

PROPYLENE OXIDATION ON Sb—Fe OXIDE CATALYSTS

B. ŠRÁMEK* and J. TICHÝ

Physical Chemistry Department,
Institute of Chemical Technology, 532 10 Pardubice

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A series of catalysts have been prepared based on antimony and iron oxides with various ratios of the both metals, and their specific surface has been measured. Properties of the individual catalysts in propylene oxidation have been tested with a flow apparatus with integral reactor. The obtained values of propene conversion and reaction selectivity with respect to acrolein have shown good overall properties of the catalysts annealed at 500°C. For the study of the influence of the reaction conditions, *i.e.* temperature and concentration of the reaction components, on the results of propene oxidation a catalyst of the Sb—Fe atomic ratio 3 : 1 has been chosen, and the optimum oxidation conditions have been determined from the experimental data.

In the previous report¹ we tested two-component oxide catalysts Sb—metal and showed the Sb—Fe contact catalyst to be highly effective for gaseous propene oxidation. This result agrees with the findings of Boreskov and coworkers²⁻⁶ who dealt extensively with the problems of oxidative dehydrogenation of butenes on this type of catalysts. Phase composition of iron—antimony oxides catalysts was studied by Malachov⁷.

Our purpose was to determine the influence of atomic ratio of the both metals, nature of the support, and reaction conditions on the reaction course. The properties of the catalysts prepared are evaluated according to the obtained propene conversion degree, reaction selectivity, and acrolein yields.

EXPERIMENTAL

Catalysts. Four catalysts were prepared having Sb—Fe atomic ratios 3 : 1, 5 : 1, 7 : 1 and 9 : 1. The starting substances were SbCl_3 and $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$, the both of *p.a.* purity grade. SbCl_3 was dissolved in 11% HCl (solution *A*), and $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ was dissolved in distilled water (solution *B*). The solution *B* was added into the solution *A* at a constant rate and with intensive stirring, whereupon pH 7 was adjusted by addition of ammonia. The suspension was heated to 70°C, evaporated with constant stirring, and finally dried at 100—150°C. The residue was further calcinated at 230—240°C and 340—360°C and then annealed at 500°C for 18 hours. A part of each catalyst was further annealed at 750°C for 8 hours. The catalyst of the 3 : 1 atomic ratio Sb—Fe was, besides that, prepared on two supports: Alon (Carbon Corporation, Boston,

* Present address: Pharmacology and Toxicology Department, Pharmacy Institute, Charles University, 500 27 Hradec Králové.

Mass. USA) and Aerosil (pyrogene Kieselsäure, Elektroschmelzwerk, Kempten, BRD). The preparation procedure was the same, the aqueous suspension of the support being added to the solution *A* before mixing. The catalysts on supports were only annealed at 500°C.

Apparatus. Propene oxidation with Sb—Fe catalysts was studied with the flow apparatus with integral reactor described in the previous report¹. Propene and CO₂ were determined by GLC,

TABLE I
Specific Surface of Catalysts

Atomic ratio Sb—Fe	Annealing temperature °C	Specific surface m ² /g	Atomic ratio Sb—Fe	Annealing temperature °C	Specific surface m ² /g
3 : 1	500	35.3	7 : 1	500	56.1
	750	18.5		750	22.1
5 : 1	500	49.1	9 : 1	500	44.5
	750	14.6		750	8.7

TABLE II
Testing of the Catalysts Annealed at 500°C

At. ratio Sb—Fe	Tempe- rature °C	Conver- sion ^a %	Yields, mmol/h		Selectivity ^b		Yields ^c , %	
			acrolein	CO ₂	acrolein	CO ₂	acrolein	CO ₂
3 : 1	381	20.2	4.46	1.53	88.0	10.1	17.8	2.0
	441	30.6	6.10	4.30	79.5	18.7	24.3	5.7
	482	34.7	6.10	7.30	70.0	27.9	24.3	9.7
5 : 1	383	25.0	5.50	2.86	87.6	15.1	21.9	3.8
	440	36.0	6.80	6.27	75.1	23.1	27.1	8.3
	482	37.4	5.90	10.2	62.7	36.3	23.5	13.6
7 : 1	385	21.0	4.45	2.03	84.5	12.9	17.7	2.7
	430	36.2	7.14	7.11	78.6	26.1	28.4	9.4
	500	35.0	5.58	9.10	63.6	34.6	22.2	12.1
9 : 1	381	20.2	4.62	1.61	90.0	10.4	18.4	2.2
	427	31.0	6.64	4.44	85.1	19.0	26.5	5.9
	493	37.5	6.29	8.78	66.9	31.1	25.1	11.7

^a Ratio of mol number of the reacted propene to mol number of propene in the feed. ^b Mol of the propene reacted to acrolein per mol of total propene reacted. ^c Mol of the propene reacted to acrolein per mol of propene in the feed.

acrolein was determined polarographically, and the carbonyl side products formed were determined qualitatively by paper chromatography. Propene for oxidation was of 99.5% purity with little propane (Slovnaft, Bratislava).

Specific surface of the catalysts was determined by the method of thermal desorption under the following conditions: Standard TiO₂ (spec. surface 7.5 m²/g), adsorbate N₂ + He (1 : 4

TABLE III
Testing of the Catalysts Annealed at 750°C

At. ratio Sb—Fe	Temperature °C	Conversion %	Yields, mmol/h		Selectivity, %		Yields, %	
			acrolein	CO ₂	acrolein	CO ₂	acrolein	CO ₂
3 : 1	385	12.1	2.79	0.90	92.0	9.9	11.1	1.2
	425	19.1	4.05	1.94	84.4	13.5	16.1	2.6
	496	31.2	5.43	6.79	69.2	28.8	2.6	9.0
5 : 1	378	11.4	2.57	1.03	90.0	12.0	10.2	1.4
	428	19.9	4.33	2.32	86.6	15.5	17.3	3.0
	507	34.2	6.09	7.99	70.9	31.0	24.3	10.6
7 : 1	380	12.4	2.69	1.05	86.8	11.3	10.7	1.4
	432	21.4	4.62	2.63	85.6	16.3	18.4	3.5
	497	33.3	5.81	7.07	69.8	28.2	23.2	9.4
9 : 1	381	6.0	1.19	0.90	78.8	19.9	4.7	1.2
	438	12.1	2.23	2.56	74.3	28.4	8.9	3.4
	493	20.0	2.98	5.83	59.1	38.5	11.9	7.7

TABLE IV
Effect of Support on Properties of Catalyst Sb—Fe (3 : 1)

Support	Reaction temperature, °C	Conversion %	Yields, mmol/h		Selectivity, %		Yields, %	
			acrolein	CO ₂	acrolein	CO ₂	acrolein	CO ₂
Aerosil	380	—	—	—	—	—	—	— ^a
	440	3.2	—	—	—	—	—	— ^b
	492	8.2	1.10	2.80	53.2	45.0	4.4	3.7
Alon	387	6.8	0.36	3.97	20.9	77.0	1.4	5.3
	475	12.3	0.0	9.10	0	98.2	0	12.0

^a Unmeasurable values, no reaction is taking place. ^b Not evaluated.

by vol.), preparation of the sample: activation in a stream of N_2 at 190–200°C for 60 min. The results are given in Table I.

Catalysts testing. The following conditions were chosen for determination of activity and selectivity of the catalysts: catalyst grain 0.4 to 0.6 mm, time factor 0.3 g h/l; composition of the starting mixture (% by vol.): oxygen 7.5, propene 7.5, water vapour 10, nitrogen 75; reaction temperature — variable within 380 to 480°C.

RESULTS AND DISCUSSION

Tables II and III give the values of propene conversion, acrolein and CO_2 yields, and reaction selectivities obtained for the catalysts annealed at 500 and 750°C, respectively. Table IV shows the influence of support on the properties of the catalyst Sb—Fe (3 : 1).

From the results of testing of the catalysts Sb—Fe of the atomic ratios 3 : 1, 5 : 1, 7 : 1 and 9 : 1 annealed at 500°C and those annealed at 750°C it follows that there are no substantial differences in activities and selectivities between the contact catalysts annealed at 500°C. They all are medium active and highly selective for acrolein. Increase in annealing temperature results in a marked activity decrease especially in the case of the catalyst Sb—Fe (9 : 1). The observed activity decrease agrees with the found decrease of the specific surface of these catalysts. If the catalyst Sb—Fe (3 : 1) was dispersed on a support, its activity was decreased. As it can be seen from the results in Tables II and IV, the propene conversion decrease and the reaction selectivity decrease were observed with the both supports mentioned.

TABLE V

Effect of Temperature and Feed Composition on the Reaction Course and Results

Besides the given variables the following parameters were kept constant: catalyst amount 5 g, flow-rate 5 l/h, propene in feed 5% by vol.

Temperature °C	Oxygen vol. %	Water vapour vol. %	Conver- sion %	Yields, mmol/h		Selectivity		Yields, %	
				acrolein	CO_2	acrolein	CO_2	acrolein	CO_2
363	12.5	10	31.4	2.99	1.71	85.4	16.3	26.8	5.1
390	12.5	10	51.9	4.07	4.50	70.4	26.0	36.4	13.4
421	12.5	10	61.7	4.28	6.95	62.1	33.6	38.4	20.8
390	5	10	34.8	3.23	1.69	83.2	14.5	29.0	5.0
390	10	10	45.3	4.00	2.86	79.2	18.9	35.8	8.5
394	12.5	0	55.8	4.87	3.79	78.3	20.3	43.6	11.3
394	12.5	15	43.4	3.73	3.14	77.0	21.6	33.4	9.4
394	12.5	20	39.9	3.24	3.48	72.8	26.1	29.0	10.4

For the optimum reaction conditions determination again the catalyst Sb—Fe (3 : 1) was chosen, as it gives the minimum yields of total propene combustion. With this catalyst the influence of reaction temperature, concentrations of oxygen and water vapour in the feedstock on the propene conversion degree, reaction selectivity, and acrolein yields was followed. The choice of oxidation conditions and results of this measurement series are given in Table V. Raising of the reaction temperature above 390°C at the constant feed composition resulted in a considerable increase of propene conversion degree accompanied by a large selectivity decrease, so that the yield of acrolein changed but little. Also the oxygen concentration increase in the feed at a constant temperature increases considerably the propene conversion degree, the reaction selectivity decreasing only little, the acrolein yield being consequently increased. The water vapour influence on the oxidation results is obviously negative. The increase of water vapour concentration in the feed diminishes both the propene conversion degree and the reaction selectivity.

The results obtained in the present work form a necessary basis for kinetic and mechanism study of propene oxidation on Sb—Fe oxides catalysts. New results in this experimental field will be presented in some further report.

REFERENCES

1. Tichý J., Šrámek B.: *This Journal* 39, 2796 (1974).
2. Borekov G. K.: *Kinet. Katal.* 10, 1350 (1969).
3. Shchukin V. P., Borekov G. K., Venjaminov S. A., Tarasova D. V.: *Kinet. Katal.* 11, 153 (1970).
4. Shchukin V. P., Venjaminov S. A., Borekov G. K.: *Kinet. Katal.* 11, 1236 (1970).
5. Shchukin V. P., Venjaminov S. A.: *Kinet. Katal.* 11, 1431 (1970).
6. Shchukin V. P., Venjaminov S. A., Borekov G. K.: *Kinet. Katal.* 12, 621 (1971).
7. Malakhov V. V.: *Kinet. Katal.* 13, 196 (1972).

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