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Phase transitions in the active component of vanadium catalyst for sulfur dioxide oxidation: crystal phase dissolving

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Abstract

As sulfur dioxide is oxidized on vanadium catalysts, phase transitions may occur in the catalyst active component, which are related to the crystallization of vanadium(IV) compounds resulting in the decrease of catalyst activity. In this paper, we report on the peculiarities of reversal process such as crystal phase dissolving, which is aimed at catalyst regeneration. We have studied how crystal phase dissolving rate depends on dissolving conditions such as temperature, gas mixture composition as well as on the conditions of crystal phase formation. Dissolving dynamics is described by a mathematical model, which was earlier suggested for the processes of crystal phase generation and growth. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Vanadium catalyst; Sulfur dioxide oxidation; Crystal phase dissolving

1. Introduction

Active component of vanadium catalysts for sulfur dioxide oxidation is proved to be a melt under reaction conditions. This melt consists of sulfates and pyrosulfates of alkaline metal that contain dissolved vanadium complexes. When reaction temperature and sulfur dioxide conversion are low, phase transitions may occur in the melt. These transitions are related to the crystallization of compounds of vanadium(IV). The crystal phase formation is known to worsen catalyst activity [1]. We have shown [2] that the rate of crystallization process depends on many parameters such as reaction conditions, active phase chemical composition, support porous structure as well as on the catalyst geometry and prehistory. Crystal phase formation peculiarities and catalyst bed activity change were well described by the mathematical model based on Gibbs–Folmer theory.

Phase transitions of vanadium(IV) compounds are of reversible character. As temperature or sulfur trioxide concentration increases, crystal phase fully or partially dissolves and catalyst activity is fully or partially regenerated. With this regard crystal phase dissolving peculiarities are of theoretical and practical interest related to the possibility of catalyst activity regeneration.

In this work, we experimentally studied and mathematically modeled the dissolving of crystal phase of vanadium(IV) in the active component melt of the catalyst for sulfur dioxide oxidation.

2. Experimental

In order to observe crystal phase dissolving, a quartz microreactor, loaded with the studied catalyst (catalyst weight 0.04 g, fraction 0.6–1 mm), was put directly into the ESR high temperature cell. This procedure allowed a direct in situ measurement of vanadium (IV) amount during experimental run. Vanadium content in the crystal phase was determined by the amplitude of the typical singlet ESR signal, while vanadium content in the liquid phase was determined by the amplitude of a well-resolved component of the super fine structure at $H = 3200\,G$. This procedure is described in detail elsewhere [3,4].

For the crystal phase to form, a reductive mixture (2–3% SO_2 in helium) was fed into the microreactor. Immediately vanadium(IV) signal in the crystal phase was registered. Singlet signal intensity quickly increased, and attained its maximum value in 15–30 min depending on the SO_2 concentration. This maximum value corresponds to the full reduction of all vanadium in the sample. As vanadium content in the crystal phase increased, its content in the liquid phase decreased, as was well seen by the decreasing amplitude of the super fine structure component. Fig. 1

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Nomenclature

c, C	molar portions of SO_2 inside catalyst grain and in gas phase
D_e	effective diffusivity in catalyst pellet (cm^2/s)
D_v	diffusion coefficient for vanadium(IV) complexes in the melt (cm^2/s)
k	the Boltzman constant (1.381×10^{-23} J/K)
k_i	the reaction rate coefficients for the corresponding stages of reaction mechanism
n	nuclei number in the melt ($nuclei/cm^3_{melt}$)
n_{max}	nuclei number at the maximum supersaturation ($nuclei/cm^3_{melt}$)
N_0	the total number of vanadium complexes per gram of catalyst
r	radius reduced to spherical crystal size (cm)
Δr	diffusion layer thickness (cm)
r_p	radius of support pores (cm)
r_0	radius of binuclear vanadium complex (cm)
$\bar{r}$	dimensionless crystal radius equal to $\bar{r} = r/r_p$
R_e	radius of catalyst pellet (cm)
S	supersaturation
T	temperature (°C)
v_0	volume of single vanadium(IV) complex (cm^3), $v_0 = 4\pi r_0^3/3$
V_L	melt volume per gram of catalyst (cm^3/g)
W	reaction rate on the catalyst grain ($cm^3/g\,s$) (observed rate)
W^s	reaction rate on the catalyst grain surface ($cm^3/g\,s$) (rate in kinetic regime)

Greek symbols

γ	bulk density of catalyst bed (g/cm^3)
γ_k	catalyst density (g/cm^3)
δ	vanadium portion in the crystal phase
η	effectiveness factor
θ_{eq}	equilibrium concentration of V(IV) complexes in the melt ($complexes/cm^3$)
θ_L	current content of V(IV) complexes in the melt ($complexes/cm^3$)
θ_∞	solubility of V(IV) complexes in the melt ($complexes/cm^3$)
ξ	dimensionless length of catalyst bed
ρ	dimensionless coordinate of grain radius
σ	interface surface energy (J/cm^2)
τ	contact time (s)
φ	$R_e(TW^s\gamma_k/273D_e)^{0.5}$—modified Thiele modulus

Fig. 1. Portion of V(IV) in the crystal (1) and liquid (2) phases at catalyst reduction by mixture 2% SO_2 in helium at 420 °C. Experimental data.

In order to dissolve the formed crystal phase, oxidative mixture ($SO_2 + SO_3 + O_2 + He$) was fed into the microreactor. Mixture composition corresponded to a high degree of sulfur dioxide conversion—not less than 0.6. To obtain this mixture, the gas mixture (2–3% SO_2 + 6–7% O_2, balance helium) was converted in a tube catalytic reactor up to desired SO_2 conversion (varying contact time). The alternation of mixtures (reductive and oxidative) fed into the microreactor was done with a 4-way valve switch. Chromatography was used to determine the composition of all the gas mixtures. A high time resolution system of temperature regulation allowed us to change the temperature in microreactor 50–70 °C in 20–30 s [4]. A tungsten–rhenium thermal couple, covered by thin boron nitride film to prevent corrosion, was inserted directly into the catalyst bed.

For the active component, initial state was the same in all runs, before reduction catalyst was heated to 485 °C, and at this temperature, it was treated with mixture $SO_2 + SO_3 + O_2 + He$ corresponding to conversion 0.9. Under these conditions, almost all vanadium in the catalyst was oxidized to valence (V), since ESR spectra showed no signals corresponding to vanadium(IV). Only then the microreactor with the oxidized catalyst was cooled to 420 °C, and reduction was performed.

Immediately at a supply of the mixture $SO_2 + SO_3 + O_2 + He$ onto reduced catalyst singlet signal amplitude started to decrease in time. The character of crystal phase dissolving essentially depended on the:

- duration of preliminary catalyst reduction (30 or 300 min);
- degree of SO_2 conversion in the mixture fed for dissolving (0.6, 0.7 or 0.8);
- dissolving temperature (400, 420 or 450 °C).

Experiments were performed with the catalyst containing 7 wt.% V_2O_5 with atomic ratio $K/V = 3.5$. Silica support had a bi-disperse structure with mean pore radiuses 10 and 100 nm. Total pore volume was 1.2 cm^3/g, the main part of

shows the typical curves of vanadium reduction, reflecting the changing portions of vanadium (IV) in crystal and liquid phases vs. time. Vanadium portion in the crystal phase (δ) was determined as a ratio of the current amplitude of the singlet signal to its maximum value, corresponding to the almost complete vanadium transition into the crystal phase.
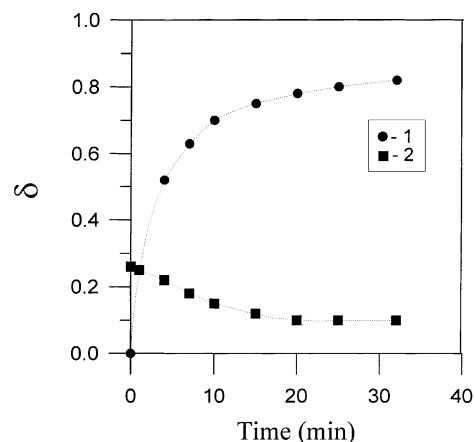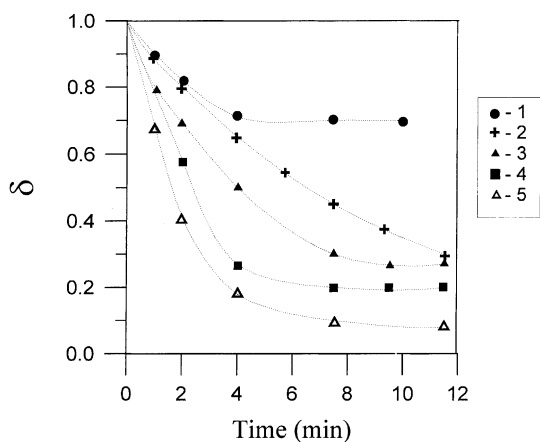
Fig. 2. Vanadium portion in the crystal phase δ vs. time at the feeding of reaction mixture for different conversions: 0.6 (3), 0.7 (1 and 4) and 0.8 (2 and 5). Preliminary reduction duration (min): 300 (1 and 2), 30 (3–5). Temperature: 420 °C. Feed gas: 3.2% SO_2 + 6.7% O_2, balance He (1 and 2) and 2.3% SO_2 + 6% O_2, balance He (3–5). Experimental data.

it (0.9 cm^3/g) accounted for pores with mean radius 10 nm, specific surface was 140 m^2/g. Catalyst was prepared by silica impregnation with the solution of sulfate vanadyl and sodium bisulfate followed by drying and calcinations at 110 and 500 °C, respectively.

Vanadium catalysts genesis studied in [5,6] shows that active component melts at calcination. Owing to a good support wetting by the melt, the latter uniformly distributes in the support pores. When a fraction of support pore volume occupied by melt is more than 0.2, at first smaller pores are filled, and then the larger ones. In the studies, catalyst pores filling is ≈0.3, and thus catalyst active component is accumulated mainly in the small pores with mean radius of 10 nm.

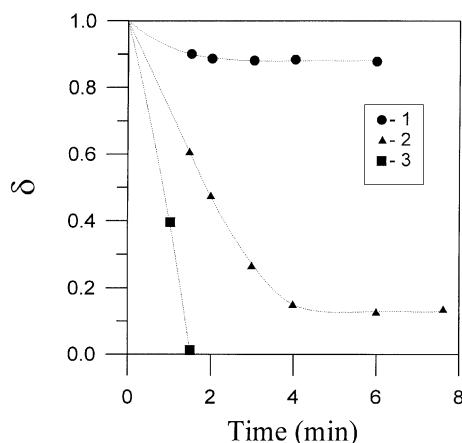Experimental data obtained are shown in Figs. 1–5.

Fig. 3. Vanadium portion in the crystal phase δ during dissolving at different temperatures (°C): 400 (1), 420 (2) and 450 (3). The gas mixture corresponds to conversion 0.8. Feed gas: 3.2% SO_2 + 6.7% O_2, balance He. Preliminary reduction duration—200 min. Experimental data.
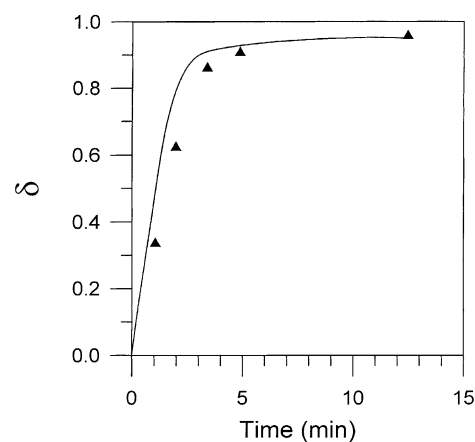

Fig. 4. Vanadium portion in the crystal phase δ vs. time during reduction by mixture 3% SO_2 in helium at 420 °C. Points—experiment, curves—calculations.
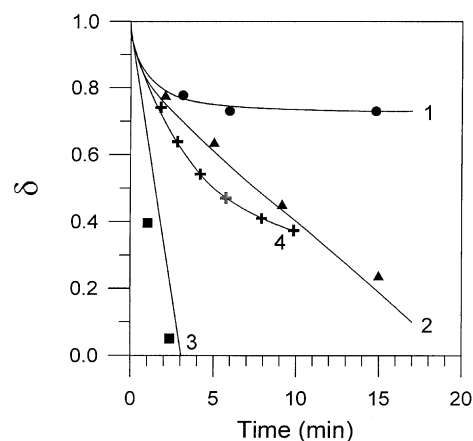

Fig. 5. Vanadium portion in crystal phase δ at a supply of reaction mixture corresponding to conversion: 0.6 (4), 0.7 (1), 0.8 (2 and 3). Temperature: 420 °C (1, 2 and 4) and 450 °C (3). Preliminary reduction duration: 300 min (1 and 2), 30 min (4), 19 min (3). Points—experiment, curves—calculations. Feed gas: 3.2% SO_2 + 6.7% O_2, balance He.

3. Mathematical model

In paper [2], a kinetic model based on Gibbs–Volmer theory for phase transitions [7,8] was used to describe the formation and growth of crystal phase. This model well enough fits the experimental data related to the crystal phase generation and its growth, and to the catalyst activity changes caused by these processes. Crystal phase growth and dissolving are mutually reversible processes. Therefore, it is quite reasonable to use the same model, equations set in particular, related to the stages of crystals growth-dissolving.

Since active component melt is a viscous liquid with a low mobility of vanadium complexes [9], crystal particles dissolving as well as their growth is limited by the diffusion of vanadium(IV) species in the melt. In this case, process

dynamics may be described by the Nernst equation [10]:

$$\frac{dr}{dt} = \frac{D_v v_0}{\Delta r}(\theta_L - \theta_{eq}) \tag{1}$$

where r is the crystal particle radius, D_v the diffusion coefficient of vanadium(IV) complex in the melt; v_0 the volume of single vanadium(IV) complex, Δr the thickness of diffusion layer near the crystal surface, θ_L the current concentration of vanadium(IV) complexes in the melt; θ_{eq} the equilibrium concentration of vanadium(IV) complexes at a given r.

Value θ_{eq} in the melt is determined by the Gibbs–Thompson equation:

$$\theta_{eq} = \theta_\infty \exp\left(\frac{2\sigma v_0}{kTr}\right) \tag{2}$$

In order to simplify the model, we assume that all crystals are of the same size and spherical. Situation $dr/dt = 0$ corresponds to a quasi-equilibrium state of the system, which tends to the true equilibrium at $r \to \infty$. Value θ_L is determined regarding reaction mechanism [11]:
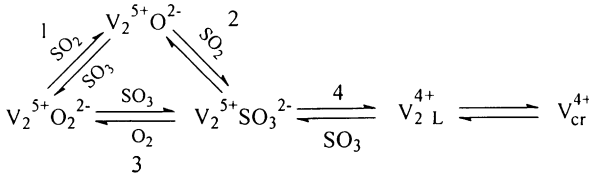
Rate of reaction stages essentially exceeds the rate of phase transitions [12]. Therefore, there is always a quasi-equilibrium ratio between V^{5+} and V^{4+} in the melt during the crystal phase (V_{cr}^{4+}) formation or dissolving. This ratio is determined by the temperature and SO_2 conversion. In our case, vanadium(IV) content in the liquid phase θ_L is determined by the formula

$$\theta_L = (1 - \delta) F \frac{N_0}{V_L},$$

$$F = \left[1 + \frac{k_{-4}}{k_4} P_{SO_3}\left(1 + \frac{k_{-2}}{k_2 P_{SO_2}} + \frac{k_3 P_{O_2}}{k_2 P_{SO_2}}\right)\right]^{-1} \tag{3}$$

where δ is the vanadium portion in the crystal phase at a given time (ratio of vanadium atoms in the crystal phase to the total number of vanadium atoms), N_0 the total number of vanadium complexes per gram of catalyst, V_L the active component melt volume per gram of catalyst, F determines the quasi-equilibrium content (portion) of vanadium(IV) in the melt according to reaction mechanism, k_i the reaction rate coefficients for the corresponding stages according to reaction mechanism. This expression for F was obtained from the full kinetic equation which suggests that far from equilibrium, $k_1 P_{SO_2} \gg k_{-1} P_{SO_3}$. The procedure was described more detail in Ref. [13].

As sulfur trioxide concentration (P_3) increases, the value of θ_L decreases. As a result, crystal particles dissolve until the new equilibrium size. As temperature increases, solubility θ_∞ also increases, and so does θ_{eq} (Eq. (2)). As a result, crystal particles partially or fully dissolve depending on the new reaction conditions.

Complete equations set for the catalyst activity calculation taking phase transitions into account is the following:

$$\frac{dC}{d\tau} = W(T, C)\gamma\eta \tag{4}$$

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2 \frac{dc}{d\rho}\right) = \frac{\varphi^2 W(T, c, \delta)}{W^s(T, C)} \tag{5}$$

$$\frac{d\bar{r}}{dt} = \alpha_D\left(\frac{1 - \delta}{1 + ((k_{-4}/k_4)P_{SO_3})(1 + k_{-2}/k_2 P_{SO_2} + k_3 P_{O_2}/k_2 P_{SO_2})} - \alpha_\infty e^{\beta/\bar{r}}\right) \tag{6}$$

where $\alpha_D = D_v v_0 N_0 / \Delta r V_L r_p$; $\alpha_\infty = \theta_\infty V_L / N_0$; $\beta = 2\sigma v_0 / kT r_p$ with initial and boundary conditions:

$$t = 0: \quad \bar{r} = \bar{r}^*; \qquad \tau = 0: \quad C = C_0, \quad T = T_0;$$
$$\rho = 0: \quad \frac{dc}{d\rho} = 0, \quad \rho = 1, c = C \tag{7}$$

where $\eta = \int_0^1 \rho^2 W(c, T, \delta)/W^s(C, T, \delta)\, d\rho$.

$$W = \frac{k_3 K_2 P_{SO_2} P_{O_2}}{1 + K_2 P_{SO_2} + K_3 P_{O_2}} \frac{1 - P_{SO_3}^2/P_{SO_2}^2 P_{O_2} K_{eq}^2}{1 + a P_{SO_3}}(1 - \delta)$$

$$\delta = \bar{r}^3 \left(\frac{r_p}{r_0}\right)^3 \frac{n}{N_0}, \quad n = n_{max} \exp\left(-b\frac{\ln^2 S_{max} - \ln^2 S}{\ln^2 S_{max} \ln^2 S}\right),$$
$$b = \frac{16}{3}\pi\sigma^3 \frac{v_0^2}{(kT)^3}$$

Eq. (4) describes the evolution of reagent concentrations in the catalyst bed in accordance to kinetic equation for reaction rate W, coming from the above-mentioned reaction mechanism. Eq. (5) describes reagents internal diffusion in the catalyst grain, while expression (6) reflects crystal particles dissolving or growth.

Mathematical model parameters were estimated regarding experimental data on the crystal phase formation and dissolving, and then were verified during modeling [2]. At 693 K, these values are: $r_0 = 0.6 \times 10^{-7}$ cm, $\sigma = 1.65 \times 10^{-5}$ J/cm^2, $D_v/\Delta r = 3.0 \times 10^{-8}$ cm/s, $\alpha_\infty = 0.0083$, $n_{max} = 1.2 \times 10^{16}$ nuclei/g. Rate constants for the chemical stages of this equation are given elsewhere [12]. Pore radius was assumed to be 10 nm since the main part of the active component melt is accumulated mainly in the small pores with mean radius of 10 nm.

4. Results and discussion

4.1. Effect of gas mixture composition and preliminary catalyst reduction duration on the rate of crystal phase dissolving

Experimental data in Fig. 2 show how the amount of V_{cr}^{4+} changes with time, when gas mixture of various conversion degree is fed onto the catalyst. When sulfur dioxide conversion in the mixture is 0.7 (curve 1) in 6 min dissolving process stops, equilibrium state is attained with 70% of vanadium remaining in the crystal phase. When SO_2 conversion is 0.8 (curve 2) dissolving goes faster, and does not stop in 11 min, the vanadium portion in the crystal phase approaches 0.3. This means that dissolving rate increases with the growing SO_3 content. This assumption is confirmed by curves 3–5, which correspond to conversions 0.6, 0.7 and 0.8, respectively.

Another important factor affecting the dissolving rate is the time of preliminary catalyst reduction. In Fig. 2, curves 1 and 4 were obtained at the same conversion ($X = 0.7$), but preliminary reduction time was different—300 and 30 min, respectively. Same difference characterizes dissolving curves 2 and 5 obtained at conversion $X = 0.8$. Thus, we may assume that the lower is the dissolving rate the longer the preliminary reduction.

According to Fig. 2, initial dissolving rate after the 30 min reduction is by 3.5–4-fold higher than after the 300 min reduction, though integral quantity of crystal phase is the same ($\delta \approx 1$). Obviously, this is related to the fact that longer reduction provides particles growing owing to the secondary crystallization process when larger particles grow by the expense of smaller particles dissolving. Therefore, according to the Nernst equation (1), small particles dissolve with a higher rate than the large ones. Electron microscopy pictures of vanadium catalysts demonstrate that the average radius of forming crystals attains 10–15 nm in several hours. Taking crystals radius after the 300 min reduction as $r_{01} = 12$ nm from the ratio of initial rates and mathematical model parameters, we may estimate the radius of crystals after the 30 min reduction as $r_{02} = 8$ nm.

4.2. Temperature influence on the rate of crystal phase dissolving

As temperature increases, crystal phase dissolves till a new equilibrium. Data given in Fig. 3 allow the estimation of temperature effect on the rate of crystal phase dissolving. Dissolving curves 1–3 correspond to different temperatures. All the other parameters such as gas phase composition at dissolving and preliminary reduction time are the same. At 450 °C, crystal phase completely dissolves in less than 2 min. At 420 and 400 °C, dissolving goes slower and is not complete. Apparently, the higher the temperature, the faster is the dissolving process.

4.3. Modeling

Using the above-described model, we studied crystal phase dissolving into the active component of vanadium catalyst for sulfur dioxide oxidation.

Figs. 4 and 5 show experimental and calculation data related to the crystal phase growth and dissolving for small catalyst grains (fraction 0.5–1 mm). Fig. 4 demonstrates the vanadium reduction under the action of mixture 3% SO_2 + He. Fig. 5 shows calculation results and experimental data for the crystal phase dissolving under various conditions (temperature and gas mixture composition) and at different times of preliminary reduction. A good agreement between experimental and calculation results tells that this particular model may be successfully used for the description of crystal phase dissolving dynamics.

Note that all the above-described experiments were done using a differential reactor with small catalyst grains (fraction 0.5–1 mm). Therefore, reaction conditions were uniform in the catalyst bed and inside the catalyst grain.

When reaction proceeds in the bed of large catalyst grains, gas phase composition along reactor length and grain radius is not the same. As a result, phase transition dynamics becomes more complex. As shown in Ref. [2], when a gas mixture containing sulfur dioxide and oxygen passes through the bed of vanadium catalyst, a moving front of crystal phase of vanadium(IV) complexes forms along the bed. Front formation dynamics and its movement depend on many factors such as gas phase composition, catalyst properties (grain size, composition and even prehistory). All experimentally observed dependencies and peculiarities are well described with the mathematical model used here and earlier with the above-mentioned set of parameters. Let us use this model to describe the dynamics of the crystal phase dissolving in the catalyst bed. The figures presented below show crystal phase distribution over the bed in coordinates $\delta(\xi)$, where ξ is the dimensionless length of the catalyst bed.

Fig. 6a gives the crystal phase front position (curve 1) in the bed of vanadium catalyst after 20 min of reductive mixture supply into the bed (1% SO_2 + 4.5% O_2, balance helium). Curve 2 corresponds to sulfur dioxide conversion along the bed without crystal phase, and curve 3 corresponds to SO_2 conversion in the presence of crystal phase front. Calculations were done for a bed of small catalyst grains (fraction 0.5–1 mm) providing no gradients over catalyst grain.

Fig. 6b demonstrates how crystal phase profile (curve 1, Fig. 6a) changes after 60 min of feeding reaction mixture of different conversions. The front part of the bed is shown. At a zero conversion ($X = 0$, curve 1), reduced vanadium portion continues to grow. At high conversions ($X = 0.8$ and 0.9, curves 2 and 3, respectively) crystal phase dissolves in the front part of the bed. The rate of dissolving increase with increasing of SO_2 conversion or partial SO_3 pressure. Note that the dissolving sulfur dioxide content in the starting mixture was 9.5%. Such mixture provides higher
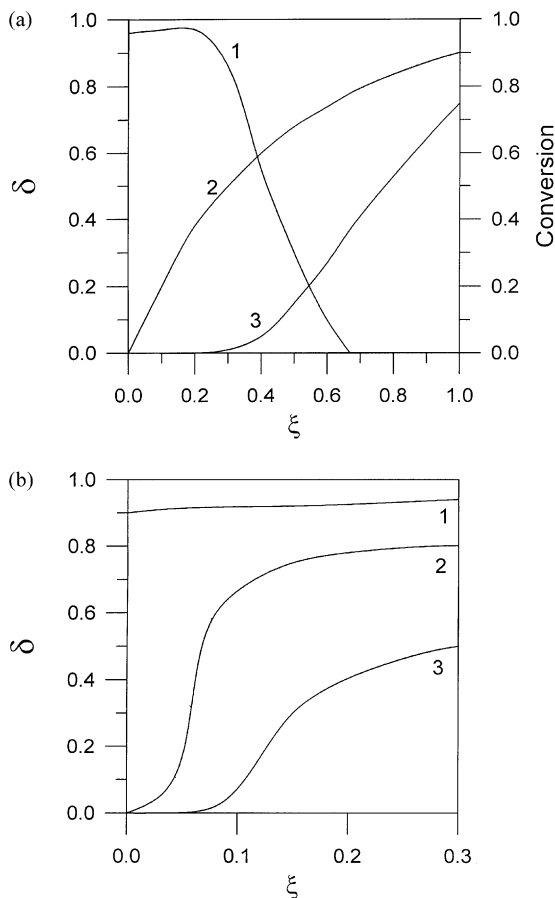
Fig. 6. (a) Crystal phase front position (curve 1) and sulfur dioxide conversion profile (curve 3) in the catalyst bed for 20 min after the supply of mixture 1% SO_2 + 4.5% O_2, balance He. Curve 2—conversion profile at the starting time moment ($\delta = 0$). Temperature: 420 °C. Catalyst fraction 0.5–1 mm. (b) Crystal phase front position (see (a)) 60 min after the supply of mixture 9.5% SO_2 + 11.5% O_2, balance He at conversion $X = 0$ (curve 1), $X = 0.8$ (curve 2), $X = 0.9$ (curve 3). Temperature: 420 °C.
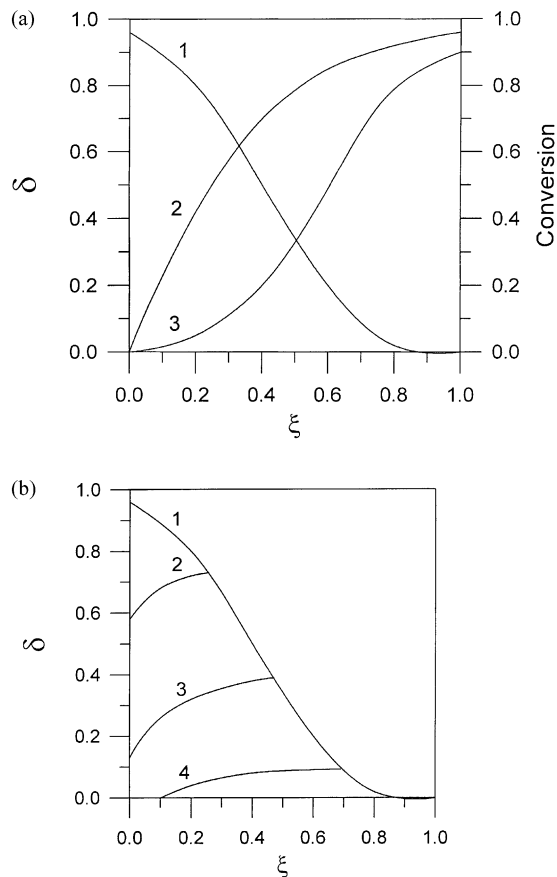
Fig. 7. (a) Crystal phase front position (curve 1) and SO_2 conversion profiles (curve 3) in the bed of catalyst grains for 250 min after a supply of mixture 0.8% SO_2 + 8.1% O_2, balance He. Curve 2—conversion profile at a starting moment ($\delta = 0$). Temperature: 430 °C, grains size: 5 × 10 mm. (b) Crystal phase front position (see (a)) after a supply of mixture 9.5% SO_2 + 11.5% O_2, balance He corresponding to conversion $X = 0.8$ at different time moments (min): 0 (curve 1), 12 (curve 2), 60 (curve 3), 300 (curve 4). Temperature: 470 °C. Grains size: 5 × 10 mm.

concentrations of sulfur trioxide thus accelerating the crystal phase dissolving.

When catalyst grains are large to describe the phase transition in the bed (crystal phase formation and dissolving), we should consider the gradients of concentration not only over the catalyst bed, but also over the catalyst grains. Gradients in the grains are caused by the internal diffusion restrictions in the pores. Owing to internal diffusion restrictions phase transition processes both formation and dissolving, go less intensively. This leads to a paradox result: under internal diffusion regime, catalyst bed activity becomes higher than under kinetic regime (no diffusion restriction) with small catalyst grains [2].

Results of numerical modeling of crystal phase formation in the bed of catalyst grains with a size of 5 × 10 mm^2 are given in Fig. 7a. Curve 1 corresponds to the crystal phase front position after 250 min of reaction mixture feeding at 430 °C. Reaction mixture composition is 0.8% SO_2 + 8.1%

O_2, balance helium. Curve 2 characterizes sulfur dioxide conversion along the bed with no crystal phase ($t = 0$), and curve 3—in the presence of crystal phase front. Calculations show that sulfur dioxide conversion at the bed outlet decreases from 0.95 to 0.88 owing to crystallization.

Fig. 7b shows the results of catalyst bed regeneration modeling. One may see crystal phase profiles along the bed at various time moments. At regeneration, catalyst bed temperature is increased to 470 °C. Calculations were performed for the gas mixture with high concentrations of reagents and high sulfur dioxide conversion.

Therefore, catalyst regeneration is indeed possible if activity decrease is caused by the crystal phase formation.

In sulfuric acid production, this situation is first of all related to the catalyst for the second stage of DC/DA (double contact) systems, where catalyst operation is characterized by low temperatures (420–440 °C), low inlet SO_2 concentration (about 1%), and by the SO_3 absence at the bed inlet. According to analysis of catalysts, unloaded from industrial

apparatuses, their activity decreases during their operation. Activity decrease is dramatic during the starting period of catalyst bed work, and then decelerates during the following months. Finally, catalysts activity attains some steady state level.

Crystallization modeling for the conditions of the fourth bed (second stage) of DC/DA system (Fig. 7) allows us to conclude that in the starting period of catalyst operation, SO_2 conversion decreases owing to the primary crystallization process. During the latter crystal phase, nuclei form and then grow to the size of support pores. The following slow decrease of activity may result from the secondary crystallization processes. According to our estimates, typical time for secondary crystallization ranges from 1 to 10 months, depending on the size of catalyst grains, support pore structure, and active component composition.

Modeling shows that it is possible to regenerate the catalyst supplying gas mixture with a high content of sulfur trioxide onto deactivated catalyst, and raising the temperature. Regarding the processes of crystal phase dissolving, we may suggest the following method for the SO_2 conversion stabilization at the second contact stage. One may switch gas flows so that third bed regime (high temperature and high SO_3 content) and fourth bed regime (low temperatures and low SO_3 content) could alternate during the process. In this case, crystal phase forming under the regime of fourth bed operation (Fig. 7a) shall dissolve under the regime of the third bed operation (Fig. 7b). Alternation time may be estimated regarding the calculation data. Curves 2–4 in Fig. 7b show how crystal phase profile changes in the bed at different moments of dissolving. Initial profile (curve 1) corresponds to the front formed in the fourth bed. Crystal phase dissolves almost completely in the same time as it forms. Therefore, switching regimes in several hours, one can maintain a higher average integral conversion of sulfur dioxide at the bed and apparatus outlet.

5. Conclusion

During the SO_2 oxidation vanadium catalyst activity decrease, caused by the formation of crystal phase of vanadium(IV) compounds, is reversible. Crystal phase dissolves when temperature and sulfur trioxide concentration become higher. The rate of crystal phase dissolving depends on the conditions of its formation as well as on dissolving conditions. Thus, as the time of catalyst reduction increases, the rate of the following dissolving decreases. As temperature and SO_3 content in the gas phase grow the dissolving rate increases.

A mathematical model, suggested for describing the dynamics of crystal phase dissolving and for the evolution of catalyst grain and bed activity provided by the dissolving process, is proved to be successfully applicable for the purpose.

Reversibility of phase transitions, related to the crystallization of vanadium(IV) compounds, allows to improve the process scheme and to increase catalyst lifetime.

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