

Розроблено нові складні оксидні каталізатори одержання акрилової кислоти альдольною конденсацією оцтової кислоти з формальдегідом у газовій фазі. Встановлено вплив компонентів $B_2O_3-P_2O_5-WO_3-V_2O_5/SiO_2$ каталізаторів і температури на здійснення процесу альдольної конденсації; визначено оптимальні умови одержання акрилової кислоти

Ключові слова: акрилова кислота, гетерогенний каталіз, альдольна конденсація

Разработаны новые сложные оксидные катализаторы получения акриловой кислоты альдольной конденсацией уксусной кислоты с формальдегидом в газовой фазе. Установлено влияние компонентов $B_2O_3-P_2O_5-WO_3-V_2O_5/SiO_2$ катализаторов и температуры на осуществление процесса альдольной конденсации; определены оптимальные условия получения акриловой кислоты

Ключевые слова: акриловая кислота, гетерогенный катализ, альдольная конденсация

COMPLEX OXIDE CATALYSTS OF ACRYLIC ACID OBTAINING BY ALDOL CONDENSATION METHOD

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1. Introduction

Acrylic acid (AA) is a valuable chemical industry product, with the world capacity over 4.5 million ton per year. The main application of AA and its derivatives is production of various polymer materials, super absorbents, paint-and-varnish materials etc.

The most common method of AA production is the two-step propylene oxidation via intermediate stage of acrolein formation. This method has worked well in terms of economic efficiency and in terms of a simple hardware design. Among the drawbacks of AA obtaining by the oxidation method, there is formation of great number of by-products, including the products of destructive oxidation (CO and CO₂) [1]. Another feature of AA obtaining by the propylene oxidation is a direct dependence of economic efficiency of the method on world price of the corresponding raw material (oil), which varies within wide limits and in the long run tends to increase. Thus a problem of diversification of raw materials base of AA production appears, which causes the high relevance of the development of new methods of its production.

2. State of the art and problem statement

Among the most promising ways of expanding of raw materials base for the acrylic monomers production is application of carbonyl group condensation processes. The great interest of chemical products manufacturers in the implementation of condensation processes by carbonyl group is related to the possibility of acrylic monomers production in low number of stages [2]. In particular, AA is obtained by aldol condensation of acetic acid (AcA) with formaldehyde (FA) [3]. In industry FA and AcA are synthesized from methanol produced from synthesis gas. And a feedstock for synthesis gas obtaining is methane or coal. The global reserves of methane and coal are much larger compared to

oil. Thus, use of these raw materials in organic synthesis industry is more promising.

Existing catalysts for AcA condensation with FA are characterized by relatively low activity and selectivity of the desired product formation. As a result, industrial production of AA by aldol condensation method has not been set up, and relevance of researches aimed to improve the efficiency of the catalysts for aldol condensation of carbonyl compounds is very high.

Aldol condensation reactions of carbonyl compounds can occur on the catalyst active sites both basic and acidic types. This is confirmed by numerous scientific works, where both basic and acidic type catalysts with different composition are suggested to be used. In most cases, the use of basic type catalysts is characterized by the satisfactory selectivity of the desired product (AA) formation, but the activity of such catalysts is relatively low [4, 5]. On the contrary, acid type catalysts provide higher conversion of the initial reactants (AcA, FA), however, their use is accompanied by formation of a large quantity of by-products [6, 7]. Thus, the problem of developing a catalyst that can provide both high activity and selectivity in the AA obtaining process by aldol condensation remains unresolved.

In earlier researches it has been determined that promoting the $B_2O_3-P_2O_5/SiO_2$ catalyst by transition metals oxides allows achieving high conversion of AcA and FA in the AA production process even at equimolar ratio of the reactants [8, 9]. These catalysts are also effective in the aldol condensation of propionic acid (PA) with FA to methacrylic acid (MAA) [10, 11]. The main regularities of aldol condensation reaction of AcA and PA with FA are the same. $B_2O_3-P_2O_5-WO_3/SiO_2$ catalytic system is the most efficient (as it provides the highest yield of target product) among developed ones [10] in acrylic acid production by aldol condensation. By the way, the highest activity (i. e. conversion of initial reactants) is observed when using $B_2O_3-P_2O_5-V_2O_5/SiO_2$ catalytic system [10, 11]. The highest activity of $B_2O_3-P_2O_5-V_2O_5/SiO_2$ catalyst correlates with high

strength of acidic active sites on its surface, while the catalyst containing tungsten oxide is characterized by higher selectivity of the desired product formation and acidic active sites of moderate strength [8, 10].

Therefore we decided to replace part of tungsten oxide to vanadium oxide in $B_2O_3-P_2O_5-WO_3/SiO_2$ catalyst to improve this catalytic system, which as expected would increase its activity at an acceptable level of the desired product formation selectivity.

Addition components that may exhibit basic properties (such as cesium and calcium oxides) to $B_2O_3-P_2O_5-MoO_3/SiO_2$ (acid type catalytic system) can slightly increase AA formation selectivity, but the activity of such catalytic systems is relatively low [12, 13].

3. The purpose and objectives of the study

The purpose of present work is to develop efficient complex oxide catalysts of AcA aldol condensation with FA to AA. The catalysts efficiency is suggested to be improved by changing their composition and by determination of optimum ratio of the catalyst components responsible for strong acid surface sites and those responsible for medium acid surface sites.

The following tasks were solved to reach the work purpose:

- to determine effect of the vanadium oxide content in the catalysts on catalytic activity of the latter;
- to determine the process temperature effect on the reactants conversion, AA formation selectivity and AA yield.

4. Catalysts preparation and characterization

The catalytic systems based on mixtures of boron and phosphorus oxides with of tungsten and vanadium oxides with different ratios have been prepared for the research. All catalysts were prepared by impregnation method. Silica with specific surface $600 \text{ m}^2/\text{g}$ was used as a support. The atomic ratio of B:P:(W+V) was 3:1:0,3 respectively. Content of WO_3 and V_2O_5 was changed so the vanadium content in transition metals oxides mixture ($WO_3+V_2O_5$) was 20 % (K_1), 40 % (K_2), 60 % (K_3) and 80 % (K_4).

The catalytic properties of the developed catalysts were studied in flow setup with fixed-bed catalyst.

Formalin obtained from paraformaldehyde immediately before usage was used as a FA source.

The process was carried out at temperature ranged from 563 to 683 K at equimolar initial reagents ratio and contact time 12 sec. The reaction products were analysed by chromatography. Average value of three parallel independent measurements was taken as final result. General variance of reproducibility of the reactants conversion values is 2.6 and that of the target product formation selectivity is 1.5.

Acetone is a by-product in the reaction conditions, and it could be separated as a marketable product.

5. Determination of the optimal composition of the catalyst and optimal conditions of the process

The results showed that increase of vanadium content in vanadium-tungsten mixture results in considerable increase

of AcA conversion (Fig. 1). Increase of the catalyst activity probably occurs due to the increase of amount of acidic active sites created by vanadium oxide [8]. It is also clear from Fig. 1 that the catalysts activity increases with temperature raise in whole investigated range (563–683 K). The most considerable increase is observed up to 653 K (75.5 % with K_4 catalyst). Further increase of the reaction temperature (up to 683 K) does not result in considerable increase of AcA conversion (78.5 % with K_4 catalyst). The slowdown of AcA conversion increase when raising the reaction temperature is most probably observed because the reaction is equilibrium.

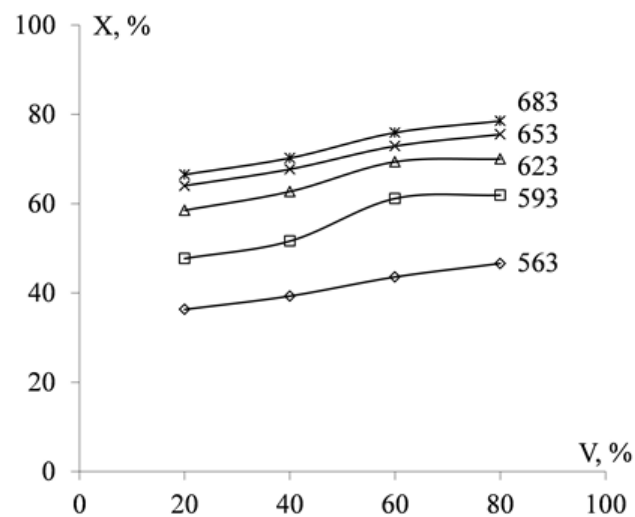


Fig. 1. Dependence of AcA conversion (X, %) on vanadium content in the vanadium-tungsten mixture in the catalysts (V, %)

Therefore, partial substitution of tungsten oxide by vanadium oxide allows achieving higher conversion of the reactants, while target product (AA) formation selectivity remains high. Thus, when vanadium content in the vanadium-tungsten mixture equals 20–60 % (K_1 , K_2 , K_3 catalysts) AA formation selectivity is high and slightly increases when vanadium content increases (Fig. 2). The increase of vanadium content in the vanadium-tungsten mixture up to 80 % (K_4 catalyst) is accompanied by considerable decrease of AA formation selectivity throughout the whole temperature range.

Maximum value of selectivity – 95.5 % – was achieved at 563 K and vanadium content in the vanadium-tungsten mixture of 60 % (K_3 catalysts). The most important fact is that the reaction temperature increase up to 593 K almost does not result in selectivity decrease (93.7 % with the same catalyst) while AcA conversion, and consequently AA yield, increase (Fig. 1, 3). When raising the reaction temperature above 593 K AA formation selectivity dramatically decreases for all studied V:W ratios in the catalyst.

The highest AA yield is achieved with K_3 catalyst (vanadium content in the vanadium-tungsten mixture is 60 %) throughout the whole studied temperature range (Fig. 3). Therefore, vanadium content of 60 % in the vanadium-tungsten mixture is optimal in terms of the target product yield.

The maximum yield of the acrylic acid – 60.3 % was obtained at 623 K. However, AA formation selectivity was only 87.0 %. Meanwhile at the temperature lower by 30 K (593 K) AA formation selectivity is much higher – 93.7 % and AA yield is lower only by 2.9 %. That's why it is inappropriate to carry out the process at 623 K.

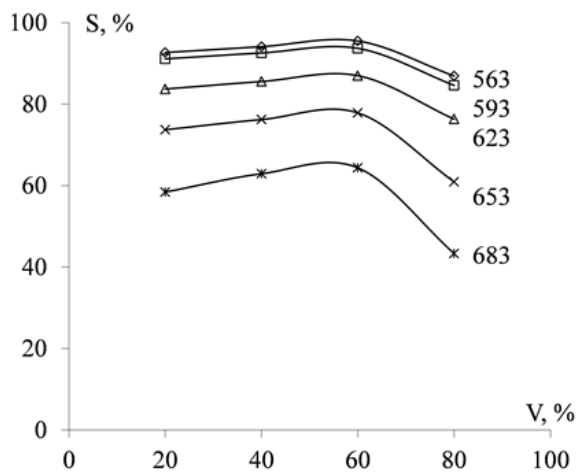


Fig. 2. Dependence of AA formation selectivity (S, %) on vanadium content in the vanadium-tungsten mixture in the catalysts (V, %)

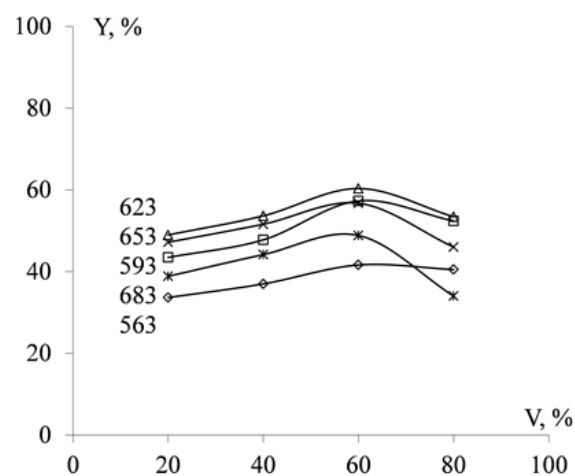


Fig. 3. Dependence of AA yield (Y, %) on vanadium content in the vanadium-tungsten mixture in the catalysts (V, %)

Thus, based on the obtained results we conclude that the optimal conditions of AcA condensation with FA to AA are temperature 593 K and vanadium content in the vanadium-tungsten mixture 60 %. Under these conditions, the yield of AA equal to 57.4 % was achieved while AA formation selectivity was 93.7 %.

On the catalyst containing no vanadium oxide ($B_2O_3-P_2O_5-WO_3/SiO_2$) acrylic acid yield was 50.6 %, while its formation selectivity was 88.8 % and AcA conversion was 57.0 % under the optimal conditions. Thus, the partial replacement of tungsten oxide in the catalyst by vanadium oxide increases catalyst activity (conversion) by 4.1 %, while desired product formation selectivity increases by 5.1 % and AA yield increases by 6.8 %. In addition, we managed to reduce the optimum temperature of the process from 653 K to 593 K that has a positive impact on the production energy efficiency.

6. Conclusions

New efficient catalysts for AcA aldol condensation with FA to the AA have been developed. The effect of vanadium oxide content in the catalyst and the process temperature on the reactants conversion and AA formation selectivity and yield has been ascertained. The optimal V:W ratio in the $B_2O_3-P_2O_5-WO_3-V_2O_5/SiO_2$ catalytic system is 3:2. The optimal temperature is 593 K.

Application of the developed catalyst at the optimal conditions allows to obtain AA with 57.4 % yield by pass, AA formation selectivity 93.7 % and AcA conversion 61.1 %. When recycling unreacted reagents, AA yield is up to 93.7 %. High efficiency of the developed catalyst justifies the use of AA obtaining method by aldol condensation as an alternative.

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Досліджено вилуговування ванадію з відпрацьованих каталізаторів конверсії сірчаного газу в розчинах сірчаної кислоти з додаванням допоміжного агента – перекису водню. При низьких концентраціях H_2SO_4 (до 10 г/л) досягнуто підвищення ступеня вилуговування на 30–40 % для каталізаторів, що містять у своєму складі сульфати рубідію та цезію. Термогідролітичне осадження п'ятивалентного ванадію можливо здійснювати без нейтралізації розчинів та зміни їх сольового складу

Ключові слова: каталізатор, ванадій, вилуговування, пероксид водню, термогідроліз

Исследовано выщелачивание ванадия из отработанных катализаторов конверсии сернистого газа в растворах серной кислоты с добавлением вспомогательного агента – перекиси водорода. При низких концентрациях H_2SO_4 (до 10 г/л) достигнуто повышение степени выщелачивания на 30–40 % для катализаторов, содержащих в своем составе сульфаты рубидия и цезия. Термогидролитическое осаждение пятивалентного ванадия возможно осуществляют без нейтрализации растворов и изменения их солевого состава

Ключевые слова: катализатор, ванадий, выщелачивание, пероксид водорода, термогидролиз

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ВПЛИВ ПЕРОКСИДУ ВОДНЮ НА КИСЛОТНЕ ВИЛУГОВУВАННЯ ВАНАДІЮ З ВІДПРАЦЬОВАНИХ КАТАЛІЗАТОРІВ

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1. Вступ

Промисловість України є активним споживачем ванадію та його сполук. Основними галузями викоринання ванадію є каталізатори та інгібітори у хімічних процесах, та легуючі добавки до спеціальних видів сталей у металургії. Для цих потреб практично весь ванадій в Україну імпортується. Власні розвідані ванадієві руди України бідні і, з екологічних та економічних причин, їх переробка не проводиться [1, 2]. В таких умовах важливе значення отримують процеси вилучення ванадію із вторинної сировини, промислових відходів та напівпродуктів переробки руд інших металів.

Серед джерел вторинної ванадієвої сировини важливе місце займають відпрацьовані ванадієві каталізатори (ВВК) синтезу сірчаної кислоти. Ці каталізатори відносяться до багатокомпонентної сировини та представляють собою формовану контактну масу, що містить у своєму складі діатомітову основу в порах якої знаходиться плав сульфатованадатів $Me^1_3VO_3SO_4$ (3–3,6 % в перерахунку на ванадій) та піросульфатів лужних металів $Me^1_2S_2O_7$ ($Me^1=K, Rb, Cs$) [3, 4]. Крім того, у відпрацьованих каталізаторах присутні домішки сульфатів заліза, марганцю, сполуки мий'яку тощо. Внаслідок високої токсичності сполук ванадію, жорстких екологічних вимог до поховання забруднених