UDC 544.47:544.344

PRODUCTION OF NANOSTRUCTURED VANADIUM OXIDE THIN FILMS ON THE SURFACE OF METAL OXIDE CARRIERS BY THERMAL DECOMPOSITION OF VANADYLIC ORGANOMETALLIC COMPLEXES $(C_5H_5)_2V=O \cdot (THF)_5$ WITH CYCLOPENTADIENYL LIGANDS

G.Z.Suleymanov

M.Nagiyevev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan

suleymanov.1948@mail.ru

Received 25.12.2017

By thermal decomposition penta-*kis* of tetrahydrofuranate solvated vanadyl complex with $(C_5H_5)_2V=O \cdot (THF)_5$ (1), produced by hydrolysis of *bis*-cyclopentadienyl of vanadium(III) chloride $(C_5H_5)_2VCl$ (2) under weak basicity vanadium oxide nanostructured thin films on the surface of metal oxide carrier were produced. It was detected that vanadium oxide thin films with thickness of 45 nm were produced at concentration 0.1 mol/100 ml solvent (THF) with capacity of 50 ml of spheric Al_2O_3 with 5–7 μm carrier.

Keywords: vanadium oxide, catalyst system, catalyst surface, oxidative dehydrogenation, isobutane, isobutylene.

Relevance of the problem

The requirement of chemical industry for C_2 – C_4 -olefins continuously grows, and the existing capacities can be insufficient [1].

At the same time among C_2 – C_4 -olefins the most flexible is C_4 – isobutylene [2], which at present is used as a monomer for producing polyisobutylene, butyl rubber and raw materials for the production of methyl acrylate and other important chemical products [3].

Presently in industry isobutylene is produced by dehydrogenation of isobutane over chromia-alumina catalyst [4]. At the beginning of 2005 total production of isobutylene by this technology [5] made up more than 3 million tonnes. It should be noted that oxidizing dehydrogenation of isobutane attracts practitioners as a potential alternative way of producing isobutylene. Unlike traditional dehydration of isobutene in the presence of an oxidizer equilibrium shifts towards isobutylene and it is an exothermic process.

Experimental part

All reactions and the yield of by-products were performed in nitrogen atmosphere.

Preparation conditions of organometallic compound of vanadium(III). For this purpose in nitrogen atmosphere 0.5 mol or 15.7 of anhydrous VCl_3 in 50 ml of dehydrated tetrahydrofuran (THF) is dissolved, then it is cooled till 10°C and NH_2Na in 50 ml of *n*-heptane which was pro-

duced in a separate reaction between 13.2 g of monocyclopentadiene (C_5H_6) and of 4.6 g sodium amide, was added by portion. Deposited sodium cyclopentadionate C_5H_5Na after decantation of heptane the whole C_5H_5Na was added into reaction mixture. After 2-hour stirring, it was stopped. Turbid solution was settled. The deposit is separated. Solution was evaporated to minimum in a volume and cooled till –10°C. In a few minutes pale blue polycrystals deposit. According to the data of elemental analysis fresh weight of a target product was 74% of its output. The compound corresponds to chemical formula $C_{10}H_{10}VCl \cdot 5(C_4H_8O)$ in which all molecules of THF are coordinated coordination bonds of vanadium(III) and THF cations. Temperatures of the beginning of decomposition $T_{b.d.}=140^\circ C$, end of decomposition $T_{f.d.}=160^\circ C$. According to thermogravimetric data decomposition of compounds occurs to 130°C.

Formation of V_2O_3 and V_2O_5 nanostructured catalytic systems over metal oxide carrier and conversion of isobutane to isobutylene by oxidizing dehydrogenation with them.

Decomposition temperature on $\gamma-Al_2O_3$ carrier is 110–120°C, *bis*-cyclopentadienyl vanadyl penta-*kis*-tetrahydrofuranate

is absorbed from 25 g of spheric Al_2O_3 which varies at the range of sizes prepared for 5–7 mm solution in 0.1mol/100 ml tetrahydrofuranate THF of I complex, then it is mixed with magnetic mixer at medium rate until only traces of the compound remain in the solution.

In the next stage the solvent is decanted and separated from Al_2O_3 , the residual solvent is fully removed from the surface of Al_2O_3 in 60–70°C temperature range. In the next stage the sample is thermally processed. Then the sample is deposited on metal oxide by thermal decomposition of $(\text{C}_5\text{H}_5)_2\text{V}=\text{O}\cdot(\text{THF})_5$ vanadyl complex. For this 0.01mol or 0.04271g of vanadyl complex is dissolved by the way of intensive mechanical mixing in nitrogen in 100 ml of hydrated tetrahydrofuran solvent. Then 7–9 mm of spheric Al_2O_3 is added at room temperature and left for absorption. Absorption process is performed till the compound in solution is fully absorbed. In the next stage solvent (THF) is heated at the temperature range of 30–40°C and is fully removed in nitrogen medium and processed at 400–500°C.

Results

As a result of investigation of the wide literature it was found out that in the production of thin films and metal coatings on the basis of both organic (R') and carbonyl (CO) ligand compounds of transition elements [6] are widely used. First of all it is conditioned with the fact that thermal decomposition of compounds with $\text{M}-\text{R}$, $\text{M}-\text{C}\equiv\text{O}$ (σ and π) bond at the temperature range of 100–200°C and are converted to thermally decomposed products by forming dimer organic products without any residual compounds. Metal or metal oxides separated from organic residue form metal or metal oxide layer on carrier and then can act as a more effective catalyst like systems with active center [6].

Considering the abovementioned the research work

describes the creation of nanostructured catalytic systems on Al_2O_3 using organometallic compound, the research of using them as a catalyst

in the conversion of isobutane into isobutylene. For this purpose 100 cm^3 of 7–9 mm spheric Al_2O_3 is added into 250 ml of three-neck flask and a solution containing 0.0427 g (I) complex and dissolved in 100 ml THF is added into it and mixed (~1.5 hour) until only traces of (I) complex remain in a solution. Then catalyst is separated from solution by decantation way in nitrogen medium and is given to furnace for thermal processing. In furnace it is mixed intensively and then is left for thermal processing for 1 hour at average temperature 140–150°C. The sample is brought till room temperature and is again left for thermal processing to be fixed on the layer. For this purpose the sample is annealed in nitrogen at 180–190°C.

The catalytic system was used in the conversion of isobutane to isobutylene. Figure 1 shows the SEM view of V_2O_3 – vanadium(III) oxide thin film deposited on Al_2O_3 carrier and its elemental composition was defined.

In SEM the thickness of V_2O_3 coating on Al_2O_3 carrier is given. Figure 1 shows the characteristic X-ray spectrum. It was confirmed that the studied dust particles consist of various size particles of aluminium oxide and vanadium oxide.

According to the results of researches it was found that 45 nm V_2O_3 coating and 100 cm^3 7–9 mm spheric Al_2O_3 which was dissolved in 0.0427 g/100 ml THF solvent on the basis of $(\text{C}_5\text{H}_5)_2\text{V}=\text{O}\cdot(\text{THF})_5$ vanadyl organometallic compound, were determined.

As to the formation of a structure between V_2O_3 on Al_2O_3 surface it should be first noted that when (I) complex is thermally decomposed the formation of coatings by chemical impact of $[\text{V}=\text{O}]$ anion radical on Al_2O_3 carrier was studied. Researches show that $[\text{V}=\text{O}]$ fragment with high energy forms

manganese oxide coating by migrating to $\text{Al}-\text{O}$ bond on Al_2O_3 .

As a result it enables to form more active nanostructured catalytic system. In the work oxidative and dehydrogenation properties of C_2-C_4 hydrocarbons of thin film nanostructured vanadium oxide were studied. It was shown on

the example of C_4 – isobutane that isobutane molecule V_2O_5 thin film on Al_2O_3 carrier conforms to the morphology of isobutane in the

range of $400\text{--}500^\circ\text{C}$ and allows performing the process more efficiently by dehydrogenating more selectively according to the scheme:

Probable mechanism of conversion process of isobutane to isobutylene.

Fig. 1. Elemental analysis and composition of SEM-substance.

Fig.2. Visual and SEM spectral image of $(C_5H_5)_2V=O \cdot 5(THF)$ complex deposited on Al_2O_3 after thermal processing.

Thus, 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 the 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 $\gamma-Al_2O_3$ 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.

References

1. Spiridonova D.V., Fokina E.A., Krylov O.V. Adsorbtsiya benzola i khlorbenczola na $\gamma-Al_2O_3$, $V_2O_5/\gamma-Al_2O_3$ i $CuCl/\gamma-Al_2O_3$ // *Kinetika i kataliz.* 2002. T.118. № 6. S.1495–1500.
2. Blasco T. Galili I., Lopez-Niello J.M., Trifiro F. Oxidative dehydrogenation of ethane and butane on VO_x/Al_2O_3 catalysts // *J. Catal.* 1997. V.169. No 1. P. 203–211.
3. Santacexaria E., Cozzolino M., Veneria I.M., Tesser R. Vanadium based catalysts prepared by grafting: preparation, properties and performances in the ODH of butane // *App. Catal. A.* 2004. V. 270. No 1–2. P. 177–192.
4. Sardarly A.M., Suleymanov G.Z., Kahramanova Sh.I., Taghiyev D.B. Study of the process of oxidative dehydrogenation of isobutene on vanadium(III) containing oxide and nanostructured vanadium(V) containing catalytic systems // *Eur. Sci.* 2017. No 8 (30). P. 6–10.
5. D.-Y. Hong, J.-S. Chang, V.P. Vislovskiy, S.-E. Park, Y.-H. Park, J.S. Yoo. Dehydrogenation of ethylbenzene with carbon dioxide over Mg-modified alumina-supported V-Sb oxide catalysts // *Chemistry Letters (Chemical Society of Japan)*. 2006. V. 35. No 1. P. 28–29.
6. D.-Y. Hong, V.P. Vislovskiy, Y.K. Hwang, J.-S. Chang. Oxidative dehydrogenation of ethylbenzene with carbon dioxide over layered double hydroxide-derived vanadium catalysts // *The 11th Korea-Japan Symposium on Catalysis (Seoul, Korea, 2007) // Book of Abstracts.* P. 34.

VANADİL METALÜZVİ KOMPLEKSİNİN $(C_5H_5)_2V=O \cdot (THF)_5$ TSİKLOPENTADIENİL LİQANDLARI İLƏ TERMİKİ PARÇALANMASINDAN İSTİFADƏ ETMƏKLƏ METALOKSİD DAŞIYICI SƏTHİNDƏ NANOSTRUKTURLAŞDIRILMIŞ VANADIUM OKSİD ÖRTÜYÜNÜN ALINMASI

G.Z.Süleymanov

bis-Tsiklopentadienil vanadium(III) xloridin $(C_5H_5)_2VCl$ (2) zəif qələvi mühitində hidrolizindən alınmış solvatlaşdırılmış penta-*kis*-tetrahidrofuranat vanadium kompleksinin $(C_5H_5)_2V=O(THF)_5$ termiki parçalanması ilə metaloksid daşıyıcı səthində nanostrukturlaşmış vanadiumoksid nazik örtük alınmışdır. Məlum olmuşdur ki, 5–7 mk ölçüdə hissəcikli sferik Al_2O_3 üzərinə çökdürülmüş 50 ml həcmli həlledicinin (THF) 0.1 mol/100 ml qatılığında 45 nm qalınlığında nazik vanadiumoksid təbəqəsi alınır

Açar sözlər: vanadium oksid, katalitik sistem, katalizatorun səthi, oksidləşdirici dehidrogenləşmə, izobutan, izobutilen.

ПОЛУЧЕНИЕ НАНОСТРУКТУРИРОВАННЫХ ВАНАДИЙОКСИДНЫХ ТОНКИХ ПЛЁНОК НА ПОВЕРХНОСТИ МЕТАЛЛООКСИДНЫХ НОСИТЕЛЕЙ ПУТЁМ ТЕРМИЧЕСКОГО РАЗЛОЖЕНИЯ ВАНАДИЛЬНОГО МЕТАЛЛООРГАНИЧЕСКОГО КОМПЛЕКСА $(C_5H_5)_2V=O \cdot (THF)_5$ С ЦИКЛОПЕНТАДИЕНИЛЬНЫМИ ЛИГАНДАМИ

Г.З.Сулейманов

Путём термического разложения пента-*кис*-тетрагидрофуранатного сольватированного ванадильного комплекса $(C_5H_5)_2V=O \cdot (THF)_5$, полученного гидролизом *бис*-циклопентадиенилванадий(III)хлорида $(C_5H_5)_2VCl$ (2) в условиях слабой основности получены ванадийоксидные наноструктурированные тонкие плёнки на поверхности металлооксидного носителя. Обнаружено, что при концентрации комплекса 0.1 моль/100 мл растворителя (ТГФ) объёмом 50 мл, нанесенного на сферический Al_2O_3 с размером частиц 5–7 мк, получена ванадийоксидная тонкая плёнка толщиной 45 нм.

Ключевые слова: оксид ванадия, каталитическая система, поверхность катализатора, окислительное дегидрирование, изобутан, изобутилен.