

CHEMICAL KINETICS
AND CATALYSIS

The Selective Catalytic Oxidation of Toluene

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Abstract—It was found for the first time that the selectivity of toluene transformations into benzaldehyde and benzoic acid decreased and into maleic anhydride and deep oxidation products increased as the ability of vanadium-containing catalysts of toluene oxidation to generate the singlet form of molecular oxygen grew. A scheme of the formation of the products of toluene oxidation with oxygen was suggested. Quinones were shown to be final rather than intermediate oxidation products. The selectivity of the reaction with respect to mild oxidation products in the presence of V_2O_5 , MoO_3 , and $V_2O_5 \cdot MoO_3$ could be increased by changing the temperature of catalyst preparation from 400 to 500°C.

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INTRODUCTION

Catalytic systems used to selectively oxidize toluene include vanadium, molybdenum, tungsten, and cobalt oxides. These oxides either are used in the pure form [1–4] or are deposited on various carriers [5]. The most characteristic product of toluene oxidation is benzaldehyde. It was noted that, when the reaction was performed on usual oxide “mild” oxidation catalysts, it terminated at the stage of benzaldehyde formation, whereas benzoic acid was present in oxidation products in insignificant amounts [6].

In [7], a series of experiments were performed to determine the most active catalyst of toluene oxidation into benzaldehyde. Molybdenum, vanadium, copper, manganese, cobalt, lead, and iron oxides were studied. It was found that, under equal conditions, the largest amounts of benzaldehyde (a 23% yield) were formed on MoO_3 . The yields were slightly lower (16%) on V_2O_5 . All the other oxides studied were active only in deep oxidation (no more than 3% benzaldehyde was obtained).

It follows that vanadium-containing catalytic systems were most active and selective in the oxidation of toluene to benzaldehyde and benzoic acid, and catalysts based on vanadium and molybdenum oxides were most simple to prepare.

An important gap in the theory of oxidative catalysis is the absence of data on the nature of the oxidizer, molecular oxygen. The participation of electronically excited molecular oxygen forms (as a rule, the $^1\Delta_g O_2$ singlet form) in these processes was suggested as early as the 1960s. However, the real possibility to study the participation of singlet oxygen in heterogeneous catalytic processes only arose in the 1980s, when high-selectivity and sensitive techniques for determining

$^1\Delta_g O_2$ were developed. These effective analytic techniques were used to reveal the ability of V and Mo oxides to generate $^1\Delta_g O_2$ [8]. Its influence on the partial oxidation of toluene, however, remained unstudied, and investigations in this field are therefore of current interest.

EXPERIMENTAL

The oxidation of toluene was performed on massive V_2O_5 and MoO_3 oxides and mixed $V_2O_5 \cdot MoO_3$ (molar ratio $V_2O_5 : MoO_3 = 3 : 1$) oxide. Massive V_2O_5 and MoO_3 oxides were prepared by the thermal decomposition of ammonium metavanadate and metamolybdate at 400–500°C for 5 h. Mixed V–Mo oxide was obtained by the coprecipitation of metal hydroxides from a saturated aqueous solution of ammonium metavanadate and metamolybdate taken in the required ratio followed by calcining.

Catalytic studies were performed on a laboratory unit with a flow reactor (working volume 3 cm³) over the temperature range 300–500°C at atmospheric pressure and toluene volume flow rate 0.5–1 h⁻¹. Toluene was supplied as a mixture with air (toluene concentration 1–2 vol %) at a rate of 200–260 ml/min.

A typical catalytic experiment was performed as follows. After the catalyst was loaded into the reactor, the reactor was heated to the required temperature in a flow of air at a rate of 283–288 K/min. When the required temperature was reached, toluene was introduced either immediately or in an hour. This did not influence the activity and selectivity of the catalysts. At the exit of the reactor, liquid products were collected in a trap with liquid nitrogen, and gaseous products, in a gas trap. In 30–60 min, supply of toluene and air was stopped, and

Yields of the main toluene oxidation products (%) and amounts of generated $^1\Delta_g\text{O}_2$ (c , molecules/g) on massive oxides at $t_{pc} = 400^\circ\text{C}$ (η is the conversion of toluene)

$t, ^\circ\text{C}$	$c \times 10^{-15}$	$\eta, \%$	BAI	BAC	MA	CO_x
$\text{V}_2\text{O}_5 \cdot \text{MoO}_3$						
300	0	17.3	2.7	1.1	0.9	12.7
400	33.9	100	0.0	12.5	28.1	59.2
500	56.1	100	0.0	9.4	23.2	67.1
V_2O_5						
300	0	29.3	3.1	5.2	0.0	21.0
400	19.5	99.6	0.8	9.6	38.9	50.3
500	34.4	100	0.0	10.0	29.0	60.5
MoO_3						
300	0	1.2	0.2	1.0	0.0	0.0
400	0.45	8.9	3.8	2.3	0.0	2.8
500	0.55	47	30.0	8.0	0.0	8.7

traps for liquid and gaseous products were changed. Carbon balance in flows before and after the reactor proved the completeness of trapping transformation products. Under constant experimental conditions, the activity and selectivity of catalysts did not decrease. No catalyst regeneration was therefore performed.

The liquid reaction products were analyzed by gas-liquid chromatography on a Cambridge GC95 chromatograph (flame ionization detector) with a capillary column 50 m long and a FFAP deposited phase under programmed heating conditions (35°C , 10 min, and $35\text{--}150^\circ\text{C}$, 278 K/min). Gases were analyzed on a Kristall-2000 gas chromatograph using a packed column (activated carbon) 5 m long under programmed heating conditions ($35\text{--}160^\circ\text{C}$, 281 K/min). The content of maleic anhydride in an aqueous solution of reaction products was determined by titration with NaOH.

The amount of $^1\Delta_g\text{O}_2$ was determined by the chemiluminescent method [9]. A catalyst sample was placed into a quartz reactor with low thermal inertia. At the exit of the reactor, air was cooled to room temperature and directed into a cell, where active oxygen selectively reacted with a chemiluminescent dye. The intensity of chemiluminescence was measured by a FEU-79 photoelectron multiplier.

The amount of stabilized singlet oxygen was estimated from its desorption into a flow passing above a sample layer. The sample was preliminarily calcined at 500°C for 1 h in a flow of air at a residual pressure of 1 kPa, rapidly cooled to minus 60°C , and again heated to $200\text{--}300^\circ\text{C}$. The amount of singlet oxygen desorbed from the sample into the air flow was measured at the exit of the reactor. The generation of singlet oxygen was studied by heating a catalyst sample in a flow of air to the required temperature at a rate of 293 K/min, and the amount of singlet oxygen was determined at the exit

of the reactor. In this work, we only considered the $^1\Delta_g$ singlet oxygen form because the $^1\Sigma_g$ form was formed in negligibly small amounts under our experimental conditions [10].

RESULTS AND DISCUSSION

The reaction on the catalysts studied occurred with the formation of benzaldehyde (BAI), benzoic acid (BAC), maleic anhydride (MA), and carbon oxides (CO_x) as the major products. In addition, benzoquinone, anthraquinone, etc. were detected as impurities. Because of their insignificant amounts (yield less than 1%), their contribution to the composition of the product was ignored. The oxidation of toluene reached stationary conditions immediately after the beginning of the process. The activity and selectivity of the catalysts remained unchanged for at least 8 h if the experimental conditions did not change during the reaction.

According to the table, the ability to generate singlet oxygen decreased in the series $\text{V}_2\text{O}_5 \cdot \text{MoO}_3 > \text{V}_2\text{O}_5 > \text{MoO}_3$. These results corresponded to the catalytic activity of the catalysts in the oxidation of toluene; that is, the catalytic activity of the samples correlated with their ability to generate $^1\Delta_g\text{O}_2$. At 300°C , the generation of $^1\Delta_g\text{O}_2$ was not observed, and conversion did not exceed 30% on the most active vanadium–molybdenum catalyst.

The fraction of deep toluene oxidation products increased as the temperature of the catalytic process grew. Already at 400°C , the products of oxidation on the most active $\text{V}_2\text{O}_5 \cdot \text{MoO}_3$ sample did not contain benzaldehyde, but the yields of benzoic acid, maleic anhydride, and CO_x increased substantially. Simultaneously, the generation of $^1\Delta_g\text{O}_2$ increased to a maximum (compared with the other samples).

The yield of benzoic acid at the same temperature was somewhat lower in the presence of V_2O_5 , and the yield of maleic anhydride was noticeably higher than on $\text{V}_2\text{O}_5 \cdot \text{MoO}_3$. The products obtained on vanadium-containing catalysts at 500°C did not contain benzaldehyde; conversely, the degree of toluene conversion into CO_x was high. At the same time, the yield of benzoic acid decreased insignificantly on the vanadium–molybdenum catalyst and even increased on vanadium oxide. On low-activity MoO_3 , the products of the oxidative destruction of the toluene benzene ring were absent over the whole temperature range ($300\text{--}500^\circ\text{C}$), but the yield of benzaldehyde increased, which is consistent with the lower ability of this catalyst to generate the singlet molecular oxygen form.

Additional evidence in favor of correlation between catalytic activity and the ability to generate $^1\Delta_g\text{O}_2$ is provided by the experimental data on the influence of the temperature of preliminary calcining on these processes (Fig. 1). At a 400°C temperature of preliminary

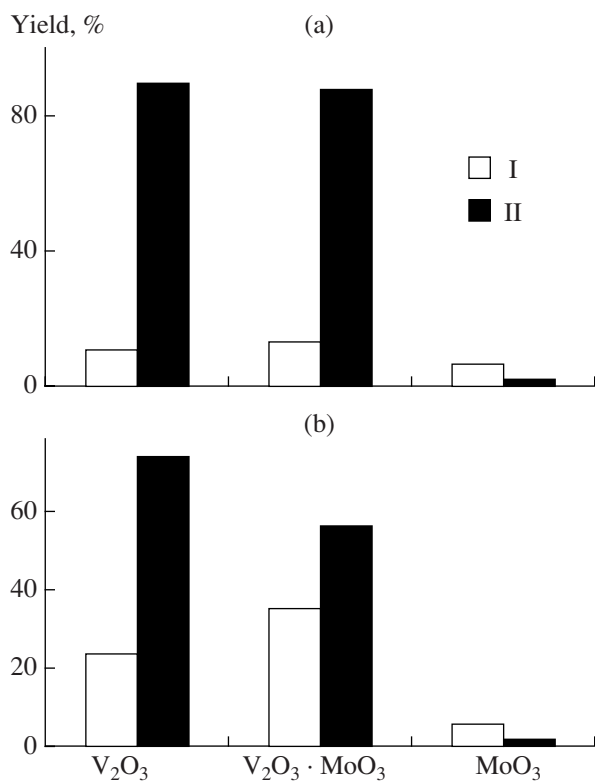


Fig. 1. Influence of the temperature of preliminary treatment of massive V_2O_5 , $V_2O_5 \cdot MoO_3$, and MoO_3 oxides with air oxygen on their (a) activity and (b) selectivity in toluene oxidation; (a) 400 and (b) 500°C; I, side chain and II, benzene ring oxidation.

calcining, the fraction of maleic anhydride and CO_x in the oxidation products was higher than that of benzoic acid and benzaldehyde. This ratio changed noticeably in favor of mild toluene oxidation products (that is, methyl group oxidation products) as the temperature of calcining increased.

This effect was most pronounced for pure V_2O_5 . At a 400°C temperature of preliminary catalyst calcining, the ratio between benzaldehyde + benzoic acid and maleic anhydride + CO_x was 1 : 10. As the temperature of calcining increased to 500°C, this ratio changed into 2 : 3. For $V_2O_5 \cdot MoO_3$ mixed oxide, the difference between side chain and benzene ring oxidation reactions was less substantial, and the yield of methyl group oxidation products increased by as little as 2.5 times. With MoO_3 , we almost did not observe changes in selectivity as the temperature of its preliminary calcining increased, and only the total toluene conversion slightly grew.

These observations well correlate with the data on changes in the amount of generated $^1\Delta_gO_2$ as the temperature increases over the same interval (Fig. 2). The intensity of the process directly depends on the temperature of calcining. At 400°C, the amount of generated $^1\Delta_gO_2$ decreases smoothly during several hours,

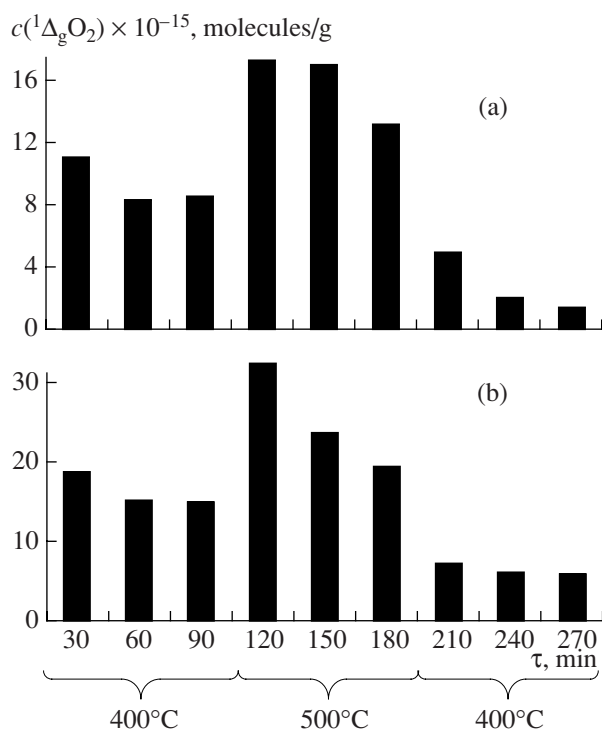


Fig. 2. Amounts of singlet oxygen on massive (a) V_2O_5 and (b) mixed $V_2O_5 \cdot MoO_3$ samples under continuous temperature variation conditions (preliminary calcining at 400°C).

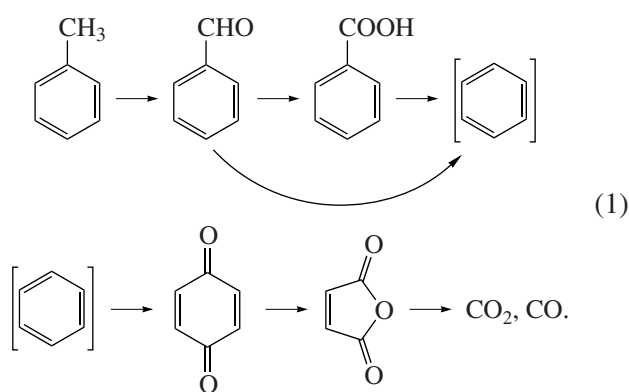
whereas, at 500°C, stable generation continues during an hour and then sharply decreases.

To refine these trends, we performed experiments with toluene oxidation on V_2O_5 and $V_2O_5 \cdot MoO_3$ (Fig. 2) and measured changes in singlet oxygen generation depending on the temperature of the preliminary calcining of the catalysts. The catalysts were heated to 400°C and held at this temperature for 1.5 h. The temperature was then increased to 500°C, and the catalysts were again held at this temperature for 1.5 h. At the concluding stage, the temperature was decreased to 400°C and maintained at this level for 1.5 h. The amount of the singlet oxygen form generated on vanadium oxide at 400°C was $(8-11) \times 10^{15}$ molecules/g. At 500°C, the generation of $^1\Delta_gO_2$ increased by a factor of 1.5. When sample temperature was reestablished at 400°C, this amount decreased by 2-3 times with respect to the initial value.

Similar results were obtained for $V_2O_5 \cdot MoO_3$ mixed oxide (Fig. 2b).

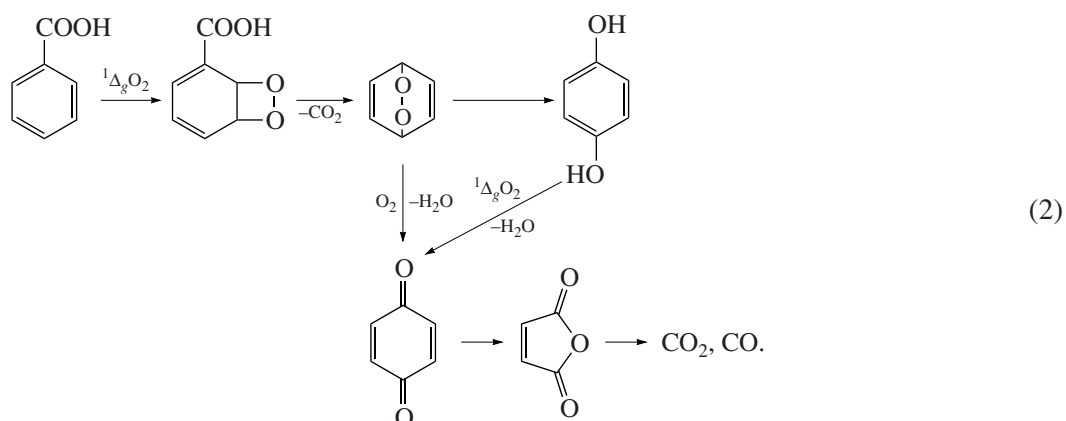
These experimental data show that there is a correlation between the ability of the oxides studied to generate singlet oxygen and their ability to oxidize toluene to maleic anhydride and carbon oxides.

The data obtained in [11-13] and the results of this work lead us to suggest the following scheme of toluene oxidation:



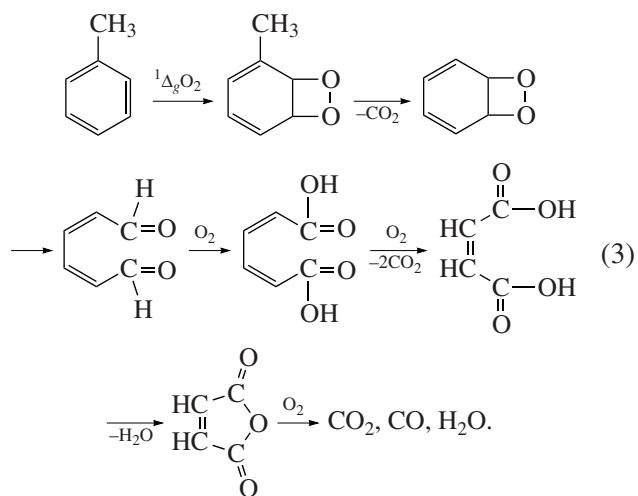
According to (1), toluene is first successively, through benzaldehyde, oxidized to benzoic acid. There is also a possibility of the formation of benzene from benzaldehyde without the formation of benzoic acid. Next, decarboxylation produces benzene, which is oxidized to benzoquinone to yield maleic anhydride and carbon oxides.

On the other hand, the following route for the oxidation of benzoic acid after its formation from benzaldehyde was suggested taking into account the characteristic chemical properties of $^1\Delta_g\text{O}_2$ [8]:



The first two stages (the formation of benzaldehyde and benzoic acid) occur independently of the ability of the catalyst to generate $^1\Delta_g\text{O}_2$. If the ability of the catalyst to generate the singlet molecular oxygen form is comparatively weak, benzaldehyde and benzoic acid are oxidized further to an insignificant degree. But if the amount of generated $^1\Delta_g\text{O}_2$ is larger, deeper oxidation occurs, and the major products are then maleic anhydride and CO_x . The concentration of $^1\Delta_g\text{O}_2$ in the immediate vicinity of the surface of a catalyst is much higher than near the detector. It can therefore be assumed that the generated singlet molecular oxygen form is in part responsible for the formation of maleic anhydride and CO_x in the presence of the catalytic systems studied.

Additional studies, however, showed that the introduction of hydroquinone into benzene had no effect on the yield of maleic anhydride. The conclusion can be drawn that the oxidation of toluene to maleic anhydride does not follow this mechanism, and hydroquinone is the final rather than intermediate toluene oxidation product. A parallel route of the oxidation of toluene is represented by the scheme



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