Recovery of Vanadium as Iron Vanadate ($FeVO_4$) from Spent Sulfuric Acid Catalysts Using Oxalic Acid Leaching

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Abstract. Abstract. Used sulfuric acid catalysts are a hazardous industrial waste and also a secondary resource enriched with valuable transition metals such as iron (Fe) and vanadium (V), which can be recycled. Improper disposal poses a severe impact on environmental pollution, while the material can easily be recycled for producing next-generation materials. This study deals with valorization and selective recovery of iron vanadate ($FeVO_4$) from a used sulfuric acid catalyst. This study proposed a hydrometallurgical method to recycle the vanadium component in used sulfuric acid catalysts, which involves the treatment with a 0.5 mol. L^{-1} oxalic acid solution under optimised conditions, such as a solid-liquid (S/L) ratio of 1:25 (g/mL), a temperature of 80°C, and stirring speed of 300 rpm. This procedure helps in the creation of a crystalline $FeVO_4$ material, which has been detected through X-ray diffraction (XRD) analysis, with a resultant recovery yield of approximately 20% vanadium. This synthesized material possesses a similar material structure to that which can be obtained from laboratory pure materials. This study, therefore, not only finds applications in producing $FeVO_4$ materials, which will have potential uses in the production of steel, batteries, and photocatalysis, etc., but also helps in recycling industrial waste material.

Keywords: Oxalic acid, Industrial catalysts, advance oxidation process; Iron vanadate.

1 Introduction

The sustainable management of industrial waste has been one of the significant environmental, economic, and technological issues over the last several decades. The metallurgical, mining, and chemical industries produce high volumes of solid and liquid residues which have high levels of transition metals especially iron (Fe) and vanadium (V). As much as these components are regarded as contaminants, they can also be recycled and used to produce high value functional materials. Such residues, in particular the spent catalysts in the production of sulfuric acid are particularly appealing due to the high quantities of recoverable metals present.

Within recent years, a rising interest has been gained in the recovery and reuse of metals in industrial wastes in order to create materials with concrete functional properties. Such an example is iron orthovanadate ($FeVO_4$), which has raised growing interest because of its outstanding photocatalytic, magnetic, and electrochemical properties. $FeVO_4$ has

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demonstrated a good potential of use in photocatalysis, lithium-ion battery electrodes and gas applications [1–4]. Most reported syntheses are however based on high-purity chemical reagents which are costly and not sustainable. Conversion of industrial residues which contain iron and vanadium directly to $FeVO_4$ is almost unexplored. This brings a major concern of the question that how is it possible to produce $FeVO_4$ using the secondary sources especially industrial wastes and retain similar structural and functional properties as those produced using pure reagents? Research conducted by Jinwei et al. [5] indicated that it is possible to make $FeVO_4$ using the industrial residues produced during the refining process of $TiCl_4$. They used a method that involved hydrometallurgical extraction paired with the control of pH levels of acidic leachates with recovery of vanadium in the 95 and above range. The article demonstrates that such approaches can be used to efficiently use waste streams of transition metals. Various $FeVO_4$ synthesis pathways are reported in scientific literature that encompass sol-gel, wet-chemical, microwave-assisted, hydrothermal, solid-state and precipitation processes [6]. Citing the example of Deng et al. [7], $FeVO_4$ was prepared by the wet-chemical method, and used as a catalyst in the Orange II dye degradation. Poizot et al. [8] also described low-temperature synthesis of crystalline $FeVO_4.1.1H_2O$ and tested its electrochemical activity, whereas Oka et al. [9] gained $FeVO_4$ -II crystals by hydrothermal route. Most recently, El Hasbaoui et al. [10] manages to recover mixed $FeVO_4$ and $AlVO_4$ phases in spent catalysts in the presence of different acids with or without H_2O_2 or even distilled water, under optimized conditions of leaching (solid-to-liquid 1:25 g/mL, 80 °C, 120 minutes). In this regard, the heroification of used catalysts is a two-fold advantage because it would reduce the impact of industrial wastes on the environment and also allow recovery of precious metals. The creation of easy, selective, and affordable methods of extracting vanadium, therefore, is a major goal. The current study can be added to this endeavor by addressing the process of recovering and converting vanadium into $FeVO_4$. The given approach involves the use of oxalic acid as a selective leaching agent at optimal operating conditions to facilitate the formation of $FeVO_4$ a compound with a great potential of being used in functional materials, steel industry as well as energy storage.

2 Material and methods

2.1 Chemicals and reagents

The catalyst used in the experiment was spent catalyst obtained from an industrial-scale sulfuric acid plant. The chemical composition of the catalyst is as follows: 1.9% vanadium (V), 0.6% Fe_2O_3, 1.8% Na_2O, 16% SO_3, and 65% SiO_2. The treatment process was done using oxalic acid ($H_2C_2O_4.2H_2O$), which was obtained from the Sigma-Aldrich chemical company, and the purity was 99%. The oxalic acid solution was prepared by dissolving the desired amount of the acid in the distilled water, and the concentration was 0.5 mol. L^{-1}. After the leaching process, the vanadium solution was treated by the addition of the ammoniacal precipitating agent in the form of the ammonia solution (NH_4OH), which has a concentration of 25%, to enable the precipitation of the iron vanadate ($FeVO_4$) compound.

2.1 Synthesis Procedure

The ground catalyst was first of all ground in a porcelain mortar and sieved through a mesh size of 250 µm in order to obtain a uniform particle size distribution. The resulting powder was dried at 100 °C over a span of 1 hour in an oven and then the powder was dried in a desiccator to inhibit future absorption of moisture before the chemical treatment. A 0.5 mol. L^{-1} oxalic acid solution was used in the leaching process and was stirred constant at 80 °C in 2 hours. After the treatment, the suspension was filtered under vacuum with the use of a 4 µm porosity filter that separated the solid residue and the filtrate that contained the dissolved

species of vanadium and iron. The potassium permanganate ($KMnO_4$) was added in small amounts to the filtered solution initially blue in color and its oxidation was subsequently continued by adding potassium permanganate ($KMnO_4$) **Fig.1**, which is a strong oxidizing agent [10], until a yellow solution was produced, which indicates that all of the vanadium has been reduced to its pentavalent form (V^{5+}), which is favorable in the precipitation of ferrovanadate. The aqueous ammonia ($NH_3.H_2O$, 1 N) was added to the solution gradually, under stirring, until the development of a stable precipitate of iron vanadate took place ($FeVO_4$). A filtering, drying and subsequent calcination of the precipitate at 600 °C using a given thermal profile (See **Fig.2**), were used to ensure that the crystallization of $FeVO_4$ occurred and this was confirmed using X-ray diffraction (XRD).

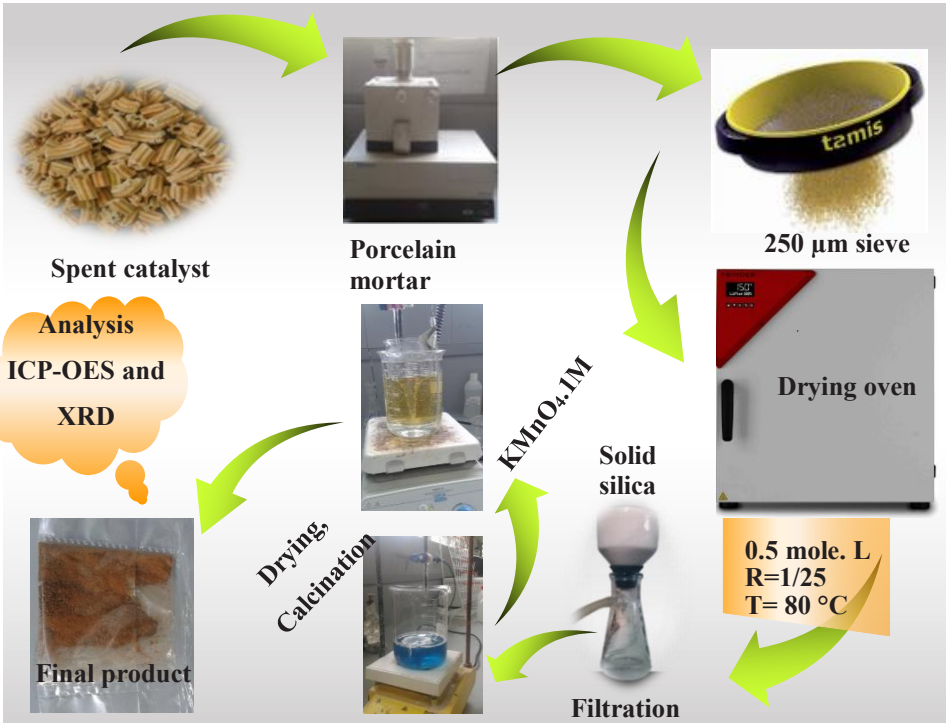

Fig. 1. Schematic Illustration of the $FeVO_4$ Valorization Process from Spent Vanadium-Based Catalyst.

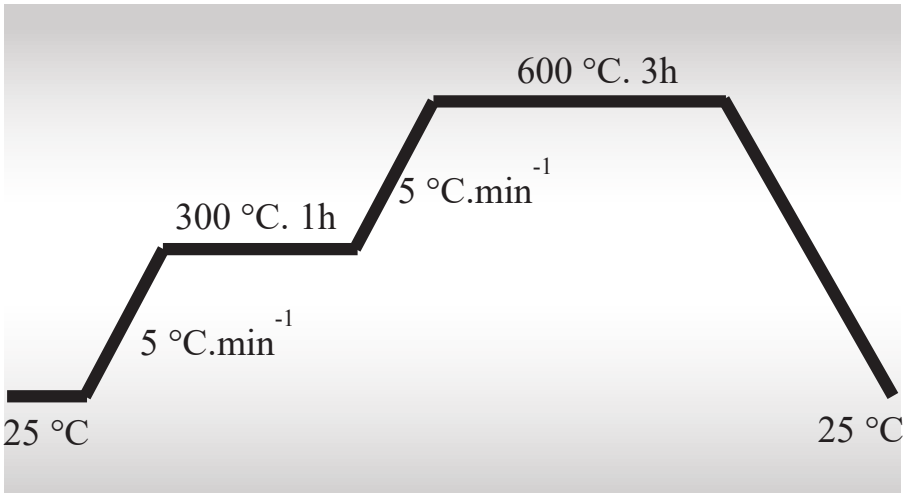

Fig. 2. Calcination profile of the recovered vanadium phase.

2.3. Characterization Techniques

The inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to analyze the chemical composition of the used catalyst and the products recovered. In this analysis, solid samples approximately 200 mg were digested through acid mineralization in Anton-Paar Multiwave Pro microwave digestion system, with 5 mL of the nitric acid (HNO_3, 65%) and 15 mL of the hydrochloric acid (HCl, 34-37%). The crystalline phases in the solid residues and final products were determined using X-ray diffraction (XRD). Bruker D8 Advance diffractometer was used in the analyses. SEM on a scanning electron microscope under this type of examination was used to study the surface morphology of the solid samples through Quanta 200 (FEI, USA).

3 Results and discussion

3.1 SEM Structural Characterization of Fresh and Spent Catalysts

The morphology of the surface of fresh and used catalysts was studied using scanning electron microscopy (SEM). The SEM images (**Fig.3**), show that there were major structural changes that took place after the oxidation reaction of sulfur dioxide (SO_2) to sulfur trioxide (SO_3). The new catalyst has surface structure of agglomerated particles with low porosity which is an indication of its original state before being used. Conversely, the used catalyst exhibits a significantly deformed morphology with the development of systematic, well-spaced block-like structures. Interestingly, one can observe rectangular facies that are about 70 μm in size and presumably relate to cristobalite that is a crystalline structure of silica. The spent catalyst also exhibits a drastic rise in the porosity of the surface. This morphological change is an indication of the high level of degradation of the material, which contributes to the pressure on the catalyst and the deactivation of catalysts, which marks the termination of the service life. In this regard, the retrieval of the active material, especially $FeVO_4$ becomes critical. Spending catalysts contain heavy metals and therefore pose health hazard to the environment without proper treatment. Hence, recycling and valorization of these materials is a crucial measure to reduce environmental impact as well as foster the principles of a circular economy in the catalytic industry.

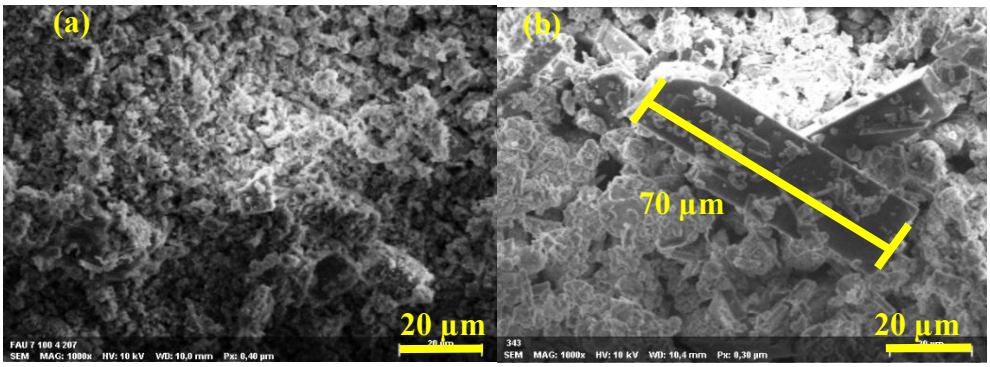

Fig. 3. SEM images of the catalyst: a) fresh, b) spent. On the right-hand side.

3.2 Characterization and Mass Balance of the Solid Residue and Final Solid Product

The X-ray diffraction (XRD) of the solid product after leaching with oxalic acid ($C_2H_2O_4.2H_2O$) is shown in **Fig.4**. The diffractogram shows that there is one crystallized phase which is crystobalite silica (SiO_2, ICPDS: 96-900-1579). This finding implies that the leaching process was fully separated and the active phase was completely separated with the support. In fact, every vanadium-containing phase dissolved successfully and silicate phase was the only remaining one in the solid residue. This is the selectivity of the leaching process that the active material can be separated to be potentially recovered or valorized.

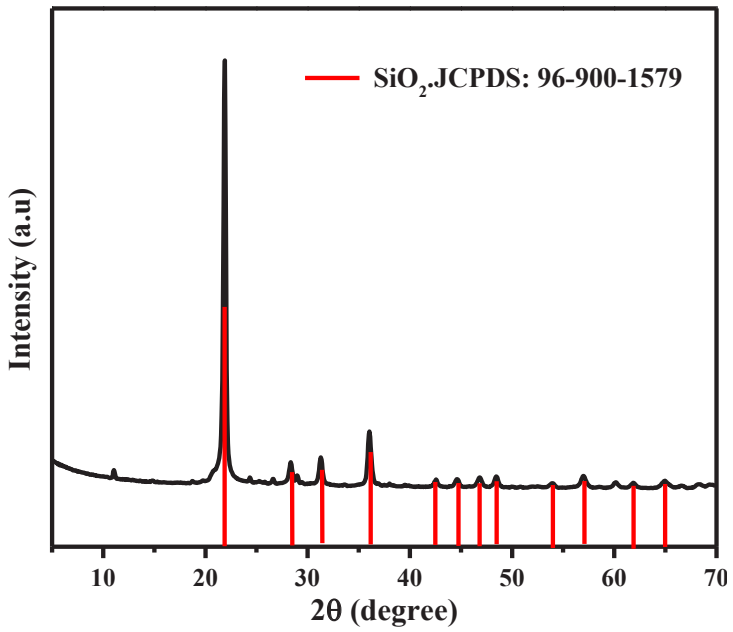

Fig. 4. XRD pattern of the final precipitate obtained by oxalic acid ($C_2H_2O_4.2H_2O$) leaching at 80°C.

The precipitate analysis that was conducted using inductively coupled plasma optical emission spectrometry (ICP-OES) showed that the precipitate obtained after the leaching process had a vanadium mass content of around 2.2% and an iron content of 1.4%. These

concentrations gave an estimate of the recovery yield of vanadium at approximately 20% using the following equation:

$$\text{Recovery yield (\%)} = \frac{\text{Mass of recovered vanadium}}{\text{Mass of vanadium in the spent catalyst}} \times 100$$

Table 1 provides the results. This recovery yield indicates the successful integration of vanadium into the precipitate phase which is largely in the form of iron vanadate ($FeVO_4$) and is accrued at neutral pH (see **Fig.5**). These observations demonstrate the effectiveness of the leaching process with the use of oxalic acid as it allows extracting and recovering vanadium in the spent catalyst selectively and partly.

Table 1. Chemical composition of the final solid determined by ICP-OES.

Element	Fe_2O_3 (%)	V (%)	SiO_2 (%)	SO_3 (%)	Vanadium Recovery Yield (%)
(wt. %)	1.4	2.2	1.1	3.0	20

The analysis of the X-ray diffraction is evident of the existence of an amorphous phase of iron vanadate ($FeVO_4$) that is associated with the reference pattern of JCPDS: 01-071-1592. Awad et al [4], in their article named Wet chemical synthesis and characterization of $FeVO_4$ nanoparticles as supercapacitor as energy storage device also confirm our experiment results in this phase. The consistency of the phases obtained with values reported in the literature supports the soundness of our strategy and evidences of the future of the synthesized $FeVO_4$, not just in terms of energy storage application, although it can also be viewed through the prism of valorizing hazardous waste obtained through the use of spent catalysts.

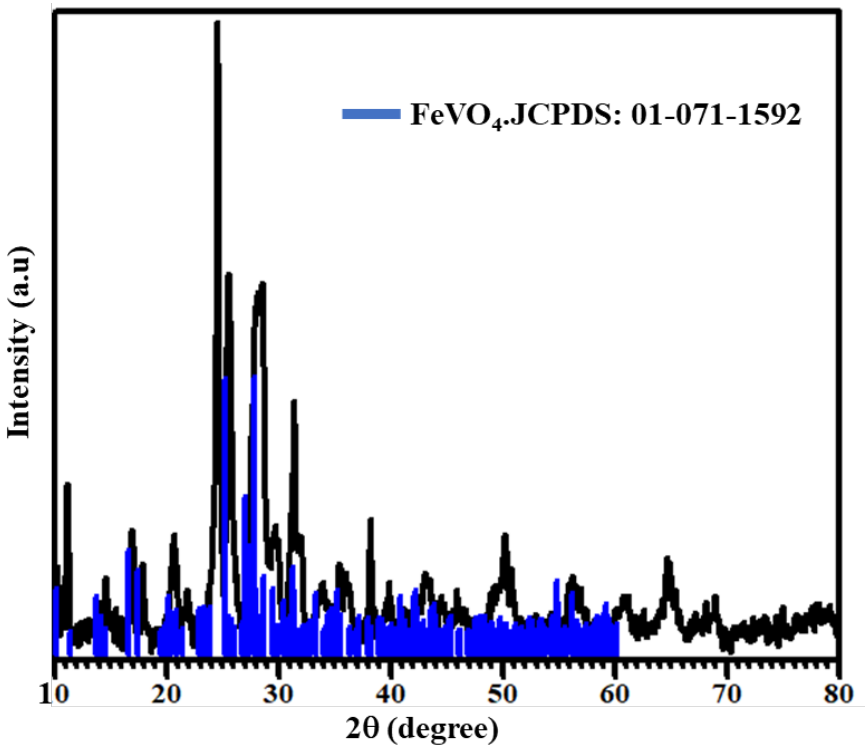

Fig. 5. XRD pattern of the final precipitate obtained by leaching with oxalic acid ($C_2H_2O_4.2H_2O$) at 80°C.

4 Conclusion

This study aimed at valorizing iron vanadate ($FeVO_4$) using a waste catalyst that was produced as a result of the oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3). To do this, a selective leaching procedure with the use of oxalic acid was generated to leach the vanadium bearing phase. At 80°C, leaching was done with a solution of 0.5 mol. L^{-1} oxalic acid. The solid residues were studied by X-ray diffraction (XRD) analysis and revealed the existence of well-crystallized silica, which was in the shape of cristobalite, whereas the precipitates formed after treatment were mainly iron vanadate phases with amorphous phase. ICP-OES elemental analysis showed that the vanadium recovery yield was about 20% in the final product obtained in $FeVO_4$ under the most favorable treatment. This compound has a specific potential in use in energy storage (including supercapacitors and batteries) and in the steel sector, with potential uses in both functional materials or metallurgical additive. These findings indicate the applicability of this simple and environmentally friendly technology in the valorization of vanadium rich industrial waste, and this technology will open the way to their incorporation into technological uses that are high in value.

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