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Catalytic Activity of Cesium Salt of 12-Molybdophosphoric Acid Containing a Vanadium Promoter in Selective Oxidation

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The vapor-phase air oxidation of *n*-butane was studied with a composite catalyst consisting of cesium salt of 12-molybdophosphoric acid and a vanadium promoter, $Cs_{2.5}H_{0.5}PMo_{12}O_{40} + 2\ VO^{2+}$. The main products were maleic anhydride, acetic acid, acrylic acid, CO, and CO_2. The selectivity to acid was as high as that obtained in the oxidation of 1-butene when the extent of the reaction was low, but it gradually decreased with an increase in the extent of the reaction because of the consecutive oxidation. For a better understanding of the catalytic performance, the activity and the product distribution were also studied for the oxidations of various compounds, such as 1-butene, 1,3-butadiene, furan, methyl ethyl ketone, acetaldehyde, acetic acid, propionic acid, acrylic acid, and maleic anhydride. Distinct differences between the oxidation of *n*-butane and those of 1-butene and butadiene were observed in the effects of the reaction variables. These differences were explained in terms of the affinity of organic compounds for the catalyst.

INTRODUCTION

Much attention has recently been given to the catalytic behavior of 12-molybdophosphoric acid, $H_3PMo_{12}O_{40}$, and its related compounds, because of their promising performances in the synthesis of methacrylic acid by means of direct oxidation (*1–4*). Thus far, the effects of counter cations have been studied extensively (*5–12*). It seems certain that the catalytic function is dependent on both the acid–base property and the oxidation–reduction property, much as in the cases of ordinary mixed metal-oxides (*13, 14*).

In a previous study (*15*), it has been found that salts of molybdovanadophosphoric acid, $H_5PMo_{10}V_2O_{40}$, and composite heteropoly compounds consisting of salts of 12-molybdophosphoric acid and a vanadium promoter are effective for the partial oxidation of *n*-butane to maleic anhydride, and that catalysts lacking in the vanadium component are quite inactive for the oxidation of *n*-butane. Thus, it seemed that it would be interesting to ascertain the characteristic features of the vanadium-containing heteropoly compounds as catalysts and also to collect data concerning the partial oxidation of paraffinic hydrocarbon. Most of the work published to date on the partial oxidation involves studies of olefins, aromatics, and oxygenates. Little information has been forthcoming on the partial oxidation of paraffinic hydrocarbons (*16*).

In this study, we first investigated the catalytic behavior of a composite heteropoly compound in the oxidation of *n*-butane and various organic compounds related to the oxidation of *n*-butane, and then, we have determined the characteristics of the reaction of *n*-butane. As a representative vanadium-containing catalyst, a composite compound consisting of cesium salt of 12-molybdophosphoric acid and a vanadium promoter, designated tentatively as: $Cs_{2.5}H_{0.5}PMo_{12}O_{40} + 2\ VO^{2+}$, was taken up, because its activity is relatively reproducible.

EXPERIMENTAL

Catalyst. 12-Molybdophosphoric acid (Kanto Chemical Co.) was dissolved in wa-

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ter, and then, twice as many moles of vanadium were added to the solution in the form of vanadyl oxalate (containing 4 × 10^{-2} mol V/g). A dark blue solution was thus obtained. Cesium carbonate, Cs_2CO_3, was then added to the solution (*17*). A yellow suspended precipitate was thus formed. The amount of Cs_2CO_3 was adjusted so that the $Cs/H_3PMo_{12}O_{40}$ mole ratio became 2.5. After 10- to 20-mesh pumice originating from volcanic rocks had been mixed with the solution, the mixture was evaporated to dryness by stirring below 200°C. The amount of pumice was about 8 liters (2.8 kg) per mole of 12-molybdophosphoric acid. The catalyst was calcined under flowing oxygen at 380°C for 4 to 5 h.

Reaction procedures. The oxidations of *n*-butane, 1-butene, 1,3-butadiene, furan, methyl ethyl ketone, acetaldehyde, acetic acid, propionic acid, acrylic acid, and maleic anhydride were carried out in a conventional continuous-flow system. The reactor was made of a steel tube, 50 cm long and 1.8 cm i.d., mounted vertically and immersed in a lead bath. The reactant–air mixed gases were fed in from the top of the reactor, with water being introduced into a preheater section by means of a micro liquid-feeder. The total flow rate (at room temperature) was 19 liters per hour (80 × 10^{-2} mol/h) and the contents of reactant and steam in the feed gas were 1.5 to 2.3 and 10.8 vol%, respectively, unless otherwise indicated. The amount of catalyst used was 10 to 40 g. The effluent gas from the reactor was led successively into three chilled water-scrubbers to recover the water-soluble compounds. At the end of 1 h, the content of the water scrubbers (about 120 ml) was collected. The overall acid and maleic anhydride were analyzed by titration with 0.1 *N* NaOH using a pH meter. The compounds, other than maleic anhydride, were analyzed by gas chromatography. The data were usually taken after the pretreatment of catalyst in a stream of *n*-butane–air mixed gas at 340°C for about 8 h. The yield of a particular product was defined as mole percentage yield on a carbon-account-for basis.

RESULTS

Catalytic Performance in the Oxidation of n-Butane

Oxidation of *n*-butane was conducted using 40 g of the $Cs_{2.5}H_{0.5}PMo_{12}O_{40} + 2\ VO^{2+}$ catalyst at the *n*-butane concentration of 2.0 vol%; the other conditions were the same as have been presented in the Experimental section. The major products were maleic anhydride, acetic acid, acrylic acid, CO, and CO_2. Small amount of unidentified polymer compounds were detected, while the amounts of the other products were negligibly small. The sum of the yields of the five main products was in accord with the overall conversion of *n*-butane obtained from the analysis of the *n*-butane content.

As may be seen in Fig. 1, the selectivities to acidic products are substantially high at a low extent of the reaction, but they gradually decrease with an increase in the extent of the reaction.

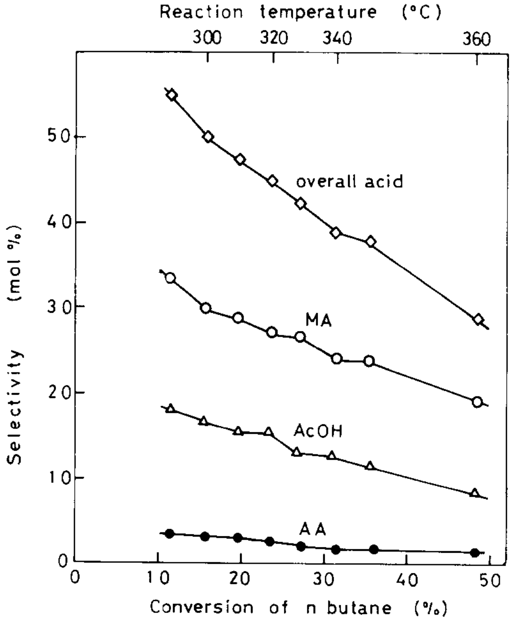


FIG. 1. Selectivities as a function of the conversion of *n*-butane. MA, maleic anhydride; AcOH, acetic acid; AA, acrylic acid.

Oxidation Activity

For a better understanding of the performance obtained in the oxidation of *n*-butane, the catalytic activity was studied for the oxidation of various compounds related to the oxidation of *n*-butane. The amount of catalyst was 40 g. The initial concentrations of each reactant were *n*-butane, 1-butene, or 1,3-butadiene = 2.0, furan = 2.2, methyl ethyl ketone = 1.8, acetaldehyde or acetic acid = 1.9, propionic acid = 2.3, maleic anhydride = ca. 1.5 vol% in air. The conversion of each reactant are plotted in Fig. 2.

The results may be summarized as follows:

(i) The catalyst shows a very low activity for the oxidation of acidic compounds, notably acetic acid and maleic anhydride.

(ii) Acrylic acid and propionic acid are a little more reactive than acetic acid.

(iii) Acrylic acid is less reactive than propionic acid.

(iv) Furan, butene, and butadiene are markedly more reactive than butane, as can reasonably be expected.

(v) Butadiene is more reactive than 1-butene.

(vi) Acetaldehyde is more reactive than the above eight compounds.

(vii) Methyl ethyl ketone is the most reactive.

Product Distribution

In the oxidation of acetaldehyde, the major products were acetic acid, CO, and CO_2. As may be seen in Fig. 3, acetaldehyde is oxidized selectively to acetic acid, and the consecutive oxidation of the formed acetic acid is small.

In the oxidations of acetic acid and maleic anhydride, CO and CO_2 are almost the sole products. The formation of formaldehyde from acetic acid did not exceed 1 mol%, unlike as in the case of the oxidation over basic metal oxides (*13*). The formation of CO_2 is usually a little greater than that of CO.

In the oxidation of acrylic acid, about 10 mol% of acrylic acid was converted to acetic acid and the rest was converted to carbon oxides.

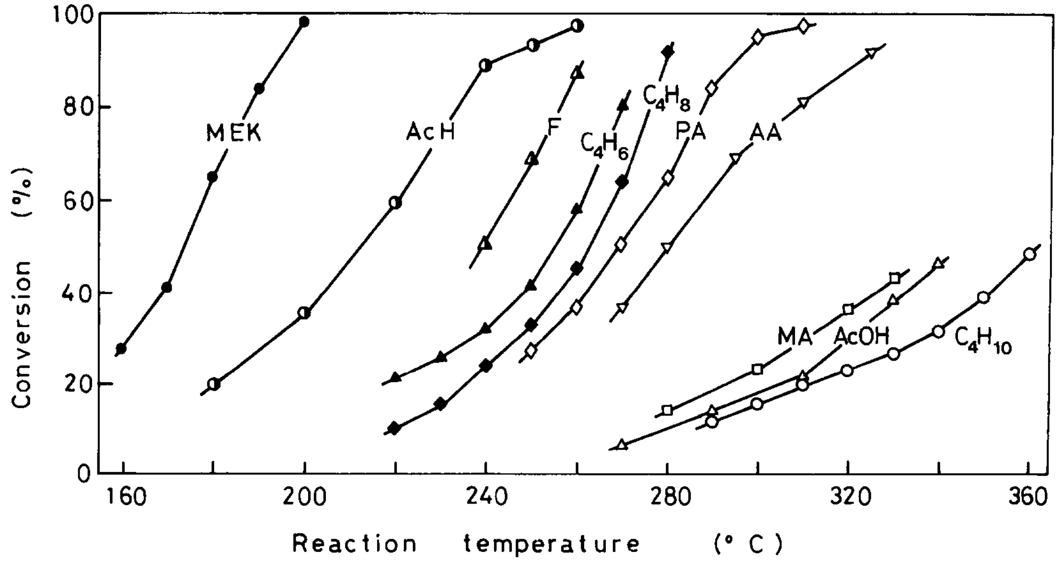


FIG. 2. Dependence of the overall conversion on the reaction temperature. C_4H_{10}, *n*-butane; C_4H_8, 1-butene; C_4H_6, butadiene; F, furan; MEK, methyl ethyl ketone; MA, maleic anhydride; PA, propionic acid; AA, acrylic acid; AcOH, acetic acid; AcH, acetaldehyde.

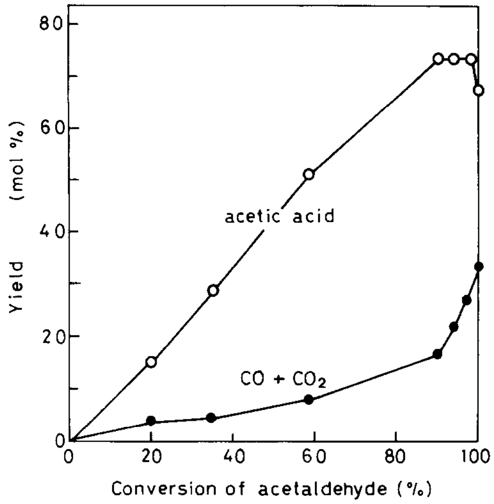


FIG. 3. Yields as a function of the conversion of acetaldehyde.

In the oxidation of propionic acid, the major products were acetic acid, acrylic acid, CO, and CO_2. The change in the yields of the two acids is shown in Fig. 4.

In the oxidation of methyl ethyl ketone, the main products are acetic acid, acetaldehyde, diacetyl (2,3-butane dione), and CO_2 (Fig. 5). It is clear that methyl ethyl ketone is converted, with a high selectivity, to acetic acid and acetaldehyde in equimolar amounts, and that a small part of the acetaldehyde is further oxidized to acetic acid.

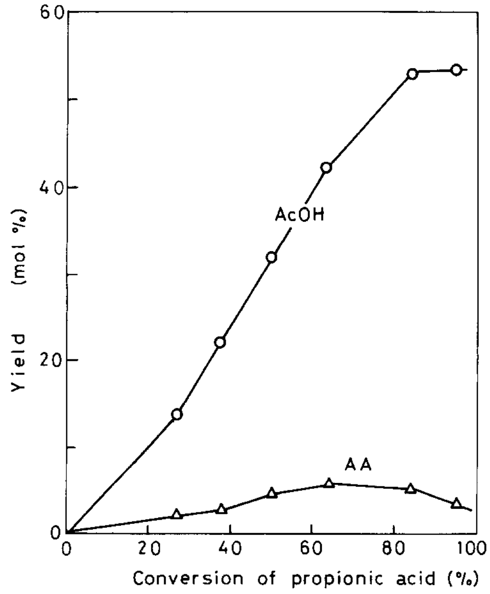


FIG. 4. Yields of acidic compounds as a function of the conversion of propionic acid. AcOH, acetic acid; AA, acrylic acid.

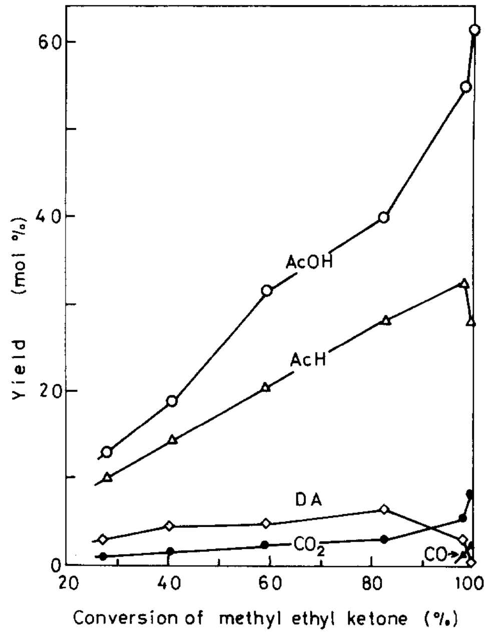


FIG. 5. Yields as a function of the conversion of methyl ethyl ketone. AcOH, acetic acid; AcH, acetaldehyde; DA, diacetyl.

The main products in the oxidations of furan, butadiene, and 1-butene are similar to those obtained in the oxidation of *n*-butane. The yields of intermediate products—for example, furan in the oxidation of butadiene and butadiene in the oxidation of 1-butene—are very small, less than 2 mol%. The distributions of products at a high conversion of the three reactants are summarized in Table 1.

Comparison of the Effects of Reaction Variables

Since the reactivity of *n*-butane is much lower than those of butene and butadiene, the aspects of the oxidation of *n*-butane can be predicted to be different from those of the oxidations of olefins, though the reaction products are similar. To confirm this,

TABLE 1

Selectivity of the $Cs_{2.5}H_{0.5}PMo_{12}O_{40} + 2VO^{2+}$ Catalyst

Reactant	Temp. (°C)	Conversion (%)	Selectivity (mol%)		
			MA	AcOH	AA
1-Butene	290	99	31	18	6
Butadiene	290	100	57	3	3
Furan	270	100	61	4	1

Note. Reactant–steam = 2.0–10.8 vol% in air, catalyst = 40 g. MA, maleic anhydride; AcOH, acetic acid; AA, acrylic acid.

the effects of the reaction variables were compared.

Effect of oxygen concentration. As may be seen in Fig. 6, the rates of the oxidation of the two olefins increase with an increase in the oxygen concentration, while the rate for *n*-butane oxidation varies only a little.

Effect of reactant concentration. The rates of acid formation are compared in Fig. 7. The rate of *n*-butane oxidation increases almost proportionally to the concentration of *n*-butane, while the rates of the two olefins increase only a little with the olefin con-

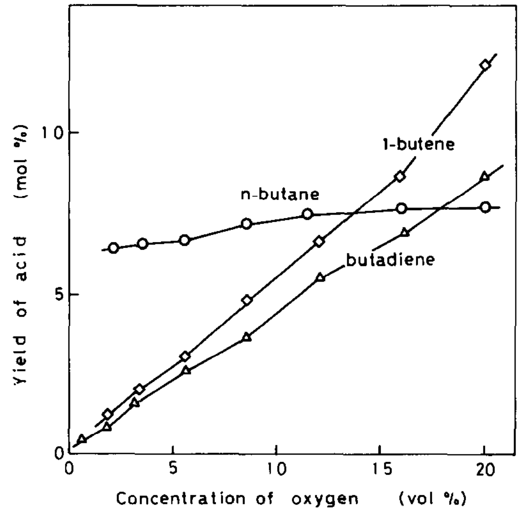


FIG. 6. Yields of acid as a function of the initial concentration of oxygen. *n*-Butane: T = 340°C, catalyst = 40 g. 1-Butene: T = 290°C, catalyst = 10 g. Butadiene: T = 280°C, catalyst = 10 g.

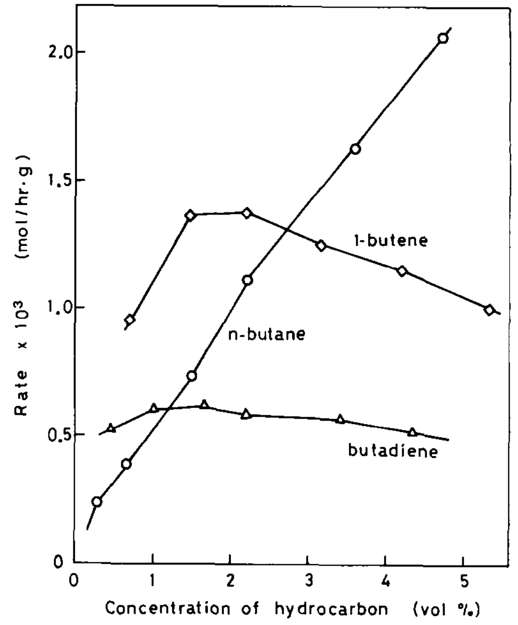


FIG. 7. Rates of acid formation as a function of the initial concentration of hydrocarbon. *n*-Butane: T = 340°C, catalyst = 40 g. 1-Butene: T = 270°C, catalyst = 10 g. Butadiene: T = 260°C, catalyst = 10 g.

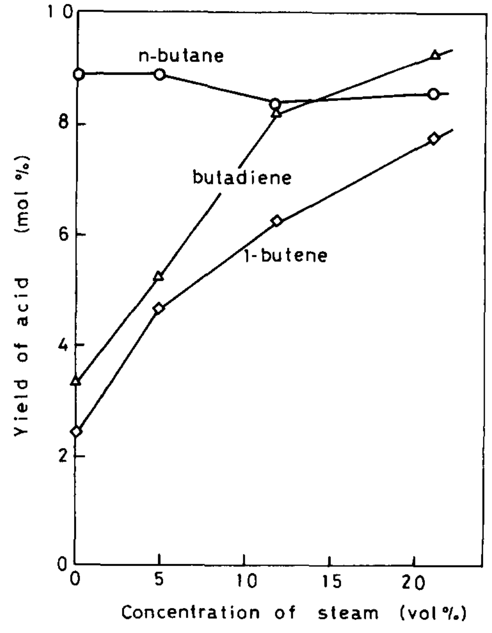


FIG. 8. Yields of acid as a function of the concentration of steam. *n*-Butane: T = 340°C, catalyst = 40 g. 1-Butene: T = 280°C, catalyst = 10 g. Butadiene: T = 270°C, catalyst = 10 g.

centration, and then decrease with a further increase.

Effect of steam concentration. The effect of steam on the oxidation of *n*-butane is also different from the oxidations of butene and butadiene (Fig. 8); the rates of olefin oxidations increase with an increase in the steam concentration, while the rate of *n*-butane is little affected by the steam concentration.

DISCUSSION

The formation of partial oxidation products other than acidic compounds is negligibly small in the oxidation of *n*-butane. This may be easily understood from the finding that maleic anhydride and acetic acid are as stable as *n*-butane, while the expected intermediates, such as butene, butadiene, furan, methyl ethyl ketone, and acetaldehyde, are markedly more reactive than *n*-butane (Fig. 2) and, accordingly, are completely consumed.

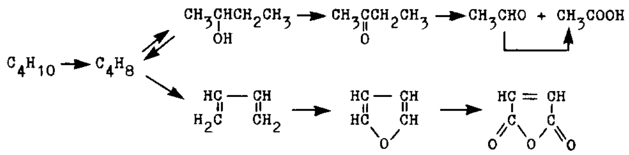
It should be noted that olefins, aldehydes, ketones, and furan act rather as electron-donating, i.e., basic, compounds and that the catalyst possesses strong acidic sites. Because of this, these organic compounds have a strong affinity for the catalyst and, as a result, can be activated extensively (*18, 19*). On the other hand, the acidic compounds are activated with difficulty, because the catalyst is poor in the basic property (*13, 14*).

As may be seen in Fig. 1, when the extent of the reaction is low, the selectivities to acidic compounds are as high as those obtained in the oxidation of 1-butene (Table 1). However, the selectivities in the oxidation of *n*-butane gradually decrease with an increase in the extent of the reaction. It may be reasonable to consider that the acidic products are stable enough under the conditions required for the oxidation of 1-butene, but that they tend to suffer from the consecutive oxidations under the conditions required for the oxidation of *n*-butane.

At any rate, it is evident that the catalyst possesses an outstanding specificity in the oxidation activity. (If not, acidic compounds having a much higher reactivity than paraffinic hydrocarbon should be consumed preferentially.) This may be ascribed to its significant acidic property.

In the oxidation of furan and butadiene, the major acidic product is maleic anhydride and the amount of acetic acid is small, while in the oxidations of butene and *n*-butane a substantial amount of acetic acid is formed (Fig. 1 and Table 1). The formation of acetic acid from 1-butene is clearly higher than that obtained with V_2O_5–P_2O_5 and MoO_3–P_2O_5 catalysts at higher temperatures, 400 to 500°C (*20*).

Possibly, the selectivity to acetic acid is related to the reaction temperature; that is, at the step of butene in a series of consecutive steps from *n*-butane to acidic products, the hydration to alcohol (*21, 22*) and the allylic oxidation to butadiene compete with each other as follows:



In view of the reaction equilibrium, the lower the temperature, the more favorable the hydration of butene becomes. In the case of catalysts based on 12-molybdophosphoric acid, it is necessary to conduct the reaction at a temperature lower than 380°C because of their low thermal stability (*8, 11, 12, 17*). Therefore, it seems hard to avoid the formation of acetic acid. This may be a characteristic of the catalyst based on 12-molybdophosphoric acid.

As is shown in Figs. 6 and 7, the oxidation rates of olefins increase with an increase in the oxygen concentration, but they increase only a little with an increase in the olefin concentration, whereas in the case of *n*-butane oxidation, the situation is reverse. This difference may be due to the difference in the reactivity and the affinity of reactant molecules. We would not like to consider that the active sites effective for the *n*-butane oxidation are different from those for the olefin oxidation.

Since olefins have a strong affinity for the acidic catalyst, the catalyst may be almost saturated with the olefin even when the concentration is low and so the oxidation rates may increase only a little with the concentration. When the concentration exceeds a limited value, the rates decrease with the concentration. This may be explained by assuming that, with the increase in the concentration, the extent of the reduction of the catalyst becomes so great that the oxidizing power of the oxygen species decreases or the reoxidation of the catalyst by gaseous oxygen becomes difficult. From the dependency on the oxygen concentration, it was felt that the rates are limited by the reoxidation of the catalyst, because olefins are easily oxidized by 12-molybdophosphoric acid.

On the other hand, paraffinic hydrocarbon is poor in the affinity for the catalyst, and so the amount of adsorbed and/or activated molecules may increase proportionally to the concentration in the gas phase. Since the reaction order is nearly zero with respect to oxygen, it may be supposed that paraffinic hydrocarbon is quite unreactive; therefore, the rate is limited by the reaction of the reactant molecule with surface oxygen species, which is controlled by the oxidizing power of surface oxygen species as well as by the extent of reactant activation on acidic sites.

Another difference in the reaction features between the oxidation of *n*-butane and that of olefins is the effect of steam (Fig. 8). As a possible explanation, it can be proposed that the steam acts to liberate the oxygenated products from the surface, especially when the reaction temperature is low. This leads us to consider that the promoting effect of steam is a common aspect observed in oxidation reactions conducted at a low temperature, regardless of the participation of steam in the reaction.

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