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Role of Singlet Oxygen in the Oxidation of Toluene on Vanadium–Molybdenum Catalytic Systems

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Abstract

It was established that the catalysts based on vanadium and molybdenum oxides exhibit activity in the generation of the singlet form of molecular oxygen. The major reaction on mixed oxides having the composition $xV_2O_5 \cdot yMoO_3$ is not the one-electron oxidation but the addition to the double bond, preferably in the *meta* position. It was demonstrated that the oxidation of toluene on individual vanadium and molybdenum oxides follows independent routes: on V_2O_5 , oxidation is realized mainly at the benzene ring, while on MoO_3 it occurs at the side chain.

Key words: singlet oxygen, toluene, heterogeneous catalysts, metal oxides

INTRODUCTION

The nature of active species taking part in oxidation transformations plays a key part in the consideration of the mechanisms of direct oxidation of hydrocarbons by molecular oxygen [1–4]. Investigations in this area were carried out mainly under the conditions of low-temperature homogeneous catalysts, while the most essential industrial processes are performed at elevated temperature and in the presence of heterogeneous catalysts.

By present, experimental and theoretical data on selective vapour phase catalytic oxidation of toluene, as well as the data on the capacity of catalysts to generate active forms of molecular oxygen, provide evidence of the existence of definite connections between them. This is especially important for heterogeneous catalysts based on such transition metals as vanadium and molybdenum. However, no systematic investigation has been carried out by present into the nature of active species that

take part in the partial oxidation of aromatic hydrocarbons on heterogeneous catalysts.

The goal of the present work was to reveal a connection between the capacity of mixed oxides $xV_2O_5 \cdot yMoO_3$ to generate the active form of molecular oxygen 1O_2 , and their selectivity with respect to toluene.

EXPERIMENTAL

Toluene oxidation was carried out on individual oxides of vanadium, molybdenum, and on mixed oxides $xV_2O_5 \cdot yMoO_3$ (molar ratio: 3 : 1, 3 : 2, 1 : 1, 2 : 3, 1 : 3), as well as on a mechanical mixture of individual oxides of vanadium and molybdenum at a ratio of 1 : 3. The samples of V_2O_5 and MoO_3 were prepared by thermal decomposition of ammonium metavanadate and metamolybdate, respectively, at 400–500 °C for 5 h. Double oxide $xV_2O_5 \cdot yMoO_3$ was obtained through co-precipitation from the saturated aqueous solution of ammonium meta-

vanadate and metarmolybdate taken in necessary proportions, followed by thermal decomposition (similarly to the case of individual oxides). The specific surface of thus prepared samples was 5–6 m²/g.

The X-ray diffraction patterns were recorded with a DRON-3 instrument (CuK_α radiation). Catalytic studies were carried out in a flow-type reactor with steady-state catalyst layer within temperature range 300–500 °C at atmospheric pressure and the volume flow rate of raw material input 0.5–1 h⁻¹. The samples of metal oxides (0.25–0.5 g) were mixed with ground quartz (1.5 m²/g) and placed into the reactor. Toluene was fed into the reactor in mixture with air at the molar ratio of toluene to oxygen equal to 1 : 10 and 1 : 6; the total rate of vapour-air mixture flow into the reactor was 90 mL/min.

Liquid reaction products were analyzed using a Cambridge GC-95 chromatograph equipped with a flame-ionization detector, capillary column (50 m) with the FFAP phase. Gaseous products were analyzed with a Kristallyuks-4000M chromatograph equipped with a katharometer, packed column (5 m) with activated carbon. Analysis of maleic anhydride and benzoic acid was carried out dissolving the obtained products in water and titrating the 0.1 M NaOH solution using an ATP-02 titrator.

Toluene oxidation with atmospheric oxygen on the catalysts under investigation proceeded with the formation of benzaldehyde, maleic anhydride (MA) and carbon oxides (CO_x). In

addition to these products, we observed the formation of small amounts (less than 1 mass %) of hydroquinone, anthraquinone *etc.* To establish the contribution from hydroquinone as a basic intermediate product forming MA, we prepared and studied reaction mixtures with the mass concentration of hydroquinone 2–10 %. According to the data of material balance with respect to carbon, the losses did not exceed 2 mass %.

The amount of ¹O₂ was determined using the jet method with the residual air pressure approximately equal to 1 kPa, and linear flow rate of 260 cm/s [5]. The weighted portion of the catalyst was placed into a quartz reactor possessing low thermal inertia. Air was cooled to room temperature at the reactor outlet and then it entered the cell in which active oxygen selectively reacted with a chemiluminescent dye. The intensity of chemiluminescence was recorded with a FEU-79 photomultiplier.

RESULTS AND DISCUSSION

The data on toluene conversion, the yields of MA and BA depending on the composition of $xV_2O_5 \cdot yMoO_3$ at different temperatures, as well as the data on the generation of singlet oxygen are presented in Table 1. One can see that the yield of MA for vanadium oxide is maximal at 400 °C, and then it decreases. The yield of benzaldehyde for V₂O₅ is maximal at 300 °C, but it becomes equal to zero at 500 °C. On molybdenum oxide, the yield of benzaldehyde increases with

TABLE 1

Summary data on toluene oxidation on $xV_2O_5 \cdot yMoO_3$ with different $x : y$ relations

$x : y$	Amount of ¹ O ₂			Toluene conversion			Yield, mol. %					
	(N), 10 ¹³ molecules/g			degree, mol. %			Maleic aldehyde			Benzaldehyde		
	Temperature, °C											
	300	400	500	300	400	500	300	400	500	300	400	500
1 : 0	1.1	2.0	4.6	3.1	89.9	89.5	0	30.9	29.0	3.1	0	0
3 : 1	0	5.1	18.5	8.5	89.3	97.2	0	32.5	16.0	8.5	0	0
3 : 2	5.5	6.7	15.0	17.8	99.9	100.0	0	33.9	18.5	17.8	7.1	0
1 : 1	2.3	8.0	14.2	24.3	99.8	100.0	0	47.8	26.9	24.3	16.4	0
2 : 3	7.0	3.9	8.5	20.0	100.0	89.8	0	36.4	34.6	20.0	8.4	0
1 : 3	5.0	3.2	3.8	19.2	42.9	82.0	0	11.5	21.4	19.2	8.1	6.7
0 : 1	0	0	0.1	0.2	6.6	39.0	0	0	0	0.2	3.8	30.3

an increase in temperature. The formation of MA did not occur on this catalyst.

Thus, toluene oxidation on individual oxides proceeds *via* different routes: on V_2O_5 oxidation proceeds mainly at the benzene ring, while on MoO_3 it proceeds at the side chain.

Inclusion of V_2O_5 into MoO_3 in all the cases causes an increase in toluene conversion degree. The samples with vanadium oxide content above 50 mol. % in fact do not differ in conversion degree from the samples of pure V_2O_5 . According to the data shown in Table 1, even the inclusion of 25 mol. % vanadium oxide promotes a substantial increase in the yield of benzaldehyde at low temperatures. The dependence of benzaldehyde yield on MoO_3 content in mixed oxides is a function with extremum: the maximal yield is observed at 300 and 400 °C for the sample containing 50 % mol. MoO_3 , while at 500 °C – for the sample with the molar concentration of MoO_3 equal to 100 %.

The XPA data for $xV_2O_5 \cdot yMoO_3$ samples point to the formation of multiphase systems. For example, for the sample with 25 mol. % V_2O_5 we revealed three phases, with the predominance of MoO_3 phase. After V_2O_5 content increased to 40 mol. %, four phases were observed, with V_2MoO_8 as the dominating phase. In the case of the sample with V_2O_5 content equal to 50 mol. %, V_2O_5 phase starts to form; its contribution increases with an increase in vanadium oxide content. The intensity of the lines corresponding to V_2MoO_8 phase decreases. For the sample with 75 mol. % V_2O_5 , the major phase is V_2O_5 .

To determine the effect of the phase composition, we prepared a sample of the mechanical mixture of individual vanadium and molybdenum oxides (75 mol. % MoO_3). Toluene conversion degree on the mechanically mixed sample at 400 °C is 15 mol. %, while at 500 °C it is 70 mol. %. These values are smaller than those obtained with co-precipitated samples but exceed (by 10 %) the value calculated using the additive scheme from the data for individual MoO_3 and V_2O_5 . In spite of the lower toluene conversion degree on mechanical mixture, benzaldehyde yield for this mixture is six times higher than that for the co-precipitated sample and completely coincides with the results for individual MoO_3 . It should be noted that the character of the temperature dependence of

benzaldehyde yield exactly coincides with that for individual MoO_3 and is opposite to the behaviour of the co-precipitated sample. The yield of MA (500 °C) turned out to be identical for the samples obtained through co-precipitation and 4mechanical mixing. The largest difference was observed for the comparison of CO_x yields: on the mechanical mixture, even at 500 °C the reaction of complete oxidation proceeds only by 14 mol. %, while on the co-precipitated sample it proceeds by 54 mol. %. This is much higher than the calculated additive estimation which is 22 mol. %. It should also be stressed that we give the values of CO_x yield in the reaction of complete oxidation that is, taking into account the oxide evolved during the formation of MA.

However, the data of X-ray phase analysis and EPR cannot explain the differences in oxidation routes on oxide vanadium-molybdenum catalysts. It is likely that different oxidizing agents take part in the formation of MA and benzaldehyde.

The assumption concerning the participation of the singlet form of molecular oxygen in oxidation reactions on oxide catalysts was made for the first time by the authors of [6]. Later on [7], the ability of V_2O_5 and MoO_3 to generate 1O_2 was discovered. However, quite different chemical nature of these oxides did not allow one form an integrated opinion concerning the mechanisms of this generation.

The data of chemiluminescence determination of the amount of 1O_2 generated into the gas phase from $xV_2O_5 \cdot yMoO_3$ are presented in Table 1. The largest amount of 1O_2 is generated on $V_2O_5 \cdot MoO_3$ and V_2O_5 ; no singlet oxygen was detected on MoO_3 . According to the EPR data [8], with an increase in vanadium oxide content, the fraction of paramagnetic centres V^{4+} increases. The VO^{2+} ions can be formed most probably through the reduction of V^{5+} by ammonia during thermal decomposition of ammonium metavanadate. On the other hand, vanadium (V_2O_5) easily passes into the tetravalent state; singlet oxygen is evolved during this process. The transition from Mo^{6+} to Mo^{5+} was not recorded in the EPR spectra; this corresponds to the data of chemiluminescence analysis on the generation of singlet oxygen with MoO_3 .

For very low vanadium oxide concentration (2 mol. %), all V^{4+} ions are isolated, and these

samples do not exhibit activity in the generation of singlet oxygen and in the formation of MA. Therefore, for MA to be formed during toluene oxidation, the associates of vanadium oxide are necessary; they are formed when vanadium oxide concentration is above 40 mol. %.

The data on the amount of carbon oxides CO_x formed in the reaction of complete oxidation (that is, taking into account the oxide evolved during the formation of MA) show that the introduction of small amounts of molybdenum oxide (up to 25 mol. %) enhances the reactions of complete oxidation that are characteristic of individual V_2O_5 . It may be assumed that an increase in the amount of CO_x , or complete oxidation of MA, with an increase in vanadium oxide content to 40 mol. % is connected with the transition of isolated centres into associates. Subsequent decrease in the concentration of CO_x can be due to the appearance of V^{5+} centres and an increase in the concentration of these centres. One cannot exclude that it is this circumstance that explains an increase in the amount of singlet oxygen generated from the surface of mixed oxides in comparison with pure vanadium oxide.

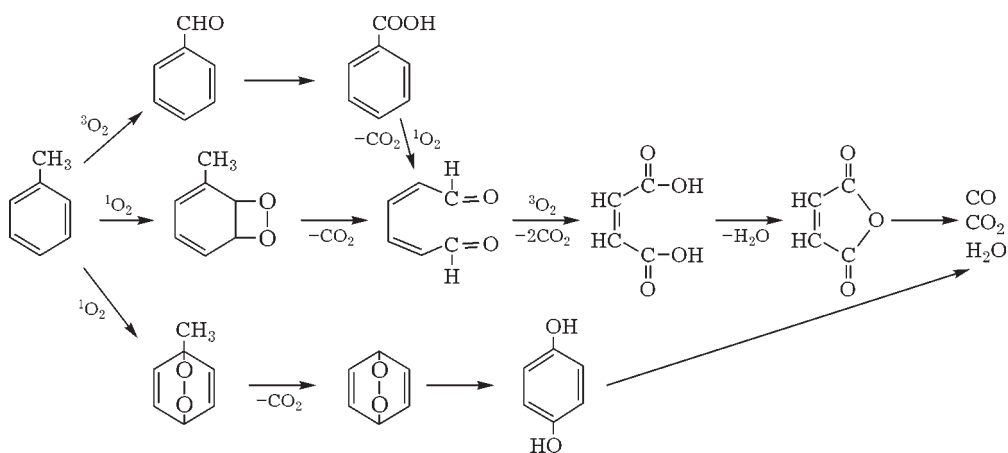
Results obtained in the study unambiguously point to the key role of the phase composition of catalysts in toluene oxidation. Judging from the same yield of MA, the generation of singlet oxygen is performed mainly by the phases V_2O_5 and VO_2 , while the presence of V_2MoO_8 phase promotes complete oxidation of substrates. Desorption of substrates from V_2MoO_8 may be hindered due to some reason, which leads to their complete oxidation.

Having compared these data with the results of catalytic transformations, we may conclude that the formation of MA and benzaldehyde follows different independent routes: the formation of benzaldehyde is participated by the triplet form of oxygen, while the singlet form is necessary for the formation of MA.

It is usually presumed [1-3] that toluene at first gets oxidized into benzaldehyde, and then into benzoic acid. Then benzene is formed in decarboxylation reaction; through hydroquinone it gives rise to MA and carbon oxides. It was important for us to find out whether this mechanism, proposed previously for silver catalyst, is actual for the systems under consideration. First of all, the absence of even the traces of benzene in reaction products should be stressed. Second, hydroquinone was indeed detected in trace amounts by means of potentiometric titration. Therefore, one might expect that its addition into the reaction mixture would cause an increase in MA yield but this did not happen. It follows from these data that toluene oxidation according to the mechanism proposed in literature does not occur in fact, and hydroquinone is not an intermediate product of toluene oxidation but the final one.

On the basis of the data obtained, we propose the scheme of toluene oxidation on vanadium-containing oxide catalysts (Scheme 1).

The first two stages leading to the formation of benzaldehyde and benzoic acid proceed independently of the ability of the catalyst to generate $^1\text{O}_2$. Then, in the case of relatively low catalyst activity in the generation of the singlet form of oxygen, benzaldehyde and ben-



Scheme 1.

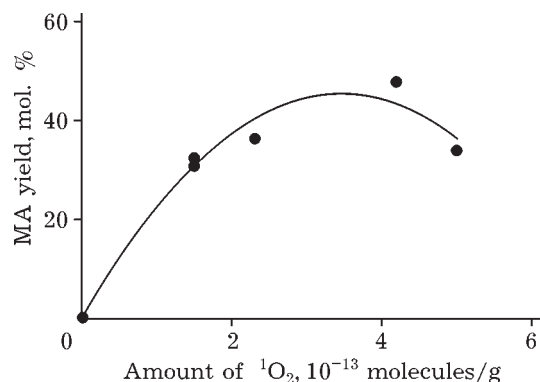
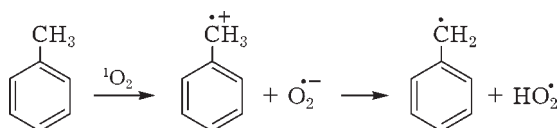


Fig. 1. Dependence of the yield of maleic anhydride (MA) on the amount of $^1\text{O}_2$ generated on $x\text{V}_2\text{O}_5 \cdot y\text{MoO}_3$ at 400 °C.

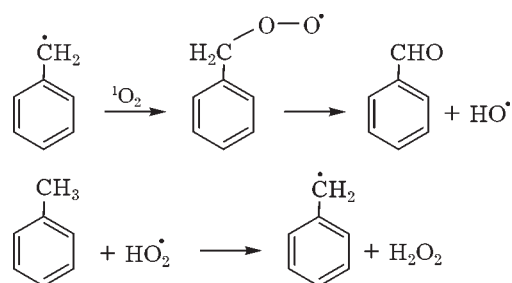
zoic acid are further oxidized only to an insignificant extent, that is, they will be the major products of toluene oxidation. However, in the case of the large amount of generated $^1\text{O}_2$, oxidation proceeds to a higher extent, and the major product is MA, and later CO_x .

The dependence of MA yield on the amount of generated $^1\text{O}_2$ on $x\text{V}_2\text{O}_5 \cdot y\text{MoO}_3$ is shown in Fig. 1. It may be concluded on the basis of these data that the optimal amount of $^1\text{O}_2$ for the formation of MA is $4.2 \cdot 10^{13}$ molecules/g. At present, two reaction routes are proposed for $^1\text{O}_2$: one-electron oxidation [9, 10] and addition at the π bond with the formation of peroxides [12].

For toluene, one-electron oxidation leads to the formation of the cation radical known as the strongest CH acid in acetonitrile, $\text{p}K_a \approx 58$ [13]. The next stage will be deprotonation of the cation radical of toluene and the appearance of toluene radical:



Then toluene radical can react with the triplet form of oxygen and form benzaldehyde:



In the case if this were the major route of the reaction of $^1\text{O}_2$, the yield of benzaldehyde would be symbate with the amount of the singlet form of oxygen. However, experimental data do not confirm this statement, as the yield of benzaldehyde on V_2O_5 and $x\text{V}_2\text{O}_5 \cdot y\text{MoO}_3$ decreases with an increase in temperature, in spite of an increase in the amount of $^1\text{O}_2$.

Thus, for $^1\text{O}_2$ on V_2O_5 and $x\text{V}_2\text{O}_5 \cdot y\text{MoO}_3$, the major route of the interaction with toluene molecule is the addition at the double bond, mainly at the meta position. The question concerning the reason of such a preference in the reaction route of $^1\text{O}_2$ remains open, and an answer can be found with the help of quantum chemical calculations.

CONCLUSION

It is demonstrated that the formation of MA and benzaldehyde in the course of toluene oxidation with molecular oxygen proceeds *via* independent routes: the formation of benzaldehyde is participated by oxygen on the surface of the catalyst, while the singlet form is necessary for the formation of MA. It is established that the generation of singlet oxygen is performed mainly by V_2O_5 and VO_2 phases; the presence of V_2MoO_8 phase promotes a complete oxidation of the substrates.

REFERENCES

- Zhu J., Anderson S. T. L., *J. Chem. Soc. Faraday Trans. 1*, 85 (1989) 3629.
- Zhu J., Andersson S. T. L., *Appl. Catal.*, 53 (1989) 251.
- Ponzi M., Duschatzky C., Carrascull A., Ponzi E., *Appl. Catal. A: Gen.*, 169 (1998) 373.
- Yan Zh., Andersson S. T. L., *Appl. Catal.*, 66 (1990) 149.
- Romanov A. N., Rufov Yu. N., *Zh. Fiz. Khim.*, 72 (1998) 2094.
- Dmuchovsky B., Freerks M. C., Pierron E. D., Munch R. H., Zienty F. B., *J. Catal.*, 4 (1965) 291.
- Zavyalov S. A., Myasnikov I. A., Zavyalova L. M., *Dokl. AN SSSR*, 284 (1982) 378.
- Tomskiy I. S., Vishnetskaya M. V., Kokorin A. I., *Khim. Fiz.*, 27, 7 (2008) 67.
- Beletskaya I. P., Makhonkov D. I., *Usp. Khim.*, 50, 6 (1981) 1007.
- Kochi J. K., Tang R. T., Bernath T., *J. Am. Chem. Soc.*, 95 (1973) 7114.
- Stockmann M., Konietzki F., Notheis J. U., Vosse J., Keunec W., Maier W. F., *Appl. Catal. A: Gen.*, 208 (2001) 343.
- Todres Z. V., *Ion-Radicaly v Organicheskom Sinteze*, Khimiya, Moscow, 1986.