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NOTE

Pyridines by Propylene Ammoxidation over Te Oxide/Silica–Alumina

Pyridines for industrial use are usually obtained from either coal tar or oil residues by distillation. However, an alternative route is synthesis by cyclization from aldehydes and ammonia (*1*). Recently some syntheses by catalytic ammoxidation of light olefins, particularly propylene, have been proposed (*2–9*). The most promising of these seems to be a vapor-phase cyclization, heterogeneously catalyzed by Te oxide (*4*), so it seemed interesting to examine certain aspects more deeply, particularly catalyst characteristics and performance. Some Te oxide/silica–alumina-based catalysts, with or without addition of other oxides, have accordingly been prepared and tested.

After some preliminary work, the chosen preparation technique was essentially a precipitation of the silica–alumina on the preformed and finely ground metallic oxide(s), since the reverse process, i.e., the precipitation of metallic oxide on preformed silica–alumina, in some cases gave unsatisfactory results. The precipitation was followed by a long (15–20 hr) homogenization step of the obtained solid, either by milling in the presence of a small quantity of water at room temperature, or by vigorous stirring in hot refluxing water. Drying at 110°C and calcination in a slow air flow at 400°C gave the final catalyst.

TABLE 1

Characteristics of the Employed Catalysts

Catalyst no.	SiO_2+ Al_2O_3 (wt%)	$\frac{Al_2O_3}{SiO_2}$ (wt ratio)	TeO_2 (wt%)	BET SA ($m^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)	Av. pore radius (Å)	Surface acidity ($mmol\ g^{-1}$)	
							pK_a + 4.0	pK_a + 4.8
1[a]	79.3	0.0270	20.7	669	0.56	20	0.2026	0.3039[b]
2[c]	82.4	0.0273	17.6	226	0.90	70	0.0384	0.2207
3[a,d]	93.3	0.0330	4.9	455	0.16 + 0.09	10/60[e]	0.1517	0.2482[b]
4[c,f]	87.1	0.0360	10.0	363	0.94	20	0.3389	0.5619
5[a,g]	87.0	0.0350	5.8	186	0.99	90	0.0870	0.1716
6[a,h]	71.1	0.0140	21.4	345	1.15	60	0.1093	0.3886

[a] Homogenization by milling overnight, room temperature.
[b] During outgassing *in vacuo* care must be taken to avoid partial decomposition of Te oxide to Te.
[c] Homogenization by reflux stirring overnight (100°C).
[d] Sb_2O_3, 1.8 wt%.
[e] Bimodal pore size distribution.
[f] Sb_2O_3, 2.9 wt%.
[g] MnO_2, 7.2 wt%.
[h] Sb_2O_3, 5.9 wt%; NiO, 1.6 wt%.

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TABLE 2

Catalyst Performance at 390°C[a]

Reaction time (hr)	C (mol%)	S_i (mol%)							
		CD[b]	AC	AL	AA	PY	LU	ME	PE
		Catalyst No. 1							
2.25	49.8	4.7	1.8	0.3	0.4	3.6	1.1	1.4	—
7	31.9	3.4	2.2	0.2	0.7	4.6	1.4	1.9	—
24	33.6	3.3	2.1	0.3	0.6	4.0	2.7	0.6	—
51	28.3	5.0	3.0	0.4	0.4	4.0	2.4	1.0	—
71	25.5	4.6	3.7	0.5	0.3	5.6	2.5	2.0	—
		Catalyst No, 2							
1.5	62.5	0.2	0.5	0.6	3.5	0.2	—	—	0.9
20	24.2	5.5	1.0	0.7	6.0	tr	—	—	4.0
45	12.4	Not determined							
		Catalyst No. 3							
2.75	71.7	2.0	2.4	1.2	tr	2.5	0.1	tr	tr
25	59.2	4.4	3.9	3.7	tr	7.0	0.2	tr	2.2
71	49.8	4.8	3.9	3.3	tr	9.1	0.3	tr	3.8
		Catalyst No. 4							
1.5	63.9	2.0	2.8	0.5	7.4	8.3	5.8	0.2	tr
45	34.3	3.2	3.0	2.1	7.0	10.7	1.7	0.3	tr
67	34.9	9.3	3.8	5.2	6.4	9.0	0.5	0.3	2.4
		Catalyst No. 5							
2	34.5	1.4	4.7	0.2	11.5	2.4	tr	—	tr
22	34.0	1.2	3.6	0.2	13.3	0.5	tr	—	7.2
		Catalyst No. 6							
1.75	34.5	0.6	1.6	0.3	1.9	0.3	tr	—	2.3
25	14.1	1.3	3.3	1.3	4.4	5.2	tr	—	14.0
46	8.4	3.0	9.1	2.7	12.4	7.8	tr	—	36.6

[a] Reaction conditions: atmospheric pressure; time factor-28.6 g hr mol^{-1}; molar ratios of fed reactants (NH_3:H_2O:C_3H_6:air) = 1:11:2:11.

[b] CD, carbon dioxide; AC, acetone; AL, acetaldehyde; AA, acetic acid; PY, pyridine; LU, lutidines; ME, methylethylpyridines; PE, diisopropylether; tr indicates less than 0.1%.

The catalysts were chemically analyzed by standard methods (*10, 11*) for their composition and were characterized by determining their specific surface area, pore volume, and pore size distribution by nitrogen adsorption at liquid nitrogen temperature, after 5 hr outgassing at 200°C and 10^{-4} Torr (ca. 10^{-2} Pa) (*12–14*). Their surface acidity was determined, after the same outgassing treatment, by titration in anhydrous solvents (*15, 16*). The characteristics are summarized in Table 1.

The activity tests were made in a small tubular glass reactor under the following conditions: 390°C; atmospheric pressure; catalyst weight, 3.00 g; feeding rates of reactants (mmol hr^{-1}): C_3H_6, 8.4; NH_3, 4.2; H_2O, 46.0; and air, 46.0. Each run was conducted continuously for several tens of hours. Reaction products were separated into a gaseous and a liquid phase, which were separately analyzed by gas chromatography (TC detector) over Porapak P and by employing the external standard technique (methyl ethyl ketone and ethylene for the liquid and gaseous phase, respectively). The catalyst activity is expressed as reported elsewhere (*17*); i.e., the overall conversion C as the mole percentage ratio of the reacted over fed propylene and the selectivity S_i to the *i*th product as the mole percentage of the converted propylene, transformed into such a product. The results are given in Table 2. In addition to the substances revealed by gas chromatography (GC) and reported in Table 2, a reddish-brown substance always formed, extremely soluble in water and partially soluble in ethyl alcohol, but practically insoluble in the usual aprotic solvents. By evaporating the collected liquid products *in vacuo* at room temperature and recrystallizing the residue from ethyl alcohol, a light-brown semisolid substance was obtained, whose characteristics indicated that the main component was probably 1-amino-ethanol, i.e., the acetaldehyde–ammonia adduct. The mass of this residue in all cases corresponded satisfactorily with the deficit of reactant unaccounted for after GC analysis of unchanged propylene and of reaction products in Table 2.

In spite of the analytical difficulties, some interesting information can be obtained about the correlations between catalyst activity and properties. Particularly one can observe that, at least for the adopted reaction conditions, the best catalysts are those containing either Te and Sb oxides together or Te oxide alone, in that order (Fig. 1). The catalysts containing additions of Mn or Ni oxides gave high overall conversion, but low selectivity and very short life (Table 2). As to the effect of the method of preparation, it may

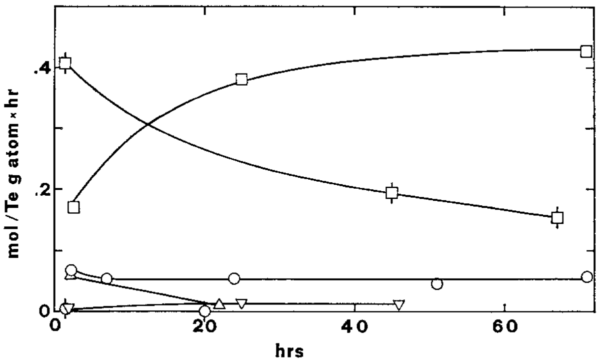

FIG. 1. Specific selective reaction rate (mol of olefin converted to pyridines/hr Te g atom) vs reaction time. (○, ϕ, □, ⌷, △, ▽) Catalysts No. 1, 2, 3, 4, 5, and 6, respectively (Table 1). See text for reaction conditions.

be noted that homogenization by wet milling at room temperature gives better results than stirring at reflux temperature, since the resulting catalysts are not only active and selective, but also more lasting (Fig. 1). Also interesting is the correlation between overall selectivity to pyridines (S_P) and surface acidity, the best catalysts being those whose concentration of surface acid centers was higher than 0.02 mmol g^{-1}, for acid strength up to pK_a +4.0, and 0.03 for acid strength up to +4.8 (Fig. 2).

The conclusions from this preliminary study are, first, that a catalyst for the direct ammoxidation of propylene to pyridines should contain (a) oxidizing centers, in the present case based on Te oxide, preferably promoted by Sb oxide, in order to favor a preliminary oxidation of the olefin to an intermediate, probably an aldehyde, and (b) acid centers, in the present case based on silica–alumina, in order to favor the cyclization with ammonia of the intermediate to the pyridine ring. This is supported by the fact that present pyridine synthesis processes from aldehydes and ammonia make use of high surface acidity catalysts (*1*). Second, as regards the preparation of the catalyst, the conditions should be those favoring the formation of a solid of the highest possible concentration of surface acid centers, at least of those of up to ca +4.8 pK_a strength.

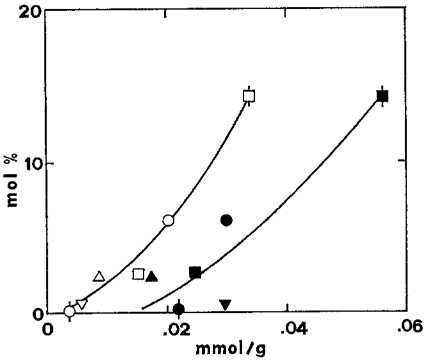

FIG. 2. Initial selectivity to pyridines vs catalyst surface acidity. Open symbols (as in Fig. 1), pK_a + 4.0; solid symbols, pK_a + 4.8.

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