UDK 546(656.87.21.22)

X-RAY STUDY OF BINARY VANADIUM OXIDE (W–V–O, SN–V–O AND MO–V–O) SYSTEMS

M.I.Aliyeva, V.L.Bagiev, E.F.Ismayilova-Orujeva*, V.A.Gasymov*

Azerbaijan State Oil and Industry University

**Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan*

*vagif_bagiev@yahoo.com,
v-gasymov@rambler.ru*

Received 13.12.2017

X-ray studies of binary vanadium-containing catalysts were carried out. The results of the investigations showed that in the W–V–O system three phases are formed, two modifications of WO_3 and one V_2O_5 . Based on the analysis of diffraction patterns, it was found that in all samples of the Sn–V–O system are observed the phases of SnO_2 and V_2O_5 oxides. It is found that in the Mo–V–O system, in addition to MoO_3 and V_2O_5 oxides, various ternary compounds and solid solutions with the general formula $\text{Mo}_m\text{V}_n\text{O}_p$ are formed.

Keywords: X-ray phase analysis, binary catalysts, tungsten oxide, solid solutions, chemical compounds.

Introduction

In previous works, we studied the oxidation of propylene on a number of binary vanadium-containing catalysts [1–3]. It was shown that the main product of the reaction of propylene oxidation over studied catalysts is acetic acid and the by-products are carbon dioxide, acetone and acetaldehyde. It is established that the yields of reaction products strongly depend on both the temperature and the composition of vanadium-containing catalysts. This may be due to a change in the phase composition of binary vanadium catalysts. In this connection, in our work, we carried out an X-ray diffraction study of binary vanadium-containing catalysts.

Experimental part

Vanadium oxide catalysts were prepared by mixing aqueous solutions of ammonium metavanadate and ammonium tungstate, ammonium molybdate and tin tetrachloride. Obtained mixture was evaporated and dried at a temperature of 100°C , after which it was transferred to a porcelain dish, and calcined at a temperature of $200\text{--}300^\circ\text{C}$ until complete separation of the nitrogen oxides. The catalyst then was calcined at 550°C during 10 hours.

X-ray studies were carried out on an automatic powder diffractometer "D2 Phaser" "Bruker" (CuK_α -radiation, Ni-filter, $3 \leq 2\theta \leq 80^\circ$).

We investigated W–V–O, Sn–V–O and Mo–V–O catalysts prepared in various ratios of

components satisfying the following conditions:

$m\text{A}/n\text{B}$, where A – W, Sn, Mo; B – V,

$m, n = 1 \div 9, m + n = 10$.

Thus, 9 samples were examined in each catalytic system.

Results and discussion

The results of X-ray studies show that three phases are formed in the W–V–O system: two modifications of WO_3 and one V_2O_5 , the crystallographic characteristics of which are presented in the Table 1. As can be seen from Table 1, WO_3 -1 differs from WO_3 -2 in that they have different symmetries and one of the parameters of the unit cell is twice that of the other, i.e. $c_2 = 2c_1$. The consequence of this is the difference in the diffraction patterns of these modifications. Figure 1 shows the diffraction patterns of all nine collected ratios of W/V. At the beginning and at the end of these diffraction patterns also represented oxides of WO_3 and V_2O_5 . X-ray analysis shows that all samples consist of three phases and in all the percentage of components is preserved, which is indicated by a regular change in the intensities of reflexes in diffraction pictures.

Analysis and interpretation of diffraction patterns in the Sn–V–O system showed that in all ratios ($m\text{Sn}/n\text{V}$) the samples consist of two phases, namely SnO_2 and V_2O_5 . Figure 2 shows the X-ray patterns of all nine collected ratios ($m\text{Sn}/n\text{V}$).

Table 1. Crystallographic characteristics of the phases formed in the W–V–O, Sn–V–O and Mo–V–O systems

Compound	Shingonia	Spatial group	Lattice parameters				Z Number of molecules	Literature
			<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	Angle, °		
WO ₃ -1	rhombic	primitive	7.384	7.512	3.846	–	4	[4]
WO ₃ -2	rhombic	<i>P2₁/n</i>	7.306	7.540	7.692	90.88	8	[5]
V ₂ O ₅	rhombic	<i>Pmnm</i>	11.510	4.369	3.563	–	3	[6]
SnO ₂	rhombic	<i>Pnmm</i>	4.708	4.720	3.195	–	2	[7]
MoO ₃	rhombic	<i>Pnma</i>	13.825	3.694	3.954	–	4	[8]
MoV ₂ O ₈	monoclinic	<i>C2</i>	19.398	3.629	4.117	144.9	2	[9]
Mo _{2,4} V _{3,6} O ₁₆	monoclinic	<i>C2</i>	19.361	3.625	4.121	90.62	1	[10]
Mo ₄ V ₆ O ₂₅	rhombic	–	11.99	6.72	8.18	–	–	[11]
(Mo _{0,88} V _{0,12})O _{2,94}	hexagonal	<i>P6₃</i>	10.593	–	3.694	–	6	[12]
(Mo _{0,08} V _{0,92}) ₂ O ₅	rhombic	<i>Pmnm</i>	11.574	3.578	4.332	–	2	[13]

Fig. 1. Diffraction patterns of tungsten and vanadium oxides, as well as all nine W–V–O catalysts: I – (W/V=1/9), II – (W/V=2/8), III – (W/V=3/7), IV – (W/V=4/6), V – (W/V=5/5), VI – (W/V=6/4), VII – (W/V=7/3), VIII – (W/V=8/2), IX – (W/V=9/1). **Fig.2.** Diffraction patterns of tin and vanadium oxides, as well as all nine Sn–V–O catalysts: I – (Sn/V=1/9), II – (Sn/V=2/8), III – (Sn/V=3/7), IV – Sn/V=4/6, V – (Sn/V=5/5), VI – (Sn/V=6/4), VII – (Sn/V=7/3), VIII – (Sn/V=8/2), IX – (Sn/V=9/1).

Fig.3. Diffraction patterns of molybdenum and vanadium oxides, as well as all nine Mo–V–O catalysts: I – (Mo/V=1/9), II – (Mo/V=2/8), III – (Mo/V=3/7), IV – Mo/V=4/6), V – (Mo/V=5/5), VI – (Mo/V=6/4), VII – (Mo/V=7/3), VIII – (Mo/V=8/2), IX – (Mo/V=9/1).

For the comparative analysis, at the beginning and at the end of these diffraction patterns, X-ray diffraction patterns of SnO_2 and V_2O_5 are also presented. X-ray analysis shows that all samples consist of two phases, namely SnO_2 and V_2O_5 . In all samples, the percentage of components is preserved, as indicated by a regular change in the intensities of the reflexes in the diffraction pictures.

X-ray diffraction studies of the Mo–V–O system showed that, in addition to the MoO_3 and V_2O_5 oxides, various ternary compounds based on Mo–V–O with the general formula $\text{Mo}_m\text{V}_n\text{O}_p$ are also formed, the crystallographic characteristics of the obtained phases are given in Table 1.

Figure 3 shows the diffraction patterns of all nine collected ratios ($m\text{Mo}/n\text{V}$). At the beginning and at the end of these diffraction patterns are also X-ray patterns of MoO_3 and V_2O_5 .

Interpretation of the obtained results shows that at the ratios of 1Mo/9V, 2Mo/8V, 3Mo/7V,

8Mo/V and 9Mo/V, three phases are formed, namely MoO_3 , V_2O_5 and $\text{Mo}_{2.4}\text{V}_{3.6}\text{O}_{16}$. And with the ratios of components 4Mo/6V, 5Mo/5V and 6Mo/4V in addition to molybdenum and vanadium oxides, other phases with different compositions of the Mo–V–O system formed.

We also calculated the degree of crystallinity of all prepared catalysts, the results of which are presented in Table 3. As can be seen from Table 3, the crystallinity of W–V–O and Mo–V–O systems does not practically change with the change of the composition, while for Sn–V–O systems the crystallinity decreases from 79.2% on the sample 1Sn-9V to 62% on the sample 9Sn-1V.

Thus, based on the X-ray investigations we conclude that the W–V–O system consists of three phases (two WO_3 modifications and one V_2O_5), Sn–V–O oxide system consists of two phases (SnO_2 and V_2O_5) and Mo–V–O system consists of MoO_3 , V_2O_5 phase and various polymolybdates.

Table 2. Phases formed in the Mo–V–O system

Ratio of components, Mo/V	Formed phases
1/9	MoO_3 , V_2O_5 , $\text{Mo}_{2.4}\text{V}_{3.6}\text{O}_{16}$
2/8	MoO_3 , V_2O_5 , $\text{Mo}_{2.4}\text{V}_{3.6}\text{O}_{16}$
3/7	MoO_3 , V_2O_5 , $\text{Mo}_{2.4}\text{V}_{3.6}\text{O}_{16}$
4/6	MoO_3 , V_2O_5 , Mo , V_2O_8 , $(\text{Mo}_{0.86}\text{V}_{0.12})\text{O}_{2.94}$, $\text{Mo}_4\text{V}_6\text{S}_{25}$
5/5	MoO_3 , V_2O_5 , $\text{Mo}_{2.4}\text{V}_{3.6}\text{O}_{16}$, $(\text{Mo}_{0.08}\text{V}_{0.92})_2\text{O}_5$
6/4	MoO_3 , V_2O_5 , $\text{Mo}_{2.4}\text{V}_{3.6}\text{O}_{16}$, $(\text{Mo}_{0.88}\text{V}_{0.12})\text{O}_{2.94}$
7/3	MoO_3 , V_2O_5 , $\text{Mo}_{2.4}\text{V}_{3.6}\text{O}_{16}$
8/2	MoO_3 , V_2O_5 , $\text{Mo}_{2.4}\text{V}_{3.6}\text{O}_{16}$
9/1	MoO_3 , V_2O_5 , $\text{Mo}_{2.4}\text{V}_{3.6}\text{O}_{16}$

Table 3. Crystallinity of the samples in the systems W–V–O, Sn–V–O and Mo–V–O

Catalytic system W–V–O to W/V	Crystallinity, %	Catalytic system Sn–V–O to Sn/V	Crystallinity, %	Catalytic system Mo–V–O to Mo/V	Crystallinity, %
1/9	77.7	1/9	79.2	1/9	82.6
2/8	78.9	2/8	74.5	2/8	78.3
3/7	80.0	3/7	76.5	3/7	79.6
4/6	80.2	4/6	74.9	4/6	75.7
5/5	79.8	5/5	73.8	5/5	80.5
6/4	80.5	6/4	72.1	6/4	77.5
7/3	79.2	7/3	70.4	7/3	81.0
8/2	80.9	8/2	63.5	8/2	77.6
9/1	80.6	9/1	62.0	9/1	77.9

References

1. Aliyeva M.I., Baghiyev V.L. Propylene oxidation over tin-vanadium oxide catalysts. // 15th International Congress on Catalysis. Munich, Germany. 2012. Poster 2.05_8063M.I.
2. Alieva M.I., Bagiev V.L. Okislenie propile-na v uksusnuiu kislotu na binarnykh V–W–O katalizatorakh. II Rossiiskii kongress po katalizu "ROSKATALIZ". 2–5 oktiabria 2014. Sb. tezisov docl. T. II. S. 239.
3. Alieva M.I., Bagiev V.L., Mirzai D.I. Vanadii-molibden oksidnye sistemy kak katalizatory okisleniya propilena v uksusnuiu kislotu // I Beynəlxalq kimya və kimya mühəndisliyi konfransı. Tezislər və məqalələr. Bakı. 2013. S. 1035–1036.
4. Roth R.S., Waring J.L. Phase equilibria as related to crystal structure in the system niobium pentoxide-tungsten trioxide // J. Res. of Nat. Bur. Stand. 1966. Sect. 70A. P. 281.
5. Loopstra B.O., Rietveld H.M. Further refinement of the structure of WO₃ // Acta Crystallographica. Section B 25. 1969. P. 1420–1421.
6. Bachmann H.G., Ahmed F.R., Barnes W.H. The crystal structure of vanadium pentoxide // Zeits. Kristallogr. 1961. V. 115. Issue 1-2. P. 110–131.
7. Gracia L., Beltran A., Andress J. Characterization of the high-pressure structures and phase transformations in SnO₂. A Density Functional Theory Study // J. Phys. Chem. B. 2007. V. 111. No 23. P. 6479–6485.
8. Anderson G., Magneli A. On the crystal structure of molybdenum trioxide // Acta Chem. Scand. 1950. No 4. P. 793–797.
9. Eick H.A., Kihborg L. The crystal structure of MoV₂O₈ // Acta Chem. Scand. 1966. V. 20. P. 1658–1666.
10. Robert C.T. Slade, A. Ramanan, Barbara C. West, Edward Prince. The structure of Mo₆V₉O₄₀ determined by powder neutron diffraction // J. Solid State. Chem. 1989. V. 82. P. 65–69.
11. Ralph H Munch, Emile D Pierron. Compound oxides present in vanadium-molybdenum oxide maleic catalysts // J. Catalysis. 1964. V. 3. Issue 5. P. 406–413.
12. Hu, Y.-T., Davies P.K. Synthesis, thermal stability and structure of (V_{0.13}Mo_{0.87}O_{2.935}) // J. Solid State Chem. 1993. V. 105. P. 489–503.
13. Haas F., Adams A.H., Buhrmester T., Schimanke G., Martin M., Fuess H. X-ray absorption and X-ray diffraction studies molybdenum doped vanadium pentoxide // Phys. Chem. Chem. Phys. 2003. V. 5. Issue 19. P. 4317–4324.

BİNAR W–V–O, Sn–V–O VƏ Mo–V–O SİSTEMLƏRİNİN RENTGENFAZA TƏDQIQI

M.İ.Əliyeva, V.L.Bağiyev, E.F.İsmaylova Orucova, V.Ə.Qasımov

Vanadiumlu binar katalizatorların rentgenoqrafik tədqiqatı aparılmışdır. Tədqiqatların nəticələri W–V–O sisteminə WO₃-ün iki modifikasiyasının və V₂O₅ əmələ gəldiyini göstərmişdir. Sn–V–O sisteminin difraksiya mənzərələrinin analizi bütün nümunələrdə SnO₂ və V₂O₅ əmələ gəldiyi məlum olmuşdur. Mo–V–O sisteminə isə MoO₃ və V₂O₅-dən əlavə ümumi formulu Mo_mV_nO_p olan üçlü birləşmələr və bərk məhlulların əmələ gəldiyi müəyyən edilmişdir.

Açar sözlər: rentgenfaza analizi, binar katalizatorlar, volfram oksidi, bərk məhlullar, kimyəvi birləşmələr.

РЕНТГЕНОГРАФИЧЕСКОЕ ИССЛЕДОВАНИЕ БИНАРНЫХ W–V–O, Sn–V–O И Mo–V–O СИСТЕМ

М.И.Алиева, В.Л.Багиев, Э.Ф.Исмаилова Оруджева, В.А.Гасимов

Проведены рентгенографические исследования бинарных ванадийсодержащих катализаторов. Результаты исследований показали, что в системе W–V–O образуются три фазы: две модификации WO₃ и одна V₂O₅. На основании анализа дифракционных картин найдено, что в системе Sn–V–O во всех образцах наблюдаются фазы оксидов SnO₂ и V₂O₅. Установлено, что в системе Mo–V–O, кроме оксидов MoO₃ и V₂O₅, образуются также различные тройные соединения и твердые растворы общей формулы Mo_mV_nO_p.

Ключевые слова: рентгенофазовый анализ, бинарные катализаторы, оксид вольфрама, твердые растворы, химические соединения.