



Recovery of vanadium and tungsten from waste selective catalytic reduction catalysts by K_2CO_3 roasting and water leaching followed by $CaCl_2$ precipitation

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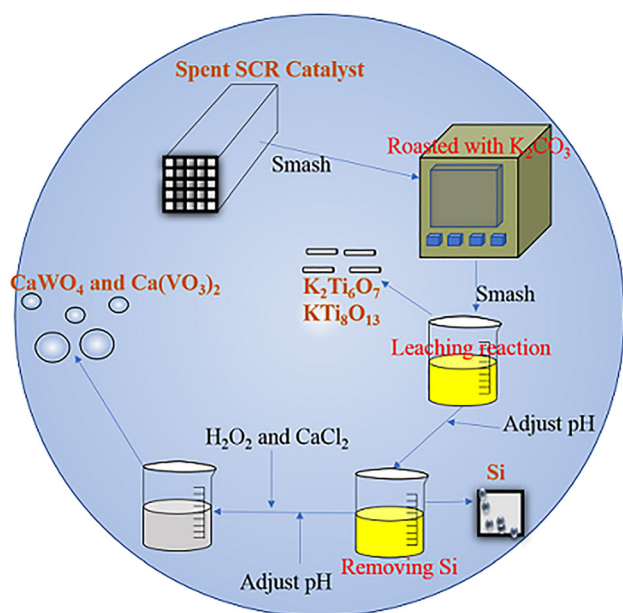
Abstract Waste selective catalytic reduction (SCR) catalysts are potential environmental hazards. In this study, the recovery of vanadium and tungsten from waste SCR catalysts by K_2CO_3 roasting and water leaching was investigated. The roasting and leaching conditions were optimized: the leaching efficiencies of vanadium and tungsten were 91.19% and 85.36%, respectively, when 18 equivalents of K_2CO_3 were added to perform the roasting at 900 °C for 2 h, followed by leaching at 90 °C for 1 h. Notably, in the described conditions, the leaching rate of silicon was only 28.55%. Titanates, including $K_2Ti_6O_{13}$ and KTi_8O_{17} , were also produced. Si removal was achieved in 85% efficiency adjusting the pH to 9.5, and the Si impurity thus isolated was composed of amorphous Si. Tungsten and vanadium were precipitated using $CaCl_2$. At pH 10 and following the addition of 0.10 mol of H_2O_2 and 16 equivalents of $CaCl_2$, the precipitating efficiencies of tungsten and vanadium were 96.89% and 99.65%, respectively. The overall yield of tungsten and vanadium was 82.71% and 90.87%, respectively.

Graphic abstract

Keywords Recovery · Waste SCR catalyst · K_2CO_3 roasting · Water leaching · $CaCl_2$ precipitation

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1 Introduction

Nitrogen oxide (NO_x) emissions can trigger environmentally hazardous phenomena like photochemical smog and haze (Du et al. 2011; Thomas 1997). Therefore, in recent years environmental laws on NO_x emissions have become increasingly strict in China. Due to its high efficiency and selectivity, the selective catalytic reduction (SCR) of NO_x by ammonia to produce water and molecular nitrogen is the most popular approach to cutting NO_x emissions (Forzatti 2001). The key component of SCR systems is the catalyst, which plays a fundamental role in the conversion of NO_x to N_2 . The $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst in NH_3 -SCR is widespread used in coal-fired power plants, as a result of the high activity of this catalyst and its tolerance to SO_2 (Baiker et al. 1992; Wang et al. 2019).

However, the lifespan of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst is limited by the activity of toxic substances present in flue gas, such as SO_2 , K_2O , CaO , As_2O_3 , and HgO (Kong et al. 2015; Li et al. 2016a, b; Li et al. 2018; Nicosia et al. 2007; Qi et al. 2017; Xu et al. 2017; Zhang et al. 2014). After several regenerations, these catalysts have been observed to become unable to catalyze NO_x SCR (Huo et al. 2015; Wu et al. 2016). Notably, waste catalysts contain leachable hazardous metals, a trait that contributes to environmental concerns associated with their storage and disposal (Imtiaz et al. 2015). The hazardous metal-based species present in SCR catalysts, such as WO_3 , V_2O_5 , As_2O_3 , and HgO , are known to be harmful to the environment and human health. On the other hand, the metals in waste catalysts are valuable (Wu et al. 2018), so recovery of such metals from the

spent catalysts is a prime environmental and economic objective.

The recovery of vanadium (V) and tungsten (W) from waste catalysts has been studied by several methods, including acid leaching, sodium hydroxide leaching, and salt roasting followed by leaching with water. Some researchers have used a range of acids to separate V from waste catalysts (Li et al. 2014). Li et al. (2016a) compared the separation efficiency of V afforded by several acids. Results from this study indicated the order of leaching ability of the various acids to be hydrochloric acid > oxalic acid > sulfuric acid > nitric acid. However, the leaching efficiency of V as made possible by acids is limited, and, applying the relevant approach, V is found in solution as a complex mixture of species. Therefore, investigating V recovery from solution is a very difficult undertaking and no further research on precipitating vanadium-containing species from acid solutions was conducted. Many researchers have shown interest in sodium hydroxide leaching. Kim et al. (2015) found that the leaching efficiency of W and V can reach values of 99.9% and 86.6%, respectively, at high temperature and pressure. Other researchers obtained similar results at atmospheric pressure (Huo et al. 2015; Wu et al. 2016). However, large amounts of hydroxides were observed to be needed in these studies. Unfortunately, excessive concentrations of sodium hydroxide in solution proved harmful to the reaction equipment and to further research about purify valuable metals.

Salt roasting followed by water leaching is another approach to W and V recovery from SCR catalysts. Na_2CO_3 and NaCl used to be widely employed as leaching agents in metallurgy (Shi et al. 2011; Zhao et al. 2016). Since NaCl roasting causes the release of harmful gas, researchers prefer to use Na_2CO_3 as leaching agent in the extraction of W and V from waste SCR catalysts. The leaching efficiency of W and V by Na_2CO_3 roasting and water leaching has been found to be considerable (Choi et al. 2018a). However, the leaching efficiency of silicon (Si) in waste catalyst was neglected, and few researchers pay attention to the leaching efficiency of Si in the roasting and leaching process. Importantly, the presence of Si in solution was found to negatively influence the efficacy of the subsequent steps, such as precipitation valuable metals W or V.

K_2CO_3 has been observed to easily react with W, V, and Si and other elements (Al, Ca and so on) and some of silicates (like CaSiO_3 , KAlSiO_8) were insoluble (Eliasson et al. 2007; Mu and Su 2009). As a result of the fact that the amount of Si and a bit of Al in waste catalyst were substantial, and it was larger than that of valuable metals (Choi et al. 2018a), the K_2CO_3 roasting method was put forward to reduce the amount of leached Si. And the more insoluble

aluminosilicate was expected. In fact, the potassium titanate obtained following K_2CO_3 roasting is widely used, for instance, as insulation and electrical insulation material (Cao et al. 2019; Li et al. 2019), rendering it more valuable than sodium titanate. In the present study the conditions for the recovery of vanadium and tungsten from waste SCR catalysts by way of K_2CO_3 roasting and water leaching were investigated. Notably, some soluble Si compounds were inevitably generated as part of the said recovery process; therefore, a procedure to remove Si from solution was also needed. Since the silicic acid precipitation or silicic acid gelatine were generated with acid added, the pH of the solution was adjusted with acid to cause these Si compounds to precipitate. Subsequently, in order to maximize the amount of recovered metals, $CaCl_2$ was added to the filtered solution to prompt the precipitation of the desired W and V compounds.

2 Materials and methods

2.1 Materials and analytical instrumentation

2.1.1 Waste SCR catalyst

The spent commercial honeycomb monolith catalyst was collected from a coal-fired power plant in China. The catalyst was purged to remove the fly ash present on its surface. The catalyst was then mashed to under $149\ \mu\text{m}$ in size in advance of the experiments described below. The powders were dried in an oven at $95\ ^\circ\text{C}$ for 24 h. A 0.1 g sample of waste catalyst was digested using a mixture consisting of 10 mL of HNO_3 , 2 mL of HF, and 2 mL of H_2O_2 ; the digested material was then analyzed by inductively coupled plasma-atomic emission spectroscopy. The waste catalyst investigated in this study includes elements Ti, V, Si, and W, each present in a weight ratio of 46.97%, 0.58%, 4.23%, and 3.21%, respectively. The X-ray diffraction (XRD) pattern of the waste catalyst is reported in Fig. 1. The main phase of the waste catalyst was anatase TiO_2 , with no obvious phases of other ingredients, due to their low contents (Choi et al. 2018a).

2.1.2 Chemicals and analytical instrumentation

K_2CO_3 , $CaCl_2$, and hydrogen peroxide were of analytical reagent grade and were provided by Beijing Chemical Industry. Hydrochloric acid, nitric acid, hydrofluoric acid of analytical reagent grade were provided by Sinopharm Chemical Reagent Co., Ltd. Structural investigations of crystalline phases were conducted by XRD (X'Pert Pro, Holland). The concentrations of V, W, and Si in solution were determined using an inductively coupled plasma-

atomic emission spectrometer (Prodigy 7, USA). The particle morphology of the leaching residue was investigated using a scanning electron microscope (SU8020, Japan).

2.2 Experimental procedures

2.2.1 Roasting and leaching experiments

A series of samples prepared pooling together a variable amount of K_2CO_3 and a fixed amount of waste catalyst were mixed for 0.5 h in a corundum crucible. The obtained mixtures were placed in a muffle furnace and roasted under the desired conditions at ambient atmosphere. The product thus obtained was allowed to cool to room temperature. It was then mixed with a fixed amount of deionized water (300 mL) in a glass beaker after milled under $149\ \mu\text{m}$. The beaker was then covered, and its contents were stirred with a magnetic stirrer at the certain leaching conditions. The mixture was then filtered, and the residue was washed with deionized water. The filter residue was dried, whereas the filtrate was collected to determine its V, W, and Si contents. After optimizing the roasting and leaching conditions, the filtrate obtained implementing the optimal roasting conditions was collected and used in subsequent experiments. The XRD patterns of the roasted products were collected, and scanning electron microscopy (SEM) images of the TiO_2 leaching residue were recorded and inspected.

2.2.2 Si removal

Since the presence of large amounts of Si in solution is not conducive to the precipitation of W and V compounds, the pH of the filtrate was adjusted to a certain value with dilute

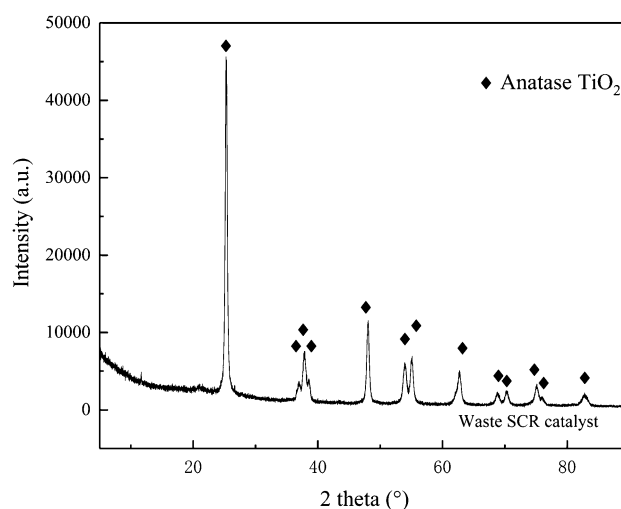


Fig. 1 X-ray diffraction pattern of the waste selective catalytic reduction (SCR) catalyst

hydrochloric acid to trigger the precipitation of silicon compounds. In detail, the mixture was kept at room temperature after the pH reached a value of 9.0. Subsequently, the sediment containing the Si-based impurity was filtered, and its XRD pattern was recorded.

2.2.3 Precipitation of W and V compounds

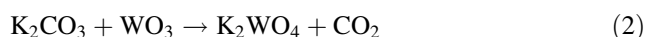
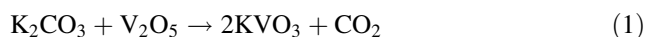
After silicon removal, CaCl_2 was added to the solution to afford the recovery of W and V. The solution containing W and V was stirred in a polytetrafluoroethylene beaker. The pH of the solution was adjusted to a certain value with a sodium hydroxide solution. Various amounts of a H_2O_2 solution (mass ratio: 30%) and solid CaCl_2 were added in the beaker. After the mixture was kept in the beaker at $90\text{ }^\circ\text{C}$ for 1 h, it was filtered. The filter residue contained precipitates of W and V compounds.

3 Results and discussion

3.1 Roasting and leaching

3.1.1 Effect of the roasting temperature on V, W, and Si leaching efficiency

As a result of the roasting process, V_2O_5 and WO_3 present in the spent catalyst were expected to generate the water-soluble KVO_3 and K_2WO_4 . The relevant chemical reactions are reported below. The amount of K_2CO_3 to be added was calculated based on the stoichiometry of the reactions described by Eqs. (1) and (2), disregarding any reaction between K_2CO_3 and other catalyst components.



The effect of the roasting temperature was initially investigated adding 14 equivalents of K_2CO_3 and performing the roasting process over 2 h. Subsequently, water leaching was conducted at $90\text{ }^\circ\text{C}$ for 1 h. Data reflecting the leaching efficiency of V, W, and Si are reported in Fig. 2. In the present study, the leaching efficiency of V was higher than that of W, indicating that V extraction from the catalyst was easier to perform. As the calcination temperature increased from 600 to $900\text{ }^\circ\text{C}$, the leaching efficiency of V and W increased by 5% and 29%, respectively. By contrast, as the calcination temperature increased further to $1000\text{ }^\circ\text{C}$, the leaching efficiency of both V and W decreased. This observation may be due to the presence of Ca in the catalyst. In fact, at high roasting temperatures, the water-insoluble CaWO_x and CaVO_x may be generated (Choi et al. 2018a). Notably, the leaching rate of Si

increased with the roasting temperature, with the leaching efficiency of Si displaying the opposite trend to V and W from 900 to $1000\text{ }^\circ\text{C}$. The presence of Si in the form of water-soluble compounds may negatively affect the extraction of W and V. At the roasting temperature of $900\text{ }^\circ\text{C}$, the leaching efficiency of W and V was 78.69% and 83.31%, respectively, whereas the leaching rate of Si was only 28.55%. Hence, at this roasting temperature, most Si remained in the filter residue. Evidence thus suggests that Si underwent complex reactions with other components of the spent catalyst or that a substantial proportion of Si-based compounds did not react with K_2CO_3 . By contrast, most W and V were extracted selectively. Therefore, a roasting temperature $900\text{ }^\circ\text{C}$ was utilized in the experiments that followed.

The XRD patterns of the filter residues obtained applying different roasting temperatures were also recorded. As can be evinced from Fig. 3, the intensity of the peak due to anatase TiO_2 decreased as the roasting temperature increased. In fact, increasing amounts of titanates, like $\text{K}_2\text{Ti}_6\text{O}_{13}$ and $\text{KTi}_8\text{O}_{17}$, formed as the roasting temperature increased. No obvious peaks attributable to compounds containing W and V were visible, due to their low abundance.

3.1.2 Effect of the relative amount of added K_2CO_3 on V, W, and Si leaching efficiencies

The leaching process was carried out after varying amounts of K_2CO_3 had been added to the spent catalyst for sample roasting, which was performed at $900\text{ }^\circ\text{C}$ for 2 h. The amount of added K_2CO_3 ranged from 8 to 20 equivalents,

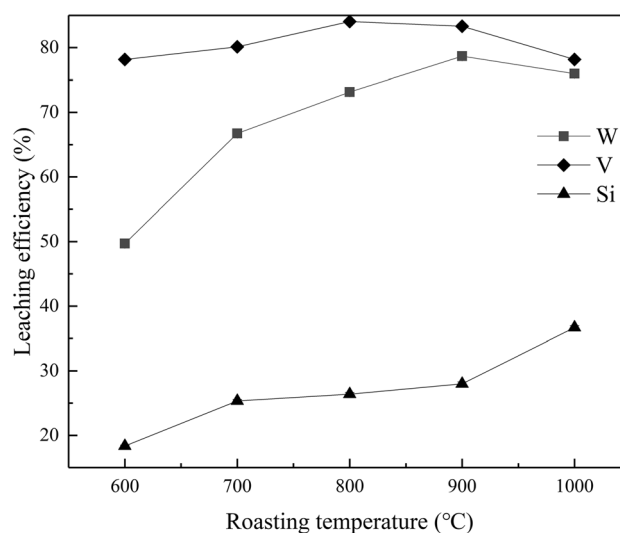


Fig. 2 Effect of the roasting temperature on the leaching efficiency of V, W, and Si. Experimental conditions: amount of K_2CO_3 added to the spent catalyst, 8 equivalents; roasting time, 2 h; leaching temperature, $90\text{ }^\circ\text{C}$; leaching time, 1 h

based on Eqs. (1) and (2). The other conditions were those described in Sect. 3.1.1. The data in Fig. 4 indicate that the leaching efficiency of V, W, and Si increased as the amount of added K_2CO_3 increased from 8 to 18 equivalents. Importantly, sufficiently high amounts of K_2CO_3 can inhibit the formation of calcium vanadate (Xing et al. 2010). However, the leaching rate of W decreased as the amount of added K_2CO_3 increased from 18 to 20 equivalents, whereas the leaching efficiency of V remained constant. Notably, increases in the amount of added K_2CO_3 favored Si leaching from the SCR catalyst, which in turn would make the solution thick and sticky. Considering leaching efficiency and material cost, we decided to add 18 equivalents of K_2CO_3 to the SCR catalyst in subsequent experiments.

The XRD patterns of the filter residues are reported in Fig. 5. Larger amounts of added K_2CO_3 favored the formation of titanates. Additionally, $Ca(Si_2O_7)(OH)_6$ formed when 18 and 20 equivalents of K_2CO_3 were added, indicating that Ca and Si were activated in the described conditions. The lower leaching efficiency of Si was probably caused by $Ca(Si_2O_7)(OH)_6$. Additionally, some $CaWO_x$ may be generated as Ca gets further activated, which might also negatively affect W leaching efficiency (Choi et al. 2018b). No obvious peaks due to anatase TiO_2 were visible when the amount of added K_2CO_3 was higher than 14 equivalents.

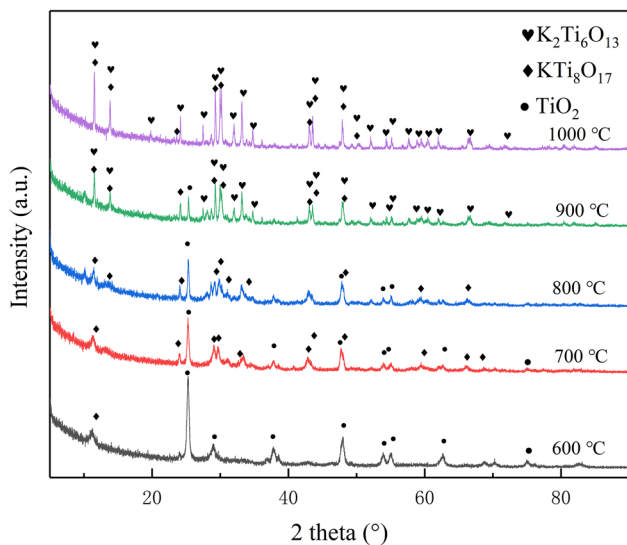


Fig. 3 X-ray diffraction patterns of roasted products obtained at different roasting temperatures. Experimental conditions: amount of K_2CO_3 added to the spent catalyst, 8 equivalents; roasting time, 2 h; leaching temperature, 90 °C; leaching time, 1 h

3.1.3 Effect of roasting time on V, W, and Si leaching efficiency

The effect that applying different roasting times, from 1 to 5 h, had on V, W, and Si leaching efficiency was examined; the results of the relevant experiments are reported in Fig. 6. The importance of the roasting time has been evaluated in many studies. Herein, the leaching process was carried out in the following conditions: roasting temperature, 900 °C; leaching temperature, 90 °C; leaching time, 1 h.

The leaching efficiency of V and W increased as the calcination time increased from 1 to 2 h. As the calcination time was extended further, no effect was measured on W and V extraction efficiency. By contrast, the leaching efficiency of Si increased with the calcination time. The XRD patterns of the filter residues isolated after applying different roasting times are reported in Fig. 7, which indicated that the roasting time was helpless to change the crystal form of the filter residue. Therefore, a roasting time of 2 h was applied in the experiments that followed.

3.1.4 Effect of the leaching temperature on V, W, and Si leaching efficiency

Applying a suitable leaching temperature can cause increased amounts of metal ions to dissolve in water. Experiments were conducted whereby the leaching temperature was made to vary from 30 to 120 °C using an oil bath (Fig. 8). The rest of the experimental conditions were those described above. At leaching temperatures below 90 °C, the leaching efficiency of V and W was below 80%.

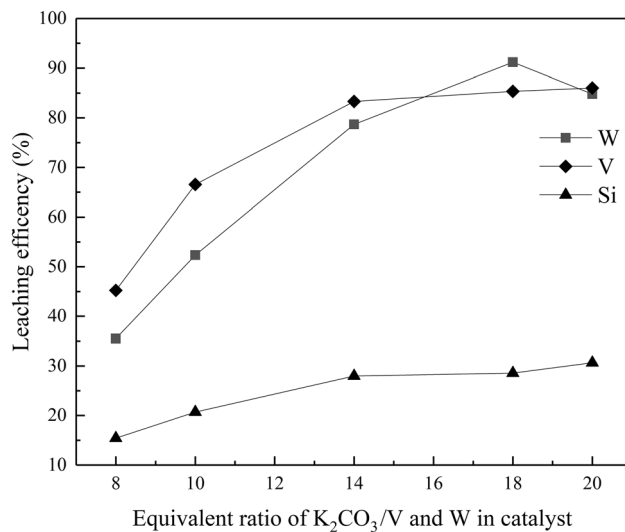


Fig. 4 Effect of the amount of K_2CO_3 added to the spent catalyst on the leaching efficiency of V, W, and Si. Experimental conditions: roasting temperature, 900 °C; roasting time, 2 h; leaching temperature, 90 °C; leaching time, 1 h

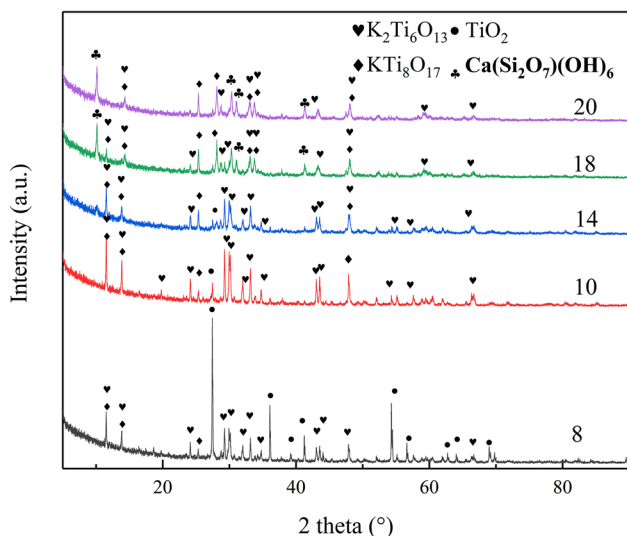


Fig. 5 X-ray diffraction patterns of roasted products obtained after adding different numbers of equivalents of K_2CO_3 to the spent catalyst. Experimental conditions: roasting temperature, $900\text{ }^\circ\text{C}$; roasting time, 2 h; leaching temperature, $90\text{ }^\circ\text{C}$; leaching time, 1 h

V exists in various forms in aqueous solution which caused V was easily to leach out below $60\text{ }^\circ\text{C}$. However, V combines more easily than W with other elements, such as $CaVO_x$ and $BaVO_x$ (Cao et al. 2017; Choi et al. 2018b). Therefore, when the leaching temperature was above $60\text{ }^\circ\text{C}$, the leaching efficiency of W was observed to be higher than that of V. The leaching efficiency of V was 85.36% and that of W was 91.19% at a leaching temperature of $90\text{ }^\circ\text{C}$. As the leaching temperature rose above $90\text{ }^\circ\text{C}$, no obvious impact was observed on the leaching

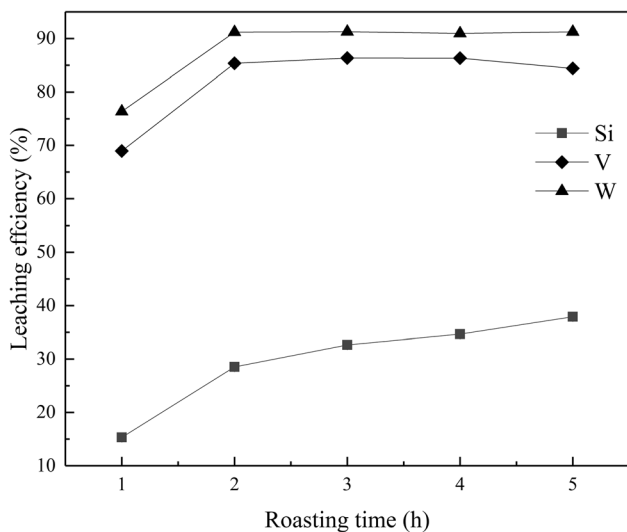


Fig. 6 Effect of the roasting time on V, W, and Si leaching efficiency. Experimental conditions: amount of K_2CO_3 added to the spent catalyst, 18 equivalents; roasting temperature, $900\text{ }^\circ\text{C}$; leaching temperature, $90\text{ }^\circ\text{C}$; leaching time, 1 h

efficiency of V and W. Importantly, the leaching temperature also affected the extraction of Si from the catalyst. Considering the leaching efficiency of valuable metals and the cost of the procedure, a leaching temperature of $90\text{ }^\circ\text{C}$ was utilized in subsequent experiments.

3.1.5 Effect of leaching time on V, W, and Si leaching efficiency

The effect of the leaching time was also investigated. Leaching experiments were conducted employing 30, 60, 90, 120, and 150 min as the leaching time. As can be evinced from Fig. 9, the leaching percentage of W and V significantly increased as the leaching time was extended from 30 to 90 min. At short leaching times, V leached out more promptly than W, given the multiple V-based species present in solution (Wu et al. 2018). Notably, W and V leaching efficiency did not change as the leaching time was extended over 90 min. By contrast, Si leaching efficiency did not markedly increase with the leaching time. The optimal leaching time for extracting W and V was thus determined to be 90 min.

3.1.6 SEM images of the leaching residue

As can be evinced from Fig. 10a, some rod structures as skeleton were not destroyed by K_2CO_3 treatment, which was one reason that most Si did not leach out. Si and Ca compounds present in the skeleton did not react with K_2CO_3 , explaining why Ca presence did not negatively affect vanadium leaching efficiency. By contrast,

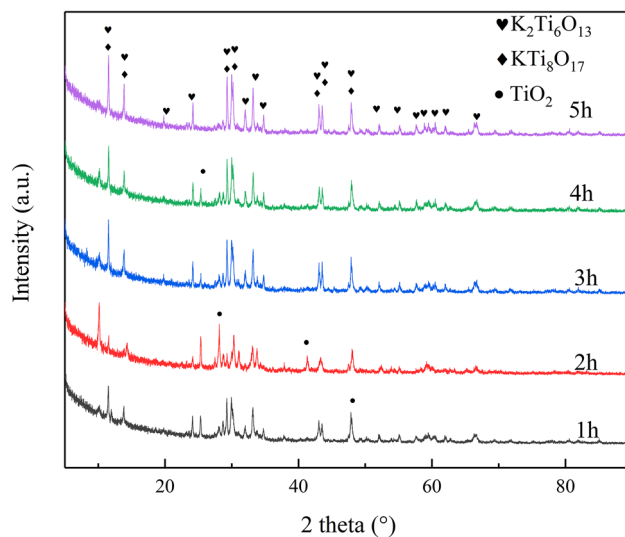


Fig. 7 X-ray diffraction patterns of roasting products obtained applying different roasting times. Experimental conditions: amount of K_2CO_3 added to the spent catalyst, 18 equivalents; roasting temperature, $900\text{ }^\circ\text{C}$; leaching temperature, $90\text{ }^\circ\text{C}$; leaching time, 1 h

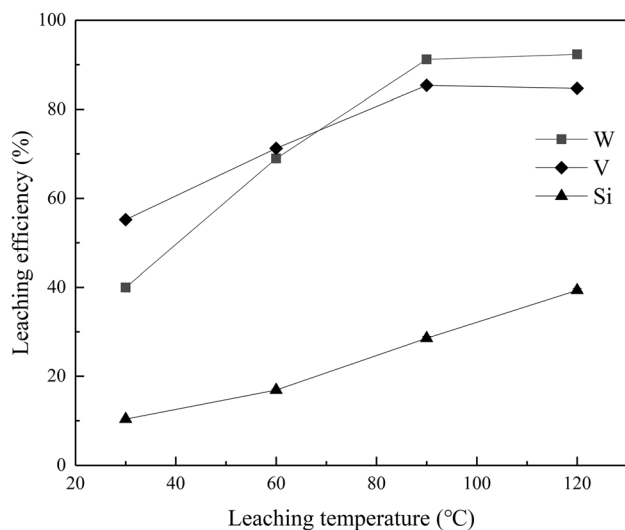


Fig. 8 Effect of the leaching temperature on V, W, and Si leaching efficiency. Experimental conditions: amount of K_2CO_3 added to the spent catalyst, 18 equivalents; roasting temperature, 900 °C; roasting time, 2 h; leaching time, 1 h

potassium titanate whiskers, appearing as rod and stick structures in Fig. 10b, c, were observed, which may be applied to other fields.

3.2 Si removal

Silicon present in the spent SCR catalyst may not only produce the skeleton structure, but it may also inhibit TiO_2 phase transition from the anatase to the rutile form (Hanaor and Sorrell 2011). Considering that Si present in solution may negatively affect W and V recovery, Si removal was performed adjusting the pH of the solution.

The leaching solution obtained after implementing the optimized roasting and leaching conditions was collected, and the W, V, and Si contents were measured. The solution pH was adjusted at this point, before centrifugal filtration. Data on the removal efficiency of W, V, and Si at different values of the solution pH are reported in Fig. 11. Evidence

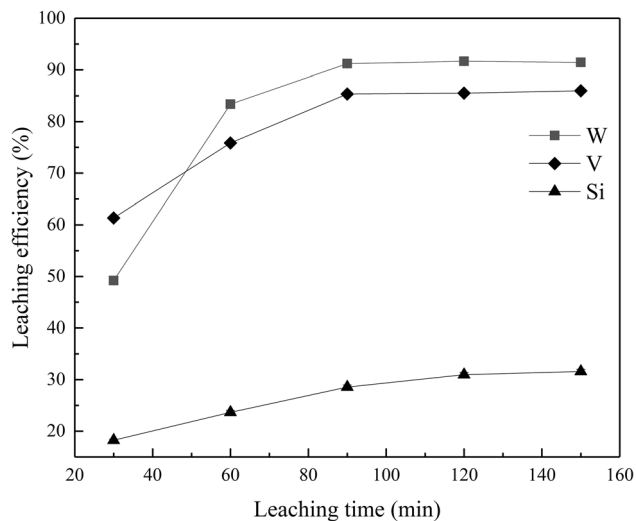


Fig. 9 Effect of the leaching time on V, W, and Si leaching efficiency. Experimental conditions: amount of K_2CO_3 added to the spent catalyst, 18 equivalents; roasting temperature, 900 °C; roasting time, 2 h; leaching temperature, 90 °C

indicates that as the pH increased, the loss rate of W and V decreased.

At pH 9.5, the removal rate of Si was 85.19%, whereas the loss rate of W and V was under 5%. The XRD pattern of the Si impurity indicated that Si was amorphous and that some KCl had separated out (Fig. 12). Notably, Si was present in ions state with the solution at pH > 13, whereas H_2SiO_3 or H_4SiO_4 formed at lower pH values.

3.3 Precipitation of W and V

3.3.1 Effect of the pH on W and V precipitation rates

A waste SCR catalyst leaching experiment was conducted implementing the optimized conditions for roasting, leaching, and impurity removal. The solutions containing W and V thus obtained were then pooled together, and the resulting liquid sample was subdivided into several

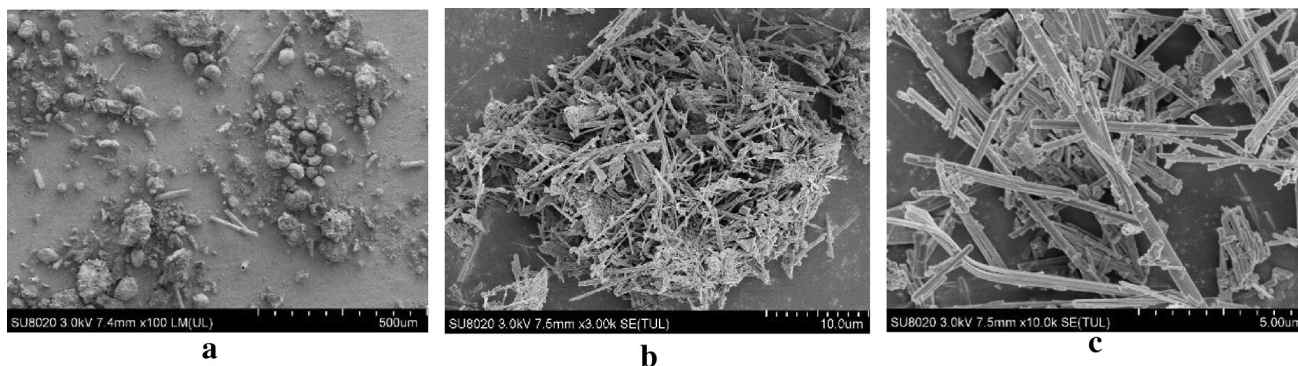


Fig. 10 Scanning electron microscopy micrographs of leaching residues (a: 500 μm; b: 10 μm; c: 5 μm)

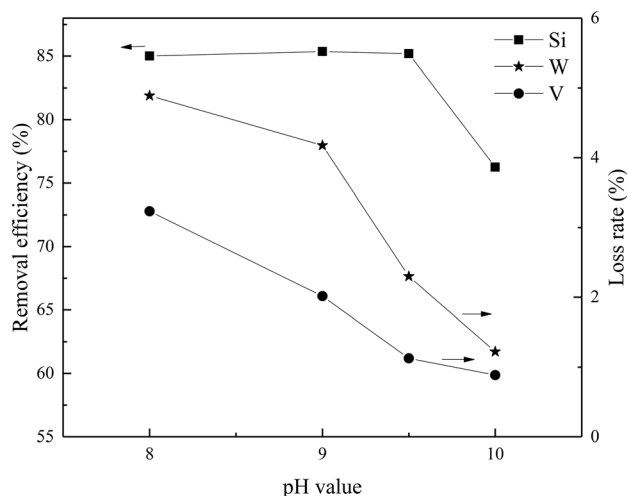


Fig. 11 Effect of the solution pH on the removal efficiency and loss rate of V, W, and Si

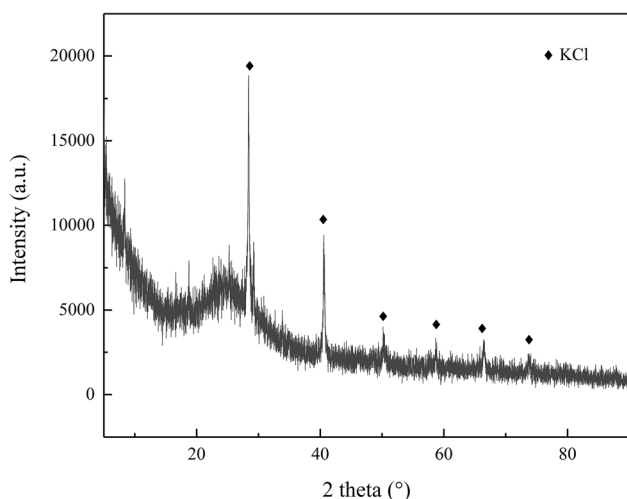
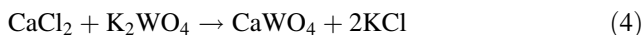
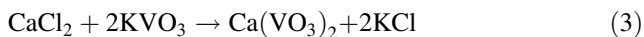


Fig. 12 X-ray diffraction pattern of the Si impurity

aliquots of equal volume. The W and V concentrations in the pooled solution were 7.13 mg/mL and 1.26 mg/mL, respectively. Notably, at this point W and V are expected to precipitate from solution in the form of CaWO_4 and $\text{Ca}(\text{VO}_3)_2$, respectively. The recycled CaWO_4 could be the feed material for W-related products (Martins et al. 2007).

The amount of CaCl_2 to be added to the solution to prompt W and V precipitation was calculated based on the reactions described by Eqs. (3) and (4). In particular, 10 equivalents of CaCl_2 were added on the basis of the theoretical reaction stoichiometries.



The pH of the filtrate after Si removal, a parameter affecting the precipitation rates of W and V, was about 9.

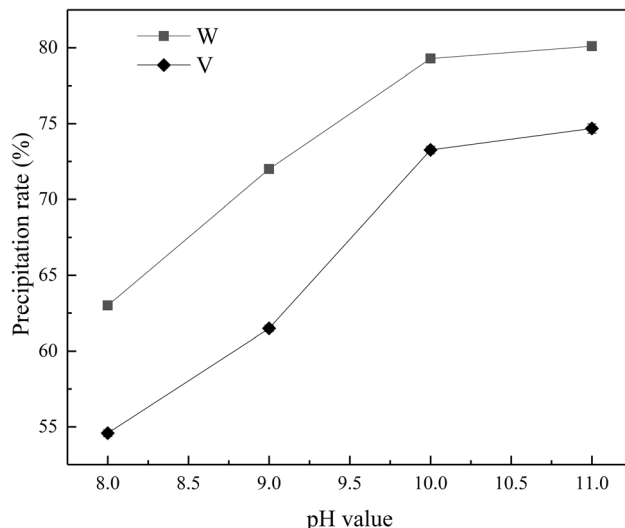


Fig. 13 Effect of pH on the precipitation rates of W and V. Notably, no H_2O_2 was added to the filtrate obtained after Si removal, and 10 equivalents of CaCl_2 were added to it

The precipitation reaction was conducted in a beaker at 90 °C for 1 h. The effect on W and V precipitation of the pH of the filtrate before precipitation was investigated. The data in Fig. 13 indicate that the proportions of W and V ions that precipitated increased as solution pH increased from 8.0 to 10.0. Moreover, the precipitation efficiency of W and V did not show any obvious changes as the pH increased further above 10. Notably, $\text{Ca}(\text{OH})_2$ forms at around pH 11.0, and the presence of this compound is known to have no positive effect on W and V precipitation (Choi et al. 2018a).

3.3.2 Effect of H_2O_2 addition on the precipitation rate of W and V

CaWO_4 is known not to be produced in solution from low-valence W ions, and complex mixtures of Ca–V salts have been observed to be produced from solutions containing V ions of different valence (Wu et al. 2018). Considering that low-valence W and V ions may appear in the solution obtained after Si removal, it was necessary to oxidize low-valence W and V ions to high valence. The addition of H_2O_2 to the filtrate was investigated for this purpose. Results from the relevant experiments (Fig. 14) indicated that H_2O_2 addition was necessary to maximize W and V precipitation. The precipitate efficiency of W and V improved by 6.6% and 15.0%, respectively, when 0.10 mol of H_2O_2 was added to the filtrate. Notably, H_2O_2 addition may contribute to the transformation of different W and V-based species into a single one.

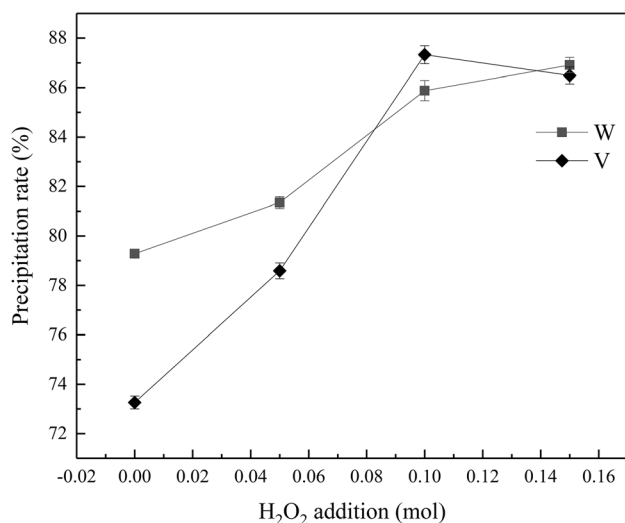


Fig. 14 Effect of H_2O_2 addition on the precipitation rates of W and V. Experimental conditions: amount of $CaCl_2$ added to the filtrate obtained after Si removal, 10 equivalents; filtrate pH, 10

3.3.3 Effect of adding different amounts of $CaCl_2$ on the precipitation rate of W and V

The precipitation efficiency of W and V was limited, so the effect of adding varying amounts of $CaCl_2$ to the filtrate obtained after Si removal was also investigated. The results of the relevant experiments indicate that W and V precipitation efficiency improved as the amount of added $CaCl_2$ increased. As can be evinced from Fig. 15, W and V precipitation efficiency reached 96.89% and 99.65%, respectively, when 16 equivalents of $CaCl_2$ were added.

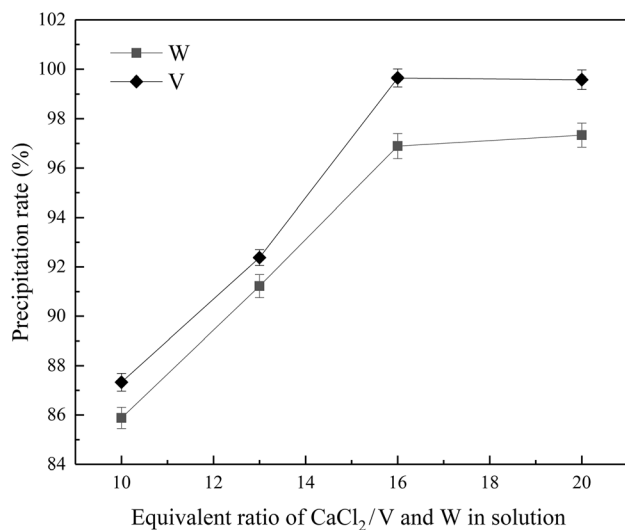


Fig. 15 Effect of adding of a different number of equivalents of $CaCl_2$ to the solution on W and V precipitation rates. Experimental conditions: pH of the filtrate obtained after Si removal, 10; amount of H_2O_2 added to the said filtrate, 0.10 mol

The addition of this relative amount of $CaCl_2$ was thus considered optimal for the experiment.

4 Conclusions

A K_2CO_3 roasting and water leaching protocol for the recovery of V and W from waste SCR catalysts was developed and optimized in the present study. The best conditions for the roasting stage were as follows: roasting time, 2 h; roasting temperature, 900 °C; equivalents of added K_2CO_3 , 18. On the other hand, the optimal conditions for the leaching process consisted of a leaching time of 1 h and a leaching temperature of 90 °C. The leaching efficiency of W and V reached values of 85.36% and 91.19%, respectively, under optimal roasting and leaching conditions; by contrast, the leaching efficiency of Si was below 28.55% in the described conditions. Notably, Si removal efficiency reached 85% as the solution pH was adjusted to 9.5. $CaCl_2$ was used to precipitate W and V from solution after Si removal. The effects on W and V precipitation efficiency of the pH of the solution before precipitation and of adding H_2O_2 to the said solution were investigated. Precipitation efficiency reached values of 96.89% and 99.65% for W and V, respectively, when the pH of the solution obtained after Si removal was adjusted to 10, before 0.10 mol of H_2O_2 and 16 equivalents of $CaCl_2$ were added to the said solution. The overall yield of W and V was 82.71% and 90.87%. Finally, XRD and SEM analyses of the residue obtained after carrying out the leaching procedure indicated this residue consists mainly of potassium titanate whiskers.

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Data availability All the data were collected in the experiments.

Code availability Not applicable.

Compliance with ethical standards

Conflict of interest No conflicts of interest between authors.

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