The dependance of an activity of vanadium catalysts on a carrier regeneration method and an active phase composition

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The results of the research studies concerning the reaction rate of SO_2 oxidation on the vanadium catalysts have been described. A carrier of the active phase – silica has been regenerated from spent vanadium mass by leaching with H_2SO_4 solution. The dependence of the oxidation reaction rate on the method of treating a catalyst carrier as well as the composition of an active phase of the new catalyst systems has been also presented.

Keywords: carrier properties, composition of active phase, SO_2 oxidation, vanadium catalysts.

INTRODUCTION

The catalysts working under industrial conditions undergo deactivation caused by changes in the structure and texture of a catalyst, and the changes are the result of loss of homogeneity of the active phase melt. One of the main reasons of these changes are iron compounds, which form with active phase components (type $KV(SO_4)_2$ or $K_3V(SO_4)_3$ compounds of $KV_{1-x}Fe_x(SO_4)_2$ and $K_3V_{1-x}Fe_x(SO_4)_3$ type with a melting point increasing when mole fraction of iron increases[1,2]. The final stage of these phase transformation are inactive systems of $KFe(SO_4)_2$ and $K_3Fe(SO_4)_3$ type.

A defining of adverse impact of iron compounds, being the components of a process gas or corrosion products, on the operating properties of vanadium catalysts[3–5] as well as an explanation of the mechanism of phase changes are important factors for the use of components recovered from the spent vanadium masses to produce fresh catalyst.

The research studies on the technology of the active phase components and silica recovery from spent vanadium catalysts by washing with concentrated acidic solutions (H_2SO_4, $H_2C_2O_4$ and $CO(NH_2)_2$)[6–13] demonstrated the possibility of reuse of K_2O and V_2O_5 to produce fresh vanadium catalyst. During acidic leaching, not only vanadium and potassium compounds but also iron ones are transferred into a solution. An absence of iron is beneficial for the silica properties and it allows a reuse of the catalyst for the production of fresh ones[7,8]. The studies have demonstrated that recovered silica can be applied if only iron content in the catalyst is below 0.5% of Fe_2O_3[14].

The paper describes the results of test studies of SO_2 oxidation rate on vanadium catalysts produced from silica after spent vanadium mass regeneration with 5% H_2SO_4 solution derived from a sulfuric acid plant.

EXPERIMENTAL

Spent vanadium mass grains were ground to a plurality of 0.16–0.75 mm, and then subjected to leaching of vanadium compounds, potassium and iron by 5% H_2SO_4 solution. The mass ratio of the catalyst to the volume of washing solution S/L was 1:15 kg/dm³. The process was carried out at 323K for 4 hours[15]. The solution was separated from the silica. The silica recovered from spent vanadium mass was filtered, washed with distilled water until pH 7.0, dried at 120°C. Part of the silica has undergone a process of heat treatment by roasting at 400°C in air. The prepared catalyst samples in a form of Raschig rings have been characterized by f12/5 mm diameters; 5, 6 or 7% of V_2O_5 with equal molar ratios of active phase components (K_2O/V_2O_5) amounting to 2/1, 2.5/1 and 3.0/1. The samples have been obtained by "dry" mixing of silica with different amounts of vanadium pentaoxide and potassium carbonate. Vanadium pentaoxide of technical grade, having 96% of V_2O_5, and technical potassium carbonate (97% of K_2CO_3) have been used as the active phase components.

Catalysts P(11–P33) have been produced on a carrier after drying in 120°C (Table 1), while catalysts P(41–P63) – after heat treatment (Table 2). Catalyst samples were also prepared on the basis of natural silica from Piotrowice (82% SiO_2) as well as vanadium pentaoxide and potassium carbonate of technical grade (P01–P09), used in amounts that ensure the same composition as the active phase of catalysts prepared on the basis of regenerated silica – Table 3.

The produced catalysts were dried in 120°C for 4 h, roasted in 400°C for further 4h and subjected to a process

Table 1. The chemical composition and the catalyst activity prepared with dried SiO_2

Component	Component content, %								
V_2O_5	5.0			6.0			7.0		
K_2O	5.2	6.5	7.7	6.3	7.8	9.1	7.2	9.0	10.8
Fe_2O_3	0.3			0.3			0.2		
Reaction rate $10^4 r$, mol $SO_3/g_c h$									
Catalyst no	P11	P12	P13	P21	P22	P23	P31	P32	P33
r^{420}	143.1	145.1	154.9	154.8	160.5	166.1	172.3	172.9	173.8
r^{480}	256.2	266.8	278.5	278.3	289.5	294.8	309.7	308.9	309.6
Decrease in the rate Δr, %									
Δr^{420}	5.7	4.7	3.9	5.4	4.6	3.7	2.1	2.8	3.7
Δr^{480}	5.6	4.4	3.7	5.1	4.1	3.4	0.8	2.3	3.0

Table 2. The chemical composition and the catalyst activity prepared with roasted SiO_2

Component	Component content, %								
V_2O_5	5.0			6.0			7.0		
K_2O	5.2	6.5	7.7	6.3	7.8	9.1	7.2	9.0	10.8
Fe_2O_3	0.3			0.3			0.3		
	Reaction rate $10^4 r$, mol $SO_3/g_c h$								
Catalyst no	P41	P42	P43	P51	P52	P53	P61	P62	P63
r^{420}	143.4	145.6	155.5	155.1	161.1	166.8	173.6	174.4	175.5
r^{480}	257.2	267.6	280.1	278.4	289.8	295.9	309.9	310.5	310.9
	Decrease in the rate Δr, %								
Δr^{420}	5.5	4.3	3.5	5.2	4.2	3.3	1.4	2.0	2.8
Δr^{480}	5.3	4.2	3.2	5.1	4.0	3.1	0.7	1.8	2.5

Table 3. The chemical composition and the catalyst activity prepared with natural silica from Piotrowice

Component	Contents, %								
V_2O_5	5.01			6.03			7.02		
K_2O	5.20	6.51	7.72	6.32	7.80	9.12	7.23	9.01	10.80
Fe_2O_3	<0.10			<0.10			<0.10		
	Reaction rate $10^4 r$, mol $SO_3/g_c h$								
Catalyst no	P01	P02	P03	P04	P05	P06	P07	P08	P09
r^{420}	151.8	152.2	161.1	163.6	168.2	172.5	176.0	177.9	180.5
r^{480}	271.5	279.2	289.3	293.2	301.9	305.3	312.1	316.1	319.0

of chemical forming in 420°C for 6h by a gas mixture (2% SO_2, 15% O_2 and 79% N_2) until no weight growth, in order to obtain a specific structure of the active phase. In catalysts formed, V_2O_5 content was determined by manganometric method, K_2O – photometric method and iron content by ASA[16] – Tables 1–3. The reaction rate of SO_2 to SO_3 oxidation in 420°C and 480°C was adopted as a measure of a catalytic activity, while the decrease of reaction rate in comparison with a reference catalyst – as a measure of an industrial usefulness of the catalysts based on recovered silica.

The kinetic studies were carried out in a specialized bench for a catalyst sample of 40.0±0.1 g; gas composition as follows 10.5% of SO_2, 10.5% of O_2 and 79% of N_2, and linear flow rate of gas 0.4 Nm/s calculated for an empty section of the reactor[16].

Sulfur dioxide concentration in the gas before and after passing the reactor was determined by microcoulometric method with $MKSO_2$ analyzer. A measurement error of SO_2 concentration was ±0.1%. On the basis of SO_2 concentration in the gas, the degree of conversion was determined according to equation (1):

$$x_t = \frac{(c_1 - c_2) \cdot 10^4}{c_1 \cdot (100 - 1,5 \cdot c_2)} \quad (1)$$

where: x_t – the degree of SO_2 conversion in temperature t (%), c_1 – SO_2 concentration before the reactor (%), c_2 – SO_2 concentration after passing the reactor (%).

The reaction rate of SO_2 oxidation was calculated from equation (2):

$$r = \frac{V_{SO_2} \cdot x_t}{21,89 \cdot m_k} \quad (2)$$

where: r –the reaction rate (mol $SO_3/g_c h$), V_{SO2} – SO_2 flow rate (Ndm^3/h), x_t – the degree of SO_2 conversion in temperature t (%), m_k – the catalyst mass (g), 21,89 –SO_3 molar volume (Ndm^3/mol).

The decrease of the reaction rate in the catalysts based on the regenerated silica was calculated from equation (3):

$$\Delta r = \frac{r_0 - r_p}{r_0} \cdot 100 \quad (3)$$

where: Dr – the decrease of reaction rate (%), r_0 – the reaction rate at the reference catalyst (mol $SO_3/g_c h$), r_p – the reaction rate at the catalyst based on regenerated silica (mol $SO_3/g_c h$).

Results and discussion

The influence of a treating method of silica after regeneration of spent vanadium mass with 5% sulfuric acid solution and the active phase composition of catalysts on the reaction rate of SO_2 oxidation (Tables 1, 2) in comparison with the activity of the catalyst based on natural silica have been studied (Table 3).

The studies have shown that the catalysts based on recovered silica were characterized by similar activity. The reaction rate in 420°C in the presence of the catalyst containing 5% V_2O_5 and 7.7% K_2O (sample P13) was 0.01549 mol $SO_3/g_c h$, while in case of roasted silica (catalyst P43) it was only slightly higher (0.01555 mol $SO_3/g_c h$). Similarly, the reaction rate of SO_2 oxidation in 480°C was 0.02785 mol $SO_3/g_c h$ and 0.02801 mol $SO_3/g_c h$ respectively. In case of the catalyst containing 6% V_2O_5 and 9.1% K_2O (catalyst P23) the reaction rate in 420°C was 0.01661 mol $SO_3/g_c h$ and catalyst P53 – 0.01668 mol $SO_3/g_c h$, while the respective rates in 480°C were as follows: 0.02948 mol $SO_3/g_c h$ and 0.02959 mol $SO_3/g_c h$ – Tables 1, 2. In case of the catalysts containing 7% of V_2O_5, the difference in the reaction rates in both temperatures was also insignificant and independent on the active phase composition.

The studies have demonstrated the correlation between the reaction rate and vanadium content as well as the active phase composition. The reaction rate increased as the vanadium content in the catalysts increased, but the nature of this increase was dependant on the active phase composition (volume) – Tables 1–3. In case of the catalysts containing 5% and 6% of V_2O_5, the reaction rate increased as K_2O/V_2O_5 ratio increased from 2 to 3, independently on silica treatment, while for the catalyst having 7% of V_2O_5 the optimal ratio (the active phase volume) was 2.0/1. At higher K_2O/V_2O_5 ratio, the reaction rate decreased as an effect of too high volume of the active phase in relation to the properties of an applied carrier.
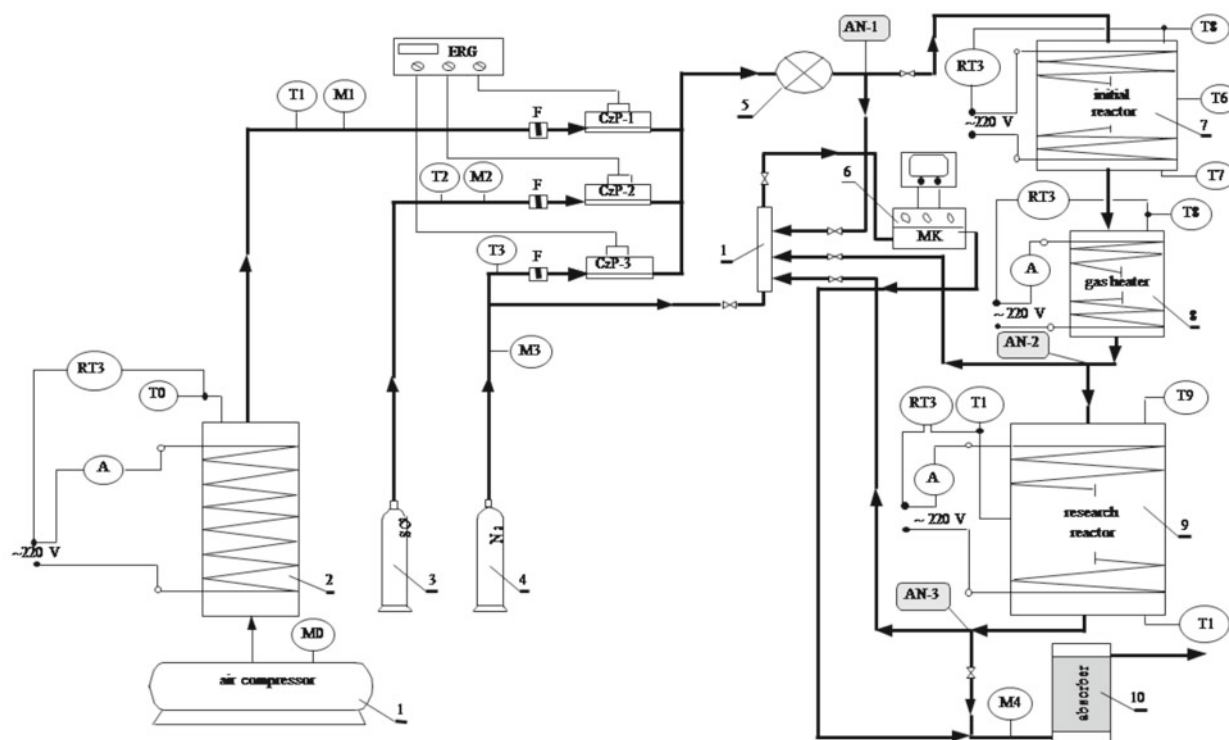
Figure 1. The schematic representation of the system used for the reaction rate determination. 1 – air compressor, 2 – air dryer, 3, 4 – bottles with technical gas SO$_2$ and N$_2$, 5 – gas mixer, 6 – gas analyzer, 7 – initial reactor, 8 – gas heater, 9 – research reactor, 10 – SO$_2$ and SO$_3$ absorber, M – pressure measurement T – temperature measurement, RT – temperature control system, AN – gas sampling point, ERG – electronic controller of flow rate, MK – microcoulometric measurement of SO$_2$ concentration

The studies have shown the necessity to optimize the active phase composition of the catalysts based on recovered silica by elution with 5% H$_2$SO$_4$ solution, taking into consideration porous properties of silica. The active phase volume should be fitted to vanadium content and the active phase composition. Too high volume can impair the catalytic properties. These parameters must be taken into consideration during a production technology development of catalysts based on recovered components.

The studies have demonstrated a negligible impact of a carrier treatment method on the catalytic activity of products based on silica recovered by elution of active components with 5% sulfuric acid solution. The maximal decrease of the reaction rate on the catalyst prepared on dried silica was about 5.7%, while in case of the optimal active phase composition was lower – only 0.8%. The parameters for roasted silica were as follows: maximal

decrease – 5.5% and the lowest one – 0.7% for the optimal active phase composition – Figure 2.

CONCLUSIONS

The regeneration method of silica recovered from spent vanadium masses by leaching with 5% H$_2$SO$_4$ solution has insignificant impact on the catalytic activity in the studied temperatures.

In the case of such recovered material, silica roasting is not necessary.

The active phase composition has an influence on a catalytic activity of the catalysts prepared by the described method and it must be optimally matched to the silica properties.

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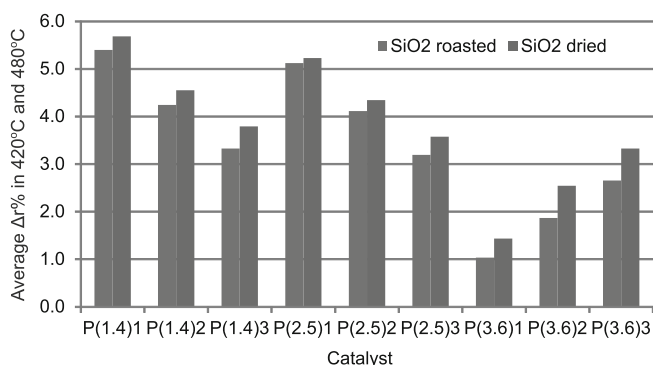
Figure 2. The rate decrease of SO$_2$ oxidation, depending on the carrier treatment

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