Vanadium leaching from V_2O_5-SiO_2 spent catalysts

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Introduction

Silica supported vanadium pentoxide (V_2O_5-SiO_2) catalysts have been widely used for the catalytic oxidation of SO_2 to SO_3 to commercially produce sulfuric acid. In spite of their high catalytic activity, they are slowly deactivated under reaction conditions (temperatures between 450 and 600 °C) [1, 2]. Characterization of spent V_2O_5-SiO_2 samples evidenced the formation of some oligomeric species of vanadium V^{4+}, such as: $K_4(VO)_3(SO_4)_{(S)}$, $KV(SO_4)_{2(S)}$, $K_2VO(SO_4)_{3(S)}$, $Na_2VO(SO_4)_{(S)}$ and $Na_4(VO)_2O(SO_4)_{4(S)}$ [1]. These species are very stable making it difficult to recover catalyst activity [1, 2]. Recycling of some catalyst components, such as vanadium, silica, and alumina has been recommended before catalyst disposal. In this contribution, we evaluated vanadium recovery by treating spent catalysts with 10% vol. H_2SO_4 solution at room temperature, as previously reported [4].

Materials and Methods

Samples of fresh (V_2O_5-F) and used (V_2O_5-U) commercial catalyst [3], were finely ground, and then treated with a solution of 10% vol. H_2SO_4 at room temperature employing a catalyst (g): acid solution (mL) ratio of 1:20 [4]. Resulting materials were coded V_2O_5-F-T and V_2O_5-U-T, respectively. Acid treated and untreated samples were characterized by TPR, FTIR, XRD, TGA-DTA and elemental chemical analysis.

Results and Discussion

The results of the elemental vanadium analyses of V_2O_5-U, V_2O_5-U-T, V_2O_5-F, and V_2O_5-F-T are shown in Table 1. Around 86 % vanadium was leached from the used sample compared to 92 % obtained from the fresh catalyst sample. The differences in percent metal leaching can be associated with the deactivated species formed.

Table 1. Vanadium chemical analyses

Sample	V_2O_5-U	V_2O_5-U-T	V_2O_5-F	V_2O_5-F-T
Vanadium weight fraction	0.0225	0.0018	0.0256	0.0020
Vanadium leaching, %		85.72		92.18

TPR profiles of fresh, used and acid treated samples are shown in Figure 1. The peaks around 480°C, 600°C and 650°C are attributed to vanadium species bounded to sodium and potassium promoters, vanadium - silicate support interaction and vanadium crystals, respectively [1,2,5,6]. The differences in the TPR profiles of V_2O_5-F and V_2O_5-U are associated to the formation of sulfovanadate species. The TPR profiles of the acid treated samples show that the peak around 600 ºC remains after the treatment, especially in the spent catalyst. The presence of FTIR bands at 600 cm^{-1}, 1004 cm^{-1}, and 1092 cm^{-1} [1] and peaks in the XRD diffraction pattern at 10°, 30°and 37° confirm the formation of sulfovanates in the deactivated catalyst samples [1]. FTIR and XRD analysis performed to V_2O_5-U-T showed that signals of sulfovanates are still present after acid treatment.

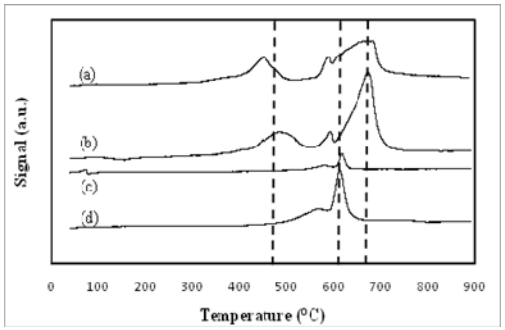

Figure 1. TPR profiles of: (a) fresh catalyst V_2O_5-F, (b) used catalyst V_2O_5-U, (c) fresh catalyst after leaching *V_2O_5-F-T* and (d) used catalyst after leaching *V_2O_5-U-T*.

From TGA-DTA analysis a weight loss around 670 ºC in V_2O_5-F-T (1.30 wt %) and V_2O_5-U-T (5.93 wt %) samples suggests the existence of K-V_2O_5 and Na-V_2O_5 species [7]. This signal might be also associated with a strong interaction of these species with the support which increases in the presence of sulfovanadates.

Significance

This preliminary study shows that the presence of alkali sulfovanadates in the spent catalyst decreases vanadium recovery when the spent catalyst is treated with a 10% vol. H_2SO_4 solution at room temperature.

Acknowledgments

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