Improvement of Acetone Yield in the Oxidation of Propylene

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The outstanding property of the SnO_2–MoO_3 catalyst in the oxidation of propylene to acetone was confirmed by tests of various oxide catalysts supported on pumice. The optimum composition was found to be SnO_2-70/MoO_3-30 mol % for the oxidation at from 170 to 260 °C. It was also found that this pumice-supported catalyst is sufficiently selective for the acetone formation even at a high temperature of 260 °C, and that it gives a high yield of acetone while keeping its high selectivity. The selectivity increases up to 90 mol % with an increase in the partial pressure of water vapor and with a decrease in the oxygen partial pressure. On the basis of such information, it can be said that a high yield of acetone can be obtained by the divided introduction of oxygen.

It has been shown that propylene can be oxidized to acetone in the presence of water vapor on molybdenum-containing catalysts,[1–5] whereas the acetone yields attained in the previous works were limited because of low conversion at low temperatures or because of low selectivity at higher temperatures.[2–5] Thus, further study is required to improve the acetone yield.

Experimental

Catalysts. A number of mixed oxide catalysts were prepared by the procedures described in previous papers.[6–8] That is, an aqueous solution or slurry containing the required quantity of metal compounds was mixed with 10—20 mesh pumice in a fixed ratio of one g-atom metal per 500 ml of pumice (in apparent volume), followed by evaporation to dryness with vigorous stirring and calcination in a stream of air at 500 °C for 4—5 h.

Procedures. The catalytic reactions were 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., which was mounted vertically and immersed in a lead bath. The reactant gas was fed from the top of the reactor, with water or isopropyl alcohol (IPA) being introduced into a preheater section by means of an injection syringe pump.

The amount of catalyst in the propylene oxidation was 20, 30, or 40 g, and the feed rates of the reactants in a standard run were as follows: propylene-20/air-20/water vapor-76 ml (volume at 25 °C)/min. The effluent gas from the reactor was led successively into three chilled water-scrubbers to recover the water-soluble compounds. At the end of a 1-h run, the contents of the scrubbers (about 50 ml) were collected and analyzed by gas chromatography. The inlet and exit gases were intermittently analyzed.

The reaction of IPA was carried out at a fixed concentration of IPA (1.65 mol% in air) and a fixed total flow rate (1.5 l/min), changing the amount of catalyst in the range from 5 to 20 g.

Results and Discussion

Catalyst Screening. *Acetone-forming Activities of Various Composite Oxide Catalysts*: It seems apparent from the previous studies[8–11] that the propylene oxidation to acetone proceeds through an alcoholic intermediate, requiring two different functions for the catalyst: the hydration of olefin and the oxidative dehydrogenation of the alcoholic intermediate. It can, accordingly, be expected that information regarding the two functions will be helpful in the exploration of an effective catalyst. Since the hydration activity may be expected to run parallel with the activity for the dehydration of IPA, the catalytic activity for the dehydration and dehydrogenation of IPA in the presence of an excess of air would be relevant as measures of the two functions.

Since the first function is generally accepted to be associated with acid catalysts, various binary or ternary mixed oxide catalysts of an acidic property were tested for the ability to form acetone from propylene. The amount of catalyst used was 20 g, and the standard feed rates of the reactants were adopted. The results are summarized in Tables 1 and 2.

Another series of experiments were carried out with each catalyst using a mixture of IPA and air as the reactant. The rates of IPA dehydration, r_p, and dehydrogenation, r_a (mol/h·g-catalyst), were measured at 175 °C. They are also shown in Tables 1 and 2.

The results in Tables 1 and 2 may be summarized as follows.

(i) Acetone is obtained, more or less, with every V_2O_5- or MoO_3-containing catalyst, at least at a low temperature. The acetone yields is likely to increase with an increase in r_p, which can be regarded as a measure of the acidity.[6–8]

(ii) Although it gives a strikingly high value of r_p, WO_3–P_2O_5 does not convert IPA to acetone; thus, it is inactive for the propylene oxidation to actone.

(iii) The SnO_2–MoO_3 catalyst gives a strikingly high yield of acetone. It should be noted that both r_p and r_a are larger on this catalyst than on other catalysts. It is also notable that the high selectivity to acetone is retained at temperatures as high as 220 °C.

(iv) The Sn-60/V-40 is the second best catalyst.

Effect of the SnO_2–MoO_3 Composition on the Yield of Acetone: Five SnO_2–MoO_3 catalysts of different compositions were tested for the yield of acetone as well as for r_p and r_a, where the feed rate of air was twice as large as in the standard condition. The yields of acetone at 175, 190, 210, and 240 °C are plotted in Fig. 1, together with the values of r_p and r_a obtained at 140 °C.

Although the highest yield of acetone is obtained at around 30 atom % Mo at each temperature, it is noticeable that the effect of the temperature increase on the acetone yield is more marked with the catalysts

Table 1. Oxidation of propylene to acetone using various MoO_3-based catalysts[a)]

Catalyst (atomic ratio)	Reactions for IPA at 175 °C[b)]		Oxidation of propylene					
			Temp (°C)	Conversion (%) of propylene to				
	r_p	r_a		Acetone	(Selectivity)[c)]	Acid[d)] (×2/3)	CO+CO$_2$ (×1/3)	Total[e)]
Mo-P (9-1)	10.6	1.2	330	0.6	(37)	0.25	0.9	1.8
Mo-S (9-1)	12.0	0.5	320	0.83	(35)	0.5	1.0	2.4
Mo-W (8-2)	0.8	1.2	320	0.91	(50)	0.1	0.8	1.8
(2-8)	25.0	8.4	293	3.21	(66)	0.3	1.4	4.9
Mo-U (8-2)	3.4	1.0	369	1.94	(39)	0.8	2.1	4.9
(2-8)	8.8	0.5	300	0.15	(7)	0.3	1.8	2.3
Mo-Ti (5-5)	36.0	5.8	248	2.12	(72)	0.3	0.5	2.9
			290	4.42	(52)	1.3	2.8	8.5
Mo-Ti-P (5-5-1)	32.0	3.2	250	1.8	(69)	0.2	0.6	2.6
			292	2.66	(41)	0.8	3.0	6.4
Mo-Sn (3-7)	217.0	205	182	19.2	(90)	0.8	1.4	21.4
			219	24.5	(87)	1.0	2.5	28.0
Mo-Fe (2-8)	42.0	22.0	235	3.0	(59)	0.9	1.2	5.1
			290	2.25	(22)	2.5	5.5	10.3
Mo-Bi (8-2)	4.6	0.9	330	1.23	(44)	0.5	1.1	2.8
Mo-Bi-P (9-1-2)	15.0	0.1	330	2.20	(46)	1.2	1.4	4.8

a) Feed rates = propylene-20/air-20/water vapor-76 ml/min, amount of catalyst used = 20 g. b) IPA concentration = 1.65 mol % in air. c) 100 × (acetone)/(total). d) Calculated as acetic acid. e) Sum of acetone, acid, CO, and CO_2.

Table 2. Oxidation of propylene to acetone using various V_2O_5- and WO_3-based catalysts[a)]

Catalyst (atomic ratio)	Reactions for IPA at 175 °C[b)]		Oxidation of propylene					
			Temp (°C)	Conversion (%) of propylene to				
	r_p	r_a		Acetone	(Selectivity)[c)]	Acid[d)] (×2/3)	CO+CO$_2$ (×1/3)	Total[e)]
V-Mo (85-15)	39.0	7.8	214	2.14	(60)	1.1	0.3	3.5
			242	2.40	(38)	1.9	2.0	6.3
V-W (8-2)	47.0	14.0	198	5.20	(53)	2.9	1.8	9.9
			214	4.28	(49)	1.1	3.4	8.8
(2-8)	5.0	2.5						
V-Ti (8-2)	37.0	36.0	209	1.20	(32)	1.7	0.8	3.7
			234	1.04	(15)	1.2	4.8	7.0
(1-9)	2.4	45.0	187	0.27	(20)	0.9	0.2	1.4
			220	0.87	(35)	0.6	1.0	2.4
V-Sn (4-6)	80.0	52.0	176	4.3	(72)	1.2	0.5	6.0
			187	6.36	(69)	1.7	1.2	9.3
			209	10.0	(70)	1.4	2.9	14.3
			234	8.86	(58)	2.4	4.0	15.2
(1-9)	2.0	105.0	220	0.90	(13)	1.8	4.2	6.9
W-P (9-1)	about 400.0	0.0	300	trace	(0)	trace	0.5	0.5

a) Feed rates = propylene-20/air-20/water vapor-76 ml/min, amount of catalyst used = 20 g. b) IPA concentration = 1.65 mol % in air. c) 100 × (acetone)/(total). d) Calculated as acetic acid. e) Sum of acetone, acid, CO, and CO_2.

with a lower Mo content, suggesting that the rate-limiting step may be different depending on the Mo content. In fact, r_p is much larger than r_a on the 40% Mo catalyst, while r_a is much larger than r_p on the 20% Mo catalyst. If r_p and r_a represent the two functions required, the rate-limiting step on the 40% Mo catalyst would be the oxidation of the alcoholic intermediate. The less extensive effect of the temperature would be reasonable, because the equilibrium concentration of the alcoholic intermediate should decrease with an increase in the temperature. On the other hand, the rate-limiting step on the 20% Mo catalyst would be the hydration to form the alcoholic intermediate; this is in agreement with the more marked effect of the temperature. Thus, r_p and r_a can be regarded as parameters for the two functions.

Effect of the Third Components Added to Sn-70/Mo-30: The effect of the third component to improve the ace-

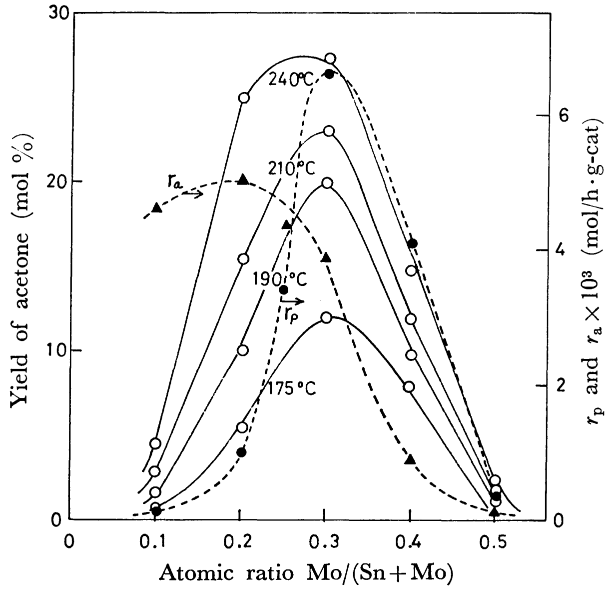

Fig. 1. Effect of SnO_2-MoO_3 composition on the yield of acetone and the values of r_p and r_a.
Oxydation of propylene; catalyst used=20 g, feed rates=propylene-20/air-40/water vapor-76 ml/min (at 25 °C). r_p and r_a; dehydration and dehydrogenation rates of IPA at 140 °C and 1.65 mol % IPA in air.

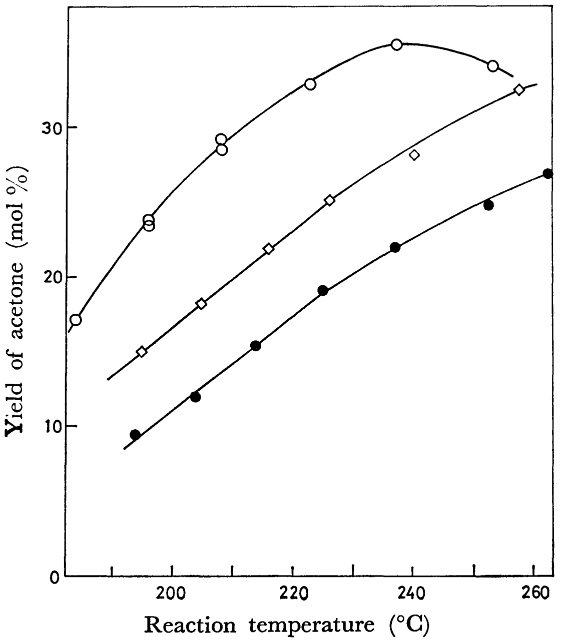

Fig. 2. Effect of reaction temperature on the yield of acetone. Feed rates; propylene-20/oxygen-15/nitrogen-24/water vapor-104 ml/min (at 25 °C), amount of catalyst used; (○)=20 g, (◇)=15 g, (●)=10 g.

tone yield was tested with P_2O_5, SO_3, V_2O_5, U_3O_8, TiO_2, Al_2O_3, Fe_2O_3, and SiO_2 by adding 2—10 atom% to Sn-70/Mo-30, whereas none of then showed any improvement.

Effect of the Reaction Conditions on the Yield of Acetone. Since the Sn-70/Mo-30 catalyst proved to be the best, the effect of the reaction conditions were investigated on this catalyst.

Effect of the Reaction Temperature: The effects of the reaction temperature on the selectivity to acetone and on the yield were tested using different amounts of the catalyst. The results are shown in Figs. 2 and 3. At the acetone yield of around 35 mol%, almost all of the oxygen fed in was consumed.

The results may be summarized as follows:

(i) The yield of acetone increases with an increase in the temperature up to about 260 °C provided the oxygen is not completely consumed.

(ii) The selectivity largely depends on the conversion of propylene (Fig. 3), the effect of the temperature being less marked.

Effect of the Feed Rate of Oxygen and Nitrogen: Two series of runs were performed, changing the feed rate of oxygen or nitrogen. The results are shown in Table 3. Except for Run 56, the conversion of oxygen was very close to 100%, so that the total conversion of propylene increased with the flow rate of oxygen.

The results in Table 3 may be summarized as follows:

(i) The selectivity to acetone decreased as the inlet oxygen concentration increases, so that there is an optimum value in the oxygen-flow rate to give the highest yield of acetone for a fixed flow rate of propylene. An acetone yield of 43 mol % was achieved with a selectivity of 78 mol %.

(ii) The selectivity to acetone can be improved by dilution with nitrogen, suggesting a suppression of complete oxidation in the presence of nitrogen.

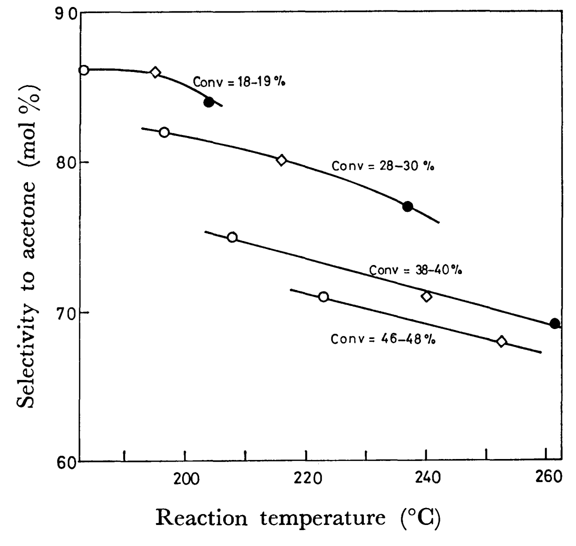

Fig. 3. Effects of reaction temperature and propylene conversion on the selectivity to acetone. Reaction conditions and notations are the same as in Fig. 2.

Effect of the Feed Rate of Water Vapor: The acetone-synthesis runs were carried out at different concentrations of water vapor. The results, shown in Table 4, indicate that the selectivity increases markedly with an increase in the water-vapor pressure. In the absence of water vapor, the catalytic activity was seriously impaired by the deposit of nonvolatile materials, while the catalyst was easily regenerated by air treatment at 500 °C. This suggests that the water vapor serves to prevent catalyst poisoning as well as to suppress complete oxidation.

Table 3. Effects of feed rates of oxygen and nitrogen on the yield of acetone[a)]

Run No.	Feed rates of (ml/min)				Conversion (%) of propylene to				
	C_3H_6	H_2O	N_2	O_2	Acetone	(Selectivity)[b)]	Acid[c)] (×2/3)	$CO+CO_2$ (×1/3)	Total[d)]
51	20	76	38	2	15.6	(92)	0.6	0.7	16.9
52	20	76	36	4	26.1	(88)	1.4	1.7	29.2
53	20	76	20	10	36.4	(89)	2.7	1.7	40.8
54	20	76	40	10	37.8	(86)	2.3	3.7	43.8
55	20	76	20	17	43.7	(78)	4.2	7.8	55.7
56	20	76	40	17	40.2	(83)	3.1	5.6	48.9
57	20	76	20	40	34.6	(35)	8.6	55.0	98.2
58	20	76	0	3	21.1	(89)	0.8	1.7	23.6
59	20	76	0	5	29.6	(87)	1.7	2.8	34.1
60	20	76	0	10	33.6	(78)	2.2	7.3	43.1
61	20	76	0	17	40.0	(75)	3.0	10.1	53.1

a) Catalyst = SnO_2-70/MoO_3-30, amount of catalyst used = 40 g, temperature = 215 °C. b) 100 × (acetone)/(total). c) Calculated as acetic acid. d) Sum of acetone, acid, CO, and CO_2.

Table 4. Effect of feed rate of water vapor on the yield of acetone[a)]

Run No.	Feed rates of (ml/min)				Conversion (%) of propylene to				
	C_3H_6	H_2O	N_2	O_2	Acetone	(Selectivity)[b)]	Acid[c)] (×2/3)	$CO+CO_2$ (×1/3)	Total[d)]
62	20	0	20	10	12.2	(66)	0.4	5.8	18.4
63	20	20	20	10	22.0	(79)	1.9	4.0	27.9
64	20	76	20	10	36.4	(84)	2.7	4.5	43.6
65	20	150	20	10	47.0	(86)	2.7	5.2	54.9
66	20	152	16	4	27.7	(92)	1.0	1.6	30.3
67	20	152	32	8	44.0	(87)	2.5	4.1	50.6
68	20	152	20	17	46.5	(75)	3.8	11.3	61.6
69	20	152	20	40	53.5	(66)	6.9	20.0	80.4

a) Catalyst = SnO_2-70/MoO_3-30, amount of catalyst used = 40 g, temperature = 215 °C. b) 100 × (acetone)/(total). c) Calculated as acetic acid. d) Sum of acetone, acid, CO, and CO_2.

Table 5. Oxidation of propylene by divided introduction of oxygen[a)]

Reactor 1		Reactor 2		Conversion (%) of propylene to				
Temp (°C)	Feed of air (ml/min)	Temp (°C)	Feed of air (ml/min)	Acetone	(Selectivity)[b)]	Acid[c)] (×2/3)	$CO+CO_2$ (×1/3)	Total[d)]
197	20	Without Reactor 2		24.5	(90)	1.2	1.6	27.3
218	20			26.8	(90)	1.1	1.9	29.8
194	40			23.3	(90)	1.4	1.3	26.0
216	40			33.0	(83)	2.7	4.1	39.8
Without Reactor 1		220	20	23.3	(85)	2.4	1.9	27.6
		220	40	25.7	(85)	2.0	2.8	30.5
193	40	210	0	31.0	(86)	2.5	2.7	36.2
194	20	210	20	35.7	(88)	2.4	2.5	40.6
203	20	210	20	42.5	(88)	2.6	3.2	48.3
220	20	215	20	43.5	(87)	2.6	3.6	49.7
220	40	215	20	48.0	(85)	3.2	4.9	56.1
220	40	218	$O_2=10$	49.5	(84)	4.0	5.6	59.1

a) Catalyst = SnO_2-70/MoO_3-30, amount of catalyst used = 20 g (Reactor 1) and 20 g (Reactor 2), feed rate of propylene = 20 ml/min, feed rate of water vapor for each reactor = 76 ml/min. b) 100 × (acetone)/(total). c) Calculated as acetic acid. d) Sum of acetone, acid, CO, and CO_2.

Improvement of the Acetone Yield. Although a high selectivity to acetone can be obtained by lowering the concentration of oxygen, the yield is limited by the oxygen feed. Thus, the reaction was performed successively in two reactor, with additional air or oxygen supplied to the second reactor. As is shown in Table 5, the yield is markedly improved by such a divided introduction of oxygen, while retaining the high selectivity. In this way, an acetone yield of 48—50 mol % is achieved with a selectivity of about 85 mol %. Although a retardation of acetone formation by product acetone was previously reported[12], the above result shows that the retardation by acetone is not strong.

Conclusion

The selective oxidation of propylene to acetone can be performed on SnO_2–MoO_3/pumice, particularly with a composition of 30% Mo; a high water partial pressure and a low oxygen partial pressure are requisites in improving the acetone yield. The superior performance of the SnO_2–MoO_3 catalyst is understood in terms of two functions: the hydration of propylene and the oxidative dehydrogenation of IPA. When the Mo content is varied, both functions, indicated by r_p and r_a, attain maxima at around 20 to 30% Mo, thus giving rise to an optimum composition of 30% Mo.

References

1) J. Buiten, *J. Catal.*, **10**, 188 (1968).
2) Y. Morooka, S. Tan, and A. Ozaki, *J. Catal.*, **12**, 291 (1968); *Bull. Chem. Soc. Jpn.*, **41**, 2820 (1968).
3) S. Ogasawara, S. Takahashi, A. Fukai, and Y. Nakata, *Kogyo Kagaku Zasshi*, **72**, 2244 (1969).
4) S. Tan, Y. Morooka, and A. Ozaki, *J. Catal.*, **17**, 132 (1970).
5) Y. Morooka, Y. Takita, and A. Ozaki, *J. Catal.*, **23**, 183 (1971).
6) M. Ai, *J. Catal.*, **40**, 318 and 327 (1975).
7) M. Ai, *J. Catal.*, **49**, 305 (1977).
8) M. Ai, *J. Catal.*, **50**, 291 (1977).
9) J. Buiten, *J. Catal.*, **13**, 373 (1969).
10) Y. Morooka, Y. Takita, and A. Ozaki, *J. Catal.*, **27**, 177 (1972).
11) J. Buiten, *J. Catal.*, **27**, 232 (1972).
12) Y. Takita, Y. Moro-oka, and A. Ozaki, *J. Catal.*, **52**, 95 (1978).