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Pyridines by Propylene Ammoxidation

III. Catalyst Optimal Composition and Process Main Parameters

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The influence of catalyst composition on reaction selectivity for propylene ammoxidation was studied and some basic information about the main practical aspects of the process was collected. Si–Al–Te–Sb–O has been used as catalyst. The catalyst performed satisfactorily within the temperature range 310–390°C and proved capable of withstanding quite rigorous operating conditions and abrupt changes in feed composition. The partial orders of reaction and at least the order of magnitude of the main kinetic parameters were also determined.

INTRODUCTION

In two recent papers (*1*, *2*) we have reported on the activity of Te oxide/silica–alumina-based solid mixtures in catalyzing the ammoxidation of propylene to pyridines. Some correlations were observed between the physicochemical properties of the solid, particularly surface acidity (*1*) and structure (*2*), and selectivity to the desired product. In addition, a comparison between the structure of selective and of unselective catalysts allowed us to propose a possible mechanism for the overall ammoxidation reaction (*2*).

In the present paper we describe the optimization of the catalyst composition with respect to reaction selectivity. As this reaction represents a potential alternative route to pyridines (*3*–*5*), it was also of interest to collect data concerning some of the more important practical aspects of the process.

EXPERIMENTAL

Materials. Propylene was a Phillips Petroleum Company "pure grade" reagent, ≥99.5 mol% pure. High purity (≥99.9 mol%) cylinder gases, "pro analysi" chemicals, and distilled water were employed to prepare the catalysts, to feed the reactor, and as reference standards for the GC analysis.

Catalysts. Thirteen different catalysts were prepared as previously described (*1*, *2*). Their composition and properties were determined as reported elsewhere (*1*, *6*) and are listed in Tables 1 and 2.

Apparatus and analysis. The propylene ammoxidation reaction was conducted in a continuous, Pyrex glass, fixed-bed, tubular microreactor. Details of the GC analysis of reactants and products are given in Ref. (*1*).

RESULTS AND DISCUSSION

All the experiments were carried out at atmospheric pressure. The results are expressed as in Ref. (*1*), in terms of overall mol% conversion (C) of the propylene and mol% selectivity (S_i) to the ith product. Due to the previously reported (*1*) analytical difficulties and to the formation of carbonaceous deposits on the catalyst surface, the carbon atoms recovered as reaction products or unconverted olefin, with respect to those fed as propylene, was less than 100%. The respective percentage recovery ($R_{\%}$) was determined and is reported, when necessary, to give an idea of the reliability of the data. The operating conditions are given in detail in Table 3. The results are shown below in either graphical or numerical form.

Influence of the Al_2O_3 concentration. As reported in our previous papers, selective

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TABLE 1

Group 1 Catalysts. Chemical Composition and Properties

Type	TeO_2 (wt%)	Sb_2O_4 (wt%)	SiO_2 (wt%)	Al_2O_3 (wt%)	BET surface area (m^2/g)	Pore vol. (ml/g)	Average pore radius (Å)	Surface acidity (mmol/g)	
								$pK_a \leq +4.0$	$pK_a \leq +4.8$
01	2.27	2.05	91.14	4.54	731	1.57	30	0.64	1.43
02	2.41	2.08	92.03	3.48	319	0.82	35	0.55	1.34
03	2.96	2.07	92.69	2.27	364	1.12	50	0.27	1.07
04	2.89	1.64	95.47	—	462	1.41	65	0.22	0.55

catalysts are characterized by a particular structure in which small particles of Te oxide-based phase(s) are embedded in a silica-based amorphous matrix (*2*), possessing surface acid centres of particular acid strength (pK_a = 4.0–4.8) in good concentration (*1*). After some exploratory work which showed that the useful range of Al_2O_3 (A) concentration in our silica–alumina matrix was from >0 to ca. 7 wt%, with respect to the sum $SiO_2 + Al_2O_3$ (SA), a first group of four catalysts were prepared and characterized (Table 1). The concentration and the relative ratio of heavy oxides were practically the same in all such solids, the ratio A/SA changing from 0 to 4.7 wt%. These catalysts were then tested by means of a first series of runs in standard conditions (see Table 3) and the results are plotted in Fig. 1. It may be noted that both the surface concentration of acid centres ($4.0 \leq pK_a \leq 4.8$) and the selectivity to pyridines (S_{pys}) go through a maximum at A/SA = 2–4 wt%, S_{pys} falling to zero in the absence of alumina.

TABLE 2

Group 2 Catalysts. Chemical Composition (wt%)

Type	TeO_2	Sb_2O_4	SiO_2	Al_2O_3
A0	8.90	—	88.18	2.92
A3	2.48	2.75	92.66	2.11
A4	1.15	2.65	92.84	3.36
A5	2.91	2.60	92.18	2.31
A9	0.52	2.57	94.47	2.44
A10	4.48	2.28	90.82	2.42
A11	1.21	3.05	92.99	2.75
A12	2.56	4.42	89.28	3.75
A14	—	11.08	85.28	3.64

Influence of the Te oxide and Sb oxide concentration. A second group of catalysts (Table 2) were prepared, by keeping the alumina content within the limits previously cited (A/SA = 2–4 wt%). The overall concentration of heavy oxides was between 3 and 11 wt% and the ratio T/TS = $TeO_2/(TeO_2 + Sb_2O_4)$ changed from 1 to 0, i.e., from pure Te oxide to pure Sb oxide. The catalysts were tested in the same standard conditions (Table 3, run series 2) and the results are shown in Fig. 2. One may observe that higher selectivity and mainly durability seem to be connected with a high (≥40 wt%) value of the T/TS ratio. Moreover, the pure Sb oxide-based catalyst is almost three times less selective than the

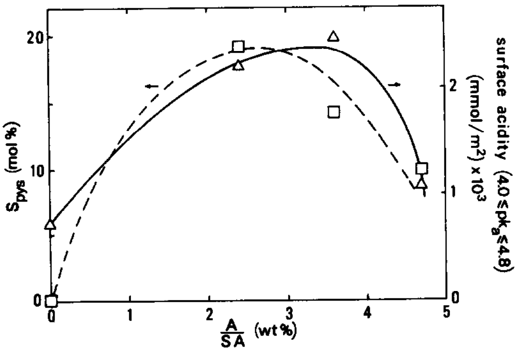

FIG. 1. Selectivity to pyridines and surface acidity vs alumina concentration in the silica–alumina amorphous matrix of the catalyst. Reaction conditions and catalysts: see Table 3, run series 1.

TABLE 3

Operating Conditions. Total Pressure 1 atm

Run series No.	T (°C)	Catalyst type (see Tables 1 and 2)	Particle size (mesh)	Reactant mol ratios ($NH_3:C_3H_6:H_2O:air$) or partial press. (Torr) in the feed	Time factor $\tau = W/F$ (g h/mol)	Results (figure)
1	390	01–04	40–80	1:2:10:20	93.2[a]	1
2	390	A0–A14	40–80	1:2:10:20	93.2[a]	2
3	310–430	03	60–100	1:2:11:22	45.2[b]	3
4	390	03	60–100	1:2:11:22	45.2[b]	4
5	390	03	60–100	1:2:11:22	14.8[c]	5
6	390	03	60–100, 100–160, 160–200	1:2:11:22	45.2[b]	6
7[d]	390	03	60–100	$O_2$21–211, $NH_3$21, $C_3H_6$42, H_2O231		
				97, 21, 13–127, 231		8
				97, 6–53, 42, 231		
				97, 21, 42, 75–482		
8[e]	310–390	03	60–100	1:2:11:22		9

[a] Catalyst weight $W = 10.0$ g, overall feed rate $F = 0.1073$ mol/h.

[b] Catalyst weight 5.0 g, overall feed rate 0.1107 mol/h.

[c] Catalyst weight 2.06–8.23 g, overall feed rate 0.1107–0.5553 mol/h, upper limits imposed by excessive pressure drop.

[d] Differential reactor technique. Constant $F = 0.1073$ mol/h. Nitrogen partial pressure adjusted to give total pressure 1 atm.

[e] Differential reactor technique. Constant $F = 0.1073$ mol/h.

pure Te oxide-based one, but the presence of antimony oxide, in relatively low concentration, shows a beneficial effect, at least on initial selectivity (Fig. 2a).

Determination of useful reaction temperature range. The useful range of reaction temperature of our catalytic system has been determined by means of a third series of runs in the conditions reported in Table 3. The mean values of the main activity parameters, averaged over the first 25 h of time-on-stream (t) are plotted in Fig. 3. It may be noticed that at 430°C higher values of conversion are accompanied by lower values of S_{pys} and by a quite high selectivity to unwelcome by-products (e.g., acetonitrile) and mainly to the total combustion product (CO_2). In addition, at such a temperature, a relatively high rate of deactivation was noted, as indicated also by the lower values of $R_{\%}$. The catalyst fouled after reacting at 430°C was also hardly regenerable.

On the other hand, at the lower end of the temperature range tested, higher selectivity to the desired product is accompanied by a very low conversion and mainly by a quite high selectivity to acetaldehyde. The formation of acetaldehyde rather than pyridines at low temperatures suggests that the former may be an intermediate in the production of the latter (*2*). At such low temperature it probably accumulates, due to the insufficient rate of conversion to pyridines.

A reasonable range of reaction temperature may thus be regarded as 300–400°C.

Catalyst life and regenerability. The test run (No. 4, Table 3) relative to these parameters has been conducted with the best catalyst of group 1 (type 03, Table 1) in quite rigorous conditions (390°C). The results are plotted in Fig. 4. During the test, accidental temporary blocking of either liquid reagents or air feed tubing caused a heavy fouling of the catalyst at the times indicated by the

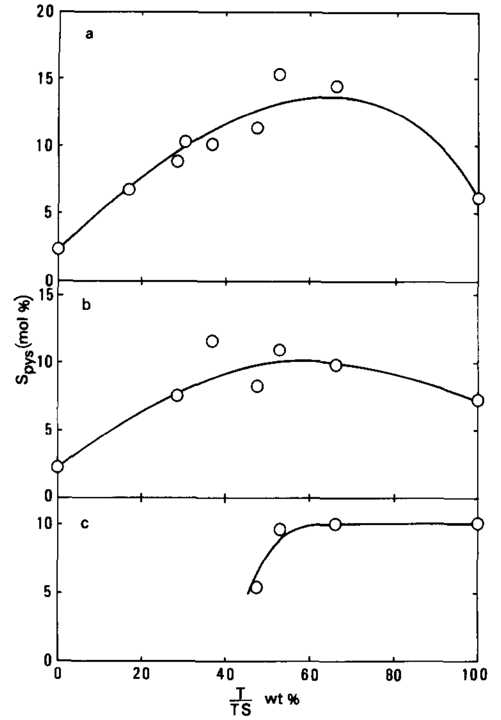

FIG. 2. Selectivity to pyridines vs Te oxide concentration in the heavy oxides phase(s) of the catalyst. (a), (b), and (c): After 2.5, 25, and 70 h time-on-stream, respectively. Reaction conditions and catalysts: see Table 3, run series 2.

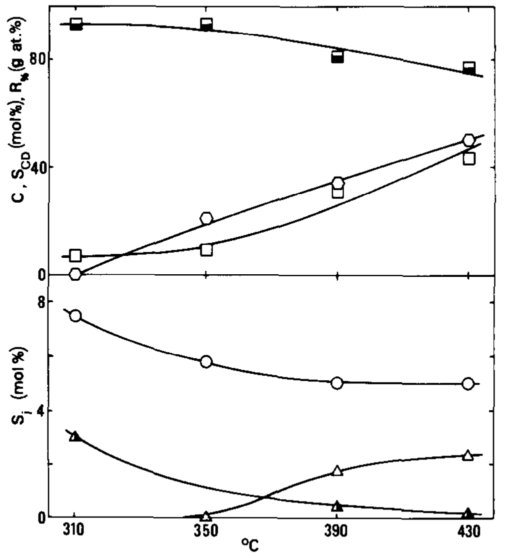

FIG. 3. Overall conversion (□), selectivity to pyridines (○), to carbon dioxide (O), to acetaldehyde (▲), to acetonitrile (△) and % recovery of carbon atoms (⬓) (values averaged over 0–25 h time-on-stream) vs reaction temperature. Reaction conditions and catalyst: see Table 3, run series 3.

dashed lines. The regeneration of the catalyst took some tens of hours and was done in all cases by simply feeding pure air at the reaction temperature. The regeneration was stopped when no more $BaCO_3$ precipitated on bubbling the effluent gas into $Ba(OH)_2$ aqueous solution for ca. 15 min. After each regeneration, the run was immediately continued at the usual conditions. The regeneration time has not been included in the overall t (Fig. 4 abscissa). The results show that, apart from the initial stabilization period, our catalyst proved to be appreciably stable, with respect to both conversion and selectivity to the various products. The regeneration procedure adopted allowed in any case to recover perfectly the conditions existing immediately before the accidental breakdowns. The relatively low selectivity to pyridines, accompanied by a relatively high selectivity to CO_2 (ca. 30%) and to acetonitrile (S_{AN} in the figure), are mainly due to the quite high temperature, chosen in order to obtain sufficiently reliable information in reasonable time.

Influence of external diffusion. A preliminary calculation of the Reynolds number Re, relative to the flow of reactants through the catalyst bed, was made by means of the well-known formula

$$Re = \frac{\bar{d}_p \bar{\rho} u_s}{\bar{\mu}(1 - \epsilon)},$$

$\bar{d}_p$ being the average diameter of catalyst particles, $\bar{\rho}$ and $\bar{\mu}$ the average density and viscosity, respectively, of the reacting gas mixture, calculated at reaction conditions by the usual methods (*7*), ϵ the external void fraction of the catalytic bed and u_s the flow rate, expressed as the ratio of the overall volumetric flow rate (cm^3/s), at reaction conditions, to the reactor cross section area (cm^2), calculated in the absence of catalyst. The calculation led to values of Re ranging

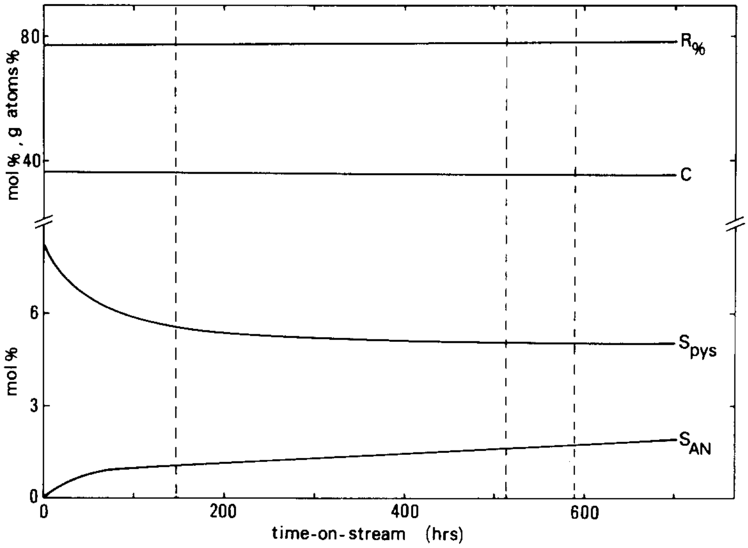

FIG. 4. Life and regenerability test run. $R_{\%}$, percentage recovery of carbon atoms; C, overall mol% conversion of C_3H_6; S_{pys}, S_{AN}, selectivity to pyridines and to acetonitrile, respectively. Reaction conditions and catalyst: see Table 3, run 4. Dashed lines: accidental feeding stops (fouling followed by regeneration).

from 0.03 to 0.2. As a consequence, it seemed advisable to perform some direct control experimental runs. Such runs (series No. 5, Table 3) were done at high temperature (390°C), in order to emphasize any eventual diffusive effect. At reactant flow rates of 0.63, 1.54, and 2.97 cm/s, selectivities (S_{pys}) of 7.3, 7.0, and 7.0 mol%, respectively, were recorded. Since all other experimental runs were performed at flow rates $u_s \geq 1$ cm/s, such results clearly show that external diffusion did not interfere in any case.

Influence of internal diffusion. Oxidations are usually quite fast exothermic reactions, so they may be easily affected by internal diffusive limitations. A check by some direct experiments (series No. 6, Table 3) at high temperature was then considered the most safe control procedure. With catalyst particles of 60–100, 100–160, and 160–200 mesh, selectivities (S_{pys}) of 7.5, 10.5, and 12.1 mol%, respectively, were obtained. These results indicate that, at least at 390°C, even very fine (160–200 mesh) catalyst particles probably could not provide kinetic data free from diffusional restrictions of this type.

Influence of partial pressures of the reagents. When employing the differential reactor technique (run series No. 7 and 8, Table 3), i.e., when the influence of reaction products may be considered negligible, the initial reaction rate r_0 (mol/h g) was expressed by the well-known empirical formula

$$r_0 = \lim_{\tau \to 0} \frac{dC}{d\tau} = k_r \prod_{i=1}^{N} p_i^{n_i} \qquad (1)$$

in which k_r (mol/h g atm$^{\Sigma n_i}$) is the rate constant, $\tau = W/F$ the time factor, W being the catalyst weight (g) and F the overall reactants flow rate (mol/h), p_i are the partial pressures (atm) of the reactants, N the number of reagents, and n_i the partial orders of reaction, with respect to the various reagents. The total pressure being the same in all runs, calculated amounts of inert gas (N_2) were added in each run to keep unchanged the partial pressures of all reagents but one. When the O_2/N_2 ratio exceeded that of air, preformed mixtures of pure O_2

and N_2 were employed. The range of partial pressure (from 0.5 to 1 orders of magnitude) explored for each reactant, including water, was the maximum allowed by our system. In the presence of a too large excess of any one of the reactants, the catalyst deactivated quite rapidly. The value of the time factor τ was chosen to ensure differential reactor conditions, i.e., to keep the overall conversion C at few mol%. To reduce the error produced by the analytical difficulties, enhanced at such low conversion, each run was conducted for some hours, with frequent sampling of the reactor effluent. The results showed a practically linear decline in activity of less than 0.3 mol% per hour, over a typical 5-h period. The value of conversion C_0 at time-on-stream $t = 0$ (i.e., with fresh catalyst) was obtained by extrapolating the best straight line, fitting the experimental data by the least-squares method. The partial orders of reaction (n_i) were then evaluated (Fig. 5) by plotting ln r_0, where $r_0 = C_0/\tau$, against $\ln p_i$ (p_i in Torr) at constant p_j ($j \neq i$). The slopes of the best straight lines (least-squares) for each set of data permitted the calculation of the partial orders 1.8, 0.3, 0.8, and 0.7 with respect to O_2, C_3H_6, NH_3, and H_2O, respectively (Eq. (1)).

Order of magnitude of kinetic parameters. The usual way to determine the values of rate constant k_r is by integrating the reaction rate differential equation, followed by optimizing (e.g., by a nonlinear regression technique) the fitting of the calculated curve with respect to a set of experimental data, obtained by the integral reactor technique. However, since an empirical rate law (Eq. (1)) was employed, the value of k_r at the various temperatures was obtained by means of a rapid, although less accurate, procedure, i.e., by conducting some runs in differential reactor conditions and by assuming as constant, within our temperature range, the partial orders of reaction previously calculated. The last series (No. 8, Table 3) of our experiments were then performed at various temperatures, by keeping the overall conversion at few mol% and the values of C_0 were evaluated as previously described. By inserting the parameters of the best straight line, drawn by the least-squares method, through the experimental points of the Arrhenius plot, in the usual equation

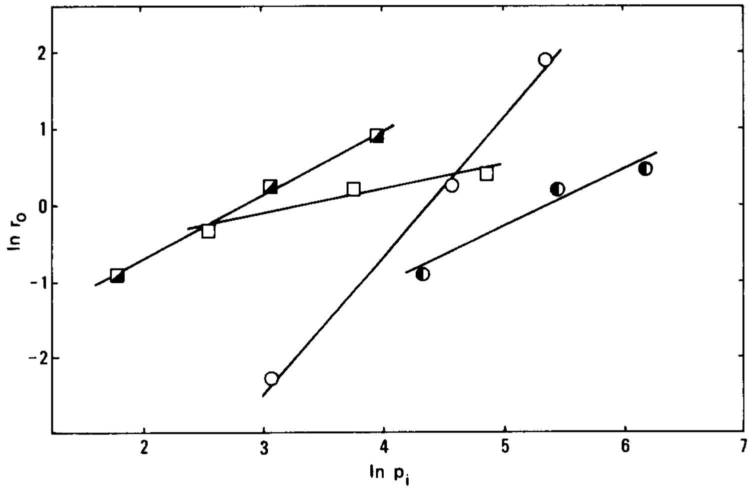

FIG. 5. Dependence of initial reaction rate r_0 (mol/h g) on partial pressures p_i (Torr) of reactants, (◪) NH_3, (□) C_3H_6, (○) O_2, (◐) H_2O. Reaction conditions and catalyst: see Table 3, run series 7.

$$\log k_r = \log A - \Delta E_a/RT \qquad (2)$$

the following values of the apparent activation energy and of the Arrhenius preexponential factor were calculated:

$$\Delta E_a = 33.1 \pm 4.8 \text{ kcal/mol},$$

$$A = 3.4 \times 10^{11} \pm 48.3 \text{ mol/h atm}^{3.6}.$$

These figures should be considered just as order-of-magnitude values, since not only are they based on an empirical equation, but also internal diffusion effects seem not to be completely absent, as noted earlier.

CONCLUSIONS

The information collected in the present work may be summarized as follows: (i) higher selectivity was obtained when the concentration of some oxides in the catalyst was neither lower nor higher than given limits; (ii) the catalyst showed a good durability and proved to be able to withstand both quite rigorous operating conditions and even shocks due to abrupt changes in feed composition; (iii) the catalyst could be regenerated easily and completely by simple burning off the carbonaceous deposits with air at reaction temperature; (iv) the upper and lower limits of reaction temperature, and the lower limit of flow rate of reactants, have been determined; (v) internal diffusion effects were probably present even with quite fine catalyst particles, so indicating that pellet shape and size may be important factors to consider in any practical application; (vi) at least the order of magnitude of the main kinetic parameters has been determined.

A useful set of basic data has thereby been provided for the evaluation of the main practical aspects of a possible larger-scale process.

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