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A New Vanadium Catalyst for Chlorine Production by Hydrogen Chloride Oxidation

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Industrial vanadia catalyst for SO_2 oxidation, IK-1-6, was shown to be efficient in a process of hydrogen chloride oxidation into molecular chlorine. The productivity of the catalyst attains values of 180 grams of chlorine per kilogram of catalyst per hour at 400 ºC. The catalyst was shown to be stable for 6 hours. A way to create a stable-operating catalytic system for chlorine production is suggested.

Key words: chlorine, hydrogen chloride, oxidation, vanadia catalyst, stability.

Regeneration of molecular chlorine by catalytic oxidation of hydrogen chloride, also known as Deacon process, (1) is an important problem of chlorine metallurgy and industrial production of chlororganic compounds [1]

$$4\,HCl + O_2 = 2\,Cl_2 + 2\,H_2O, \qquad (1)$$
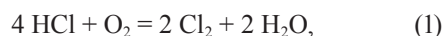
but an efficient catalyst for the reaction, except for patent data on expensive RuO_2 system, has not been found. Recently we found that vanadium catalyst $V_2O_5*nKCl*mLiCl$ is very active, but not stable enough in hydrogen chloride oxidation at 250 – 350 ºC [2]. This corresponds to data by Benson et al. [3], whose experiments with vanadia catalyst resulted in its quick evaporation in the form of $VOCl_3$.

Decreasing the vanadium volatilization and increasing the stability of vanadium catalysts can be attained by two ways:

(a) use of the compounds which are more stable under reaction conditions than vanadium oxide, and

(b) creating reactant concentrations, which suppress $VOCl_3$ formation according to equations:

$$KVO_3 + 4\,HCl = VOCl_3 + KCl + 2\,H_2O, \quad (2)$$
$$[VOCl_3] = K\,[HCl]^4/[H_2O]^2, \qquad (3)$$

where K is equilibrium constant of reaction (2). According to eqs. (1) – (3), the dependence of vanadyl chloride equilibrium pressure versus hydrogen chloride conversion decreases proportionally to 4th power of HCl pressure and negative 2nd power of H_2O pressure, i.e. $VOCl_3$ pressure decreases proportionally to at least 4th power of HCl conversion ratio.

Indeed, we have found that industrial vanadium catalyst IK-1-6 (8 % V_2O_5, 30 % K_2SO_4 supported on SiO_2) for SO_2 oxidation

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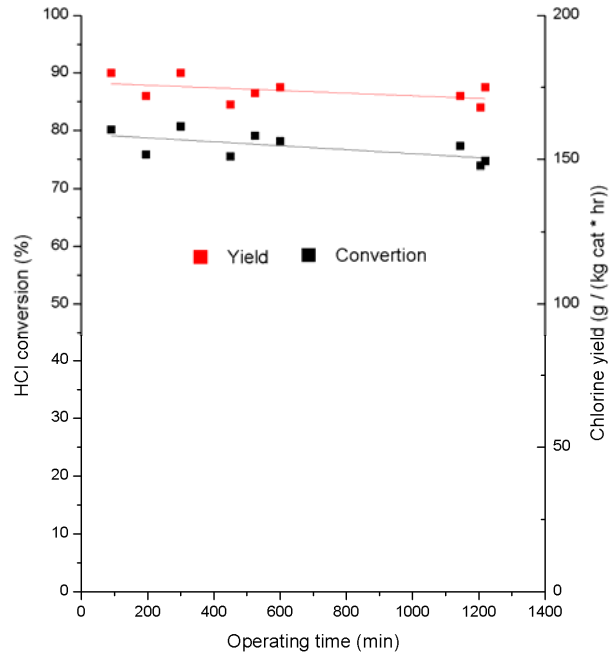*   Corresponding author E-mail address: veta@icct.ru

Fig. 1. Influence of process duration of HCl oxidation by air on the activity of IK-1-6 catalyst at 400 °C. Reactor i.d. 21 mm, gas flow rate 13 l/h, initial catalyst mass 14.98 g, catalyst grain size 0.63-1 mm. HCl concentration in the gas phase - 17 vol.%
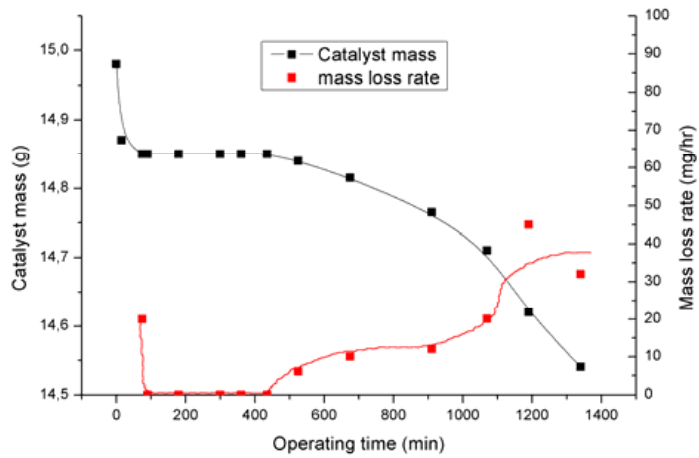

Fig. 2. The dependence of mass and mass decrease rate for IK-1-6 catalyst versus operation duration

is stable and active enough at HCl conversion ratio close to equilibrium (Fig. 1, 2). The catalyst productivity and HCl conversion do not exhibit significant decrease over the 20 hours of operation. The experiments were carried out as described in [2].

Fig. 2 displays the dependencies of catalyst mass decrease versus time on stream while HCl conversion is kept above 60 %. The integral and differential curves of mass decrease consist of three principal sections: the short initial section (1 hour) with high weight loss rate, the prolonged middle section (6 hours) during which no weight loss is observed at all, and the trailing section with weight loss rate of 20 - 30 mg/hr.

The initial weight loss (130 mg) may be due to dehydration of the catalyst. Along the middle section (lasting approx. 6 hours) no weight loss is detected, but discoloration of the catalyst layer on the inlet side is observed, and thickness of discolored catalyst layer increases with operation duration. So there is the time period along which vanadium is volatilized in the gas entry side layer and is completely absorbed in the following layers. Such phenomenon indicates that vanadyl chloride formation-hydrolysis processes are mainly determined by the thermodynamic parameters of the system, i.e., are of equilibrium nature. While reacting gas mixture moves along the catalyst sample, concentration of HCl decreases and concentration of H_2O increases in the gas phase due to the catalytic reaction (1) taking place.

Both these changes lead to substantial decrease of $VOCl_3$ equilibrium concentration, according to equations (2) – (3).

The trailing section of weight loss curve is characterized by the increase of catalyst mass loss rate along with lack of notable change in productivity and HCl conversion. The latter means that concentrations of hydrogen chloride, water, and equilibrium concentration of vanadyl chloride do not change as well. Under such conditions, the catalyst mass loss can be explained by the low rate of $VOCl_3$ hydrolysis - as thickness of the active vanadium-containing catalyst layer decreases, so decreases the time during which $VOCl_3$ can contact to both the gas mixture described by high HCl conversion and the catalyst itself. As the result, vanadyl chloride does not have enough time to be completely hydrolyzed into solid vanadium compounds while within the catalyst bed bounds. Thus unhydrolyzed portion of $VOCl_3$ is carried away from the catalyst, resulting in the observed catalyst mass loss.

The obtained results demonstrate high activity and stability of the industrial vanadium catalyst, normally used for SO_3 production, in a process of HCl oxidation. These allow concluding that a stable vanadium catalytic system for HCl oxidation can be created. For example, under the used condition the catalyst sample of 30 g (190 mm of layer height) will operate for more than 6 hours without loss of vanadium, and after this period the gas flow direction may be reversed etc.

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Новый ванадиевый катализатор получения хлора окислением хлористого водорода

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Показано, что промышленный ванадиевый катализатор окисления диоксида серы ИК-1-6 активен в процессе окисления хлористого водорода в молекулярный хлор (производительность до 180 грамм хлора на килограмм катализатора в час при 400 °C). Показано, что катализатор стабилен в течение 6 часов и предложены пути создания стабильно работающей каталитической установки для производства хлора.

Ключевые слова: хлор, хлористый водород, окисление, ванадиевый катализатор, стабильность.