The Production of Furan by the Vapor-Phase Oxidation of Butadiene Using Heteropoly Compounds as Catalysts

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Supported heteropoly compounds, such as salts of 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$), were found to be effective as catalysts for the synthesis of furan in the vapor-phase oxidation of 1,3-butadiene. The rate of the reaction increases with the contents of oxygen and steam in the feed gas, whereas it decreases with the butadiene content. The yield of furan attains a maximum at a conversion of about 70%, regardless of the reaction conditions and the catalysts. From tests on 18 salts of 12-molybdophosphoric acid with an M^{n+}/Mo atomic ratio of $1/12n$ ($M_{1/n}H_2PMo_{12}O_{40}$) as catalysts, it was found that the best results for furan formation are obtained with the cesium, sodium, and ammonium salts. The effect of cesium content was also studied. The best results for both the yield of furan and the oxidation activity are obtained at a Cs/Mo atomic ratio of from $1/12$ to $1.5/12$. The results were discussed in the light of the acid–base properties of the cataysts.

INTRODUCTION

Furan is a raw material for tetrahydrofuran, which is in great demand as a solvent and as a starting material for polymer compounds. Tetrahydrofuran has been manufactured by three methods: the furfural process, the hydrolysis of 1,4-dichloro-2-butene, and the hydrogenation of maleic anhydride (*1*). Attempts have also been made to obtain furan by the direct oxidation of butadiene or crotonaldehyde (*2–5*). There have, however, been very few academic works. Adams *et al.* (*6, 7*) have reported a 9 mol% yield of furan in the oxidation of butadiene and a 40 mol% yield in the oxidation of crotonaldehyde using a bismuth molybdate catalyst. The present author has also reported that furan is an intermediate in the oxidation of *cis*-2-butene, butadiene, or crotonaldehyde to form maleic anhydride (*8*), and that the yield of furan cannot exceed 3 mol% with a V_2O_5 or V_2O_5–MoO_3 catalyst and is less than 7 mol% even with V_2O_5–P_2O_5 (P/V atomic ratio = 1.6), this showing a good selectivity in the oxidation from *cis*-2-butene to maleic anhydride because furan is fairly reactive compared with *cis*-2-butene or butadiene (*9*). After a survey of the performances obtained from various mixed oxide catalysts, it was concluded that the MoO_3–P_2O_5 catalysts with a P/Mo atomic ratio of about 1/10 are effective for furan synthesis. The yield of furan attained 11 mol% in the oxidation of butadiene (*10*).

Recently, we found that heteropoly compounds such as the salts of 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$) are more effective as catalysts for furan synthesis than the ordinary MoO_3–P_2O_5-based mixed oxides. In this study we focused our attention on the formation of furan from butadiene and attempted to clarify the effect of the catalyst and of reaction variables, since no detailed information about this oxidation reaction has yet been reported.

EXPERIMENTAL

Catalysts

A number of heteropoly compounds were used as catalysts. They were prepared as follows. 12-Molybdophosphoric acid, $H_3PMo_{12}O_{40} \cdot \alpha H_2O$ (Kanto Chemical Co.), was dissolved in water, and the required

quantities of the second metallic components were added to the solution. As the starting materials of the second components, we used, in some cases, two different compounds: (A) carbonates (if they are unobtainable, nitrates or acetates), and (B) metal powders, which can be dissolved in the aqueous solution because of the oxidizing function of 12-molybdophosphoric acid. After 10- to 20-mesh pumice originating from volcanic rocks had then been mixed with the solution, the mixture was evaporated to dryness with stirring below 200°C. The amount of pumice was about 8 liters per mole of 12-molybdophosphoric acid. The catalysts were calcined under flowing oxygen at 380°C for 4 to 5 hr.

Reaction Procedures

The oxidation of 1,3-butadiene was carried out in a conventional continuous-flow system. The reactor was made of a steel tube coated with aluminum, 50 cm in length and 1.8-cm i.d., mounted vertically and immersed in a molten lead bath. The oxygen–nitrogen mixed gases were fed in from the top of the reactor, with water being introduced into a preheater section by means of an injection syringe pump. The total flow rate was kept constant at 1.0 liter/min. The amount of catalyst used was 20 g, and the content of butadiene, oxygen, steam, and nitrogen in the feed gas was 1.0, 4.0, 7.5, and 85.7 vol%, respectively, unless otherwise indicated. The effluent gas from the reactor was led successively into four chilled water-scrubbers to recover the water-soluble compounds. At the end of 1 hr, the contents of the water-scrubbers were collected (about 300 ml). The maleic anhydride was analyzed by titration with 0.10 N NaOH using a pH meter, while the other compounds were quantitatively analyzed by gas chromatography. The inlet and exit gases were intermittently analyzed. In order to measure the catalytic behavior in the stationary state, the data were taken more than 7 to 8 hr after the start of each run.

RESULTS AND DISCUSSION

Effects of Reaction Variables

The fact that furan is reactive and easily oxidized to maleic anhydride (11, 12) leads us to predict that the yield of furan is strongly influenced by the reaction conditions. In addition, it is known that heteropoly compounds are decomposed at temperatures higher than 400°C (13). It therefore seems necessary to know the characteristics of the reaction. Thus, at first, the effects of the reaction variables were studied, using supported 12-molybdophosphoric acid as the catalyst.

Product distributions. The main products in the oxidation of butadiene were furan, maleic anhydride, acetic acid, CO, CO_2, and unidentifiable polymer compounds. The amount of acetic acid was found to be less than 5 mol% of the maleic anhydride, and that of the polymer compounds, less than 10 mol% from the material balance between inlet and exit gases. The yields of the other products, such as acetaldehyde and acetone, were less than 0.5 mol%. The change in the yields of the main products with the extent of reaction was studied by changing the reaction temperature from 315 to 365°C (Fig. 1).
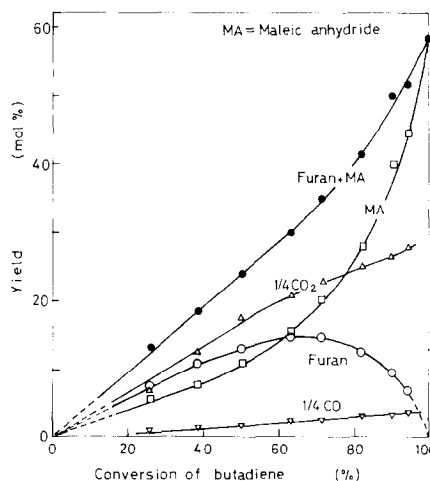

FIG. 1. Oxidation of butadiene over supported 12-molybdophosphoric acid. Catalyst = 20 g; $C_4H_6-O_2-H_2O-N_2$ = 1.0–4.0–18.6–76.4 vol%; total flow rate = 1.0 liter/min; T = 315–365°C.

When the conversion is low, less than 40%, the yield of each product increases almost in parallel as the reaction proceeds. This means that the products are formed competitively. However, at a higher conversion around 70% the yield of furan attains a maximum value and it decreases above this conversion being accompanied by an increase in the yield of maleic anhydride. These results suggest that maleic anhydride is formed also by the oxidation of the produced furan. The slope of the curve representing the sum of the yields of furan and maleic anhydride increases with the conversion especially at a conversion of more than 70%. This reveals that some of the polymer compounds also act as precursors of maleic anhydride. It was also found that the catalyst is inactive for the oxidative degradation of maleic anhydride.

Effect of steam content. The reaction was carried out by changing the steam content in the feed gas from zero to 18.6 vol%. The conversion (overall consumption) of butadiene is plotted as a function of the temperature in Fig. 2. It is evident that the reaction rate increases markedly with an increase in the steam content.

In Fig. 3 the yield of furan at different steam contents is plotted as a function of the extent of the reaction. It was found that
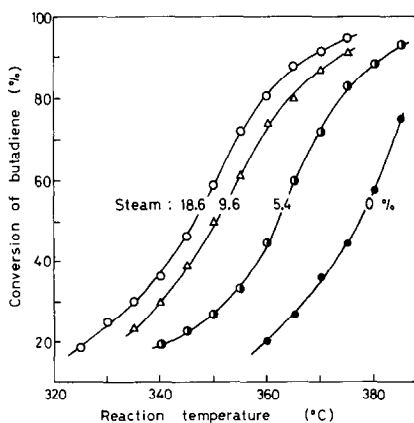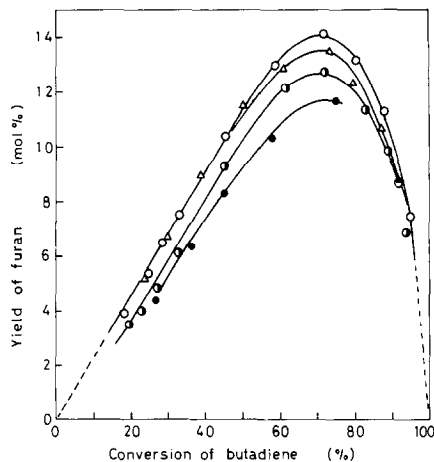

FIG. 3. Effect of the steam content on the yield of furan. Reaction conditions and symbols are the same as for Fig. 2. Steam content: (●) 0%; (◑) 5.4%; (△) 9.6%; and (○) 18.6%.

the addition of steam up to 18 vol% is favorable for furan formation and that the conversion of butadiene at the maximum yield of furan is as high as about 70%, regardless of the steam content. It was also found that the yield of maleic anhydride at a high conversion (90–95%) is not affected by the addition of steam.

Effect of oxygen content. The oxygen content was varied, and the rate of butadiene consumption calculated from the low-level conversion (less than 30%) was compared. As may be seen in Fig. 4, the rate increases almost proportionally with the oxygen content.

The yield of furan at three different oxygen contents is shown in Fig. 5. The maximum yield decreases slightly with an increase in the oxygen content. It was also found that the conversion of butadiene at the maximum yield of furan and the yield of maleic anhydride at higher conversion (90–95%) are almost insensitive to the oxygen content.

Effect of butadiene content. The effect of the butadiene content was also examined. As may be seen in Fig. 6, the rate of butadiene consumption decreases with an increase in the butadiene content. The yield of furan at the conversion of about 70%,
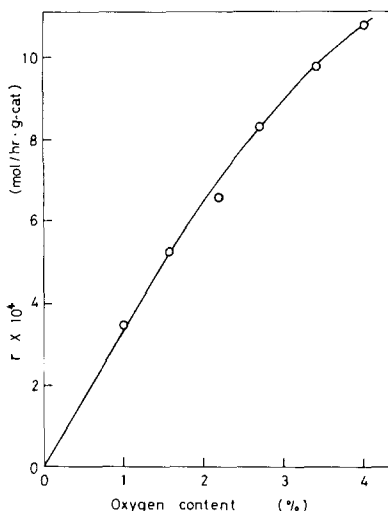

FIG. 2. Effect of the addition of steam to the feed gas on the rate of butadiene oxidation. Catalyst = 20 g; content of C_4H_6 and O_2 = 1.0 and 4.0 vol%; total flow rate = 1.0 liter/min.

FIG. 4. Rate of butadiene consumption as a function of the initial oxygen content in the feed gas. Catalyst = 5–20 g; $T = 362°C$; contents of C_4H_6 and steam = 1.0 and 7.6 vol%; total flow rate = 1.0 liter/min.

corresponding to the maximum yield of furan, also decreases slightly with the butadiene content.

Discussion. The 12-molybdophosphoric acid catalyst, much like the MoO_3–P_2O_5 and WO_3–P_2O_5 mixed oxide catalysts, is strongly acidic, but is lacking in basic property. From these acid–base characteristics, the catalytic behavior can be understood, to a certain extent. That is, the catalyst has a strong affinity for basic compounds, such as butadiene and furan, whereas it has little affinity for acidic compounds, such as maleic anhydride. Accordingly, the catalyst is active for butadiene and furan, but inactive for maleic anhydride. Thus, the selectivity to maleic anhydride at a high conversion (90–95%) remains constant, regardless of the reaction conditions. The facts that the reaction rate increases almost proportionally with the oxygen content, while it decreases with an increase in the butadiene content, lead us to consider that the reaction is limited by the reoxidation step of a redox cycle, in contrast with the reaction over a basic catalyst such as Bi_2O_3–MoO_3, and that the increase in butadiene content causes an increase in the reduction degree

of the catalyst, making the reoxidation of the catalyst difficult. On the other hand, from the fact that the oxidation rate increases with the addition of steam, we must consider the possibility that the steam serves to remove certain oxidation products which are strongly adsorbed on the surface and obstruct the reaction of butadiene.

Since furan is an intermediate product, the yield is affected by two factors (*8, 14, 15*): (i) the relative reactivity of furan to butadiene, and (ii) the affinity of the catalyst for furan and the oxidizing power of the catalyst; this means that the stronger the furan adsorption and the oxidizing power become, the larger the portion of the adsorbed furan species which goes to the next oxidation, without desorbing to the gas phase. The fact that the conversion at the maximum yield of furan remains constant at 70% with the variation in the conditions suggests that the reactivity ratio of furan to butadiene is unchanged. The results obtained from a special run of competitive oxidation between furan and butadiene indicated that the reactivity ratio of furan to butadiene is about unity. Accordingly, it may be said that the yield of furan
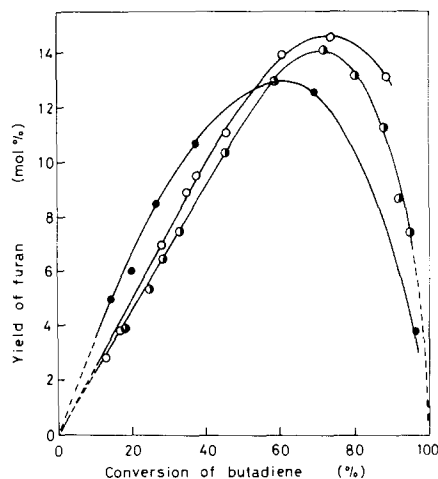

FIG. 5. Effect of oxygen content on the yield of furan. Catalyst = 20 g; contents of C_4H_6 and steam = 1.0 and 7.6 vol%; total flow rate = 1.0 liter/min; oxygen content: (○) 2.6%; (◑) 4.0%, and (●) 20%; T = 300–375°C.
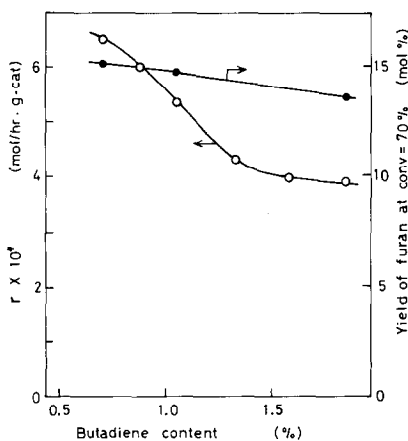
FIG. 6. Effect of the initial butadiene content on the rate and yield of furan. Catalyst = 10–20 g; contents of oxygen and steam = 20 and 7.5 vol%; (O) rate of butadiene consumption at 340°C; (●) maximum yield of furan at T = 350–370°C.

depends only on the second factor. The increase in the oxygen content brings about an increase in the oxidizing power for furan, which results in a decrease in the yield. On the other hand, the effect of steam addition on the yield of furan can also be understood by assuming that the steam serves to remove the adsorbed furan, as has been mentioned above.

Catalyst Screening

In order to improve the yield of furan, attention was given to the modification of the 12-molybdophosphoric acid catalyst by adding various kinds of second metallic components. It can be predicted that if all three protons of 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$) are replaced by metal cations, the acidic property will be strongly extinguished and that, as a result, the catalytic function for mild oxidation will also disappear. Accordingly, a series of salts of 12-molybdophosphoric acid with an M^{n+}/Mo atomic ratio of $1/12n$ ($M_{1/n}^{n+}$ $H_2PMo_{12}O_{40}$) were tested.

Four examples of the change in the yields of furan and maleic anhydride with the extent of reaction are shown in Fig. 7. The results obtained from each catalyst at conversions of 70 and 80% are listed in Table 1.

As may be seen in Figs. 1 and 7, the yield of furan at a 70% conversion corresponds to the maximum yield and the main product at an 80% conversion is maleic anhydride. The reaction temperature required to achieve two fixed conversions represents the relative oxidation activity of each catalyst. The catalyst marked "m" in the first column of Table 1 are the catalysts prepared by mixing metal powder with the 12-molybdophosphoric acid solution.

The results may be summarized as follows:

(i) The effect of the difference in the kind of second metallic component on the oxidation activity is not large, whereas in the case of $MoO_3–P_2O_5$-based mixed oxide catalysts (16) the activity varies greatly with the difference in the kind of second metallic component.

(ii) No clear correlation is found between the oxidation activity of salts of heteropoly acid ($M_{1/n}^{n+}H_2PMo_{12}O_{40}$) and the acid–base properties or the oxidation activity of the metal oxide corresponding to the second metallic component (M_2O_n).
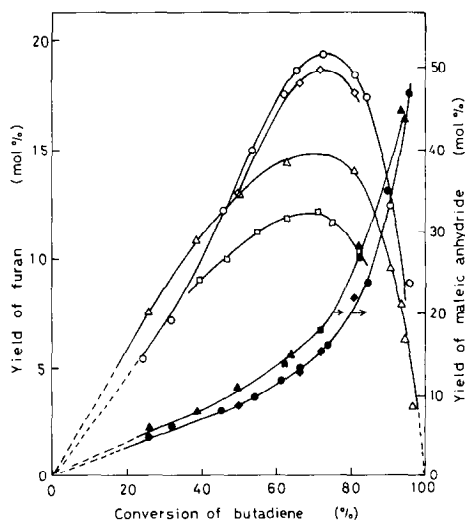

FIG. 7. Yields of furan and maleic anhydride as a function of the conversion of butadiene. T = 320–380°C; $C_4H_6–O_2–H_2O–N_2$ = 1.0–4.0–14.2–80.8 vol%; total flow rate = 1.0 liter/min; catalyst = 20 g; (△,▲) $H_3PMo_{12}O_{40}$; (O,●) $CsH_2PMo_{12}O_{40}$; (◇,◆) $NH_4H_2PMo_{12}O_{40}$; (□,■) $NiHPMo_{12}O_{40}$.

TABLE 1

Oxidation of Butadiene with Various $M_{1/n}{}^{n+}H_2PMo_{12}O_{40}$ Catalysts[a]

Catalyst M^{n+}	Data at conversion = about 70%				Data at conversion = about 80%			
	React. temp. (°C)	Total conv. (%)	Furan yield (mol%)	MA yield (mol%)	React. temp. (°C)	Total conv. (%)	F + MA yield (mol%)	F + MA select. (mol%)
H^+	352	67	14.5	18.7	355	80	40.2	50
$NH_4{}^+$	370	72	18.6	17.4	380	81	39.2	50
Na^+	360	68	17.7	17.1	370	83	47.3	57
K^+	330	74	14.5	20.1	335	80	35.4	44.5
Cs^+	340	72	18.8	16.1	352	84	40.4	48
Mg^{2+}	350	66	12.0	20.5	360	87	46.6	53.5
Ba^{2+}	355	63	16.2	13.8	360	80	41.5	52
Zn^{2+} m	340	68	14.0	19.7	350	92	51.3	56
Te^{4+} m	355	67	12.0	15.6	360	79	31.6	40
Bi^{3+}	350	74	15.0	19.8	360	78	37.6	48
Sn^{4+} m	352	71	16.1	20.0	360	76	39.0	51
Pb^{4+} m	345	76	13.0	22.0	350	86	42.2	49
U^{4+}	350	77	16.0	21.2	360	89	43.1	49
Fe^{3+}	340	73	14.3	19.4	345	79	36.7	47
Fe^{3+} m	355	62	13.2	15.5	360	79	41.1	52
Ni^{2+}	350	57	13.2	13.5	360	79	37.6	48
Ni^{2+} m	350	70	12.0	17.7	—	—	—	—
Cu^{2+}	355	66	10.6	20.4	360	83	41.9	50.5
Cu^{2+} m	350	50	10.5	15.1	355	86	41.5	48
Ag^+	375	74	14.6	20.5	380	84	42.1	50
Ag^+ m	350	71	12.6	16.9	355	75	34.2	45.5
P	370	67	15.0	18.0	380	79	39.2	50

[a] Feed gas: C_4H_6–O_2–H_2O–N_2 = 1.0–4.0–14.2–80.8 vol%; total flow rate = 1.0 liter/min; catalyst = 20 g. F, furan; MA, maleic anhydride.

(iii) The difference in the starting material of the second component (whether carbonate or metal powder) does not cause any marked difference in the catalytic activity.

(iv) The selectivity to maleic anhydride at a high conversion is not affected by the addition of a second metallic component as long as the M^{n+}/Mo atomic ratio is less than $1/12n$. It is believed that the $M_{1/n}{}^{n+}H_2PMo_{12}O_{40}$ catalysts are acidic enough to produce acidic products (17).

(v) The most favorable ions for furan formation are Cs^+, Na^+, and $NH_4{}^+$. The next best ions are Ba^{2+}, Sn^{4+}, and U^{4+}. The addition of Cu^{2+}, Ag^+, Ni^{2+}, and Fe^{3+}, in contrast, decreases the yield.

It is difficult at present to understand the effect of the difference in the kinds of metal ions added to heteropoly acid on the catalytic behavior as well as the difference in the catalytic behavior between heteropoly compounds and ordinary mixed oxides. Further experimental evidence is awaited.

Effect of Catalyst Composition

Since it was found that the best result is obtained with the cesium salt of 12-molybdophosphoric acid, the effect of the catalyst composition was studied using cesium salt as a model system. As may be seen in Fig. 8, the oxidation activity for butadiene consumption increases with the cesium con-
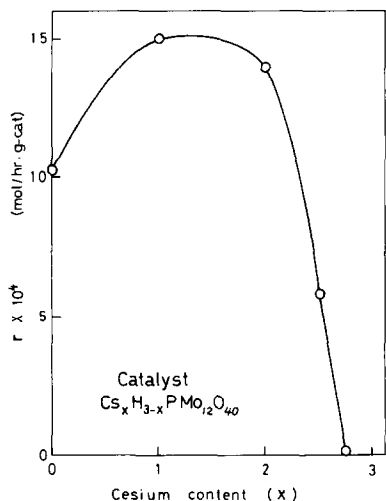
FIG. 8. Effect of the cesium content in the acid salt of $H_3PMo_{12}O_{40}$ on the catalytic activity for butadiene oxidation. $T = 326°C$; $C_4H_6 = 1.0$ vol% in air.

tent, passes through a maximum at a Cs/Mo atomic ratio of about 1.5/12, and then declines sharply with a further increase in the cesium content.

We would like to explain the results as follows. The oxidation activity is generally governed by two functions (18): (i) the activation of butadiene and furan on acidic sites and (ii) the activation of gaseous oxygen on basic sites. Since 12-molybdophosphoric acid is eminent in acidic character,
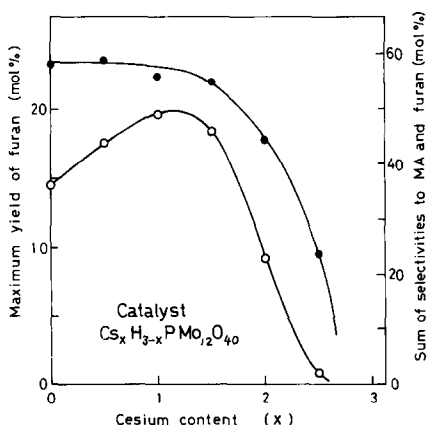
but deficient in basic character, the reaction is limited by the function of the basic sites. Accordingly, it is reasonable that the activity increases with an increase in the basic sites. On the other hand, when the content of cesium is high, the catalyst becomes deficient in acidic property, and, as a result, the reaction is limited by the function of the acidic sites. Therefore, the activity decreases with a decrease in the acidity. A maximum in the activity is obtained when the acid–base properties become proper to the reaction, that is, at Cs/Mo = 1.5/12.

The maximum yield of furan, obtained at about a 70% conversion, and the sum of the selectivities to furan and maleic anhydride at a conversion of from 90 to 96%, are shown as functions of the cesium content in Fig. 9. It was found that the best result for furan formation is obtained with the catalysts having Cs/Mo atomic ratios of from 1/12 to 1.5/12. The selectivity to maleic anhydride seems to be almost the same in the Cs/Mo range from zero to 1.5/12, whereas it sharply decreases with a further increase in the cesium content.

From these results, we are induced to consider that the addition of cesium reduces the affinity of the catalyst for furan, which facilitates the desorption of the adsorbed furan and increases the yield of furan, and that with the addition of more cesium so that the Cs/Mo ratio exceeds 1.5/12, the catalyst loses its acidic property so greatly that it becomes improper for use in the acid-formation reaction, because one of the necessary conditions for an effective catalyst for the acid-formation reaction is the possession of a sufficient acidic property (18).

FIG. 9. Effect of the cesium content on the yield of furan and the sum of selectivities to maleic anhydride and furan. Catalyst = 20 g; $C_4H_6–O_2–H_2O–N_2$ = 1.0–4.0–18.6–76.4 vol%; total flow rate = 1.0 liter/min; T = 310–380°C.

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