







Insight studies on the deactivation of sulfuric acid regeneration catalyst

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Highlights

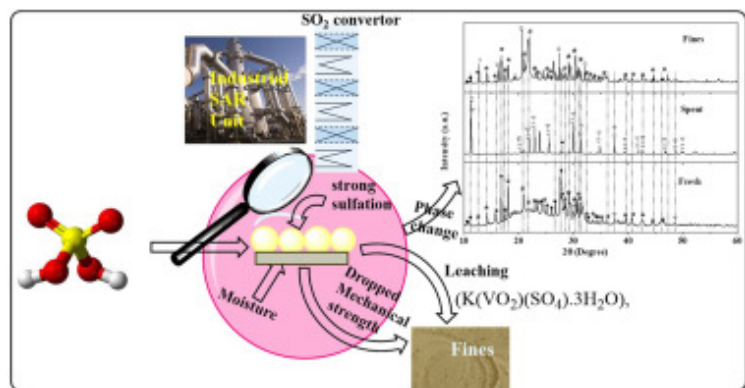
- Root-cause analysis of deactivation of Industrial SAR catalyst.
- Structural changes and their impact on catalyst property were determined using various physico-chemical characterization methods.
- Identified active phase leaching and determined undesired phase transformation of catalyst using XRD.
- Strong sulfation at catalyst surface validated using simulated experiment and FTIR analysis.

Abstract

The SAR unit is used for regenerating spent sulfuric acid for alkylation reactions. In the SAR unit, the converter employs a potassium and vanadium-based catalyst for conversion of SO₂ to SO₃. The multiple bed fixed bed reactor is there to ensure that almost entire amount of SO₂ is converted to

SO₃. On observing the generation of large amounts of fines in the reactor catalyst, the spent catalyst and fines are collected for insight studies. The current study enlightens the possible causes of catalyst deactivation and fines generation. Structural changes in potassium/vanadium based catalyst during the oxidation of sulfur dioxide identified as the major cause of catalyst deactivation. Such structural changes and their impact on catalyst property were determined using various physico-chemical characterization methods like crushing strength, Loss on drying (LOD), XRF, XRD, FTIR and XPS analysis. LOD analysis shows the higher moisture and volatile content in spent and fines compared to fresh catalyst. High moisture content in spent catalyst decreases hardness of catalyst resulting in leaching of vanadium salt and carrier degradation due to thermal cycling. Chemical analysis data found to show the active vanadium content in fines is higher compared to spent which indicates vanadium has leached out from fresh catalyst and is deposited on fines. These observations are further correlated with XRD and XPS results. XPS analysis shows the relative distribution of V⁴⁺ and V⁵⁺ species on the catalyst surface are altered and found very low concentration of V⁴⁺ sites on spent catalyst. The XRD analysis demonstrates the leaching of the active component, potassium vanadyl sulfate K(VO₂)(SO₄)·3H₂O, which then accumulated in the fines fraction. FT-IR and XRD results further shows increase in sulfate accumulation on spent catalyst surface along with phase changes. FTIR analysis of simulated spent catalyst are well correlated with these findings.

Graphical abstract



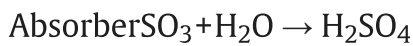
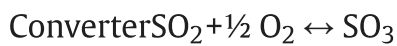
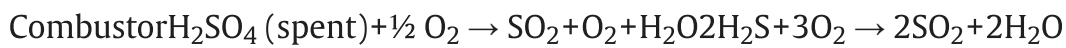
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Introduction

Sulfuric acid is an important commodity chemical with versatile applications for numerous process industries, such as fertilizer manufacturing, oil refining, chemical synthesis, pharmaceuticals, and lead-acid batteries [1]. To minimize the risk associated with its transportation, sulfuric acid production plants are usually located near their point of use, as it is a corrosive and risky chemical to transport. Alkylation identified as the most important organic reactions to produce many industrially relevant products over the decades. Alkylation in the refinery denotes to a process for making of high-octane motor fuel (gasoline range material) from the olefin derivatives [[1], [2], [3]]. Acid

catalysts, Sulfuric acid or HF, is well known for majority of industrial operations in this front [[1], [2], [3]]. Superfluous quantities of industrial waste acid create a serious threat to the environment. Hence, spent acid used for the alkylation would be safely disposed or used in other processes or regenerated back to pure and concentrated acid for reuse in the main process. The sulfuric acid regeneration (SAR) exists as supporting unit of majority of industrial alkylation units, with attention given to the organic and inorganic contaminants, overall water balance, and the desired product specifications. In alkylation plant, SAR unit designed to meet high purity sulfuric acid requirement, where the spent acid and H₂S oxidized to SO₂ in a high temperature furnace. SO₂ is then converted in to SO₃ using vanadium-based catalyst in a fixed-bed converter unit. Further, SO₃ is absorbed with H₂O in absorption tower to form H₂SO₄. The major reactions occur in the SAR process are depicted in equations (1)–(4) [4,5].



Among different steps, SO₂ to SO₃ conversion step (equation (3)) is decisive step for final sulfuric acid recovery. This reaction is exothermic and favours at low temperature (450°C) and high pressure. Vanadium based catalyst is used for the conversion of SO₂ to SO₃ [4,5]. Although Iron-based catalysts are more stable, they are not much in practice due to lower activity and high-temperature conditions (>600°C) [6,7]. Noble metal catalysts [[8], [9], [10]] and systems based on activated carbon [11] are in laboratory scale with limited research. V₂O₅ based catalyst follows the redox cycle mechanism [12,13] as shown in the equation below.

$$\text{V}_2\text{O}_5 + \text{SO}_2 \leftrightarrow \text{V}_2\text{O}_4 + \text{SO}_3 \quad \text{V}_2\text{O}_4 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{V}_2\text{O}_5$$

However, to improve the redox property of the catalyst, a suitable promoter or support is necessary in combination V₂O₅ phase to produce SO₃ at high turnover frequency. The addition of potassium pyro sulfate or other additives along with suitable transition metal support helps to maintain the fast redox cycle. Therefore, catalyst contains an active substance like vanadium, promoter like alkali metal compounds and sulfate assists to improve the rate of reaction. The naturally occurring diatomaceous earth founded as an effective support for such system. Another type of important vanadium-based catalyst is the porous silicate coated with a thin molten film of alkali pyrosulphates.

The spectroscopic studies show that an active component exists as a melt forming a very thin liquid layer on the surface of the support. In the melt, vanadium oxides are dissolved in the form of coordination complexes and the most active component of this catalyst identified as octahedral [(VO)₂O(SO₄)₄]⁴⁻ complex dissolved in the melt [14,15]. In an industrial process, V₂O₅ based catalyst in combination with alkali pyrosulphates and fixed bed systems employed to obtain 99.8% conversion of SO₂. The life of catalyst used in SAR converter is generally varied between 2 and 3 years. However, there is a possibility of deactivation of catalyst and thus unusual fine generation occurs within short duration of operation due to unknown reasons. Because of this, the beds might need to be replenished with fresh catalyst to match the earlier performance of the reactor and thus leads to increase of operation cost. To minimize/avoid such unexpected phenomena via catalyst

deactivation/fines generation, it is essential to understand the cause of such incidences. Hence, the current study focusses to unravel the cause of increased fines generation and catalyst deactivation by comprehensive physico-chemical characterization of fresh, spent and fine catalysts.

Section snippets

SAR catalyst sampling

SAR converter reactor is multiple bed fixed bed reactor. During inspection of SAR converter reactors, it was found that fines generation are higher than usual. Thus, the catalyst samples for current study are collected after 4–5 months of operations, which was undergone for deactivation therefore processed for comprehensive characterization. Physico-chemical characterization of spent catalyst obtained from reactor bed was collected and screened with Retsch made 1.7 mm/ASTM [E11](#) ↗ (Serial No. ...

Results and discussion

Physical appearance of fresh and spent catalyst appeared different in colour. Fresh catalyst appeared as yellow with greenish shade, good strength, and dustless during the screening, whereas spent catalyst sample collected (SAR reactor), exhibit colour change with light brown coloured deposition over the surface. Surface of the spent catalyst was not intact with respect to fresh and high dust found during screening. This is due to surface contamination of the catalyst, which leads to reduction ...

Conclusions

The formation of moisture, active metal oxide phase changes and vanadium leaching during the process identified by compositional and structural analysis of spent catalyst/fines received from SAR unit. The fines formation with higher concentration of active metal caused by higher moisture content, which is evident from the LOD analysis. This is further supported with 24 % decrease in crushing strength of spent catalyst in comparison to fresh catalyst. The other possible causes of catalyst ...

Credit authors statement

Jasmin Akola: Conceptualization, Formal analysis, Investigation, Validation, Methodology, Visualization, Writing – original draft. **Unnikrishnan P:** Formal analysis, Investigation, Validation, Methodology, Writing – original draft. **Mehul B Joshi:** Formal analysis, Methodology, Writing – original draft. **Chinthala Praveen Kumar:** Supervision, Resources, Project administration, Writing – review & editing. **Bhavin Dhaduk:** Supervision, Resources, Project administration, Writing – review & editing. ...

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. ...

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