JOURNAL OF CATALYSIS **120**, 206–215 (1989)

Oxidation of α-Methylstyrene to Phenylacrolein on MoO_3–WO_3–TeO_2 Catalysts

MAMORU AI

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Received February 7, 1989; revised June 26, 1989

Various kinds of metal oxides were tested as catalysts for vapor-phase oxidation of α-methylstyrene to form α-phenylacrolein (atropoaldehyde). The best performance was obtained with the Mo/W/Te atomic ratio of 10/4/4 catalyst; one-pass yield of α-phenylacrolein attained 59 mol% at α-methylstyrene conversion of 91%. The rate of reaction increased proportionally to the oxygen concentration, while it was almost insensitive to the concentrations of α-methylstyrene and water vapor. Studies of reaction variables showed that an optimal yield of α-phenylacrolein is obtained under the conditions of long contact times, low temperatures, high oxygen concentrations, α-methylstyrene concentration of 1 to 2.4 mol%, and absence of water vapor. The results are discussed in the light of both the acid–base property and the oxidizing function of the metal oxides.

INTRODUCTION

It is well known that propylene is oxidized to acrolein with a very high selectivity over Bi–Mo and Sb-based mixed-oxide catalysts and that *n*-butene and isobutene are also oxidized to butadiene and methacrolein, respectively, over a similar type of catalyst. However, in the oxidation of aromatic compounds, these catalysts cannot exhibit an excellent performance. Indeed, the metal oxides proposed to be effective in the oxidation of ethylbenzene to styrene (*1*) are different from those used in the oxidation of propylene and the butenes. Further, coke deposited on a catalyst carrier is generally considered to be responsible for the catalytic action (*2–5*). On the other hand, V–P oxides (*6*), Mo–P oxides (*7*), Mo–P-based oxides (*8*), Mo-based oxides (*9*), and V–Ti oxides (*10*) have been proposed to be effective for the oxidation of toluene to benzaldehyde.

As for the oxidation of α-methylstyrene [2-phenylpropene] to form α-phenylacrolein [atropoaldehyde, 2-phenylpropenal] (abbreviated hereafter as PhA), there have been very few studies. Adams (*11*) reported that Bi–Mo oxide is not effective; the PhA yield is about 3 mol% at the α-methylstyrene conversion of 45%. Recently, Grasselli *et al.* (*12*) reported a 30 mol% yield of PhA at the α-methylstyrene conversion of 50% using Nb-promoted Sb–U oxide catalysts.

In this study, we focused our attention on the oxidation of α-methylstyrene to form PhA and attempted to explore effective catalysts for this reaction and also to clarify the characteristic features of this oxidation reaction.

EXPERIMENTAL

Catalysts. The catalysts used in this study were various kinds of single, binary, and ternary oxides. Some of them were the same as those used in our previous studies (*13–15*). The metal oxides were supported on 8- to 20-mesh-size pumice originating from volcanic stone consisting of macropores (packing density = 0.4 g/ml and specific surface area = 0.3 to 0.6 m^2/g).

For example, the Mo/W/Te atomic ratio = 10/4/4 catalyst was prepared as follows. $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (35.3 g) was dissolved in hot water and 20.9 g of

0021-9517/89 $3.00

$(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$ was also dissolved in hot water using oxalic acid. The two solutions were mixed and 18.0 g of H_6TeO_6 was dissolved in the solution. Excess water was evaporated off with vigorous stirring with the aid of a hot air current, yielding a sticky syrup. Thereafter, 100 ml of 8- to 20-mesh-size pumice was added to the sticky syrup and the mixture was evaporated to dryness with stirring by means of a hot air current. The solid obtained was evaporated again in an oven at 200°C for 4 h and then it was calcined at 450°C for 6 h in a stream of air.

Reaction procedures. The vapor-phase contact oxidation of α-methylstyrene was conducted with 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. Air or a mixture of oxygen and nitrogen was introduced from the top of the reactor, with α-methylstyrene being injected into the preheating section of the reactor by means of a micro liquid feeder (a syringe pump).

Unless otherwise indicated, the feed rates were fixed as follows; air, 400 ml (at 20°C)/min (ca. 1.0 mol/h); α-methylstyrene, 11.9 mmol/h (ca. 1.19 mol% in the feed). The effluent gas from the reactor was led successively into four chilled scrubbers containing 2-propanol to recover the 2-propanol-soluble compounds. After 1 h time-on-stream, the content of the 2-propanol scrubbers was collected (120 ml). The reaction products and unreacted α-methylstyrene were analyzed by gas chromatograph: a 1-m column of molecular sieve 13× for CO; a 6-m column of propylene carbonate for CO_2; a 2-m column of PEG 20M at 160°C for α-methylstyrene, benzaldehyde, and 2-propanol; a 1-m column of AT-1200 + H_3PO_4 at 160°C for PhA, maleic anhydride, benzaldehyde, and benzoic acid. The amount of total acid was also checked by titration with 0.1 *N* NaOH using a pH meter. The titration was in accord with the sum of the amounts of maleic anhydride and benzoic acid measured by gas chromatograph.

Since PhA is not available as a chemical agent, the identification was performed by means of GC-MS (Hitachi H-80) and the quantity was determined on the basis of the approximation that the peak area of PhA recorded in gas chromatograph (FID) is equal to that of cinnamaldehyde [β-phenylacrolein, 3-phenylpropenal].

The yield and selectivity of a particular product were defined as mole percentage yield and selectivity on a carbon-accounted-for basis. As for the yield of carbon oxides [CO_x], the CO_x accompaning the formation of benzoic acid, benzaldehyde, and maleic anhydride was excluded.

RESULTS

Performance of Various Metal Oxide Catalysts

Since little information has been reported on the oxidation of α-methylstyrene, it seemed necessary to make a character sketch of the catalytic function for this reaction. Therefore, various kinds of metal oxides were tested. The results are listed in Tables 2 to 5, according to the classification of metal oxide in view of both acid–base and oxidizing functions shown in Table 1 (*15, 16*).

Table 2 shows the results obtained with single-oxide catalysts. Over WO_3, the main product is carbon dioxide and the PhA yield does not exceed 5 mol%. The MoO_3 possesses sufficient catalytic activity for this oxidation and it exhibits the highest selectivity to form PhA among the tested oxides; the PhA yield attains 20.5 mol% at α-methylstyrene conversion of 90%. The V_2O_5 is very active; almost all of the α-methylstyrene is consumed even at 295°C, but the main products are unidentifiable polymer compounds and maleic anhydride, and PhA is not formed. The Sb_2O_5 is inactive. At a high temperature of 500°C, 46% of α-methylstyrene is consumed even in the absence of catalyst and the yield of PhA attains 14 mol%.

TABLE 1

Acid–Base Properties of Metal Oxides

(i) Oxides with oxidation activity

No.	1	2	3	4	5	6	7	8	9	10				
Oxide	W	Mo	V	U	Ti	Sn	Fe	Bi	Zn	Mn	Cr	Co	Ni	Cu
Group	*A*	*A*	*A*	*B*	*B*	*B*	*B*	*B'*	*B'*	*C*	*C*	*C*	*C*	*C*

(ii) Oxides without oxidation activity

No.	1'	2'	3'	4'	5'	6'	7'	8'	9'	
Oxide	S	P	B	As	Sb	Al	Mg	Ca	Na	K
Group	*A'*	*A'*	*A'*	*A'*	*A'*	*A'*	*D*	*D*	*D*	*D*

acidic ←——————————————→ basic

The results obtained over various Mo-based binary oxides at the optimal temperatures are listed in Table 3.

The results may be summarized as follows:

(1) The best results are obtained with the Mo–Te oxides. Both the activity and selectivity increase with an increase in the tellurium content up to the Te/Mo atomic ratio of 0.4. The PhA yield attains 48.5 mol% at the α-methylstyrene conversion of 96.3% with the Te/Mo = 0.4 catalyst.

(2) The second-best results are obtained with the Mo–P and Mo–B oxides. As the content of phosphorus or boron increases, the activity decreases gradually, while the selectivity increases up to P/Mo = 0.7 or B/Mo = 1.2.

(3) The combination of vanadium or tungsten with molybdenum enhances markedly the activity, but it cannot improve markedly the selectivity.

(4) The combination of sulfur or aluminum also enhances the activity to a certain extent, but it cannot improve the selectivity.

(5) The effect of antimony is small.

(6) The combination of a basic oxide such as U_3O_8, TiO_2, SnO_2, and Fe_2O_3 enhances the activity, but it decreases markedly the selectivity.

TABLE 2

Performances of Single-Oxide Catalysts

Catalyst oxide	(g)	*T* (°C)	Conv. (%)	Yield (mol%)						S_{PhA} (mol%)
				PhA	Baci	Bald	MA	CO_x	Other	
W	7	410	29.	4.7	0.	0.	0.	15.	8.	16.
Mo	8	450	81.5	18.5	12.5	15.9	5.6	4.1	24.9	23.
		460	90.	20.5	13.8	17.1	7.0	6.4	15.2	23.
V	10	295	99.	0.	2.4	0.	27.	7.8	63.	0.
Sb	5	500	55.	14.6	3.	3.6	0.	8.6	25.	27.
None[a]	0	500	46.	14.4	5.6	3.	0.	4.2	19.	33.

Note. T, temperature; PhA, phenylacrolein; Baci, benzoic acid; Bald, benzaldehyde; MA, maleic anhydride; CO_x, carbon oxides; other, [(overall conversion of α-methylstyrene) − (yields of PhA + Baci + Bald + MA + CO_x)]; S_{PhA}, selectivity to phenylacrolein.

[a] The reactor is packed only with about 100 ml of ceramic cylinders (3 mm long, 3 mm o.d., 1.5 mm i.d.).

TABLE 3

Performances of Mo-Based Binary Oxide Catalysts

Catalyst atom ratio	(g)	T (°C)	Conv. (%)	Yield (mol%)						S_{PhA} (mol%)
				PhA	Baci	Bald	MA	CO_x	Other	
Mo alone	8	460	90.	20.5	13.8	17.1	7.0	6.4	15.2	23.
W/Mo 2/8	10	360	50.	20.1	16.2	7.2	3.8	4.5	8.2	33.5
V/Mo 2/8	10	295	81.	21.	20.	5.	7.	8.	20.	26.
U/Mo 2/8	10	400	34.	14.4	4.8	2.4	1.8	6.8	3.8	42.5
		415	95.	9.4	20.2	19.	12.	20.	14.4	10.
Ti/Mo 1/9	10	380	60.	13.8	17.	3.6	4.6	8.8	12.2	23.
Sn/Mo 1/9	10	380	52.5	12.8	8.3	3.0	4.5	11.	12.9	24.5
Fe/Mo 1/9	10	380	90.	10.9	23.3	19.1	11.	10.	15.7	12.
S/Mo 4/10	10	420	86.5	23.3	24.5	12.5	5.5	5.7	15.0	27.
8/10	20	430	87.5	20.7	22.2	12.5	6.5	4.0	21.6	23.5
P/Mo 2/10	10	440	76.	26.4	11.8	3.0	5.3	9.9	19.6	35.
4/10	10	460	68.	22.	7.	2.	5.3	6.7	25.	32.5
		470	91.	26.5	18.	5.	7.	8.5	25.	29.0
5/10	10	460	85.	24.5	11.9	3.8	7.5	9.4	27.9	29.0
7/10	20	460	92.	27.8	20.3	5.0	7.5	6.7	24.7	33.2
B/Mo 2/10	10	430	74.	20.9	21.3	2.5	3.5	5.5	20.3	28.
4/10	10	430	91.5	20.1	22.6	10.	6.5	3.4	28.9	22.
8/10	10	470	92.6	26.3	17.2	4.5	5.	2.3	37.3	28.5
12/10	20	480	80.	27.3	10.3	3.0	4.6	1.7	33.1	34.
		490	96.7	33.3	15.3	4.0	6.	2.	36.	34.5
Te/Mo 2/10	10	430	83.0	42.0	9.2	3.2	2.1	3.3	23.2	50.5
4/10	10	430	92.5	45.0	11.3	2.5	2.1	4.4	27.2	48.5
		440	96.3	45.0	13.7	2.0	2.0	5.0	25.1	50.5
2/3	10	440	95.0	45.0	10.4	4.5	2.0	7.3	25.8	47.5
Sb/Mo 4/10	10	450	66.0	19.2	13.3	11.3	3.	7.	12.2	29.
1/1	20	450	78.5	23.8	16.2	9.0	5.5	6.5	17.5	30.2
2/1	20	420	60.	16.7	14.0	4.5	3.5	7.0	14.3	28.0
Al/Mo 2/8	10	410	89.	20.2	20.2	16.0	10.	14.7	7.9	22.6

Note. Abbreviations are the same as those used for Table 2.

Table 4 shows the results obtained with metal phosphate catalysts. It is clear that, except for Mo–P, metal phosphates are not effective as catalysts for this oxidation.

In order to improve the performance of the Te/Mo = 0.4 catalyst, the metal oxides which can improve the performance of MoO_3 (Table 3) were combined with the Te/Mo = 0.4 oxide. The results are shown in Table 5. They may be summarized as follows:

(1) The combination of tungsten improves markedly both the activity and selectivity. The PhA yield attains 53.5 mol% at the α-methylstyrene conversion of 93.5%.

(2) The second-best results are obtained with the combination of vanadium. The PhA yield attains 46.5 mol% at the α-methylstyrene conversion of 88.5%.

(3) The combination of phosphorus, boron, or antimony decreases both the activity and selectivity.

Effects of Reaction Variables

The study in the preceding section reveals that the best results for the formation of PhA are obtained with the Mo/W/Te cat-

TABLE 4

Performances of Metal Phosphate Catalysts

Catalyst atom ratio		(g)	T (°C)	Conv. (%)	Yield (mol%)						S_{PhA} (mol%)
					PhA	Baci	Bald	MA	CO_x	Other	
Mo alone		8	460	90.	20.5	13.8	17.1	7.0	6.4	15.2	23.
P/Mo	0.7	10	460	92.	27.8	20.3	5.	7.5	6.7	24.7	33.2
P/W	0.1	10	480	29.	2.5	1.	0.	0.	15.	10.	8.5
P/V	1.06	6	370	43.	5.7	3.	2.	0.	14.	18.3	13.
	1.6	6	390	46.	6.1	3.3	0.	0.	13.7	22.9	13.
	2.0	6	460	41.	2.9	1.1	0.	0.	18.1	18.9	7.
P/Ti	2.0	5	350	71.	2.0	2.8	0.	0.	62.	4.2	3.
	2.2	5	440	45.	3.9	2.1	0.	0.	24.	15.	8.5
P/Sn	0.5	7	460	43.	1.5	0.	0.	0.	16.	25.5	3.5
P/Fe	1.0	7	420	3.8	1.3	1.3	0.	0.	14.	12.8	12.
	1.5	10	450	31.	7.7	3.0	0.	0.	18.	2.7	25.

Note. Abbreviations are the same as those used for Table 2.

alyst with atomic ratio of 10/4/4. Thus, the study to clarify the characteristic features of the reaction was performed using this catalyst.

Product distribution. The reaction was conducted at 400°C by changing the amount of catalyst used from 1 to 30 g; the contact time, which was defined as volume of catalyst (ml)/total flow rate (ml/sec) at 20°C, was varied from 0.18 to 5.4 s (the packing density of the catalyst was 0.83 g/ml), while fixing the other conditions as presented under Experimental. No variations in the catalytic activity was observed during the reaction. The main products were PhA, benzoic acid, benzaldehyde, maleic anhydride, and carbon oxides. A large deviation was observed between the overall consumption of α-methylstyrene and the sum of the five products. This deviation is as-

TABLE 5

Performances of Mo–*X*–Te Ternary Oxide Catalysts

Catalyst atom ratio		(g)	T (°C)	Conv. (%)	Yield (mol%)						S_{PhA} (mol%)
					PhA	Baci	Bald	MA	CO_x	Other	
Mo/W/Te	10/4/4	10	390	54.	37.	6.0	2.4	1.5	1.8	5.3	69.
			410	93.5	53.5	11.3	4.5	1.6	5.0	17.6	57.
			420	98.	46.5	12.1	5.7	3.0	7.3	23.4	47.5
Mo/V/Te	10/3/4	10	435	88.5	46.5	15.8	6.7	2.5	2.9	14.1	52.5
			440	95.	45.5	14.1	7.1	2.5	6.0	19.8	48.
Mo/P/Te	10/4/4	10	460	85.	35.3	7.9	3.8	3.5	7.5	27.	41.5
			468	95.7	44.0	12.4	4.3	4.5	8.1	22.4	46.
Mo/B/Te	10/8/4	10	500	58.5	26.5	3.9	2.5	2.0	3.3	20.3	45.
Mo/Sb/Te	10/4/4	10	490	78.	42.	8.2	7.7	3.0	4.8	12.7	54.
			500	87.	43.	9.5	9.4	1.5	6.3	17.3	50.

Note. Abbreviations are the same as those used for Table 2.

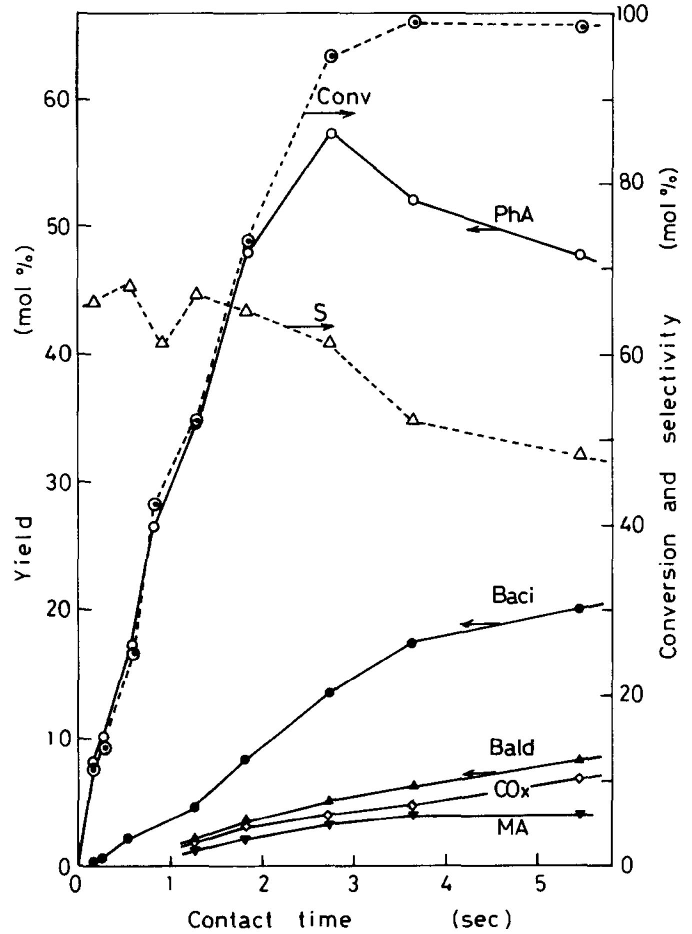

FIG. 1. Product distributions on the Mo/W/Te = 10/4/4 catalyst. (○) PhA; (●) benzoic acid; (▲) benzaldehyde; (▼) maleic anhydride; (◇) carbon oxides; (⊙) conversion of α-methylstyrene; (△) selectivity to PhA.

cribed to the formation of polymer compounds in the reactor. Indeed, the presence of dimer of PhA was detected by the GC-MS analysis.

The results are shown in Fig. 1. The PhA yield attains a maximum (56 mol%) at the α-methylstyrene conversion of 95%. With a further increase in the extent of the reaction, the yield falls gradually.

Effect of temperature. The reaction was conducted by changing the amount of catalyst used from 2 to 40 g (the contact time from 0.36 to 7.2 s), while fixing the other conditions. In order to compare the selectivities at the same level of the α-methylstyrene conversion, the reaction temperatures were adjusted so as to achieve an overall conversion of 90 to 95%. The results obtained at each contact time and temperature are listed in Table 6. By lowering the temperature, the selectivity to PhA increaases, while the formation of benzaldehyde and unidentifiable polymer compounds decreases.

Effect of oxygen concentration. The effect of the oxygen concentration was studied by changing the initial concentration of oxygen in the feed gas from 3 to 99 mol%, while fixing the other conditions; the sum of the feed rates of oxygen and nitrogen was

TABLE 6

Effect of the Reaction Temperature on the Yield and Selectivity

Contact time (s)	T (°C)	Conv. (%)	Yield (mol%)						S_{PhA} (mol%)
			PhA	Baci	Bald	MA	CO_x	Other	
0.36	455	92.6	47.	11.8	8.3	2.9	3.3	19.3	51.
0.81	433	95.2	50.5	10.4	6.0	2.0	4.4	21.9	53.
1.8	410	93.0	56.7	14.3	3.6	2.8	2.4	12.2	62.
2.7	400	93.1	57.2	13.6	4.8	4.0	3.3	10.2	62.
3.6	390	91.7	56.6	11.5	3.6	2.6	3.6	13.8	62.
7.2	375	90.8	59.	14.6	3.0	2.3	3.7	8.2	65.

Note. Abbreviations are the same as those used for Table 2.

fixed at 400 ml (at 20°C)/min. Figure 2 shows the yields of PhA and benzoic acid obtained at 390°C with a contact time of 1.8 s. The formation of both products increases steadily with the oxygen concentration up to the concentration of 99 mol%.

Effect of α-methylstyrene concentration. The reaction was conducted by changing the initial concentration of α-methylstyrene from 0.25 to 1.19 mol% in air, while fixing the other conditions: contact time, 0.36 s; temperature, 400°C. Figure 3 shows the rate of PhA formation as a function of the α-methylstyrene concentration. The rate varies only a little with the change in the concentration.

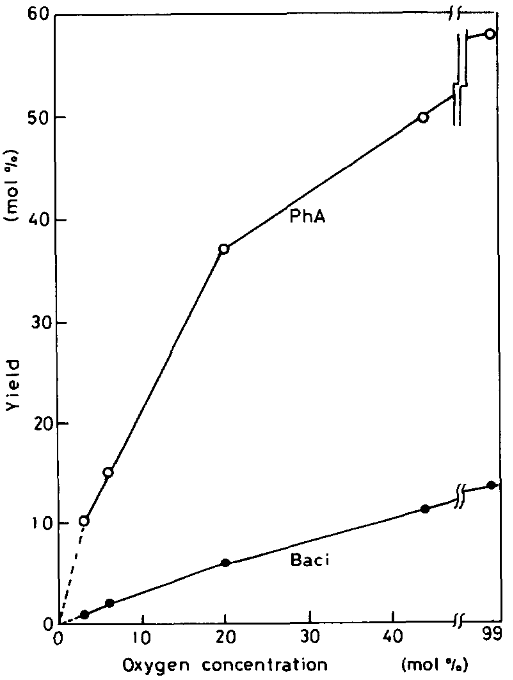

FIG. 2. Effect of the oxygen concentration on the yield of PhA and benzoic acid. (○) PhA; (●) benzoic acid.

Effect of addition of water vapor. The reaction was conducted by changing the initial concentration of water vapor from zero to 19.6 mol% in the feed gas. The yield of PhA obtained at 400°C with a contact time of 0.36 s is plotted as a function of the water vapor concentration in Fig. 4. The effect of water vapor on the rate is small. The yield and selectivity obtained in the presence of

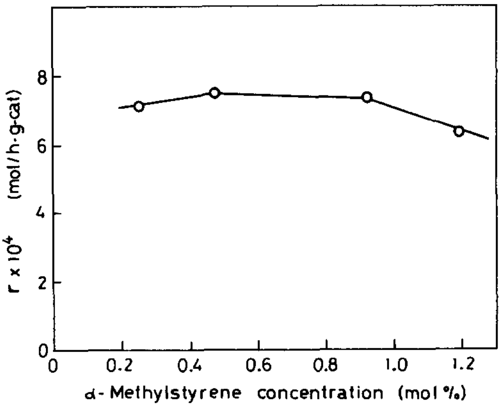

FIG. 3. Effect of the α-methylstyrene concentration on the rate of PhA formation.

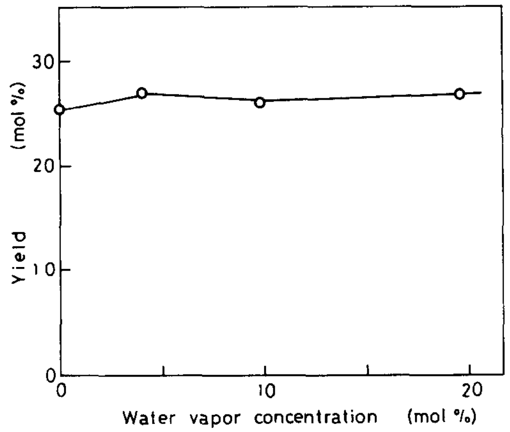

FIG. 4. Effect of the water vapor concentration on the yield of PhA.

water vapor (19.6 mol% in the feed gas) were compared with those obtained in the absence of water vapor in Table 7. The selectivity to PhA decreases, to a small extent, with the presence of water vapor.

DISCUSSION

Single MoO_3 is known to exhibit a low catalytic activity for oxidation of propylene and butenes, but it shows a good activity for oxidation of α-methylstyrene. Further, this oxidation reaction takes place even in the absence of catalyst, i.e., on the ceramic cylinders (3 mm long, 3 mm o.d., 1.5 mm i.d.,) packed in the reactor, at a temperature of about 500°C. These findings indicate that α-methylstyrene is oxidized much more easily than propylene and butenes.

Among acidic metal oxides with oxidizing function such as WO_3, MoO_3, and V_2O_5 (*15, 16*), only MoO_3 is effective as the main component of the catalysts; W- and V-based oxides promote predominantly C–C bond fission. It is difficult to clearly explain the reason at present. However, we consider that the basic and/or oxidizing function of V-based oxides is too strong to suppress the C–C bond fission (*17, 18*).

As the second component added to MoO_3, acidic oxides without oxidizing function such as SO_3, P_2O_5, B_2O_3, TeO_2, and Sb_2O_5 (*15, 16*) improve the selectivity. Some of them also improve the activity, whereas the addition of U_3O_8, TiO_2, SnO_2, and Fe_2O_3 which are more basic than WO_3, and MoO_3, and V_2O_5 (*15, 16*) markedly increases the activity, but they decrease the selectivity.

We explain the results as follows. The oxidation activity is governed by two functions (*16*): (i) the activation of α-methylstyrene on acidic sites and (ii) an intrinsic oxidation activity, which is connected with both the basic character and the metal–oxygen bonding strength. The combination of an acidic oxide with MoO_3 usually enhances the acidic property, but it also plays a role in extinguishing the basic property. The oxidation activity increases with an increase in the acidic property, but when the basic property is extinguished to a great extent, it decreases. On the other hand, the combination of a basic oxide with MoO_3 enhances the basic property and, sometimes, also the acidic property. Therefore, the activity increases.

As for the selectivity, it is governed

TABLE 7

Effect of the Addition of Water Vapor on the Yield and Selectivity

Water vapor (mol%)	*T* (°C)	Conv. (%)	Yield (mol%)						S_{PhA} (mol%)
			PhA	Baci	Bald	MA	CO_x	Other	
0.	410	92.	56.7	14.0	3.6	2.8	2.4	10.2	62.
19.6	405	91.	53.2	17.2	3.6	1.5	1.0	15.5	58.5

Note. Abbreviations are the same as those used for Table 2.

mainly by the rate of the consecutive oxidation of PhA relative to that of the PhA formation. From the results (Table 3) we feel that the selectivity is improved by the suppression of the basic property.

It is also difficult to clearly explain the reason why the best performance is obtained by the combination with TeO_2. Possibly, the balance of acid–base properties obtained by the combination with TeO_2 is the best fit for the oxidation of α-methylstyrene.

As the third component added to the Te/Mo = 0.4 oxide, WO_3 and V_2O_5, which possess oxidizing functions are better than P_2O_5, B_2O_3, and Sb_2O_5, which do not have oxidizing functions. It is considered that the addition of P_2O_5, B_2O_3, and Sb_2O_5 decreases the basic property at a great extent, while that of WO_3 and V_2O_5 maintains the basic property at a certain level.

Let us now discuss the characteristic features of the reaction on the Mo/W/Te = 10/4/4 catalyst. As may be seen in Fig. 1, the yield of PhA increases with the extent of the reaction up to the overall conversion of 95%, indicating that the PhA produced is relatively stable on the catalyst. The selectivity to PhA is in the range 60 to 70 mol%. However, with a further increase in the extent of the reaction, the PhA yield decreases by the consecutive oxidation. On the other hand, benzoic acid, benzaldehyde, maleic anhydride, and carbon oxides are formed in parallel with PhA. A part of these products is also produced by the consecutive oxidation of PhA.

As the reaction temperature is raised, the selectivity to PhA decreases. Possibly, the C–C bond fission is promoted preferentially by an elevation of temperature. It should be noted that the formation of benzaldehyde increases with temperature. This finding is in conformity with the results of earlier studies (*6–8*); a high temperature of 500 to 600°C is required to obtain a high yield of benzaldehyde in the oxidation of toluene.

The rate of reaction increases steadily with the oxygen concentration up to a high concentration of 99 mol% and it is insensitive to the α-methylstyrene concentration. The same feature is usually observed in the oxidation with acidic catalysts, for example, oxidation of methacrolein, butadiene, butene, and methyl ethyl ketone on heteropoly compound catalysts (*19, 20*) and isobutyric acid, acrolein, and methacrolein on V_2O_5–P_2O_5 catalysts (*18, 21, 22*). This finding indicates that the reaction is controlled mainly by the regeneration of reduced catalyst by gaseous oxygen rather than by the activation of α-methylstyrene on the acidic sites.

Since the rate is zero order with respect to the concentration of α-methylstyrene, when the concentration is high, a long contact time is required to achieve the same level of conversion without elevation of the reaction temperature. This may be a defect of this reaction.

The effect of the addition of water vapor was found to be small. This may be ascribed to the fact that that the PhA produced desorbs easily from the catalyst, unlike the case of the production of acidic compounds (*18, 22*).

REFERENCES

1. Emig, G., and Hofman, H., *J. Catal.* **84,** 15 (1983).
2. Alkhazov, T. G., Lisovskii, A. E., Safarov, M. G., Lapin, V. B., and Kurbanow, N. A., *Kinet. Katal.* **17,** 434 (1976).
3. Lisovskii, A. E., Kozaharov, A. I., and Feizullaeva, Sh. A., *Kinet. Katal.* **19,** 605 (1978).
4. Fiedorow, R., Przystajko, W., Sopa, M., and Dallalana, I. G., *J. Catal.* **68,** 33 (1981).
5. Vrieland, E. G., *J. Catal.* **111,** 1 (1988).
6. Ai, M., *Kogyo Kagaku Zasshi* **73,** 946 (1970).
7. Ai, M., *Kogyo Kagaku Zasshi* **74,** 1636 (1971).
8. Ai, M., *Nippon Kagaku Kaishi,* 1151 (1972).
9. Nag, N. K., Frasen, T., and Mars, P., *J. Catal.* **68,** 77 (1981).
10. Van Hengstun, A. G., Van Ommen, J. G., Bosch, H., and Gellings, P. J., *Appl. Catal.* **8,** 369 (1983).
11. Adams, C. R., *J. Catal.* **10,** 355 (1968).
12. Grasselli, R. K., Burrington, J. D., Suresh, D. D., Friedrich, M. S., and Hazle, M. A. S., *J. Catal.* **68,** 109 (1981).
13. Ai, M., *J. Catal.* **50,** 291 (1977).
14. Ai, M., *J. Catal.* **83,** 141 (1983).
15. Ai, M., *J. Catal.* **106,** 273 (1987).

16. Ai, M., "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), p. 1060. Kodansha, Tokyo/Elsevier, Amsterdam, 1981.

17. Ai, M., *Polyhedron* **5,** 103 (1986).

18. Ai, M., *J. Catal.* **98,** 401 (1986).

19. Ai, M., *J. Catal.* **71,** 88 (1981).

20. Ai, M., *J. Catal.* **85,** 324 (1984).

21. Ai, M., *Appl. Catal.* **27,** 167 (1986).

22. Ai, M., *J. Catal.* **116,** 23 (1989).