

OXIDATION OF PROPYLENE ON TWO-COMPONENT OXIDE CATALYSTS

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A series of two-component Sb-metal oxide catalysts have been tested in gas phase oxidation of propylene in a flow apparatus with integral reactor. The catalysts were evaluated according to the conversion degree of propylene and reaction selectivity with respect to acrolein. The experimental results have shown very good properties of Sb-Fe oxides system for this oxidation.

Among the catalysts proposed for selective oxidation and ammo-oxidation of propylene in gas phase there are important two-component catalysts containing antimony oxides as the main component. Hadley, McCain and others¹⁻³ studied properties of the catalysts based on antimony and tin oxides. Due to Graselli^{4,5} a highly selective $\text{UO}_2\text{-Sb}_2\text{O}_5$ catalyst is known nowadays. Recently, Boreskov and coworkers⁶ described composition and activity of $\text{Fe}_2\text{O}_3\text{-Sb}_2\text{O}_5$ contact catalyst for propylene ammo-oxidation.

The aim of this work was a study of activity and selectivity of further catalysts of this type for gas phase propylene oxidation with molecular oxygen. Two-component oxide catalysts having the 1 : 1 atomic ratio Sb-metal are evaluated according to their activity measured by degree of propylene conversion and according to the reaction selectivity with respect to acrolein yields.

EXPERIMENTAL

Catalysts. The following *p.a.* chemicals were used for preparation of catalysts: SbCl_3 , $\text{Co}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Ce}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$. A series of two-component oxide catalysts having the 1 : 1 Sb-metal ratio were prepared in the following way. Solutions A and B were prepared by dissolving SbCl_3 in 11% HCl and the other metal salt in water, respectively (except for $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ where 11% HCl had to be used, too). The solution B was uniformly added into the solution A under continual vigorous mixing, and then pH was adjusted at 7 by addition of ammonia. The precipitate formed was concentrated by heating at 70°C and then dried at 100 to 150°C. Calcination and annealing was carried out at 230 to 240°C for 2 to 3 hours and then at 500°C for 18 hours. One half of the catalyst obtained was annealed at 750°C for another 8 hours.

Apparatus. Propylene oxidation with individual catalysts was carried out in a flow apparatus with integral reactor. The reagents, *i.e.* oxygen, propylene and nitrogen, were measured with the

accuracy of 3% using capillary flowmeter. The required water vapour concentration was obtained by saturating the calculated nitrogen amount with water vapour in a two-step saturator. The stainless steel reactor⁷ was electrically heated, and the temperature was measured with a chromel-

TABLE I
Tests of the Catalysts Annealed at 500°C

Catalyst	Temperature °C	Conversion ^a % C ₃ H ₆	Selectivity ^b for acrolein %	Side product	Note
Sb-Fe	431	28.8	12.4	no	only acrolein and CO ₂
Sb-Ni	434	23.8	2.7	acetaldehyde	
Sb-Cr	430	22.3	—	no	only CO ₂
Sb-Sn	430	30.5	22.6	no	only acrolein and CO ₂
Sb-Pb	430	—	—	—	no reaction, unmeasurable conversion
Sb-Cu	430	23.2	14.9	acetaldehyde	
Sb-Ce	430	16.1	—	no	only CO ₂
Sb-Mn	435	26.0	1.0	no	only CO ₂
Sb-Co	430	24.1	3.8	acetaldehyde, formaldehyde	

^a mol of the propylene reacted per mol of the propylene in the feedstock, ^b mol of the acrolein formed per mol of the propylene reacted.

TABLE II
Tests of Catalysts Annealed at 750°C

Catalyst	Temperature °C	Conversion ^a % C ₃ H ₆	Selectivity ^b for acrolein %	Side products	Note
Sb-Fe	432	41.2	15.3	acetaldehyde (traces)	
Sb-Ni	431	16.1	1.7	acetaldehyde	
Sb-Cr	430	24.2	—	—	only CO ₂
Sb-Sn	435	17.2	19.4	acetaldehyde	
Sb-Pb	429	3.2	not evaluated	—	too low conversion
Sb-Cu	432	30.6	—	—	only CO ₂
Sb-Ce	431	29.7	—	—	only CO ₂
Sb-Mn	434	23.3	—	—	only CO ₂
Sb-Co	434	15.8	7.5	acetaldehyde	

^{a, b} See Table I.

-alumel thermocouple and maintained with a $\pm 3^\circ\text{C}$ accuracy by means of an automatic regulation apparatus. The samples of reaction mixtures for chromatographic analysis were withdrawn before and after the reaction by means of a gas dispenser with a four-way and a six-way cocks. The last part of the apparatus consisted of a laboratory gas chromatograph and a countercurrent water absorber.

Analysis of reaction mixtures. Two kinds of samples were used for analyses of propylene oxidation products, *viz.* a sample of gaseous reaction mixture at the reactor outlet and a sample of the solution from the absorber.

The gaseous sample was chromatographically analyzed to determine the unreacted propylene and the carbon dioxide formed by reaction. The analysis was carried out with a $2200 \times \text{mm}$ stainless steel column packed with the Porapak N 60/80 mesh activated in a stream of nitrogen at 150°C ; the temperature of the column and katharometer was 90°C , hydrogen was used as carrier-gas, flow-rate 2.5 l/h. The solution from the absorber was analyzed polarographically (acrolein) by the method of Moshier⁸ modified for the reaction conditions. The solution was also used for identification of the carbonyl compounds formed (paper chromatography with standard substances). At first the products were precipitated with a solution of 2,4-dinitrophenylhydrazine, the precipitate was filtered off, dissolved in acetone and chromatographed on paper Whatman No 4 using acetone-formamide 1 : 1 and cyclohexane as stationary and mobile phases, respectively. The spots were made visible with sodium methoxide.

Starting material. Propylene of 99.5% purity was used for oxidation containing small amounts of propane.

RESULTS AND DISCUSSION

The following constant conditions of measurements were chosen for comparing the activity and selectivity of the catalysts prepared: Temperature 430°C , catalyst grain diameter 0.4 to 0.6 mm, time factor 0.3 g/h/l, composition of the starting mixture (% by vol.) oxygen 7.5, propylene 7.5, water vapour 10, nitrogen 75. The measured values of propylene conversion and reaction selectivity are given in Tables I and II for the catalyst series annealed at 500 and 750°C , respectively.

According to the propylene conversion results obtained the studied catalysts can be divided into four activity groups. Catalysts annealed at 500°C : 1) the most active Sb-Sn, Sb-Fe, 2) medium activity Sb-Mn, Sb-Co, Sb-Ni, Sb-Cr, Sb-Cu, 3) little activity Sb-Ce, 4) inactive Sb-Pb; at 750°C : 1) the most active Sb-Fe, 2) medium Sb-Mn, Sb-Ce, Sb-Cr, Sb-Cu, 3) little active Sb-Ni, Sb-Sn, Sb-Co, 4) inactive Sb-Pb. Increase in annealing temperature results in an activity increase only in the case of catalysts Sb-Fe, Sb-Cu, Sb-Ce, whereas Sb-Cr, Sb-Mn did not substantially change their activity, and in the case of Sb-Co, Sb-Ni and Sb-Sn systems a lower degree of propylene conversion was found.

Similarly the selectivity can be compared with respect to the oxidation of propylene into acrolein. Catalysts annealed at 500°C : 1) selective Sb-Sn, 2) medium selectivity Sb-Cu, Sb-Fe, 3) little selectivity Sb-Co, Sb-Ni, 4) non-selective Sb-Mn, Sb-Ce, Sb-Pb, Sb-Cr; at 750°C : 1) selective Sb-Sn, Sb-Fe, 2) little selectivity Sb-Co, Sb-Ni, 3) non-selective Sb-Cu, Sb-Cr, Sb-Pb, Sb-Ce, Sb-Mn.

TABLE III
Effect of Temperature on Catalytic Oxidation of Propylene

Catalyst	Catalyst annealing temperature, °C	Reaction temperature, °C	Conversion ^a % C ₃ H ₆	Selectivity ^b		Side products	Note
				acrolein	CO ₂		
Sb-Ni	500	351	4.4	15.5	85	acetaldehyde	
		435	24.4	2.1	98	acetaldehyde	
		482	36.5	0.2	99	no	only CO ₂
Sb-Ni	750	382	4.5	—	97	no	
		431	17.4	2	96	acetaldehyde	only traces of acrolein
		483	30.5	1.1	100.2	acetaldehyde	
Sb-Co	500	408	14.6	3.5	92.1	acetaldehyde	
		430	24.1	3.8	94.2	acetaldehyde	
		478	33.7	2.5	96.3	no	
Sb-Co	750	373	not evaluated				very low conversion of propylene
		383	not evaluated				
		434	15.8	7.5	91.5	acetaldehyde	
		491	31.5	5	92.4	no	
		351	11.8	61.5	43.1	no	
Sb-Fe	750	360	21.1	38.6	63.1	no	
		391	38	18	80.7	acetaldehyde	in both cases only
		432	41.2	15.3	91.4	acetaldehyde	traces of acetaldehyde

^{a,b} See Table I.

The two-component systems Sb-Pb, Sb-Mn, Sb-Ce and Sb-Cr prepared by the described way cannot be used for oxidation of propylene to the intermediate degree. The same holds for the contact catalyst Sb-Cu annealed at 750°C. The activity increase of this catalyst heated at higher temperature is connected with a steep selectivity decrease.

Comparison of the measured values of propylene conversion with those of reaction selectivity gives the final order of the catalysts with respect to the yield of acrolein (mol of the acrolein formed per mol of propylene in the feedstock). Annealing temperature 500°C: Sb-Sn, Sb-Fe, Sb-Cu, Sb-Co, Sb-Ni; 750°C: Sb-Fe, Sb-Sn, Sb-Ni.

For the selected two-component oxide catalysts Sb-Fe, Sb-Co, Sb-Ni the influence of temperature on the oxidation course of propylene was further investigated, the experimental conditions being in each case: 2.25 g catalyst of 0.4 to 0.6 mm grain

diameter, flow-rate 7.5 l/hour (NTP), composition of the feedstock (% by vol.) oxygen 7.5, propylene 7.5, water vapour 10, nitrogen 75.

The data obtained for the propylene conversion, reaction selectivity and side products of propylene oxidation are given in Table III. The results presented show that the system Sb-Fe (besides the already studied contact catalyst Sb-Sn) needs to be further investigated. A complete study of propylene oxidation on Sb-Fe oxide catalysts including the oxidation kinetics will be dealt with in some later report.

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