Jointly published by
Akadémiai Kiadó, Budapest
and Kluwer Academic Publishers, Dordrecht

React.Kinet.Catal.Lett.
Vol. 73, No. 2, 357-365
(2001)

RKCL3912

# POTASSIUM VANADATES OF MIXED VALENCE AS SULFURIC ACID CATALYST PRECURSORS

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*Received May 7, 2001*
*Accepted May 31, 2001*

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**Abstract**

The kinetics of hydrolytic precipitation of potassium vanadates $K_xV_{12}O_{31-\delta}\cdot nH_2O$ ($0 < x \leq 2.25$; $0 < \delta \leq 1.15$) from a $KVO_3$ solution at pH = 1.7 and 80°C in the presence of $K_2SO_4$ and $VOSO_4$ is controlled by second and third order reactions respectively occurring on the precipitate surface. This difference is due to the effect of $VO^{2+}$ ions on the polymer anion $[V_{12}O_{31-\delta}]^n$ formation. Potassium vanadates $K_xV_{12}O_{31-\delta}\cdot nH_2O$ and $K_xV_3O_{8-\delta}\cdot nH_2O$ ($1.02 \leq x \leq 1.91$; $0 \leq \delta \leq 0.22$) can be used as vanadium-containing precursors for sulfuric acid catalysts.

*Keywords*: Vanadates, sulfuric acid catalysts

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## INTRODUCTION

Hydrochemical utilization of spent vanadium catalysts of sulfur dioxide oxidation [1] results in production of acid solutions containing $V^{4+}$ and $V^{5+}$. Vanadium can be precipitated from these solutions in the form of potassium vanadates $K_xV_{12}O_{31-\delta}\cdot nH_2O$ and $K_xV_3O_{8-\delta}\cdot nH_2O$. However, their formation kinetics and their potential as vanadium-containing precursors of the sulfuric acid catalysts have not been studied.

The objective of the present work is to investigate the hydrolytic precipitation of potassium vanadates from the system $KVO_3$–$VOSO_4$–$K_2SO_4$–$H_2O$ and their applicability in the synthesis of sulfuric acid catalysts of the CVD type [2].

0133-1736/2001/US$ 12.00.

## EXPERIMENTAL

$KVO_3$, $VOSO_4$, $K_2SO_4$ and KOH of analytically pure grade were used as reactants. The hydrolytic precipitation of vanadium was carried out in a thermostat, which provided the temperature control within ±1°C. Potassium and vanadium content in the samples was determined by an absorption and volumetric analysis, respectively. The precipitate content was controlled using IR-spectra measured with a Specord-75 spectrometer, and X-ray diagrams recorded with a DRON-0,5 apparatus under Cu Kα-radiation.

The following vanadium-containing precursors were used for the catalyst synthesis: $V_2O_5$ (I), $K_{1.9}V_{12}O_{30.2}\cdot nH_2O$ (II), and $K_{1.4}V_3O_{7.8}\cdot nH_2O$ (III). The molar ratio $K_2O:V_2O$ was 4:1. The content of the active $V_2O_5$ form was 8% of the total catalyst weight. Natural macroporous diatomite was used as a carrier. The calculated amount of $KHSO_4$ was added to vanadium compounds pre-powdered with diatomite. The mixture was dried at 100-150°C, pressed into briquettes and then caked at 550-580°C for 3 h. In this process, the $V^{4+}$ ions of the precursor were converted into the $V^{5+}$ form, which was confirmed by the volumetric analysis. After the process, the $V^{4+}$ ions could not be detected within the limits of the experimental error. The selected fraction of 1-2.5 mm was sieved.

Before studying the catalytic properties, we exposed the samples to the reacting medium with the initial $SO_2$ concentration of 10-15% at 450°C for 6 hours. The catalyst activity in the $SO_2$ oxidation was determined according to the $SO_2$ conversion in a flow glass reactor at 485°C and the gas mixture flow rate of 6350 $cm^3\ h^{-1}$. The initial $SO_2$ concentration in the air was 15%. Ten milliliters of the catalyst was mixed with the equal amount of quartz. The reaction temperature was controlled within ±1.5°C, using a thermocouple placed in the center of the catalyst bed. The conversion X (%) was calculated by the equation:

$$X = \frac{(c_o - c)\cdot 10000}{c_o \cdot (100 - 1{,}5c)},$$

where $c_0$ and c are the initial and final $SO_2$ concentrations in the reactor as determined by iodometric titration.

## RESULTS AND DISCUSSION

The preliminary experiments have shown that the X-ray amorphous vanadate $K_xV_{12}O_{31-\delta}\cdot nH_2O$ ($1.5 \leq x \leq 2.25$ and $0.4 \leq \delta \leq 1.5$) is produced in the $KVO_3$–$VOSO_4$–$H_2O$ system at 90°C and $1 < pH < 3$. At $pH > 5$, the tetragonal crystalline $\varphi$-phase $K_xV_3O_{8-\delta}\cdot nH_2O$ ($1.02 \leq x \leq 1.91$; $0 \leq \delta \leq 0.22$) is precipitated. Within the range $3 < pH < 5$, the mixture of these two compounds exists. The IR-spectra of these vanadates are shown in Fig. 1. The X-ray diagrams of $K_xV_3O_{8-\delta}\cdot nH_2O$ compounds are similar to those known in the literature [3]. If vanadium is being precipitated from $KVO_3$ at pH = 1.7, where the $VO_2^+$ ions dominate, the reaction can be described by eq. 1.

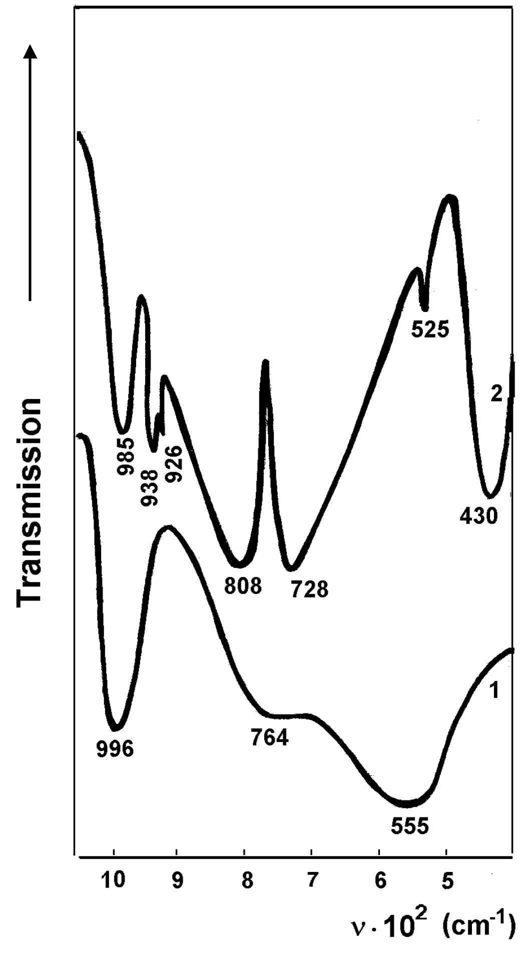

**Fig. 1.** IR-spectra of vanadates: 1) $K_xV_{12}O_{31-\delta}\cdot nH_2O$; 2) $K_xV_3O_{8-\delta}\cdot nH_2O$

$$2K^+ + 12VO_2^+ + 7H_2O = K_2V_{12}O_{31} + 14H^+ \qquad (1)$$

A decrease in pH detected at the end of the experiment supports the validity of the equation.

The $V^{4+}$ ions are involved in the potassium polyvanadate formation according to the equation:

$$2K^+ + (12\text{-}y)VO_2^+ + yVO^{2+} + (7+0.5y)H_2O = K_2V_{12\text{-}y}^{5+}V_y^{4+}O_{31\text{-}0.5y}^{+} + (14+y)H^+ \qquad (2)$$

The precipitation of the compound in reaction (1) is characterized by an induction period of the solid cluster formation. At the initial $KVO_3$ concentration of 0.05 M, the induction period changes from 5 to 135 min with the temperature decrease from 90 to 60°C. The addition of potassium sulfate with the concentrations up to 0.25 mol/L decreases the induction period, whereas the higher $K_2SO_4$ concentrations lead to an increase in the cluster formation time.

The hydrolytic vanadium precipitation is more significantly affected by the $VO^{2+}$ ions. In the presence of vanadyl sulfate (0.01 mol/L), the induction period completely vanishes. In accordance with the IR-spectra, these precipitates have the same structure. However, in this case, they contain $V^{4+}$ (2).

After the potassium polyvanadate clusters were formed, their further growth can be limited either by the $K^+$, $VO_2^+$, $VO^{2+}$ diffusion or by the surface formation of the $VO_5$ tetragonal pyramid chains with the subsequent formation of the double V-O layers with the potassium cations and water molecules in between [4].

Since $[V_{12}O_{31}]^{2-}$ does not exist in the solution, and the conditions created (pH and temperature) correspond to the $K_xV_{12}O_{31\text{-}}\delta{\cdot}nH_2O$ polyvanadate crystallization, this solution may be considered as oversaturated in respect to this compound.

The observed hydrolysis under the stationary conditions revealed almost an instantaneous formation of the polyvanadate clusters in the whole solution volume, which allows the use of equations 3-4 for the kinetic data analysis:

$$k'_D \cdot \tau = \int_0^{\alpha} \alpha^{-\frac{1}{3}} (1-\alpha)^{-1} \cdot d\alpha = I_D \qquad (3)$$

$$k'_N \cdot \tau = \int_0^{\alpha} \alpha^{-\frac{2}{3}} (1-\alpha)^{-N} \cdot d\alpha = I_N \,. \qquad (4)$$

These equations were developed by Nilsen [5] for the heterogeneous autocatalytic solid-phase growth from oversaturated solutions without further nucleation [5]. Here, $k'_D$ and $k'_N$ are the apparent rate constants of the diffusion controlled growth and of the surface-reaction controlled growth, respectively. N indicates the order of the surface reaction with respect to the precipitate; $\alpha$ is the fraction of the total vanadium precipitate formed at time $\tau$; $I_D$ and $I_N$ are the integrals of the corresponding kinetic equations.

If the growth rate on the particle surface is controlled by a reaction of the order N [5], then:

$$\frac{dr}{d\tau} = Vk_N C^N . \tag{5}$$

Here, $r$ is the particle radius, $V$ is the molar volume of the material, $k_N$ is the rate constant, and $C$ is the precipitate concentration. Since $C >> S$, where $S$ is solubility, one may consider $C \approx const = C_O$ and $k_N = \dfrac{k'_N r_\infty}{3V(C_O - S)}$. Considering also that $r = r_\infty \alpha^{1/3}$, where $r_\infty = r$ at $\tau = \infty$, equation (5) can be transformed to

$$\frac{dr}{d\tau} = \frac{1}{3} r_\infty \alpha^{-2/3} \frac{d\alpha}{d\tau} = Vk_N C_O^N (1-\alpha)^N \tag{6}$$

or

$$\frac{d\alpha}{d\tau}\alpha^{-2/3} = \frac{Vk_N C_O^N}{\frac{1}{3} r_\infty}(1-\alpha)^N \tag{7}$$

The logarithm of eq. 7 is

$$\lg\frac{\Delta\alpha}{\Delta\tau}\alpha^{-2/3} = \lg\left(Vk_N C_O^N\right) - \lg\left(\frac{1}{3} r_\infty\right) + N\lg(1-\alpha) \tag{8}$$

The replacement of $\frac{d}{d\tau}$ onto $\frac{\Delta}{\Delta\tau}$ in eq. 8 implies the use for the interpolation of finite differences delivered from the experiment. From eq. 8, a $\lg\frac{\Delta\alpha}{\Delta\tau}\alpha^{-2/3} - \lg(1-\alpha)$ plot yields a straight line with the slope equal to N.

Suitability of these equations, shown previously in ref. [6], is confirmed in the present work for potassium metavanadates by the detected direct dependence of $\lg(\Delta\alpha / \Delta\tau \cdot \alpha^{-2/3})$ on $\lg(1-\alpha)$ (Fig. 2). It is found that after the induction period, the kinetic results can be described by the equation $b + k'_N \cdot \tau = I_N$ (Fig. 3) (where $b$ is a parameter).

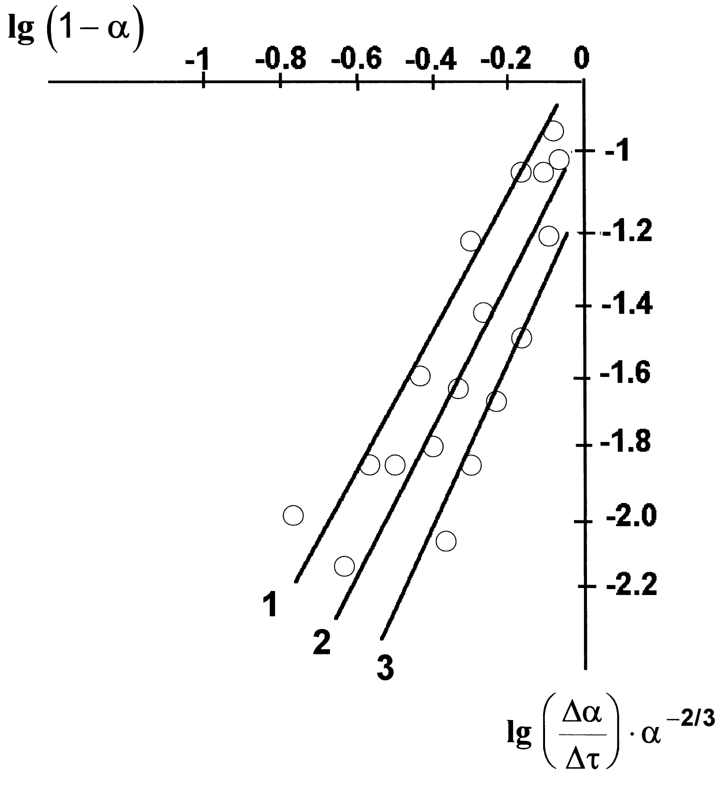

**Fig. 2.** Dependence of $\lg(\Delta\alpha\ /\ \Delta\tau \cdot \alpha^{-2/3})$on $\lg(1-\alpha)$ for the vanadium compound precipitation from the 0.05 M $KVO_3$ solution at different $K_2SO_4$ concentrations: (1) 0.05 M; (2) 0.25 M; (3) 0.5 M (pH = 1.7, T = 80°C)

The polyvanadate potassium precipitation in the system $KVO_3$-$K_2SO_4$-$H_2O$ is controlled by the second order reaction occurring on the solid surface. The reaction rate constant varies in the range of 0.17, 0.20, 0.13, 0.06 for the $KVO_3$ solutions containing 0, 0.05, 0.25, 0.50 mole of $K_2SO_4$ per liter, respectively. In the case of the vanadyl sulfate addition, the third order reaction is the limiting one. The presence of small quantities of $VOSO_4$ (0.01-0.02 mol/L) in the $KVO_3$ solution sharply increases the rate constant of the precipitation. With the further vanadyl sulfate concentration growth, the rate constant $k_N$ decreases remaining greater than that for pure $KVO_3$ (Fig. 4).

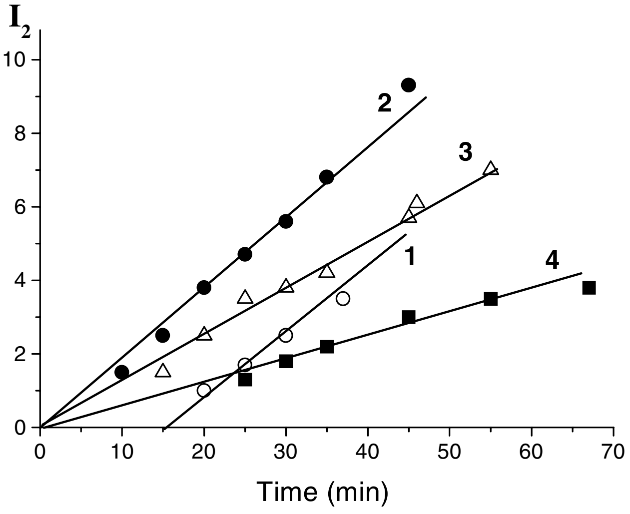

**Fig. 3.** Dependence of $I_2$ on time of the vanadium compound precipitation from the 0.05 M $KVO_3$ solution at the different $K_2SO_4$ concentrations: (1) 0; (2) 0.05 M; (3) 0.25 M; (4) 0.5 M (pH = 1.7; T = 80°C)

The second polyvanadate $K_xV_3O_{8-\delta}\cdot nH_2O$ containing the $V^{4+}$ and $V^{5+}$ cations is formed at a sufficiently high rate when heated up to 80°C with the subsequent cooling of the solution with the molar ratio $KVO_3 : VOSO_4 = 1$ and pH = 7:

$$2K^+ + 2VO_3^- + VO^{2+} + 2OH^- \longrightarrow K_2V_3O_8 + H_2O \qquad (9)$$

This process kinetics was not investigated due to the high reaction rate.

The reactivity of the potassium vanadates studied containing the cations $V^{4+}$ and $V^{5+}$ toward the pyrosulfate system can differ from that of commonly used $V_2O_5$, when converted to a molten phase. In this connection, the suitability of these vanadates for the synthesis of the catalysts for the $SO_2$ to $SO_3$ oxidation should be examined.

The table shows the activity of the catalysts synthesized from $V_2O_5$ or from potassium vanadates containing the cations $V^{4+}$ and $V^{5+}$. The activities of all the catalysts under investigation are shown to be the same in the limits of the experimental error. Thus, it has been found that the formation of $K_xV_{12}O_{31-\delta}\cdot nH_2O$ vanadate is limited by the surface chemical reaction and not by the ion diffusion to the developing solid phase, as was proposed earlier [6]. In total, this process is controlled by the formation of the polymer anion $[V_{12}O_{31-\delta}]^{n-}$, which in conjunction with the potassium cation develops the $K_xV_{12}O_{31-\delta}\cdot nH_2O$ vanadate structure (second order reaction).

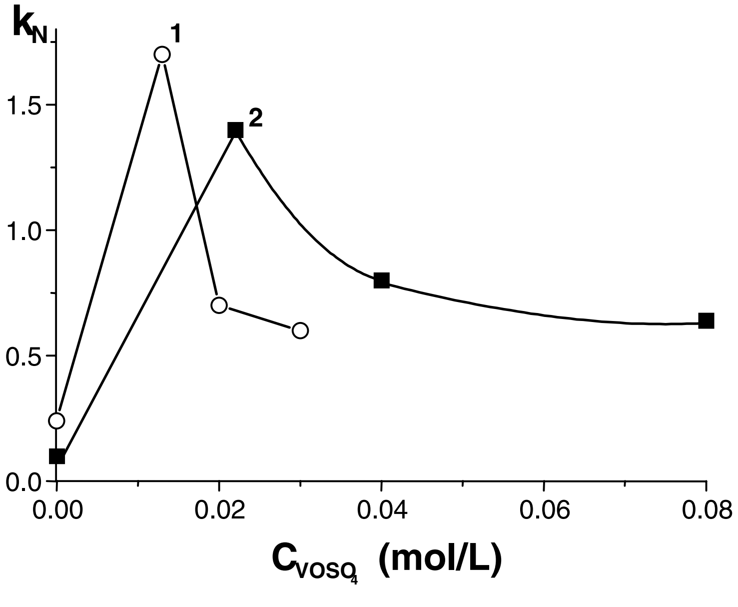

**Fig. 4.** The rate constants of the vanadium compound precipitation from 0.05 M (1) and 0.2 M (2) $KVO_3$ solutions depending on the $VOSO_4$ content (pH 1.7; T = 80°C)

If the solution contains both $V^{4+}$ and $V^{5+}$, the polymerization proceeds faster. The $VO_2^+$, $VO^{2+}$ and $K^+$ ions are involved in the surface reaction of the third order. These data show that in the practice of vanadium extraction from the spent sulfuric acid catalysts, the presence of $V^{4+}$ has a positive effect on the polyvanadate hydrolytic precipitation kinetics. Potassium vanadates of mixed valence produced in the reaction can be used as the precursors of the catalyst synthesis for $SO_2$ oxidation.

**Table 1**

$SO_2$ conversion on the catalysts synthesized with the different vanadium-containing precursors

| Sample number | Vanadium-containing precursor | Conversion, x (%) |
|---|---|---|
| I | $V_2O_5$ | 60.4 |
| II | $K_{1.9}V_{12}O_{30.2}\cdot nH_2O$ | 62.9 |
| II | $K_{1.4}V_3O_{7.8}\cdot nH_2O$ | 60.0 |

**Acknowledgment.** This study was supported by the Russian Foundation for Basic Research (Grant No. 00-15-97418).

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