UTILIZATION OF VANADIUM FROM USED INDUSTRIAL CATALYST FOR THE OXIDATION OF SULPHUR DIOXIDE

M.D. Stancheva, L.E. Makedonski

Medical University – Varna
55, Marin Drinov Str., 9002 Varna, Bulgaria
Phone: (+359 52 606786/269), Fax: (+359 52 222584)

Abstract
Used vanadium oxide catalysts are still not completely exhausted and be utilized as regenerated catalysts. The present paper reports data on the extraction of vanadium and other useful components from used vanadium oxide catalysts for the oxidation of sulphur dioxide under industrial conditions of sulphuric acid production.

The effect of various factors affecting the extraction (extragent concentration, temperature, duration, stirring intensity, solid/liquid phase ratio and grain size) has been investigation and the optimum conditions of acid ($H_2C_2O_4$) extraction of V_2O_5 and other components established.

Introduction

The limited number of investigations on the regeneration of these catalysts seems to be due to their low cost, the irreversible changes occurring in the support and relatively low vanadium content. Hence after finding an optimum method for the extraction of vanadium, the used catalyst may be considered as a possible source of vanadium products.

Experimental

A used and partly deactivated industrial catalyst (G VEB Bitterfeld, Germany) was used throughout. The composition of the catalyst as determined according to standard [1] procedures recommended by the producer was as follows:

Table 1 Chemical composition of the used catalysts

Components	Composition, wt.%
V_2O_5	4.67
SiO_2	59.11
K_2O	4.96
Fe_2O_3	3.36
Na_2O	3.66
Al_2O_3	0.82

For the extraction with mixture of sulphuric acid and oxalic acids, distilled water, concentrated sulphuric acid and a stoichiometric amount of oxalic acid calculated according to ref. [2,3]. Were added to a catalyst mass preliminary ground to a certain particle size (0.13 mm), constant liquid/solid phase ratio being maintained. The pulp obtained was heated for 20 min at 75-80 ^oC in a thermostated

glass vessel. The Na_2O and K_2O contents were determined according to the standard procedure recommended by the producer [1]. The silicate support was studied by X-ray diffraction with a DRON-1 apparatus using Cu K_α radiation. The infrared spectra were obtained by a SPECORD 75 IR apparatus in a potassium bromide tablet. Thermogravimetry studies were performed with a MOM 1500 derivatograph at a 0-1000 ^oC and a mean heating rate of 10 ^oC/min, aluminium oxide being used as a standard.

Results and Discussion

Extraction with Oxalic Acid

The oxalate vanadates were obtained using a stoichiometric amount of oxalic acid calculated according to Eqn. (1) [2]:

$$V_2O_5 + 4\,H_2C_2H_4 = H_2V_2O_2(C_2O_4)_3 + 3H_2O + 2CO_2 \quad (1)$$

The effect of concentrated sulphuric acid was studied. The influence of the addition of 0-10 cm^3 concentrated sulphuric acid, the extraction degree of V_2O_5 and other useful catalyst components, such as sodium potassium oxide, also increases (fig.1).

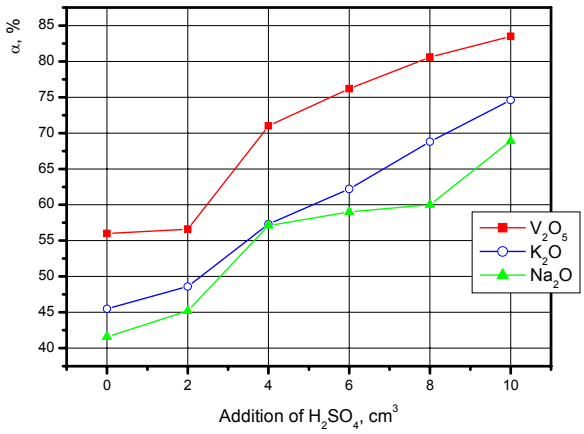

Figure 1 Dependence of the degree of primary vanadium extraction on the amount of concentrated sulpuric acid added to the solution during oxalate extraction

Considerable extraction degree of V_2O_5 (83.5%), K_2O (69.9%) and Na_2O (74.6%) were achieved in the presence of 10 cm^3 concentrated H_2SO_4 in the reaction mixture. The effect of the duration of the extraction process on the extraction degree of V_2O_5 and the remaining useful components of the used catalysts was also studied. The experimental results evidence that the major amount of useful catalyst components pass into the solution during the first 20 minutes from the beginning of the dissolution, after which noticeable increase in extraction degree of the components is observed. Experiments aimed at establishing the temperature dependence of the transition of V_2O_5 and other useful catalyst components into the solution as well as of the extraction degrees were also performed.

Figs.2 and 3 evidence that the temperature has no substantial effect on the degree of extraction. For that and for econimic reasons we have performed further extraction at relatively low temperature (25^oC). The active phase of V_2O_5 and other useful catalyst components are dispersed in the granule volume. The extraction degree depends strongly on the grinding degree of the catalyst mass and on the stirring intensity of the suspension. It has been established that a stirring intensity of the

order of 400-600 rev./min and a grain size of the catalyst of 0.13-0.063 mm essentially increase the extraction degree of the useful catalyst components.

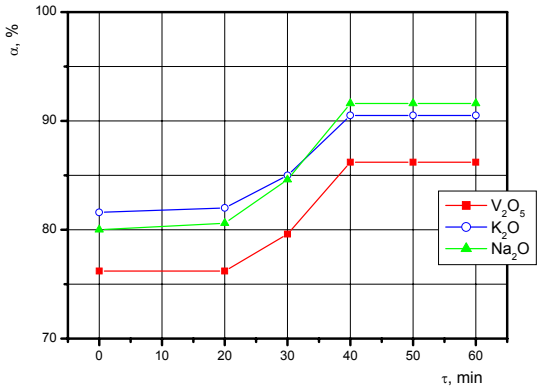

Figure 2 Kinetic curves of primary extraction with oxalic acid and addition of 10 cm^3 of concentrated H_2SO_4, intensity of stirring: 600 rev/min, grain size 0.13 mm, T = 25 ^oC

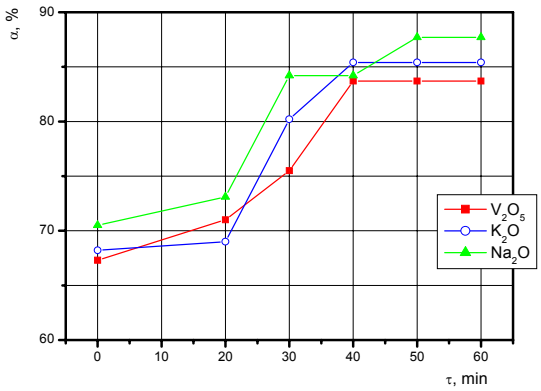

Figure 3 Kinetic curves of primary extraction with oxalic acid and addition of 10 cm^3 of concentrated H_2SO_4, intensity of stirring: 600 rev/min, grain size 0.13 mm, T = 80 ^oC

Table 2 Chemical composition of the regenerated silicate support

Components	Composition, wt.%
SiO_2	86.6
V_2O_5	0.7
K_2O	1.2
Na_2O	1.1
Fe_2O_3	1.3
SO_3	4.7
Mg, Ca, Al, Mn	traces

After the first acid extraction, secondary acid extraction with oxalic acid under the optimum conditions chosen has been applied to the solid residue obtained after filtration. The two successive acid extractions have led to a V_2O_5 extraction degree of 98.6%.

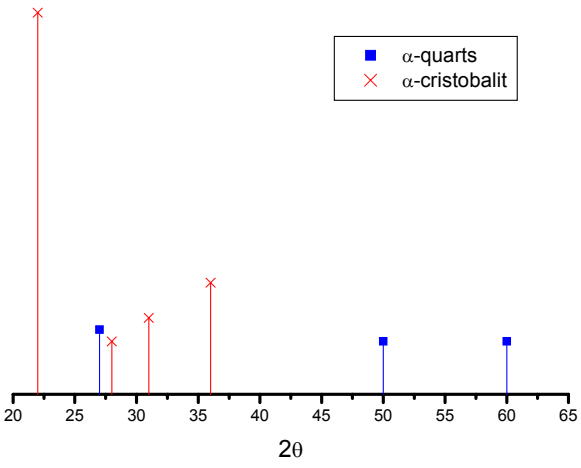

Figure 4 X-ray spectroscopy of the silicate support

We have carried out a single oxalate dissolution followed by water extraction of the solid residue. The pulp obtained was allowed to stay for 12 h or was intensively stirred for 3 h. The extraction degree reached 87.3% for V_2O_5, 86.2% for K_2O and 90.0% for Na_2O.

Recovery of the Catalyst Support

The chemical analysis (see Table 2) show that the major silica component is mixed with minimum amounts of oxides of vanadium, sodium, potassium and iron, which are also present in the natural diatomite support, and there is no obstacle to its second application.

The high working temperatures lead to phase conversions in the silicate support. The X-ray analysis of the regenerated silicate support (Fig.4) has shown that, in addition to the lines (with d = 3.34, 2.45 and 1.97 Å) characteristic of the α-quartz phase, there are also lines (with d= 4.05, 3.53, 3.14, 2.84, 2.43 and 2.01 Å) typical of the new phase of α-cristobalite. This indicates a gradual transition of α-quartz into of α-cristobalite.

The formation of α-cristobalite in the presence of vanadium compounds in used catalysts at relatively low temperatures is an indication of chemical interaction between silica and the molten salts of the active catalyst components. The presence of α-cristobalite in the regenerated silica support has been confirmed by IR spectroscopy.

Isolation of Vanadium

Vanadium was isolated from the extracts by precipitation with ammonium hydroxide solution [4]. The rate and degree of hydrolytic vanadium precipitation are essentially affected by a number of factors such as pH, temperature and duration of hydrolysis. The analysis of the experimental results has shown that there is a range of pH values (7.7 – 8.1) in which the precipitation degree of vanadium is above 95%.
The yield of precipitated ammonium metavanadate is 98%. Its composition is present in Table 3.

Table 3 Chemical composition of the precipitated ammonium metavanadate

Components	Composition, wt. %
NH_4VO_3	97.70
SO_4^{2-}	1.20
Fe	0.05
Si	0.30

The DTA analysis of the sample of precipitated ammonium metavanadate shows that its decomposition begins already at 30^{o}C and is intense above 220 ^{o}C. The decomposition proceeds according to the reaction:

$$2\ NH_4VO_3 = V_2O_5 + 2\ NH_3 + H_2O \qquad (2)$$

Experiments on thermal decomposition of precipitated ammonium metavanadate at different temperatures with to obtaining divanadium pentoxide of a high purity and of a large specific surface area were performed.

The chemical composition of V_2O_5 obtained at a temperature that corresponds to the maximum specific surface area is shown in Table 4.

Table 4 Chemical composition of utilized V_2O_5

Components	Composition, wt.%
V_2O_5	98.20
Fe	0.05
SO_4^{2-}	1.20
Si	0.30
K	0.15
Na	0.10

Conclusions

The present studies have revealed optimum conditions of vanadium extraction and precipitation from the extracts.

The optimum vanadium extractions with oxalic solutions are: stoichiometric amount of oxalic acid, temperature 25^{o}C, contact time 20 min., grain size 0.13 mm, stirring intensity 600 rev./min. The extraction degree of vanadium is 86.25%.

The optimum conditions of vanadium precipitation from the extracts are: hydrolytic precipitation with an ammonium hydroxide solution (25%), intense stirring, temperature 60^{o}C, pH 7.7-8.1. The precipitation degree of vanadium is above 97%.

References

1. Standard SVK 2 132, VEB Bitterfeld – Germany (1983).
2. Patent Germany 11 669 (1975).
3. I. VOLNOV, Peroksokompleksy vanadia, niobia, tantala, Nauka, Moskva (1972).
4. S. FOTIEV, Vanadievye cristalofosfory, Nauka, Moskva (1976).