{2-} on commercial catalysts for selective catalytic reduction of NO_x with NH_3 . *Chem. Eng. J.* **2016**, *293*, 118–128.
- (59) Wu, Y.-w.; Zhou, X.-y.; Mi, T.-g.; Hu, B.; Liu, J.; Lu, Q. Effect of WO_3 and MoO_3 doping on the interaction mechanism between arsenic oxide and V_2O_5 -based SCR catalyst: A theoretical account. *Molecular Catalysis* **2021**, *499*, 111317.
- (60) Yu, J.; Zhang, E.; Wang, L.; Song, Z.; Kong, F.; Ma, Y.; Zhao, H.; Sun, L. The Interaction of NH_4HSO_4 with Vanadium-Titanium Catalysts Modified with Molybdenum and Tungsten. *Energy Fuels* **2020**, *34*, 2107–2116.
- (61) Qiu, K.; Song, J.; Song, H.; Gao, X.; Luo, Z.; Cen, K. A novel method of microwave heating mixed liquid-assisted regeneration of V_2O_5 - WO_3/TiO_2 commercial SCR catalysts. *Environ. Geochem Health* **2015**, *37*, 905–914.
- (62) Xu, L.; Wang, C.; Chang, H.; Wu, Q.; Zhang, T.; Li, J. New Insight into SO_2 Poisoning and Regeneration of CeO_2 - WO_3/TiO_2 and V_2O_5 - WO_3/TiO_2 Catalysts for Low-Temperature NH_3 -SCR. *Environ. Sci. Technol.* **2018**, *52*, 7064–7071.
- (63) Kato, T.; Sakusabe, K.; Mochizuki, Y.; Okawa, H.; Sugawara, K. Removal of arsenic from a denitration catalyst by reduction using methanol as a carbon source. *React. Chem. Eng.* **2019**, *4*, 1208–1215.
- (64) Zheng, Y.; Guo, Y.; Wang, J.; Luo, L.; Zhu, T. Ca Doping Effect on the Competition of NH_3 -SCR and NH_3 Oxidation Reactions over Vanadium-Based Catalysts. *J. Phys. Chem. C* **2021**, *125*, 6128–6136.
- (65) Hu, W.; Gao, X.; Deng, Y.; Qu, R.; Zheng, C.; Zhu, X.; Cen, K. Deactivation mechanism of arsenic and resistance effect of SO_4^{2-} on commercial catalysts for selective catalytic reduction of NO_x with NH_3 . *Chem. Eng. J.* **2016**, *293*, 118–128.
- (66) Qian, L.; Ding, L.; Liu, W.; Ren, S.; Long, H. Simultaneous removal of NO and dioxins over V_2O_5 - WO_3/TiO_2 catalyst for iron ore sintering flue gas: The poisoning effect of Pb. *Fuel* **2022**, *324*, No. 124483.
- (67) Li, X.; Li, X.; Yang, R. T.; Mo, J.; Li, J.; Hao, J. The poisoning effects of calcium on V_2O_5 - WO_3/TiO_2 catalyst for the SCR reaction: Comparison of different forms of calcium. *Molecular Catalysis* **2017**, *434*, 16–24.
- (68) Cao, Y.; Han, F.; Wang, M.; Han, L.; Zhang, C.; Wang, J.; Bao, W.; Chang, L. Regeneration of the Waste Selective Catalytic Reduction Denitrification Catalyst by Nitric Acid Washing. *ACS Omega* **2019**, *4*, 16629–16637.
- (69) Peng, Y.; Li, J.; Si, W.; Luo, J.; Wang, Y.; Fu, J.; Li, X.; Crittenden, J.; Hao, J. Deactivation and regeneration of a commercial SCR catalyst: Comparison with alkali metals and arsenic. *Appl. Catal., B* **2015**, *168*–*169*, 195–202.
- (70) Li, J.; Zhang, P.; Chen, L.; Zhang, Y.; Qi, L. Regeneration of Selective Catalyst Reduction Catalysts Deactivated by Pb, As, and Alkali Metals. *ACS Omega* **2020**, *5*, 13886–13893.
- (71) Yu, Y.; Wang, J.; Chen, J.; He, X.; Wang, Y.; Song, K.; Xie, Z. Regeneration of commercial selective catalyst reduction catalysts deactivated by Pb and other inorganic elements. *J. Environ. Sci. (China)* **2016**, *47*, 100–108.
- (72) Tian, Y.; Yang, J.; Liu, L.; Liu, Q.; Kong, B.; Lin, F.; Kong, M.; Hu, G. Insight into regeneration mechanism with sulfuric acid for arsenic poisoned commercial SCR catalyst. *Journal of the Energy Institute* **2020**, *93*, 387–394.
- (73) Li, J.; Zhang, P.; Chen, L.; Zhang, Y.; Qi, L. Regeneration of Selective Catalyst Reduction Catalysts Deactivated by Pb, As, and Alkali Metals. *ACS Omega* **2020**, *5*, 13886–13893.
- (74) Yu, Y.; He, C.; Chen, J.; Yin, L.; Qiu, T.; Meng, X. Regeneration of deactivated commercial SCR catalyst by alkali washing. *Catal. Commun.* **2013**, *39*, 78–81.
- (75) Qi, L.; Li, J.; Yao, Y.; Zhang, Y. Heavy metal poisoned and regeneration of selective catalytic reduction catalysts. *J. Hazard Mater.* **2019**, *366*, 492–500.
- (76) Jia, Y.; Zhou, J.; Bai, J.; Li, M.; Wang, Y.; Zhong, Q. Hybrid regeneration of selective catalytic reduction denitration catalyst poisoned by arsenic and potassium. *Kuei Suan Jen Hsueh Pao/Journal of the Chinese Ceramic Society* **2016**, *44*, 1025–1032.
- (77) Lou, W.; Zhang, Y.; Zheng, S.; Li, P.; Zhang, Y.; Zhang, Y.; Zhao, B.; Li, Z.; Jin, W. Efficient recovery of scrapped V_2O_5 - WO_3/TiO_2 SCR catalyst by cleaner hydrometallurgical process. *Hydrometallurgy* **2019**, *187*, 45–53.
- (78) Li, X.; Li, X.; Chen, J.; Li, J.; Hao, J. An efficient novel regeneration method for Ca-poisoning V_2O_5 - WO_3/TiO_2 catalyst. *Catal. Commun.* **2016**, *87*, 45–48.
- (79) Li, X.; Liu, C.; Li, X.; Peng, Y.; Li, J. A neutral and coordination regeneration method of Ca-poisoned V_2O_5 - WO_3/TiO_2 SCR catalyst. *Catal. Commun.* **2017**, *100*, 112–116.
- (80) Gao, F.; Tang, X.; Yi, H.; Zhao, S.; Zhang, T.; Li, D.; Ma, D. The poisoning and regeneration effect of alkali metals deposited over commercial V_2O_5 - WO_3/TiO_2 catalysts on SCR of NO by NH_3 . *Chin. Sci. Bull.* **2014**, *59*, 3966–3972.
- (81) Yu, Y.; Meng, X.; Chen, J.; Yin, L.; Qiu, T.; He, C. Deactivation mechanism and feasible regeneration approaches for the used commercial NH_3 -SCR catalysts. *Environmental Technology (United Kingdom)* **2016**, *37*, 828–836.
- (82) Xue, Y.; Zhang, Y.; Zhang, Y.; Zheng, S.; Zhang, Y.; Jin, W. Electrochemical detoxification and recovery of spent SCR catalyst by in-situ generated reactive oxygen species in alkaline media. *Chem. Eng. J.* **2017**, *325*, 544–553.
- (83) Li, W.; Du, X.; Li, Z.; Tao, Y.; Xue, J.; Chen, Y.; Yang, Z.; Ran, J.; Rac, V.; Rakić, V. Electrothermal alloy embedded V_2O_5 - WO_3/TiO_2 catalyst for NH_3 -SCR with promising wide operating temperature window. *Process Safety and Environmental Protection* **2022**, *159*, 213–220.
- (84) Kapkowski, M.; Siudyga, T.; Sitko, R.; Niemczyk-Wojdyła, A.; Zelenka, T.; Zelenková, G.; Golba, S.; Smolinski, A.; Polanski, J. Toward a viable ecological method for regenerating a commercial SCR catalyst – Selectively leaching surface deposits and reconstructing a pore landscape. *J. Clean Prod.* **2021**, *316*, 128291.
- (85) Zheng, Z.; Du, X.; Wang, X.; Liu, Y.; Chen, K.; Lu, P.; Rac, V.; Rakić, V. Experimental investigation on the decomposition of NH_4HSO_4 over V_2O_5 - WO_3/TiO_2 catalyst by NH_4NO_3 at low temperature. *Fuel* **2023**, *333*, 126443.
- (86) Tang, X.; Wu, P.; Wang, Y.; Liu, Y. Recent advances in heavy metal poisoning mechanism and regeneration methods of selective catalytic reduction (SCR) denitration catalyst. *Fuel* **2024**, *355*, 129429.
- (87) Zhang, Q.; Wu, Y.; Li, L.; Zuo, T. Sustainable Approach for Spent V_2O_5 - WO_3/TiO_2 Catalysts Management: Selective Recovery of Heavy Metal Vanadium and Production of Value-Added WO_3 - TiO_2 Photocatalysts. *ACS Sustainable Chemistry & Engineering* **2018**, *6*, 12502–12510.
- (88) Nie, Z.; Ma, L.; Xi, X.; Guo, F.; Nie, Z. Studying the leaching mechanism of spent SCR catalyst with different leaching agents ($NaOH$, H_2SO_4 , HCl and HNO_3) using DFT calculations. *Appl. Surf. Sci.* **2022**, *584*, 152577.
- (89) Yao, J.; Cao, Y.; Wang, J.; Zhang, C.; Wang, W.; Bao, W.; Chang, L. Successive calcination-oxalate acid leaching treatment of spent SCR catalyst: A highly efficient and selective method for recycling tungsten element. *Hydrometallurgy* **2021**, *201*, 105576.
- (90) Wu, W.; Wang, C.; Bao, W.; Li, H. Selective reduction leaching of vanadium and iron by oxalic acid from spent V_2O_5 - WO_3/TiO_2 catalyst. *Hydrometallurgy* **2018**, *179*, 52–59.
- (91) Su, Q.; Miao, J.; Li, H.; Chen, Y.; Chen, J.; Wang, J. Optimizing vanadium and tungsten leaching with lowered silicon from spent SCR catalyst by pre-mixing treatment. *Hydrometallurgy* **2018**, *181*, 230–239.
- (92) Wu, W.C.; Tsai, T.Y.; Shen, Y.H. Tungsten recovery from spent SCR catalyst using alkaline leaching and ion exchange. *Minerals* **2016**, *6*, 107.

- (93) Cao, Y.; Yuan, J.; Du, H.; Dreisinger, D.; Li, M. A clean and efficient approach for recovery of vanadium and tungsten from spent SCR catalyst. *Miner Eng.* **2021**, *165*, 106857.
- (94) Kim, J. W.; Lee, W. G.; Hwang, I. S.; Lee, J. Y.; Han, C. Recovery of tungsten from spent selective catalytic reduction catalysts by pressure leaching. *Journal of Industrial and Engineering Chemistry* **2015**, *28*, 73–77.
- (95) Choi, I. H.; Moon, G.; Lee, J. Y.; Jyothi, R. K. Extraction of tungsten and vanadium from spent selective catalytic reduction catalyst for stationary application by pressure leaching process. *J. Clean Prod.* **2018**, *197*, 163–169.
- (96) Wang, S.; Xie, Y.; Yan, W.; Wu, X.; Wang, C. T.; Zhao, F. Leaching of vanadium from waste V_2O_5 - WO_3 / TiO_2 catalyst catalyzed by functional microorganisms. *Sci. Total Environ.* **2018**, *639*, 497–503.
- (97) Liu, Q.; Quan, S.; Liu, Z.; Liu, Q. Leaching of vanadium and tungsten from spent V_2O_5 - WO_3 / TiO_2 catalyst by ionic liquids. *Hydrometallurgy* **2022**, *213*, 105938.
- (98) Zhang, Q.; Wu, Y.; Zuo, T. Titanium Extraction from Spent Selective Catalytic Reduction Catalysts in a NaOH Molten-Salt System: Thermodynamic, Experimental, and Kinetic Studies. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science* **2019**, *50*, 471–479.
- (99) Cueva Sola, A. B.; Jeon, J.H.; Jyothi, R.K.; Lee, J.-Y. *Novel Environmentally Friendly Leaching Process for Vanadium and Tungsten Recovery from Spent SCR Catalyst*; Ouchi, T., Azimi, G., Forsberg, K., Kim, H., Alam, S., Neelameggham, N.R., Baba, A.A., Peng, H., Eds., Rare Metal Technology; Springer International Publishing: Cham, 2022; pp 111–117.
- (100) Choi, I. H.; Kim, H. R.; Moon, G.; Jyothi, R. K.; Lee, J. Y. Spent V_2O_5 - WO_3 / TiO_2 catalyst processing for valuable metals by soda roasting-water leaching. *Hydrometallurgy* **2018**, *175*, 292–299.
- (101) Moon, G.; Kim, J.H.; Lee, J.Y.; Kang, J. Leaching of spent selective catalytic reduction catalyst using alkaline melting for recovery of titanium, tungsten, and vanadium. *Hydrometallurgy* **2019**, *189*, 105132.
- (102) Yang, B.; Zhou, J.; Wang, W.; Liu, C.; Zhou, D.; Yang, L. Extraction and separation of tungsten and vanadium from spent V_2O_5 - WO_3 / TiO_2 SCR catalysts and recovery of TiO_2 and sodium titanate nanorods as adsorbent for heavy metal ions. *Colloids Surf. A Physicochem Eng. Asp.* **2020**, *601*, 124963.
- (103) Wang, B.; Yang, Q. Optimization of roasting parameters for recovery of vanadium and tungsten from spent scr catalyst with composite roasting. *Processes* **2021**, *9*, 1923.
- (104) Choi, I.-h.; Moon, G.; Lee, J.-Y.; Jyothi, R. K. Hydro-metallurgical processing of spent selective catalytic reduction (SCR) catalyst for recovery of tungsten. *Hydrometallurgy* **2018**, *178*, 137–145.
- (105) Yuting, T.; Yaping, Z.; Ling, W.; Peng, W. Recovery of Titanium, Vanadium and Tungsten from Waste Scr Denitration Catalyst by Dry-Wet Process. *Environment Engineering* **2020**, *38*, 163–167.
- (106) Yang, B.; Zhou, J.; Wang, W.; Liu, C.; Zhou, D.; Yang, L. Extraction and separation of tungsten and vanadium from spent V_2O_5 - WO_3 / TiO_2 SCR catalysts and recovery of TiO_2 and sodium titanate nanorods as adsorbent for heavy metal ions. *Colloids Surf. A Physicochem Eng. Asp.* **2020**, *601*, 124963.
- (107) Kim, J. W.; Hwang, I. J. Separation of valuables from spent selective catalytic reduction catalyst leaching solution by fabricated anion extraction resins. *J. Environ. Chem. Eng.* **2018**, *6*, 1100–1108.
- (108) Mahandra, H.; Singh, R.; Gupta, B. Recovery of vanadium(V) from synthetic and real leach solutions of spent catalyst by solvent extraction using Cyphos IL 104. *Hydrometallurgy* **2020**, *196*, 105405.
- (109) Xiao, H.; Chen, L.; Qin, Z.; Yin, R.; Weng, D.; Wang, Z.; Luo, D. Separation of vanadium, tungsten and molybdenum from spent SCR catalysts solution by solvent extraction with primary amine N_{1923} . *Waste Management* **2022**, *150*, 301–309.
- (110) Qian, X.; Ao, W.; Wang, X.; Sun, S.; Zhang, J.; Ding, H. Preparation of fly ash based titanium dioxide composite photocatalysts using spent SCR catalyst carriers. *J. Environ. Chem. Eng.* **2022**, *10*, 107980.
- (111) Cueva Sola, A. B.; Parhi, P. K.; Lee, J. Y.; Kang, H. N.; Jyothi, R. K. Environmentally friendly approach to recover vanadium and tungsten from spent SCR catalyst leach liquors using Aliquat 336. *RSC Adv.* **2020**, *10*, 19736–19746.
- (112) Wang, Y.; Chang, Z.; Blamo, B. J.; Wu, X.; Liu, S.; Li, W. Preparation of Photocatalytic $Zn_3(VO_4)_2/ZnWO_4$ from Waste V_2O_5 - WO_3 / TiO_2 SCR Catalyst. *Waste Biomass Valorization* **2017**, *8*, 2423–2430.
- (113) Wen, J.; Hou, X.; Yao, M.; Chen, J.; Tian, M.; Feng, E.; Huang, G.; Xu, S. Tuning of vanadium valence for value-added recycling and utilization of vanadium from spent Selective Catalytic Reduction Catalysts. *J. Clean Prod.* **2023**, *390*, No. 136151.
- (114) Ma, B.; Qiu, Z.; Yang, J.; Qin, C.; Fan, J.; Wei, A.; Li, Y. Recovery of Nano- TiO_2 from Spent SCR Catalyst by Sulfuric Acid Dissolution and Direct Precipitation. *Waste Biomass Valorization* **2019**, *10*, 3037–3044.
- (115) Zhang, Q.; Wu, Y.; Zuo, T. Green Recovery of Titanium and Effective Regeneration of TiO_2 Photocatalysts from Spent Selective Catalytic Reduction Catalysts. *ACS Sustain Chem. Eng.* **2018**, *6*, 3091–3101.
- (116) Zhang, Y.; Lei, Y.; Ma, W.; Shi, Z.; Chen, Q.; Li, Z.; Wang, C. A green approach for simultaneously preparing Ti_5Si_3 and Ti_3Si_4 - $TiAl_3$ alloys using spent SCR catalyst, Ti-bearing blast furnace slag, and Al alloy scrap. *Chem. Eng. J.* **2022**, *430*, 132916.
- (117) Chen, H. J.; Wang, R.; Yang, Y. L.; Shi, X. L.; Lu, S.; Chen, Z. G. Environmentally-friendly harvesting TiO_2 nanospheres and V_2O_5 microrods from spent selective catalytic reduction catalysts. *Progress in Natural Science: Materials International* **2021**, *31*, 858–864.
- (118) Bai, X.; Shang, X.; Wan, H.; Che, Y.; Yang, B.; He, J.; Song, J. Sustainable recycling of titanium from TiO_2 in spent SCR denitration catalyst via molten salt electrolysis. *J. Energy Chem.* **2021**, *58*, 557–563.
- (119) Long, H.; Ding, L.; Yang, J.; Qian, L.; Tao, J.; Yang, T.; Meng, Q.; Xu, C. C. Novel resource utilization approach of spent catalyst from flue gas denitrification: Preparing high quality titanium-bearing pellets. *Fuel* **2023**, *340*, 127581.
- (120) Zhou, Z.; Liu, X.; Liao, Z.; Shao, H.; Hu, Y.; Xu, Y.; Xu, M. A novel low temperature catalyst regenerated from deactivated SCR catalyst for HgO oxidation. *Chem. Eng. J.* **2016**, *304*, 121–128.
- (121) Tian, B.; Zhao, W.; Cui, Y.; Chu, H.; Qi, S.; Wang, J.; Xin, B. Utilizing waste Zn-Mn batteries in combination with waste SCR catalyst to construct a magnetically recoverable and highly photocatalytic materials. *Chem. Phys. Lett.* **2022**, *796*, 139530.
- (122) Zhang, H.; Zhang, J.; Ding, H.; Li, Y.; Sun, S.; Ao, W.; Liang, Y. Solid-phase synthesis of perovskite using spent SCR catalyst and calcium carbonate and its application as ceramic opacifier. *Journal of Industrial and Engineering Chemistry* **2022**, *114*, 499–507.
- (123) Jin, Q.; Shen, Y.; Cai, Y.; Chu, L.; Zeng, Y. Resource utilization of waste V_2O_5 -based $deNO_x$ catalysts for hydrogen production from formaldehyde and water via steam reforming. *J. Hazard Mater.* **2020**, *381*, 120934.
- (124) Liu, J.; Zhou, S.; Gu, P.; Zhang, T.; Chen, D.; Li, N.; Xu, Q.; Lu, J. Conjugate Polymer-clothed $TiO_2@V_2O_5$ nanobelts and their enhanced visible light photocatalytic performance in water remediation. *J. Colloid Interface Sci.* **2020**, *578*, 402–411.
- (125) Cai, Z.; Hao, X.; Sun, X.; Du, P.; Liu, W.; Fu, J. Highly active $WO_3@anatase-SiO_2$ aerogel for solar-light-driven phenanthrene degradation: Mechanism insight and toxicity assessment. *Water Res.* **2019**, *162*, 369–382.
- (126) Li, Y.; Wang, L.; Li, Z.; Liu, Y.; Peng, Z.; Zhou, M.; Zhang, C.; Jin, W. Synthesis and photocatalytic property of $V_2O_5@TiO_2$ core-shell microspheres towards gaseous benzene. *Catal. Today* **2019**, *321*-322, 164–171.
- (127) Anwer, H.; Mahmood, A.; Lee, J.; Kim, K.-H.; Park, J.-W.; Yip, A. C. K. Photocatalysts for degradation of dyes in industrial effluents: Opportunities and challenges. *Nano Res.* **2019**, *12*, 955–972.