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Oxidation of α-Methylstyrene to Phenylacrolein

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Various kinds of Mo-based oxides were tested as catalysts for the vapor-phase oxidation of α-methylstyrene to form phenylacrolein (atropoaldehyde). The best performance was obtained with the Te/Mo atomic ratio = 0.4 catalyst; the one-pass yield of phenylacrolein attained 48.5 mol% at the α-methylstyrene conversion of 96.3%.

It is well known that propylene is oxidized to acrolein with a very high selectivity over Bi-Mo and Sb-based oxide catalysts, and that n-butene and isobutene are also oxidized to butadiene and methacrolein, respectively, over similar type of catalysts. However, for the oxidation of aromatic compounds, these catalysts cannot exhibit an excellent performance. As for the oxidation of α-methylstytene [2-phenylpropene] to form phenylacrolein [atropoaldehyde, 2-phenylpropenal] there have been very few studies. Adams[1] reported that Bi-Mo oxide is not effective; the yield is 3 mol%. Recently, Grasselli et al.[2] reported a 30 mol% yield using Nb-promoted Sb-U oxide catalysts. In this study, we attempted to explore more effective catalysts for this oxidation.

The catalysts used were various kinds of Mo-based binary oxides. For example, the Te/Mo atomic ratio = 0.4 catalyst was prepared as follows. 35.3 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 18.0 g of H_6TeO_6 were dissolved in 200 ml of hot water and 100 ml of natural pumice (8- to 20-mesh size) was added to the solution. The mixture was evaporated to dryness with stirring and by means of hot air current. The obtained solid 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.

The reaction was conducted with a continuous-flow system.[3] Air was introduced from the top of the reactor (400 ml/min, ca. 1.0 mol/h), with α-methylstyrene being injected into the preheating section of the reactor by means of a syringe pump with a fixed rate of 11.9 m mol/h (ca. 1.19 mol% in air). The effluent gas from the reactor was led successively into four chilled scrubbers containing 120 ml of 2-propanol to recover the 2-propanol-soluble compounds.

The results obtained for each catalyst at the optimal reaction temperatures are listed in Table 1. They 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 Te content up to the Te/Mo atomic ratio of 0.4. The yield attains 48.5 mol% at the conversion of 96.3%.

(2) The second best results are obtained with the Mo-P and Mo-B oxides. As the content of P or B increases, the activity decreases gradually, while the

selectivity increases up to P/Mo = 0.7 or B/Mo = 1.2.

(3) The combination of V or W enhances markedly the activity, but it cannot improve the selectivity.

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

(5) The effect of Sb 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 1. Performances of Mo-based binary oxide catalysts[a)]

Catalyst atomic ratio		(g)	T °C	Conv %	Yield / mol% PhA	Bacid	Balde	MA	CO_x	other	S_{PhA} mol%
W/Mo	2/8	10	360	50.0	20.1	16.2	7.2	3.8	4.5	8.2	33.5
V/Mo	2/8	10	295	81.0	21.0	20.0	5.0	7.0	8.0	20.0	26.0
U/Mo	2/8	10	400	34.0	14.4	4.8	2.4	1.8	6.8	3.8	42.5
Ti/Mo	1/9	10	380	60.0	13.8	17.0	3.6	4.6	8.8	12.2	23.8
Sn/Mo	2/8	10	380	52.5	12.8	8.3	3.0	4.5	11.0	12.9	24.5
Fe/Mo	1/9	10	380	90.0	10.9	23.3	19.1	11.0	10.0	15.7	12.0
S/Mo	4/10	10	420	86.5	23.3	24.5	12.5	5.5	5.7	15.0	27.0
	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	76.0	26.4	11.8	3.0	5.3	9.9	19.6	35.0
	4/10	10	470	91.0	26.5	18.0	5.0	7.0	8.5	25.0	29.0
	5/10	10	460	85.0	24.5	11.9	3.8	7.5	9.4	27.9	29.0
	7/10	20	460	92.0	27.8	20.3	5.0	7.5	6.7	24.7	33.2
B/Mo	2/10	10	430	74.0	20.9	21.3	2.5	3.5	5.5	20.3	28.0
	4/10	10	430	91.5	20.1	22.6	10.0	6.5	3.4	28.9	22.0
	8/10	10	470	92.6	26.3	17.3	4.5	5.0	2.3	37.3	28.5
	12/10	20	490	96.7	33.3	15.3	4.0	6.0	2.0	36.0	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	440	96.3	48.5	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	3.0	7.0	12.2	29.0
	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 0	16.7	14.0	4.5	3.5	7.0	14.3	28.0

a)T = temperature, PhA = phenylacrolein, Bacid = benzoic acid, Balde = benzaldehyde, MA = maleic anhydride, CO_x= carbon oxides, other = [(conv.) - (yields of PhA + Bacid + Balde + MA + CO_x], S_{PhA} = selectivity to phenylacrolein.

References

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2) R.K. Grasselli, J.D. Burrington, D.D. Suresh, M.S. Friedrich, and M.A.S Hazle, J. Catal., 68, 109 (1981).

3) M. Ai, J. Catal., 101, 473 (1986).

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