A Review on Resource Utilization of Spent V-W-Ti Based Selective Catalytic Reduction Catalysts

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Abstract: To address the environmental pollution caused by nitrogen oxides, V$_2$O$_5$-WO$_3$/TiO$_2$ is widely used as a catalyst based on selective catalytic reduction (SCR) technology. However, spent SCR catalysts pose a potential hazard to the environment due to the presence of heavy metals. This problem continues to plague countries with predominantly thermal power generation, and landfills as the dominant disposal method wastes significant metal resources. Previous research into the recovery of these metal resources has received considerable attention. Here, we summarise the methods of recovery and find that research trends are beginning to move towards improving the added value of recovered products. One very promising application is photocatalysts; however, the atomic efficiency of current methods is not satisfactory. Therefore, this review first focuses on the regeneration of spent SCR catalysts and the processes used for elemental extraction to clarify what forms of V, W and Ti can be obtained from existing processes. This is followed by providing directions for the conversion of spent SCR catalysts into photocatalysts with improvements based on such processes. From a different perspective, this also provides a new resource for photocatalysts and is expected to significantly reduce the cost of photocatalyst production.

Keywords: SCR; photocatalyst; vanadium; tungsten; titanium; resource utilization

1. Introduction

Industrial gas emission has been a concern for decades, and nitrogen oxides (NO$_X$) are one of the most important toxic industrial gases [1,2]. A selective catalytic reduction catalyst (SCR catalyst) is widely used for coal-fired boilers as a flue gas denitrification catalyst to convert NO$_X$ into harmless N$_2$ emission [3]. Furthermore, V$_2$O$_5$-WO$_3$/TiO$_2$-based SCR catalysts are the most common type. At high temperatures, the presence of H$_2$O, SO$_2$, alkali metals, heavy metals and halogens causes the SCR catalyst to be poisoned and, after deactivation, become a spent SCR catalyst [4]. Spent SCR catalysts have several characteristics: (i) increasing waste generation [5], (ii) containing large amounts of metal resources [6], and (iii) causing serious threats to soil and water bodies [7]. The severity and urgency of the problem is reflected in the increase in patents for the recycling of spent SCR catalysts in China since 2013 [8].

The treatment process must prevent toxic elements (e.g., V, As, Pb, etc.) from entering soil and water bodies to avoid secondary pollution. Conventional treatment is landfill for spent SCR catalysts as hazardous solid waste [9]. According to the policy guidelines, such wastes are required to be roasted above 1000 °C with flux to prevent the leaching of toxic elements [10]. Recent research has tended to add spent catalysts to production lines that require significant use of SCR catalyst for denitrification, thus avoiding transportation. For instance, spent SCR catalysts can be blended into the iron-ore sintering process [11], with heavy metals being recovered from the sintering dust [12]. However, the addition of spent SCR catalysts will reduce several indicators [13]. Alternatively, the spent SCR catalyst can...
also be mixed into cement and the leaching of As and Pb is significantly inhibited after sintering [14].

However, spent SCR catalysts have a high recovery value with components of over 80wt% consisting of V₂O₅, WO₃ and TiO₂ and should, therefore, be regenerated or recovered in order to recycle the resource [15–17]. Although spent SCR catalysts may contain oxides such as SiO₂, Al₂O₃ and CaO that constitute the ceramics, as well as compounds of elements including As and Pb deposited from the flue gas, the extraction of these materials is not reviewed in this article. Regeneration methods can extend the life of SCR catalysts by focusing on detoxification and reactivation. The major problems to be addressed during regeneration are the deactivation and loss of active sites as well as blocking of pores [4,18–20]. Specific regeneration methods for different types of deactivations can achieve promising results [21]. However, current regeneration processes are unable to achieve the expected results when the catalyst is severely deactivated or has undergone several regenerations. In this case, the SCR catalyst will reach the end of its life and be recycled by recovery [22]. Conventional recovery methods focused on the extraction and purification of metals (V, W and Ti) [23]. However, recent research has increasingly turned to the added value of the product with a view to increasing the economic benefits of recycling. For instance, after separation, NH₄VO₃, ammonium paratungstate and anatase TiO₂ are produced, respectively [24].

Under light conditions, photocatalysts produce photogenerated electrons and holes and, further, form active species such as hydroxyl (·OH) and oxygen (O₂⁻) radicals. Due to the strong redox properties of the active species, photocatalysts can address pollutions caused by heavy metals, organics and other substances [25]. Anatase TiO₂ is a classical photocatalyst with excellent photocatalytic activity. Studies have often used doping to build heterostructures to extend the wavelength range of light and to suppress the separation of photogenerated carriers [26,27]. On the other hand, to inhibit the agglomeration of nano TiO₂ and to assist recycling, the preference is to use carrier-loaded nano TiO₂ [28]. Spent SCR catalysts contain a large amount of anatase TiO₂ and are cost-effective; therefore, recovery as photocatalysts not only increases the recovery benefit, but also overcomes the high cost of conventional photocatalysts. In addition, V [29,30] and W [31,32] in spent SCR catalysts have the potential to build heterostructures with TiO₂.

This paper will first review the research on the recycling of spent SCR catalysts carried out between 2013 and 2022. Thereafter, it will continue with a discussion of the studies on the recycling of spent SCR catalysts between 2019 and 2022, including both the regeneration and recovery of spent SCR catalysts. The discussion will focus on the use of reagents with acid, base, complexing, oxidising, or reducing properties in these studies and will summarise the different effects of the different reagents. For the recovery methods, the extraction process of the elements is discussed. This is followed by an introduction to the idea of converting spent SCR catalysts into photocatalysts. Finally, the developments in the recycling of spent SCR catalysts are concluded.

2. Progress in Research on Spent SCR Catalysts

2.1. Methodology

Articles were retrieved on 24 July 2022 from Web of Science (www.webofscience.com) database. The articles were found using the following search formula: TS = (selective-catalytic-reduction OR NH3-scr or deNO(x)-catalysts OR scr) AND TS = (spent OR waste) AND TS = (recovery OR recycling OR leaching OR extraction OR management) AND TS = (titanium OR vanadium OR tungsten). Patents were found through the European Patent Office (www.epo.org) on 24 July 2022. The keywords used are selective-catalytic-reduction, NH3 scr, deNO, scr, spent, recovery, recycling, leaching, extraction, management, titanium, vanadium, tungsten. Patents and articles between 2013 and 2022 were counted using the search method described above to give a general trend of research on recycling spent SCR catalysts. Other sections review articles for 2019 to 2022.
2.2. Research Process

The data on articles and patents described in 2.1 are plotted in Figure 1, where Figure 1a shows the number of articles and patents issued with the year, and Figure 1b shows the proportion of patent disclosures in different countries or organisations. From 2013 onwards, the number of studies addressing the recovery and regeneration of spent SCR catalysts continues to rise and reaches a peak in 2020. The proportion of patents is higher than that of articles, reflecting the huge demand for practical applications in this field. In Figure 1b, significant interest in the disposal of waste SCR catalysts is shown, since the energy structure in China, Korea and Japan is dominated by thermal power generation. Take China as an example: the Emission standard of air pollutants for thermal power plants (GB 13223-2011) limits NO\textsubscript{X} emissions to <100 mg/m\textsuperscript{3}. With increasingly stringent restrictions on NO\textsubscript{X} emissions, the use of SCR catalysts will also increase. In view of the limited effect of regeneration on spent SCR catalysts, the cycle time of regeneration has been limited to ensure that gas emissions comply with standards [22]. As a result, there is a growing interest in the development of regeneration processes and the reuse of resources through recycling.

![Figure 1. (a) Annual number of publications of papers and patents. (b) Patent issuance by countries and organizations between 2013 and 2022.](image-url)

The principles of green chemistry and green engineering by Ziemmerman et al. [33] in 2020 also emphasise the importance of this idea of recycling. The principles point to a shift in future industry from mostly linear processes to circular processes and a shift from “waste” treatment to “waste” utilisation. In this field, the main idea is to avoid landfills in favour of efficient regeneration of spent SCR catalysts and recycling those that cannot be regenerated. Current research has explored several methods for recycling spent SCR catalysts, but these methods have not been replicated in industry, so there is still much scope for research into recycling methods. Factors limiting their application include the process, waste generation, material consumption, and equipment requirements and, in the case of recycled production products, the value of the product is also important [22].

3. Regeneration of Spent SCR Catalysts

SCR catalysts under a high-temperature flue gas condition are subjected to deactivation due to multiple factors including pore blocking, catalytic-site poison and catalytic-component loss [4,18–20]. In recent years, most regeneration processes have employed ultrasonic instead of stirring to obtain better results (Table 1). Regeneration processes have been designed to address the poisoning of spent SCR catalysts and to attempt to restore the
structure of spent SCR catalysts. Following this effort, some studies have supplemented the regenerated catalysts with active sites by impregnation. NH$_4$VO$_3$ solutions are usually used to reload V$_2$O$_5$ [34], and, relatively, Ce(NO$_3$)$_3$ solutions can be used instead to load CeO$_2$ avoiding the use of V [35].

Table 1. Regeneration process for SCR catalysts.

| Process | Testing Condition | Performance | Ref. |
|---------|-------------------|-------------|------|
| Mixed acid immersing, NaOH immersing, CH$_3$COOH immersing | 0.2% NO$_2$ + 0.2% NH$_3$, 2 L min$^{-1}$, 400 °C | NO$_X$ conversion = 73.0% (used: 17.1%, virgin: 89.9%) | [36] |
| H$_2$SO$_4$ immersing | 0.05% NH$_3$ + 0.05% NO, 0.2 L min$^{-1}$, 400 °C | NO$_X$ conversion ≈ 100% (comparable to fresh) | [37] |
| Ultrasonic water immersing, ultrasonic acid immersing, NH$_4$VO$_3$ impregnation, roasting, and loading | 335 mg m$^{-3}$ NO + 513 mg m$^{-3}$ NO$_2$, 1L min$^{-1}$, 230 °C | NO$_X$ conversion = 93.5% (higher than fresh) | [34] |
| Ultrasonic water immersing, ultrasonic EDTA+LAS immersing, and roasting | 0.05% NH$_3$+0.05% NO, 0.1 L min$^{-1}$, 400 °C | NO$_X$ conversion = 86% (poisoned: about 40%, fresh: nearly 100%) | [38] |
| Ultrasonic TMT103 immersing, ultrasonic EDTA+LAS+H$_2$SO$_4$ immersing, Ce(NO$_3$)$_3$·6H$_2$O impregnation, and roasting | 0.08% NH$_3$+0.08% NO, 0.1 L min$^{-1}$, 400 °C | NO$_X$ conversion = nearly 99% (comparable to fresh) | [35] |

EDTA: ethylenediaminetetraacetic acid. LAS: dodecylbenzene sulfonic acid. TMT103: 2,4,6-trimercaptotriazine.

Improvement of the pore landscape of regenerated SCR catalysts can effectively increase catalytic activity without reloading the active site. Various data can be used to characterise the pore landscape, such as: mesopore volume, mesopore surface area, BET surface area, acidic sites etc. Here, the mesopore volume data obtained with thermoporometry measurements (TPM) provides a reliable indication of the effect of the immersing method [36]. In addition to regenerating the activity by improving the pore landscape, pore size and specific surface area can also be enhanced by loading the regenerated SCR catalyst powder onto the cloth surface. Shi et al. [34] regenerated the spent SCR catalyst in H$_2$C$_2$O$_4$ and NH$_4$VO$_3$ solutions after sequential blowing, grinding, deionised water washing and 0.5 M sulphuric acid washing. The regenerated catalyst was then loaded onto a P84 filter cloth by impregnation and used as a catalytic filter for low-temperature flue gas denitrification achieving 91.6% of the catalytic effect of the fresh catalyst.

The regeneration process attempts to achieve better results for catalysts that are severely deactivated as well as repeatedly experiencing deactivation–regeneration [22]. Complex processes can effectively extend the life cycle of SCR catalysts. However, the complexity of the process also results in higher costs. Therefore, despite the fact that complex processes can be used for longer cycle times, the difficult regenerated spent SCR catalysts need to be further recovered as metal (V, W, and Ti) resources to reduce costs.

4. Extraction of Elements from Spent SCR Catalysts

Two common methods can be used to effectively extract V and W from spent SCR catalysts: the leaching method [39,40] and the roasting method [16,41]. The leaching method is a process dissolving certain components from the catalyst. Leaching reagents are typically employed to selectively separate specific components with acid [42], base [43], complexation [44], reduction [44], oxidation [45] and other properties. In most cases, TiO$_2$ will be retained in the residue to be recycled [46,47]. The roasting method is a process in which reagents eutectic with spent SCR catalyst under high-temperature conditions form salts. This process generally forms soluble salts which are subsequently separated from the solid phase in a leaching step [48,49]. Table 2 summarises the studies of extracting by roasting or leaching methods for V, W and lists the final form of Ti.
Table 2. Extraction process for spent SCR catalysts.

| Process                                                                 | Form of Ti                                      | Leaching Efficiency of V | Leaching Efficiency of W | Ref. |
|-------------------------------------------------------------------------|------------------------------------------------|--------------------------|--------------------------|------|
| (NH₄)₂CO₃+H₂O₂ leaching                                                | Anatase TiO₂                                    | 98%                      | 99%                      | [45] |
| NaOH leaching                                                          | Anatase TiO₂                                    | 40.0–51.0%/66.8–69.9%    | 44.6–57.3%/38.0%–52.6%  | [50] |
| NaOH leaching in residue                                                |                                                  | 95.76% on average        | 98.63% on average        | [51] |
| NaOH leaching                                                          | Anatase TiO₂                                    | 82.4%                    | 54.3%                    | [52] |
| HCl leaching                                                           | Anatase TiO₂                                    | 52.5%                    | 0.1%                     | [52] |
| HNO₃ leaching                                                          | Anatase TiO₂                                    | 42.2%                    | 0.0%                     | [52] |
| H₂SO₄ leaching                                                         | Anatase TiO₂                                    | 69.0%                    | 0.6%                     | [52] |
| NaOH leaching, H₂SO₄ leaching, carbothermic reduction, flotation        | Metallic Ti (purity of 99.5 wt%)                | 91%                      | 67%                      | [6]  |
| operation, and electrochemical process                                 |                                                |                          |                          |      |
| NaOH+NaCl roasting, and water leaching                                 | In residue                                      | 93.25%                   | 99.17%                   | [53] |
| K₂CO₃ roasting, water leaching, Si removal, and CaCl₂ precipitation    | Potassium titanates                             | 99.65%                   | 96.89%                   | [54] |
| Na₂CO₃+NaCl roasting, and water leaching                               | Nano TiO₂ and sodium titaneate nanorods         | 94.9% of leaching 93.4%  | 95.5% of leaching 96.2%  | [49] |
| Resin enrichment, NaOH stripping, NH₄Cl precipitation                  |                                                |                          |                          |      |
| Na₂CO₃ roasting, water leaching, and HCl leaching                      | TiOCl₂                                         | 99.3%                    | 99.2%                    | [55] |
| Na₂CO₃ roasting, and water leaching                                     | Anatase/rutile TiO₂                             | >99%                     | >99%                     | [48] |
| Roasting, H₂C₂O₄ leaching, repeat, HCl precipitation, and roasting     | Anatase/rutile TiO₂                             | None                     | 87%                      | [56] |
| Soda roasting, and water leaching                                       | In residue                                      | >99.9% of extraction 71.31% of stripping | >99.9% of extraction 71.31% of stripping | [24] |
| Aliquat 336 extraction, and NaOH+NaCl stripping                        |                                                |                          |                          |      |
| NaOH+Na₂CO₃ roasting, HCl immersing, and calcination                   | Rutile/anatase TiO₂ nanosphere                  | None                     | None                     | [7]  |

Aliquat 336: trioctylmethylammonium chloride.

4.1. Leaching Method

Leaching is a process of separating V₂O₅, WO₃ from the catalyst carrier using a solvent to break the V-O, W-O and Ti-O bonds [52]. The separation can be achieved by selectively dissolving V₂O₅, WO₃ and TiO₂ into different solvents based on the difference in solubility. Whereas V₂O₅ is usually well soluble in acids and bases, WO₃ is only soluble in bases and stable to acids, while TiO₂ is always retained in residues. Therefore, leaching with normal acid (e.g., H₂SO₄ [52]) allows a highly selective separation of V from the catalyst, and, conversely, extracts both V and W.

In the case of V extraction, V(III) is not easily soluble and can be oxidised by adding an oxidant or V(V) under an acidic condition. H₂O₂ is commonly used as an oxidant to convert low-valent V to V(V) under alkaline conditions, contributing to the leaching efficiency in both leaching [45] and precipitation [54] processes. In contrast, the reaction between V(III) and V(V) will take place at 5wt% H₂SO₄ at 95 °C and will eventually be converted to VOSO₄ in the presence of the reducing agent Na₂SO₃ (leaching efficiency is nearly 100%) [57]. Theoretical calculations show [52] that (i) with alkaline reagents, OH⁻ reacts directly with V and W atoms; and (ii) with acidic reagents, H⁺ reacts with O atoms. Organic acids such as H₂C₂O₄ exhibit complexation reaction activity as well, e.g., V can be separated out as V(OH)₂(OH)₄ using 1.0 mol/L H₂C₂O₄ at 90 °C in a reaction of 3 h at a liquid-to-solid ratio of 20 mL g⁻¹ (leaching efficiency of 84.22%) [44]. Among the organic acids, H₂C₂O₄ is more effective than citric and tartaric acids for the extraction of V [58].

The extraction of W was also facilitated by the addition of the oxidising agent H₂O₂ but the leaching efficiency remained at a low level [54]. Additionally, at high V content, the leaching efficiency of W is limited due to the strong V-W-Ti interaction [50]. WO₃ has good stability in acid and requires alkaline reagents for dissolution. Leaching of W generally uses NaOH as the leaching agent and requires heating. For instance, heating a 1.5 mol L⁻¹ NaOH solution to 100 °C at atmospheric pressure for a 4 h leaching (liquid-to-
solid ratio = 15) resulted in leaching efficiencies ranging from 38.0% to 57.3% for W [50]. In contrast, applying a pressure condition to heat a 4.75 mol L\(^{-1}\) NaOH solution to 190 °C for 44.5 min leaching reaction (liquid-to-solid ratio = 10) could achieve 98.63% leaching efficiency [51]. When the temperature was increased to 300 °C, 96% W (liquid-to-solid ratio = 10) was leached after 2 h of immersing using a 2 mol L\(^{-1}\) NaOH solution [39]. Further studies have found that mixing NaOH with spent SCR catalysts using a ball-mill premix promotes leaching at lower temperatures [59]. After premixing NaOH to a catalyst at a mass ratio of 0.9, leaching with the addition of water for 20 min at 25 °C (liquid-to-solid ratio = 15) could achieve the same result as a 4 h reaction at 100 °C under the same conditions (see Figure 2 for SEM images). The final leaching efficiencies for V and W were 67.7% and 56.3%, respectively.

Ammonium salt can form water-soluble NH\(_4\)VO\(_3\) and (NH\(_4\))\(_2\)WO\(_4\) with V and W, respectively. Cao et al. [45] leached V and W using a solution of 2 mol L\(^{-1}\) (NH\(_4\))\(_2\)CO\(_3\) and 1.5 mol L\(^{-1}\) H\(_2\)O\(_2\). After 0.5 h leaching at 70 °C, the leaching efficiencies of V and W reached 98% and 99% (liquid-to-solid ratio = 25). The addition of H\(_2\)O\(_2\) has a promoting effect on V but is not sensitive to the concentration. The use of alkaline leaching agents requires the further separation of V and W. For example, diethylhydroxydodecanoneoxime (LIX 63) can selectively separate V from W [45]. Similar extractants are trioctylphosphine oxide (TOPO), triisobutylphosphine sulphide (TIBPS), trioctylmethylammonium chloride (Aliquat 336) and di-2-ethylhexylphosphoric acid (HDEHP) [60]. Aliquat 336 can simultaneously extract V and W [24]. After separation, W can be converted to ammonium paratungstate, while V can be converted to NH\(_4\)VO\(_3\).

Figure 2. SEM images of (a) the original catalyst, (b) the catalyst treated by the premixing method and (c) the catalyst treated by the common method (from 1 to 3 at 100×, 1000× and 10,000×, respectively). Reproduced with permission [59]. Copyright 2018, Elsevier.
4.2. Roasting Method

Roasting is a method of converting oxides of V and W into soluble salts with the assistant of alkaline reagents by high-temperature solid-state reactions. The main reagents used are NaOH, Na₂CO₃ and NaCl. NaOH and Na₂CO₃ are the major alkaline reagents, which can react with W more effectively than NaCl [53]. The Na₂CO₃ will decompose above the melting temperature, accompanied by the occurrence of alkali fusion. When the CaO content is low and the Na₂O content is high, V and W tend to form soluble NaVO₃ and Na₂WO₄, thereby avoiding the formation of insoluble CaV₂O₆ and CaWO₄ during the process [48]. Due to the different proportions of Na₂O and metal oxides, the catalyst will exhibit different states after the reaction (Figure 3). Studies have shown that mixing NaCl with Na₂CO₃ [49] (NaCl:Na₂CO₃ = 8.8:16) and NaOH [53] (NaCl:NaOH = 3:2) can effectively promote leaching efficiency. NaCl will produce Cl₂ in the process of high-temperature calcination, acting as catalyst and oxidant, thus reducing the reaction temperature (from 1000 °C to 750 °C) [53].

Figure 3. Actual appearance of samples after alkali fusion reactions for 20 min at 950 °C in various molar ratios (MOₓ/Na₂O+MOₓ, M = Ti, Si, W): (a) 0.3, (b) 0.4, (c) 0.5, (d) 0.6, (e) 0.7. Reproduced with permission [48]. Copyright 2019, Springer Nature.

After roasting with an alkaline reagent, the obtained solid can be selectively extracted using the leaching method. In this condition, water is able to dissolve the sodium salts formed during roasting, including NaVO₃, Na₂WO₄, etc. [49]. Thus, V and W are transferred to water. Since Si affects the leaching efficiency of V and W, Si needs to be removed first in the case of high Si content. At room temperature, 85% of Si can be removed in the form of silicate precipitation by reducing the pH to 9.5 by HCl, avoiding the loss of W and V. Water leaching can reach more than 99% leaching of V and W, and is less affected by leaching conditions [55]. Afterwards, V and W can be precipitated from water with Ca²⁺ ions [54]. Alternatively, highly selective extraction can be achieved with the help of the
selective complexation of V and W by organic ammonium salts (e.g., \([R_3NCH_3]^+\text{Cl}^−\) [24]). Following a stripping process using a solution of NaOH and NaCl, the stripping step has a leaching efficiency of around 70% for V and W.

Leaching processes are limited for the efficient leaching of W due to the stability of the W-O bond. In contrast, roasting methods are highly efficient in breaking such stable bonds at high temperatures, thus reducing the requirement for a leaching reagent. However, roasting reagents require NaOH or Na₂CO₃ for alkali fusion at high temperatures, raising the equipment requirements and, therefore, making it difficult to promote. To solve this problem, the leaching process can be adjusted to reduce the reliance on alkaline reagents during roasting. In the case of leaching with HCl instead, for example, CaO can be added to the spent SCR catalyst instead of the alkaline reagent [17]. Such acid leaching takes place by the selective dissolution of the calcium salts (e.g., CaV₂O₆ and CaWO₄) formed from roasting step. The use of a high concentration (4 mol L⁻¹) of HCl promotes the dissolution of V and inhibits the dissolution of W, thus achieving the separation of V and W. The undissolved W will be deposited on the surface of CaWO₄ in the form of H₂WO₄. The H₂WO₄ precipitation should be dissolved in a low-concentration (1 mol L⁻¹) NaOH solution to inhibit the dissolution of Fe, Al, and V. Subsequently CaCl₂ is added to once again precipitate W from the solution as CaWO₄ (CaWO₄ content was 96.1%). Using H₂C₂O₄ (0.5 mol L⁻¹) instead of HCl (1 mol L⁻¹) was found to increase the dissolution efficiency of W as well as reduce the dissolution of V [56]. In contrast to HCl, the use of H₂C₂O₄ does not produce H₂WO₄, but is further converted to soluble H₂[WO₃(C₂O₄)H₂O]. This dissolution process is accompanied by a precipitation of CaC₂O₄. A secondary roasting of the leach residue converts this precipitate into CaO. Further H₂C₂O₄ leaching after the secondary roasting leads to an increase in the leaching of W to 87% and directly obtaining a H₂WO₄ product.

4.3. Separation of Ti

The content of Ti is the highest in spent SCR catalysts and Ti will be retained in the residue after the extraction of V and W. With similar leaching efficiencies of V and W, differences in the form of Ti are presented due to the different processes. During roasting above 500 °C, anatase TiO₂ tends to change to rutile TiO₂ [7] and a portion of TiO₂ is converted to titanate [54], yet the leaching process is relatively gentle and does not affect the structure of TiO₂ [45]. The form of Ti varies depending on the recovery method (Figure 4): (i) roasting with Na₂CO₃ and NaCl at 750 °C gives a mixture of rutile TiO₂, anatase TiO₂ and sodium titanate [49]; (ii) roasting with K₂CO₃ gives potassium titanate [54]; (iii) electrolysis of Ti₂CO (obtaining by a carbothermal reduction) gives Ti metal [6]; and (iv) adding hot concentrated HCl to the roasting residue gives a TiOCl₂ solution [55], etc.
Figure 4. The different recovery products of Ti: (a) mixture of rutile TiO$_2$, anatase TiO$_2$ and sodium titanate. Reproduced with permission [49]. Copyright 2020, Elsevier. (b) Potassium titanate. Reproduced with permission [54]. Copyright 2020, Springer Nature. (c) Ti metal [6]. Reproduced with permission [6]. Copyright 2021, Elsevier. (d) TiOCl$_2$ solution. Reproduced with permission [55]. Copyright 2019, Elsevier.

5. Conversion of Spent SCR Catalysts into Photocatalysts

Recent research has explored new recycling methods to convert spent SCR catalysts into products rather than raw materials, such as a pigment [61] and ceramic opacifier [62]. The idea of recycling spent SCR catalysts as photocatalysts for pollution treatment is in-line with the concept of “treating waste with waste” [63].

5.1. Catalyst Carriers

Photocatalytic degradation is a promising technology to address environmental pollution with economic and environmental efficiency [64]. However, as most photocatalysts are nanoparticles, they are difficult to recycle and, therefore, present the potential risk of secondary pollution [65]. On the other hand, the tendency of nanoparticles to agglomerate can also limit their catalytic activity [66]. To solve these problems, photocatalysts can be loaded onto carriers, such as fly ash [67] and activated carbon [68]. The carriers not only provide dispersion and easier recycling, but specific carriers can also improve the catalytic activity of the catalyst by forming a specific heterostructure [69].
Spent SCR catalysts contain a variety of oxides with catalytic activity, which can be used as carriers to enhance catalytic activity. However, it is important to ensure that components such as V$_2$O$_5$ and As$_2$O$_5$ do not enter the environment during utilization and cause secondary contamination. Jin et al. [70] investigated spent SCR catalysts by grinding into powder and adding Al$_2$O$_3$, diatomite and agglomerant to calcine at 1000 °C to obtain ceramics. This was followed by impregnation and sintering in an 8wt% Ni(NO$_3$)$_2$ solution to obtain NiO loading (Figure 5). The prepared NiO-based catalysts were used for the reforming of formaldehyde and water vapour for hydrogen production with a selectivity of 100% for H$_2$, 31.9% for CO and 53.2% for CO$_2$ at 500 °C, and a conversion of formaldehyde above 93.0%. The analysis of the XPS data and the mechanism of the reforming reaction revealed that the presence of oxides on the surface had a positive effect on the performance of the catalysis. Based on the work of Jin et al., it can be demonstrated that spent SCR catalysts have potential as catalyst carriers. Particularly, TiO$_2$ shows typical photocatalytic activity and research on recycling spent SCR catalysts as photocatalyst carriers for this feature awaits further exploration.

Figure 5. (a) Process of converting spent SCR catalysts into NiO-based catalysts, (b) XPS test results of spent SCR catalysts after sintering into ceramics, (c) catalytic performance test results of NiO-based catalysts. Reproduced with permission [70]. Copyright 2020, Elsevier.
5.2. Photocatalysts

V₂O₅, WO₃ and TiO₂ from spent SCR catalysts can be used for the preparation of photocatalysts. V₂O₅ and WO₃ can form crystals with cations such as Bi³⁺ in the form of VO₄³⁻ and WO₆⁶⁻, respectively [71], while TiO₂ exists as anatase TiO₂ mostly [72]. Zhang et al. [57] used a solution of H₂SO₄ and Na₂SO₃ to leach out V from spent SCR catalyst, followed by dissolving the Ti-containing residue in HF solution to obtain WO₃-TiO₂ photocatalyst after a hydrothermal reaction. In another case, V and W were leached out using a NaOH solution, followed by the addition of Bi(NO₃)₃ for a hydrothermal reaction to obtain BiVO₄/Bi₂WO₆ photocatalysts [71]. Wang et al. [73] also used NaOH to retain Ti in the leach residue for separation. Subsequently, Na₃PO₄ and Mg(NO₃)₂ were used to precipitate Ca²⁺, SiO₄⁴⁻, and PO₄³⁻, respectively. This was followed by the precipitation of Al³⁺ and Mg²⁺ using HNO₃ and NaOH to adjust the pH. The solution retains VO₃⁻ and WO₄²⁻, but additional NH₄VO₃ is required due to the low V. The addition of Zn(NO₃)₂ eventually leads to a visible light responsive Zn₃(VO₄)₂/ZnWO₄ photocatalyst by hydrothermal reaction.

Qian et al. [74] used NaOH to leach the V element from the catalyst, followed by a hydrothermal reaction using 96% H₂SO₄ to convert the TiO₂ to TiOSO₄ after roasting at 200 °C (Figure 6). V is removed after reaction with NaOH, while W remains in the residue. This method overcomes the difficulty of separating Ti and W and makes effective use of Ti. The prepared photocatalyst exhibits similar catalytic activity to P25 at a lower Ti content and demonstrates the feasibility of dissolving and converting Ti to nano TiO₂. Furthermore, loading TiO₂ onto the fly-ash surface also overcomes the shortcomings of nano TiO₂, which is difficult to recover and prone to agglomeration.

![Image](a) Microscopic view of Ti-FA surface by TEM, (b) XRD pattern, (c) XRF test results and (d) UV degradation of rhodamine B catalytic performance test results; (e) UV-DRS test results. Reproduced with permission [74]. Copyright 2022, Elsevier.

Current research has focused on the separation of TiO₂ from V₂O₅ and WO₃ with some progress being achieved. Figure 7 illustrates the transformation relationships of substances in these works. Since the goal is no longer to separate and purify V, W and Ti, the process can be simplified based on current separation processes. New extraction processes can also be developed, such as the dissolution of TiO₂ with sulphuric acid under hydrothermal conditions [75]. Mechanochemical methods also have potential applications in the preparation of TiO₂ [76]. Ball milling as a pre-treatment has proven to be effective in the recycling of spent SCR catalysts [59]. On the other hand, both BiVO₄ [77] and Bi₂WO₆ [78] can form corresponding heterostructures with TiO₂. Moreover, V and W can be extracted directly into solution as NH₄VO₃ and (NH₄)₂WO₄ [45], which would assist in the further synthesis of bismuth salt.
The common elemental extraction processes include leaching and roasting methods. The efficiency can be improved by combining with a reducing agent (e.g., Na$_2$SO$_3$) under leaching method can achieve the extraction of elemental V at lower temperatures, and common elemental extraction processes include leaching and roasting methods. The cation. Recycling process is necessary to address these shortcomings to achieve broader application. Nevertheless, further exploration of green chemistry, it is difficult to promote because of its complexity, high cost, low economic efficiency, and the risk of secondary pollution. Consequently, even though the recycling process is more in-line with the principles of spent SCR catalysts at present; although wasteful of resources, it is much easier to process. Regeneration processes are currently employed in industry to extend the life of SCR catalysts, but catalysts that have undergone three to four regenerations are eventually abandoned as they are difficult to regenerate. Landfill is the main disposal method for catalyst (e.g., NaCl) to reduce the temperature and time for the reaction, and (iii) application of acid leaching rather than water leaching to avoid the use of an alkaline reagent in the roasting process. With the above method, V$_2$O$_5$ can be recovered as CaV$_2$O$_6$, NH$_4$VO$_3$, CaWO$_4$, and TiO$_2$ can be utilized as photocatalysts for environmental management, respectively. Additional, both BiVO$_4$/Bi$_2$WO$_6$, and Zn$_3$(VO$_4$)$_2$ and TiO$_2$ can be utilized as photocatalysts for environmental management, respectively. Further research should explore photocatalyst conversion processes with higher atomic efficiency. The selective conversion of V, W and Ti into their salt or oxide can be applied in the treatment of...
spent SCR catalysts, and attempts can be made to combine these substances into a heterogeneous photocatalyst. In addition, new treatment technologies such as mechanochemical processes to reduce contamination during the recycling of spent SCR catalysts need to be introduced. The process should avoid high-temperature and pressure-reaction conditions and reduce the production of wastewater, waste gases and residues.

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**References**

1. Busca, G.; Lietti, L.; Ramis, G.; Berti, F. Chemical and mechanistic aspects of the selective catalytic reduction of NOx by ammonia over oxide catalysts: A review. *Appl. Catal. B-Environ.* 1998, 18, 1–36. [CrossRef]

2. Han, L.; Cai, S.; Gao, M.; Hasegawa, J.-y.; Wang, P.; Zhang, J.; Shi, L.; Zhang, D. Selective Catalytic Reduction of NOx with NH3 by Using Novel Catalysts: State of the Art and Future Prospects. *Chem. Rev.* 2019, 119, 10916–10976. [CrossRef]

3. Wang, D.; Chen, Q.; Zhang, X.; Gao, C.; Wang, B.; Huang, X.; Peng, Y.; Li, J.; Lu, C.; Crittenden, J. Multipollutant Control (MPC) of Flue Gas from Stationary Sources Using SCR Technology: A Critical Review. *Environ. Sci. Technol.* 2021, 55, 2743–2766. [CrossRef]

4. Szymaszek, A.; Samojeden, B.; Motak, M. The Deactivation of Industrial SCR Catalysts-A Short Review. *Energies* 2020, 13, 3870. [CrossRef]

5. Yuan, L.; Qiu, Z.; Yang, J.; Ma, B.; Cao, L.; Zhang, W. Research progress of alkali(alkaline earth) metal poisoning and modified regeneration of scr catalyst. *Environ. Eng.* 2018, 36, 117–121.

6. Bai, X.; Shang, X.; Wan, H.; Che, Y.; Yang, B.; He, J.; Song, J. Sustainable recycling of titanium from TiO2 in spent SCR denitration catalyst via molten salt electrolysis. *J. Energy Chem.* 2021, 85, 557–563. [CrossRef]

7. Chen, H.-J.; Wang, R.; Yang, Y.-L.; Shi, X.-L.; Lu, S.; Chen, Z.-G. Environmentally-friendly harvesting TiO2 nanospheres and V2O5 microrods from spent selective catalytic reduction catalysts. *Prog. Nat. Sci. Mater. Int.* 2021, 31, 858–864. [CrossRef]

8. Ferella, F. A review on management and recycling of spent selective catalytic reduction catalysts. *J. Clean. Prod.* 2020, 246, 118990. [CrossRef]

9. Choi, I.-H.; Cho, Y.-C.; Moon, G.; Kang, H.-N.; Oh, Y.; Lee, J.-Y.; Kang, J. Recent Developments in the Recycling of Spent Selective Catalytic Reduction Catalyst in South Korea. *Catalysts* 2020, 10, 182. [CrossRef]

10. Zhou, H.; Xing, Y.-j.; Xu, J.-n.; Zhou, M.-x. In-situ investigation of melting characteristics of waste selective catalytic reduction catalysts during harmless melting treatment. *J. Zhejiang Univ. Sci. A* 2022, 22, 207–221. [CrossRef]

11. Long, H.-m.; Zhang, Y.-d.; Yang, T.; Qian, L.-x.; Yu, Z.-w. A promising method to recover spent V2O5-WO3/TiO2 catalyst: Treatment by vanadium–titanium magnetite sintering process. *J. Iron Steel Res. Int.* 2021, 29, 1176–1184. [CrossRef]

12. Qian, L.; Yang, T.; Long, H.; Ding, L.; Xu, C.C. Recycling of Waste V2O5-WO3/TiO2 Catalysts in the Iron Ore Sintering Process Via a Preballing Approach. *ACS Sustain. Chem. Eng.* 2021, 9, 16373–16383. [CrossRef]

13. Zhou, H.; Ma, P.; Lai, Z.; Zuo, Y.; Xing, Y.; Shi, H.; Cen, K. Harmless treatment of waste selective catalytic reduction catalysts during iron ore sintering process. *J. Clean. Prod.* 2020, 275, 122954. [CrossRef]

14. He, C.; Kong, F.; Bao, Q.; Zhang, F.; Wang, L.; Ma, Y.; Yao, Y. Cement solidification/stabilization of the toxicants from spent commercial SCR catalyst. *J. Technol. Biotechnol.* 2021, 96, 514–520. [CrossRef]

15. 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 V2O5-WO3/TiO2 SCR catalysts and its concurrent activation by bioleaching through a novel mechanism. *Chem. Eng. J.* 2021, 420, 127722. [CrossRef]

16. Choi, I.-H.; Kim, H.-R.; Moon, G.; Jyothi, R.K.; Lee, J.-Y. Spent V2O5-WO3/TiO2 catalyst processing for valuable metals by soda roasting-water leaching. *Hydrometallurgy* 2018, 175, 292–299. [CrossRef]
17. Liu, X.; Yang, Q. Research on the deactivation mechanism of a denitration catalyst WO$_3$–V$_2$O$_5$ on a coal-fired power plant. RSC Adv. 2020, 10, 44025–44033. [CrossRef]

18. Zytkowski, M.; Motak, M.; Samojeden, B.; Szczepanek, K. Deactivation of V$_2$O$_5$–WO$_3$/TiO$_2$ DeNOx Catalyst under Commercial Conditions in Power Production Plant. Energies 2020, 13, 6260. [CrossRef]

19. Zhang, Q.; Wu, Y.; Yuan, H. Recycling strategies of spent V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst: A review. Resour. Conserv. Recycl. 2020, 161, 104983. [CrossRef]

20. Wang, B.; Liu, Z.; Lin, D.; Cao, Z.; He, F.; Lu, G.; Xiao, Y. A Review on Recovery and Utilization of Spent V$_2$O$_5$-WO$_3$/TiO$_2$ Catalyst. Mater. Rev. 2021, 35, 15001–15010.

21. 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. [CrossRef]

22. Nair, R.V.; Gummaluri, V.S.; Matham, M.V.; Vijayan, C. A review on optical bandgap engineering in TiO$_2$. Adv. Mater. 2019, 31, 1807660. [CrossRef]

23. Nair, R.V.; Gummuluri, V.S.; Matham, M.V.; Vijayan, C. A review on optical bandgap engineering in TiO$_2$ nanostructures via dopant and intrinsic vacancy modulation towards visible light applications. J. Phys. D Appl. Phys. 2022, 55, 313003. [CrossRef]

24. Capkowska, M.; Siudyga, T.; Sitko, R.; Niemczyk-Wojdyla, 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. [CrossRef]

25. Huang, X.; Wang, D.; Zhao, H.; Yang, Q.; Peng, Y.; Li, J. Severe deactivation and artificial enrichment of thallium on commercial SCR catalysts installed in cement kiln. Appl. Catal. B Environ. 2020, 277, 119194. [CrossRef]

26. Zhou, K.; Li, G.; Lu, B.; Wang, S.; Zhang, Y.; Teng, Y.; Li, J. Regeneration of Deactivated V$_2$O$_5$-WO$_3$/TiO$_2$ Selective Catalytic Reduction Denitration Catalyst. J. Chin. Ceram. Soc. 2019, 47, 940–449. [CrossRef]

27. 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. J. Ind. Eng. Chem. 2015, 28, 73–77. [CrossRef]

28. Li, Q.; Liu, Z.; Liu, Q. Kinetics of Vanadium Leaching from a Spent Industrial V$_2$O$_5$/TiO$_2$ Catalyst by Sulfuric Acid. Ind. Eng. Chem. Res. 2014, 53, 2956–2962. [CrossRef]

29. Kim, H.-R.; Lee, J.; Kim, J. Leaching of Vanadium and Tungsten from Spent SCR Catalysts for De-NOx by Soda Roasting and Water Leaching Method. J. Korean Inst. Resour. Recycl. 2012, 21, 65–73. [CrossRef]

30. Qi, C.; Bao, W.; Wang, L.; Li, H.; Wu, W. Study of the V$_2$O$_5$-WO$_3$/TiO$_2$ Catalyst Synthesized from Waste Catalyst on Selective Catalytic Reduction of NOx by NH$_3$. Catalysts 2017, 7, 110. [CrossRef]

31. 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. [CrossRef]

32. 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. [CrossRef]

33. Chen, Y.; Xie, Z.; Wang, C. Study of the TiO$_2$ Recovery from SCR Catalyst Waste in Coal-Fired Power Plants. Electr. Power 2016, 49, 151–156,180.
47. Wang, S.; Xie, Y.; Yan, W.; Wu, X.; Wang, C.-T.; Zhao, F. Leaching of vanadium from waste V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst catalyzed by functional microorganisms. Sci. Total Environ. 2018, 639, 497–503. [CrossRef]

48. Choi, I.-H.; Moon, G.; Lee, J.-Y.; Jyothi, R.K. Alkali fusion using sodium carbonate for extraction of vanadium and tungsten for the preparation of synthetic titanium tinate from spent SCR catalyst. Sci. Rep. 2019, 9, 12316. [CrossRef]

49. Yang, B.; Zhou, J.; Wang, W.; Liu, C.; Zhou, D.; Yang, L. Extraction and separation of tungsten and vanadium from spent V$_2$O$_5$-WO$_3$/TiO$_2$ SCR catalysts and recovery of TiO$_2$ and sodium tinate nanorods as adsorbent for heavy metal ions. Colloids Surf. A Physicochem. Eng. Asp. 2020, 601, 124963. [CrossRef]

50. Su, Q.; Yi, X.; Miao, J.; Chen, Y.; Chen, J.; Wang, J. A Comparative Study in Vanadium and Tungsten Leaching from Various Sources of SCR Catalysts with Local Difference. Sustainability 2020, 12, 1499. [CrossRef]

51. Liu, N.; Xu, X.; Liu, Y. Recovery of vanadium and tungsten from spent selective catalytic reduction catalyst by alkaline pressure leaching. Physicochem. Probl. Miner. Processing 2020, 56, 407–420. [CrossRef]

52. Nie, Z.; Ma, L.; Xi, X.; Guo, F.; Nie, Z. Studying the leaching mechanism of spent SCR catalyst with different leaching agents (NaOH, H$_2$SO$_4$, HCl and HNO$_3$) using DFT calculations. Appl. Surf. Sci. 2022, 584, 152577. [CrossRef]

53. 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. [CrossRef]

54. Liu, X.; Yang, Q. Recovery of vanadium and tungsten from waste selective catalytic reduction catalysts by K2CO$_3$ roasting and water leaching followed by CaCl$_2$ precipitation. Int. J. Coal Sci. Technol. 2021, 8, 727–736. [CrossRef]

55. 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. [CrossRef]

56. Yao, J.; Cao, Y.; Wang, J.; Zhang, C.; Wang, W.; Bao, W.; Chang, L. Successive calcination-oxidative acid leaching treatment of spent SCR catalyst: A highly efficient and selective method for recycling tungsten catalyst. Hydrometallurgy 2021, 201, 105576. [CrossRef]

57. Zhang, Q.; Wu, Y.; Li, L.; Zhuo, T. Sustainable Approach for Spent V$_2$O$_5$–WO$_3$/TiO$_2$ Catalysts Management: Selective Recovery of Heavy Metal Vanadium and Production of Value-Added WO$_3$–TiO$_2$ Photocatalysts. ACS Sustain. Chem. Eng. 2018, 6, 12502–12510. [CrossRef]

58. Chen, F.; Cui, C.; Qi, L. Utilizing organic acids for V$_2$O$_5$ recovery from denitrification catalyst alkaline inactivation. CIESC J. 2017, 68, 4717–4722.

59. 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. [CrossRef]

60. Foulon, C.; Pareau, D.; Durand, G. Thermodynamic and kinetic studies of palladium (II) extraction by extractant mixtures containing LIX 63: Part I. Thermodynamic study. Hydrometallurgy 1999, 51, 139–153. [CrossRef]

61. Moon, G.; Cho, Y.-C.; Lee, J.-Y.; Kang, J. Desilication of Highly Acidic Titanyl Chloride Solution for the Production of High-Purity Titania Pigment from a Spent Selective Catalytic Reduction Catalyst. Mater. Trans. 2019, 60, 988–996. [CrossRef]

62. Ao, W.; Ding, H.; Sun, S.; Lin, C.; Zhang, X. Processing of Waste Selective Catalytic Reduction Denitrification Catalyst Used for Preparing Composite Opacifier for, e.g. Ceramics by Mixing e.g. Pre-Treated Waste Selective Catalytic Reduction Catalyst and Wollastonite, and Crushing. CN Patent CN110981199-A; CN110981199-B, 10 April 2020.

63. Son, B.T.; Long, N.V.; Nhat Hang, N.T. Fly ash-, foundry sand-, clay-, and pumice-based metal oxide nanocomposites as green functional microorganisms. J. Water Process Eng. 2022, 30, 601–610. [CrossRef]

64. Wang, B.; Yang, L. Extraction and separation of tungsten and vanadium from spent SCR catalyst catalyzed by ZnWO$_4$/TiO$_2$ modified chitosan biopolymer composite. J. Water Process Eng. 2022, 49, 102993. [CrossRef]

65. Ao, W.; Qu, J.; Yu, H.; Liu, Y.; Liu, C.; Fu, J.; Dai, J.; Bi, X.; Yuan, Y.; Jin, Y. TiO$_2$/activated carbon synthesized by microwave-assisted heating for tetracycline photodegradation. Environ. Res. 2022, 214, 113837. [CrossRef]

66. Mohan, H.; Vadivel, S.; Rajendran, S. Removal of harmful algae in natural water by semiconductor photocatalysis- A critical review. Chemosphere 2022, 302, 134827. [CrossRef][PubMed]

67. Shabir, M.; Yasin, M.; Hussain, M.; Shafiq, I.; Akhter, P.; Nizami, A.-S.; Jeon, B.-H.; Park, Y.-K. A review on recent advances in the treatment of dye-polluted wastewater. J. Ind. Eng. Chem. 2022, 112, 1–19. [CrossRef]

68. Li, X.; Simon, U.; Bekhheet, M.F.; Gurlo, A. Mineral-Supported Photocatalysts: A Review of Materials, Mechanisms and Environmental Applications. Energies 2022, 15, 5607. [CrossRef]

69. Gajera, R.; Patel, R.V.; Yadav, A.; Labhasetwar, P.K. Adsorption of cationic and anionic dyes on photocatalytic flyash/TiO$_2$ modified chitosan biopolymer composite. J. Water Process Eng. 2022, 49, 102993. [CrossRef]

70. Jin, Q.; Shen, Y.; Cai, Y.; Chu, L.; Zeng, Y. Resource utilization of waste V$_2$O$_5$-based deNO(x) catalysts for hydrogen production from formaldehyde and water via steam reforming. J. Hazard. Mater. 2020, 381, 120934. [CrossRef]

71. Li, Z.; Chang, Z.; Cai, Y.; Chu, L.; Zeng, Y. Resource utilization of vanadium from waste V$_2$O$_5$-WO$_3$/TiO$_2$ SCR Catalyst. Waste Biomass Valorization 2015, 6, 159–165. [CrossRef]

72. Kim, J.B.; Seol, D.-H.; Shin, H.K.; Kim, G.-J.; Kim, J.-H. Preparation and Characterization of Titania Nanoparticles from Titanium Tetrachloride and Titanium Sulfate Floucculation of Dye Wastewater. J. Jpn. Pet. Inst. 2010, 53, 167–172. [CrossRef]

73. Wang, Y.Z.; Chang, Z.D.; Blamo, B.J.; Wu, X.; Liu, S.X.; Li, W.J. Preparation of Photocatalytic Zn-3(VO$_4$)$_2$/ZnWO$_4$ from Waste V2O5-WO3/TiO2 SCR Catalyst. Waste Biomass Valorization 2017, 8, 2423–2430. [CrossRef]
74. 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. [CrossRef]

75. Ao, W.; Ding, H.; Sun, S.; Qian, X.; Jiang, C.; Jiang, J. Use of Waste Selective Catalytic Reduction Catalyst in Preparing Silicon Dioxide-Titanium Dioxide Composite Photocatalyst. CN Patent CN113145093-A, 23 July 2021.

76. Giannakoudakis, D.A.; Chatel, G.; Colmenares, J.C. Mechanochemical Forces as a Synthetic Tool for Zero- and One-Dimensional Titanium Oxide-Based Nano-photocatalysts. Top. Curr. Chem. 2019, 378, 2. [CrossRef]

77. Sajid, M.M.; Alomayri, T. Synthesis of TiO$_2$/BiVO$_4$ Composite and Cogitation the Interfacial Charge Transportation for Evaluation of Photocatalytic Activity. Arab. J. Sci. Eng. 2022. [CrossRef]

78. Zhang, L.; Meng, G.; Liu, B.; Ge, X. Heterogeneous photocatalytic ozonation of sulfamethoxazole by Z-scheme Bi$_2$WO$_6$/TiO$_2$ heterojunction: Performance, mechanism and degradation pathway. J. Mol. Liq. 2022, 360, 119427. [CrossRef]