

STUDY OF THE PROCESS OF OXIDATIVE DEHYDROGENATION OF ISOBUTANE ON VANADIUM (III) CONTAINING OXIDE AND NANOSTRUCTURED VANADIUM (V) CONTAINING CATALYTIC SYSTEMS

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Abstract: experimental results on the oxidative dehydrogenation of isobutane in the presence of vanadium-containing oxide and nanostructured catalysts are presented. The features of the structures of catalytic systems on the efficiency of their action on the activity and selectivity of the dehydrogenation process are studied. Oxidative dehydrogenation of isobutane, an industrial promising process for the preparation of isobutylene, was studied in the presence of vanadium oxide catalysts deposited on the surface of $\gamma\text{Al}_2\text{O}_3$ by decomposition with organometallic complex compounds of vanadium (III) and (V). The catalytic effect in the target and side reactions is compared with the results of studying the characteristics of their volume and surface by X-ray diffraction, X-ray photoelectron spectroscopy, temperature-programmed hydrogen reduction, and a number of others. Physicochemical method of investigation established that, depending on the initial vanadium metal complex taken, either the amount of reactive mobile oxygen increases or decreases, thereby promoting more efficient course of the oxide-reduction cycle and more stable operation of the catalyst.

Keywords: oxidative dehydrogenation of isobutane $\text{V}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ dehydrogenation catalysts.

ИЗУЧЕНИЕ ПРОЦЕССА ОКИСЛИТЕЛЬНОГО ДЕГИДРИРОВАНИЯ ИЗОБУТАНА НА ВАНАДИЙ(III) СОДЕРЖАЩИХ ОКСИДНЫХ И НАНОСТРУКТУРИРОВАННЫХ ВАНАДИЙ(V) СОДЕРЖАЩИХ КАТАЛИТИЧЕСКИХ СИСТЕМАХ

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Аннотация: окислительное дегидрирование изобутана - промышленно-перспективный процесс получения изобутилена – исследован в присутствии нанесённых на поверхность $\gamma\text{Al}_2\text{O}_3$ оксидных ванадиевых катализаторов разложением металлоорганическими комплексными соединениями ванадия(III) и (V). Каталитическое действие в целевой и побочных реакциях сопоставлено с результатами изучения характеристик их объёма и поверхности методами рентгеновской дифракции, рентгеновской фотоэлектронной спектроскопии, температурно-программированного восстановления водородом и рядом других. Физико-химическим методом исследования установлено, что в зависимости от взятого исходного ванадиевого металлокомплекса либо увеличивается, либо уменьшается количество реакционноспособного мобильного кислорода, способствующего тем самым более эффективному протеканию окисльно-восстановительного цикла и более стабильной работе катализатора.

Ключевые слова: окислительное дегидрирование изобутана $\text{V}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ катализаторы дегидрирования.

INTRODUCTION

Appropriate nanostructured catalytic systems were started to be observed frequently on the surface of different structured carrier by using plenty of one and multi-core metal complex compounds containing organic and metalorganic ligands obtained by synthesis experiments that made recently [1]. These systems help to provide more effective selective transformations of saturated or multi-group compounds. On the other side, using compounds having organic and metal-organic ligands is firstly based with, such compounds generate nanostructured metal and

metal oxide layer placing more effectively on the surface of carrier like metal and metal oxide at high temperatures [2]. Aim of introduced work is research about properties of using metal-complexes as raw material in creating nanostructured catalytic systems for more effective oxidative dehydrogenation processes of C₂-C₄ paraffins [3-7].

TECHNIQUE OF EXPERIMENTS

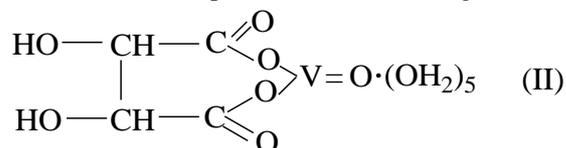
New vanadium metal complexes that more easily saturated in organic solvents and splitting in low temperatures were synthesized on the basis of the compounds of vanadium with organic ligands, new methods providing the compounds with no lost and high quality were developed. Due to accomplishing the aimed investigation work properties of the synthesis of the π - and ion type complexes of vanadium(+4 oxidation state) with cyclopentadienyl and organic acid ligand and establishing nanostructured catalytic systems on the surface of carrier were investigated. 2 type reaction were explored for this reason. One of them is the reaction of getting bis (π -cyclopentadiene) vanadium bis (tetrahydrofuran) dichloride, (π -C₅H₅)₂VCl₂(OC₄H₈)₂ I metal complex by VCl₄ reaction in the monocyclopentadienyl C₅H₆ THF solvent(activated by diethylamine). Easy oxidation and hydrolyzation of I metal complex is resulted with the conversion of it to the relatively stable II-vanadyl type metal complex (π -C₅H₅)₂V²⁺=O·(THF)₅ and heating of it in reaction environment is resulted of conversion to the more stable III- dymersolvate complex. It was observed from NMR ¹H spectrum, in contrast to the I and II III dioxovanadyle complex determines asymmetric form of the cyclopentadiene rings and vanadium for them to have $\delta_{C_5H_5}$ =6.17m.h. and $\delta_{C_5H_5}$ -6.38m.h chemical sliding. Thermal stable I transforms into new compounds after staying much in the solution. According to thermogravimetric analysis I-III cyclopentadienyl organic ligand containing metal complexes decompose (I-T_{deco} .120⁰C; II-T_{deco} .128⁰C; III-T_{deco} .170⁰C) and melt(I T_{melt} - 87-88⁰C; II-T_{melt} -107-108⁰C; III-T_{melt} .114-115⁰) in very low temperatures. According to the results of the microanalysis method, the brutto formula confirming the composition of new synthesized I-III complexes coincides with the theoretical calculations given to them. As for their solubility in polar and nonionic solvents, it should be noted that all three methaccomplexes are soluble good in DMSO, DMFO, acetone-like solvents and soluble bad in non-polar solvents. For the synthesis of the vanadium ion-type metal complex, according to the reaction between 2 dosed 2,3-dihydrocarboxybutandyol carbon (wine) acid HOOC(OH)-CH(OH)-COOH (IV) and vanadyle cation V²⁺=O V-bis 2,3-dihydroxybutanediol decahydrate vanadyle two-core metal complex was synthesized and investigated. V carboxylate complex with a high yield (84%) and a clear purity color crystal, T. = 136-137⁰C melting, T = 194⁰C, a degradation temperature was obtained for removing the obtained carboxylate type vanadium complex from the reaction mixture by applying liquid phase extraction method. According to the results of microanalysis, the content of the element obtained for the V complex coincides with theoretically calculated composition. Thus, methods were developed for getting new synthesized organic ligand containing metal complexes from reaction mixtures with high purity and without loss. Their solubility in many organic solvents, having low degradation temperatures, allows them to tan on the carrier surface (Al₂O₃, silica).

RESULTS and CONCLUSION

π -type bicyclopentadienyl bentetrahydrofuranate vanadium metal complex (π -C₅H₅)₂V=O(THF)₂ (I) having organic ligand, low decomposition temperature, high ability to be solved and 2-core ion-type bis-2,3 dihydrocarboxybutane dialpentahydrate divanadine complex was synthesized for the production of vanadium-based nanostructured new and more effective catalytic systems in the problem of oxidative dehydrogenation of C₂-C₄ paraffins.

Methods based on liquid phase extraction were developed for removal of the obtained new compounds from the reaction mixture without loss and high purity, their composition, structure and thermal properties were investigated. Both types of vanadyl metal complexes have good solubility in strong polyaric solvents and have low degradation (I - 120 °C, II - 194 °C), and the high oxophilic character of the final splitting product can be useful as raw material in future for creation of nanostructured vanadium oxide based catalytic systems.

Nanostructured catalytic systems based on vanadium-oxid were created by thermal decomposition on the surface of oxide carrier by using organic ligand containing π -type cyclopentadiene (C₅H₅)₂V=O(THF)₅ (I) vanadium complex which is changeable at T=180-194⁰C temperature interval, having low decomposition temperature and



acid ligand containing ion-type vanadyl carboxylate which is changeable at T=180-194⁰C high temperature interval. Solution was prepared by tetrahydrofuran solvent which is strong solvent former and plays the role of stabilizer of metal-ligand chemical communication. The second reason of choosing this solvent is its complex can be hydrolyzed easily. Solution of complex was made using H₂O. Al₂O₃/I·(THF)_n(I) and Al₂O₃/II·(H₂O)_m (II) solvent containing samples were obtained by tanning.

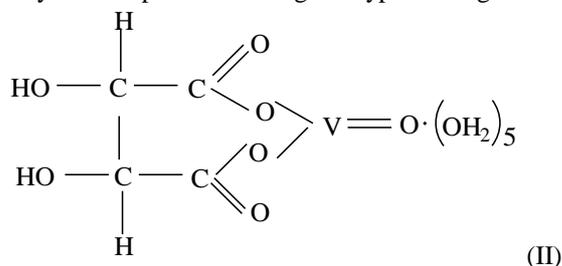
They desolvate by heating in I - 40-60⁰C temperature for 2 hours; II in 80-90⁰C interval for 5 hours in N₂ environment, respectively, for full separation of solvents in I and II samples and solvate samples containing Al₂O₃/I (III) and Al₂O₃/II (IV) are obtained. Desolvated III and IV samples are tanned to oxide carrier surface by thermal decomposition. Samples are placed in the oven which has special mixing mechanism and the temperature regime is determined.

A catalytic system containing $\text{Al}_2\text{O}_3/\text{V}_2\text{O}_4$ (V) was obtained by tanning of I-II sample- $\text{Al}_2\text{O}_3/\text{I}$ for 0.5 hours to the surface of oxide carrier in the inert gas (N_2) or open air environment at 120-180 $^\circ\text{C}$ temperature interval.

By the same way, a catalytic system containing $\text{Al}_2\text{O}_3/\text{V}_2\text{O}_5$ (VI) was obtained by tanning of $\text{Al}_2\text{O}_3/\text{II}$ (IV) for 1 hours to the surface of oxide carrier in the inert gas (N_2) or open air environment at 180-300 $^\circ\text{C}$ temperature interval.

Obtained both of catalytic systems containing $\text{Al}_2\text{O}_3/\text{V}_2\text{O}_4$ (V) and $\text{Al}_2\text{O}_3/\text{V}_2\text{O}_5$ (VI) were glowd for effective connection in N_2 environment at 400-500 $^\circ\text{C}$ temperature interval. It should be noted that, paramagnetic sample holds its paramagnetivity during subsequent thermal processes.

π -type metalorganic complex of vanadium (IV) which has low split temperature ($T_{\text{split}} > 110 \div 120^\circ\text{C}$) – $(\text{C}_5\text{H}_5)_2\text{V}=\text{O} \cdot (\text{THF})_5$ (I) and carboxylate complex containing ion-type acid ligand



First of all, they are absorbed to carrier surface from their tetrahydrofuran and water solutions, then obtained samples were heated up to 180-200 $^\circ\text{C}$ and 180-300 $^\circ\text{C}$ temperature intervals, respectively. Thin layer samples with vanadium oxide on the carrier surface were obtained during this experiments.

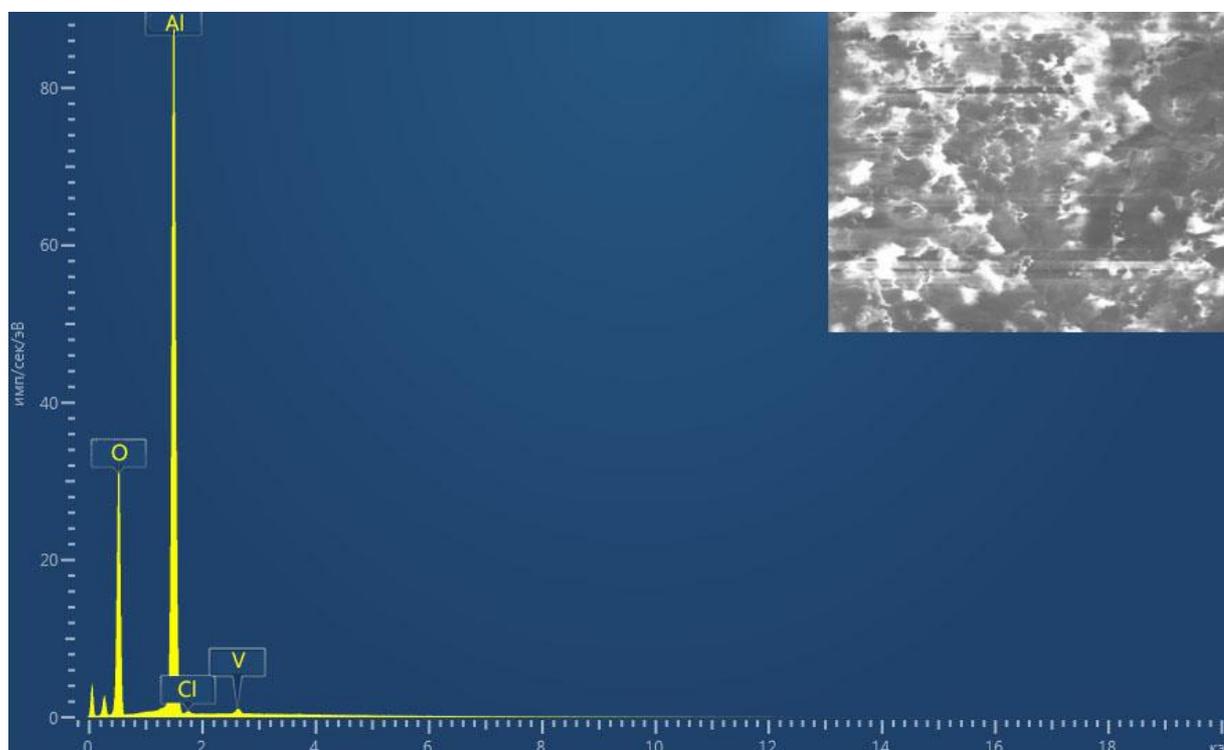


Fig. 1. Elemental analysis and SEM image of the products

Elemental analysis and SEM image of the products were given in figure above. The morphological analysis and recognition of element structure were made by JEOL 7600F scanner electron microscope and X-MAX50(Oxford Instruments) detector configured on it. Results were shown by map of sharing elements on chosen field and characteristic rentgen ray spectrum. It was observed, the investigated pollens 90 consist of vanadium particles of different sizes of aluminum oxide. As it is seen from pictures, particles are spherically formed. It is also possible to observe the uniform distribution of particles on the surface. Glowing of samples obtained by this way at 400-500 $^\circ\text{C}$ temperature interval led to structure and phase changes.

As a result of the investigated spectral IR and structure (RFA, Gas Chromatographic Analysis), some distinctive aspects are observed in structure and composition of obtained coatings depending on the organic ligand and thermal working environment. This gives rise to the idea that they are formed on the basis of vanadyl complexes taken as raw material V(IV) and (V) which have different oxidation grades

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