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Catalytic Dehydrogenation of Alkylpyridines

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The selective dehydrogenation of 2-ethyl-3,5-dimethylpyridine to 2-vinyl-3,5-dimethylpyridine can be accomplished with calcium nickel phosphate or aluminum nickel phosphate catalyst (95% selectivity at 22% conversion). Increasing conversion results in lower selectivity due to dealkylation and cracking. The behavior of various catalysts in the dehydrogenation of alkylpyridines follows a different pattern from that with alkyl aromatics or olefins.

INTRODUCTION

An improved synthesis of alkylpyridines has recently become available (*1*), based on the reaction of aldehydes and ammonia over selective catalysts. The product from propanal, 2-ethyl-3,5-dimethylpyridine, is of particular interest, since its synthesis can be based on the inexpensive raw materials: ethylene, synthesis gas, and ammonia. We have investigated the conversion of this pyridine to the corresponding 2-vinyl-3,5-dimethylpyridine in a number of dehydrogenation systems.

The literature on dehydrogenation of alkylpyridines is restricted almost exclusively to patents (*2*). The use of chromia-alumina catalyst has been described (*3*, *4*), but the selectivity was either low or not reported. Cislak (*5*) has disclosed the use of tungsten oxide, vanadium pentoxide, and ceric oxide, but no data are given. 2-Methyl-5-ethylpyridine was dehydrogenated to the corresponding vinylpyridine with calcium oxide–magnesium oxide in 73% selectivity at 39% conversion (*6*). Promoted zinc oxide catalysts have also been patented (*7*, *8*); 2-methyl-5-vinylpyridine was obtained in 88% selectivity at 52% conversion (*8*). The use of promoted iron oxide dehydrogenation catalysts has been frequently reported in the patent literature (*9–11*). With 2-methyl-5-ethylpyridine, a catalyst containing 93% Fe_2O_3, 5% Cr_2O_3, and 2% KOH gave a selectivity of 78% at 43% conversion (*9*), while 5% Fe_2O_3, 43% Cr_2O_3, and 52% K_2CO_3 gave 89% selectivity at 43% conversion (*11*). Very good selectivities (90–100%) at low conversions (12–30%) were reported for the dehydrogenation of 2- and 4-ethylpyridine with calcium cobaltous phosphate (*12*). There are, therefore, several reports of good results in the literature, but when these processes were applied to 2-ethyl-3,5-dimethylpyridine, quite low selectivities were obtained. A broader investigation of the deyhdrogenation of this pyridine was therefore initiated.

EXPERIMENTAL

Except where noted, the reactions were carried out in a fixed-bed (catalyst particle diameter 1–2 mm) quartz reactor (about 50-ml volume) heated in a cylindrical oven. With the steam dilution catalysts a preheater was used consisting of an identical reactor filled with quartz chips. Liquid feeds were fed with motor-driven syringe pumps and gaseous feeds with

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calibrated rotameters. Products were condensed (usually at 0°C) and the liquid product analyzed by gas-liquid chromatography. Hydroquinone or 4,4′-methylenebis(2,6- di-*tert*-butylphenol) was used as stabilizer for the vinylpyridines.

The 2-ethyl-3,5-dimethylpyridine was made (*1*) from propanal and ammonia over cobalt aluminum phosphate. For some of the experiments, the fractionated pyridine contained about 5% of a ketone impurity, 2-ethyl-3,5-dimethyl-2-cyclopenten-1-one, an aldol condensation product from the propanal. For dehydrogenation, it is not necessary to remove this ketone, since it is quantitatively converted to gaseous products by the catalyst, even at low pyridine conversions. Experiments indicated it did not affect the activity, selectivity, or stability of the catalyst.

Products were identified by elemental analyses and spectroscopy (mass, NMR, IR).

The catalysts were prepared in the usual ways or following directions given in the literature. The calcium nickel phosphate was prepared as follows: 2.0 moles of $(NH_4)_2HPO_4$ was dissolved in 2 liters of water and a solutions of 1.75 moles of $Ca(NO_3)_2$ and 0.25 moles of $Ni(NO_3)_2$ in 2 liters of water slowly added, with stirring, and the pH maintained at 8 with aqueous ammonia. The precipitate was filtered and washed with 9 liters of water, dried 2 hr at 115°C, calcined in air for 2 hr at 500°C, crushed, and sieved to size (1–2 mm diameter). The aluminum nickel phosphate was prepared in an analogous way.

NORMAL DEHYDROGENATION CATALYSTS

By this term we mean those catalysts which are used for dehydrogenation without the aid of oxidation or self-regeneration reagents.

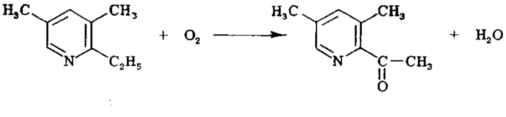
Chromium oxide on alumina is widely used as a dehydrogenation catalyst. We used a coprecipitated catalyst containing 20% Cr_2O_3. Since the reaction is equilibrium-limited, various diluents (helium, nitrogen, benzene) were used. In all cases, selectivity was low due to dealkylation and cracking. At 575°C, GHSV* = 930, 14% pyridine in feed, conversion was 50% and selectivity to 2-vinyl-3,5-dimethylpyridine was 31%. Lower conversion did not substantially increase selectivity. When hydrogen was used as the diluent, no vinylpyridine was formed and appreciable (32% selectivity at 48% conversion) amounts of 2,3,5-trimethylpyridine were produced. Platinum catalysts are also frequently used for dehydrogenation. Hydrogen diluent is required to prevent excessively rapid decline of activity. When 2-ethyl-3,5-dimethylpyridine (EDP) (4% in H_2, GHSV = 2100) was passed over 2% Pt/SiO_2 at 500°C, selectivity to vinylpyridine was only 20% at 10% conversion. Lower amounts (50%) of hydrogen diluent did not increase selectivity.

A catalyst containing 4% CoO, 10% MoO_3, and 1% K_2O on alumina was also examined. At 600°C, 90% N_2, GHSV = 375, selectivity to the vinylpyridine was only 30% at 54% conversion. Other conditions did not increase this selectivity. When hydrogen was used, no vinylpyridine was formed and increased amounts of 2,3,5-trimethylpyridine were made.

It thus appears that normal dehydrogenation catalysts will not give good selectivity for this reaction, primarily due to dealkylation and cracking.

OXIDATIVE DEHYDROGENATION

The use of certain catalysts with molecular oxygen gives very good results for the oxidative dehydrogenation of butylene to butadiene (*13–15*). Several of these catalysts were examined with EDP. Some typical results are shown in Table 1. The 2-vinyl-3,5-dimethylpyridine is made in only fair selectivity (maximum of 46%). A surprising result is that a ketone, 2-aceto-3,5-dimethylpyridine, is made in appreciable



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* Gas hour space velocity = gas volumes of total feed (calculated at 0°C and 1 atm) per bulk volume of catalyst per hour.

TABLE 1

OXIDATION OF 2-ETHYL-3,5-DIMETHYLPYRIDINE WITH OXYGEN

Temp. (°C)	GHSV	Pyridine conversion (%)	Selectivity (%)	
			2-Vinyl	2-Aceto
	Bismuth Molybdate			
250	50	25	28	32
300	100	51	15	33
350	240	66	29	10
450	240	40	36	4
500	1630	55	18	1
	Bismuth Tungstate			
250	40	34	6	40
450	250	33	46	14
	Bismuth Phosphate			
300	240	24	44	17
450	1000	49	32	0
	Cobalt Molybdate			
450	4000	40	37	0

amounts at low temperatures. The kinetic results are not clear, but the ketone may possibly be formed from the vinyl compound, rather than a primary product from the ethylpyridine. This is the first time that a ketone has been made with this type of catalytic oxidation.

DEHYDROGENATION WITH STEAM DILUTION

A widely used method of catalytic dehydrogenation involves high dilution with steam, in which the steam reacts with any coke deposited on the catalyst to form CO_2 and H_2. Current commercial production of styrene uses Shell 105 catalyst, an iron oxide promoted with about 5% each of Cr_2O_3 and K_2CO_3. However, when 2-ethyl-3,5-dimethylpyridine and water were fed over this catalyst, only low selectivities to the vinylpyridine were obtained (36% selectivity at 36% conversion at 600°C). Furthermore, when various mixtures of EDP and ethylbenzene were fed, the presence of the pyridine very severely inhibited the dehydrogenation of the ethylbenzene.

One of the best catalysts reported in the literature for the dehydrogenation of 2-methyl-5-ethylpyridine is a promoted zinc oxide (*8*). However, when EDP was dehydrogenated over this catalyst (60% ZnO, 14% CaO, 7% Al_2O_3, 2% Cr_2O_3, 2% K_2O) at 600°C and pyr:H_2O = 20:1, the selectivity was only fair and decreased rapidly with increasing conversion:

Pyridine conversion	24	34	44
Vinyl selectivity	57	41	26

Calcium cobaltous phosphate is also reported (*12*) to be a good catalyst for the dehydrogenation of 2- and 4-ethylpyridine, but when 2-ethyl-3,5-dimethylpyridine and steam were passed over this catalyst dealkylation to 3,5-dimethylpyridine was extensive and only low yields of the vinyl compound were obtained.

Calcium nickel phosphate is a known steam dilution catalyst for *n*-butene to butene and butadiene (*16, 17*). It was tried for the dehydrogenation of 2-ethyl-3,5-dimethylpyridine and found to give good selectivity at low conversion (Fig. 1); 91% selectivity at 14% conversion or 80% selectivity at 24% conversion was obtained, but the selectivity drops off rapidly with increasing conversion, due to increased dealkylation and formation of high-boiling products and polymer (Table 2). Aluminum nickel phosphate $AlNi(PO_4)_x$ was found to be equally effective while cobalt aluminum phosphate, $Co_3Al_3(PO_4)_x$, gave somewhat lower selectivity at lower conversions (Fig. 1). These data were obtained at 600°C EDP:H_2O = 1:20 molar. Figure 2

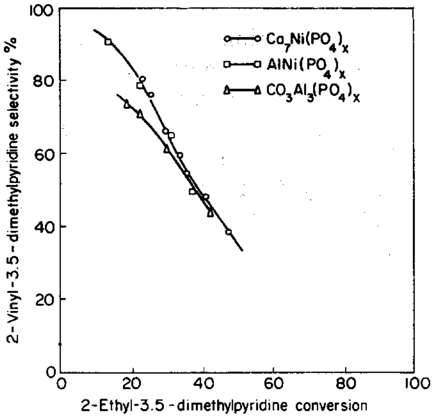

FIG. 1. Dehydrogenation of 2-ethyl-3,5-dimethylpyridine: 600°C; atmospheric pressure; EDP:H_2O = 1:20.

TABLE 2
PRODUCT DISTRIBUTION FOR THE DEHYDROGENATION OF 2-ETHYL-3,5-DIMETHYLPYRIDINE[a]

GHSV: Pyridine conversion %:	1100 24	480 41
	Selectivity (%)	
2-Vinyl-3,5-dimethylpyridine	80	48
2,3,5-Trimethylpyridine	11	16
3,5-Dimethylpyridine	6	4
High-boiling (>230°C, several unidentified products by GLC)	3	16
Nonvolatile products	—	16

[a] $Ca_7Ni(PO_4)_x$; 600°C; EDP:H_2O = 1:20.

shows that substantially better results are obtained at somewhat higher temperatures; 650°C gave 74% selectivity at 40% conversion. Increasing the temperature to 675°C gave no further increase in selectivity, nor did further dilution with steam (Fig. 2).

Normal operation of calcium nickel phosphate for butylene dehydrogenation involves frequent (approximately in a 30-min cycle) regeneration with air. After an initial drop in the first 2 hr, we have found activity to be constant for periods up to 18 hr (Fig. 3). Long-term studies would be required to tell whether regeneration is necessary. However, inadvertently coked catalyst has been air-regenerated with no difficulty. It has been found (*16*, *17*) that a small amount of chromium oxide is beneficial for the long-term activity of the catalyst in butylene dehydrogenation. A calcium nickel phosphate containing 2% Cr_2O_3 was prepared and the results showed that the chromium oxide is not detrimental to the selectivity.

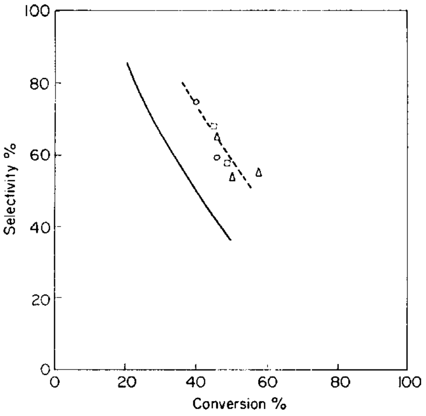

FIG. 2. Dehydrogenation of EDP with $Ca_7Ni(PO_4)_x$: —, 600°C, EDP:H_2O = 1:20; ○, 650°C, EDP:H_2O = 1:20; □, 675°C, EDP:H_2O = 1:20; △, 650°C, EDP:H_2O = 1:50.

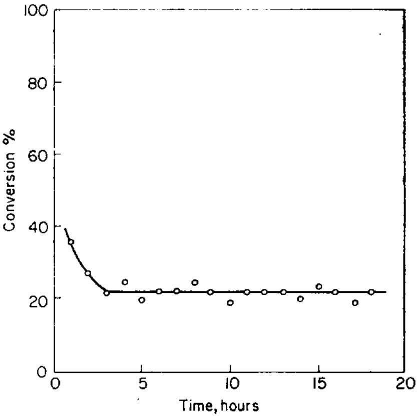

FIG. 3. Catalyst activity with time in dehydrogenation of EDP: regenerated $Ca_7Ni(PO_4)_x$ catalyst; 625°C; GHSV = 2400; EDP:H_2O = 1:20.

The results described above were obtained in a small (40 ml of catalyst) glass reactor. The reaction was also carried out in a larger (800 ml catalyst, 1 m long) stainless steel reactor. Some typical results are given in Table 3 and Fig. 4. After the first half hour, the activity is constant for 3 hr and the selectivity is better than that

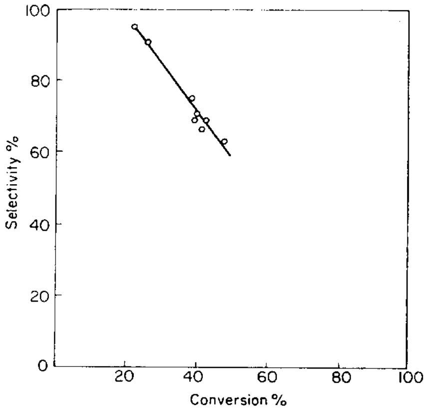

FIG. 4. Dehydrogenation of EDP with $Ca_7Ni(PO_4)_x$ in large stainless steel reactor; data from Table 3.

TABLE 3

Dehydrogenation of 2-Ethyl-3,5-dimethylpyridine in a Stainless Steel Reactor[a]

	GHSV = 3200		GHSV = 1400					
Time (hr)	0.3	0.7	0.5	1.0	1.5	2.0	2.5	3.0
EDP conversion (%)	26	22	48	39	43	41	39	40
Selectivity (%)								
Vinyl DP	91	95	63	75	69	66	69	70
2,3,5-Collidine	6	3	13	13	15	12	10	13
3, 5-Lutidine	—	—	11	10	9	8	11	6

[a] Reactor, 1 m long; $Ca_7Ni(PO_4)_x$, 800 ml, 475 g; 1 – 2 mm particle diameter; EDP:H_2O = 1:20 molar, 580–630°C.

obtained in the small glass reactor at 600°C and equal to that obtained at 650°C (compare with Fig. 2).

2-Methyl-5-ethylpyridine was also dehydrogenated with calcium nickel phosphate with good results. At 650°C and 5 mole % pyridine and 95% H_2O, 78% selectivity to 2-methyl-5-vinylpyridine at 33% conversion was obtained at 2400 GHSV, while 400 GHSV gave 58% selectivity at 70% conversion.

Discussion

These results show that 2-ethyl-3,5-dimethylpyridine can be dehydrogenated to 2-vinyl-3,5-dimethylpyridine in good selectivity with calcium nickel phosphate or aluminum nickel phosphate. Similar to certain other dehydrogenation processes, the single-pass conversion must be restricted to prevent degradation of the product. The structure of the alkylpyridine is also important since catalysts reported to be selective for other alkylpyridines gave poor selectivity with 2-ethyl-3,5-dimethylpyridine.

The dehydrogenation of alkylpyridines follows a different behavior with various catalysts as compared to the dehydrogenation of olefins or alkyl aromatics. Some catalyst systems which give good results for these latter two materials give very poor results with alkylpyridines. The obverse is also true. Aluminum nickel phosphate and cobalt aluminum phosphate, both of which give good results with 2-ethyl-3,5-dimethylpyridine, were examined for the dehydrogenation of ethylbenzene and both were very inactive and unselective. Table 4 gives a comparison of various catalysts for the dehydrogenation of ethylbenzene and of 2-ethyl-3,5-dimethylpyridine. It is quite ap-

TABLE 4

Comparison of Various Catalysts for the Dehydrogenation of Ethylbenzene and 2-Ethyl-3,5-dimethylpyridine[a]

Catalyst	Ethylbenzene	Ethyllutidine
Chromia-alumina	Good A Good S	Fair A Very poor S
Iron oxide	Good A Good S	Poor A Poor S Severe inhibition
Calcium nickel phosphate	Good A Good S	Good A Good S
Aluminum nickel phosphate	Very poor A Fair S	Good A Good S
Cobalt aluminum phosphate	Very poorA Fair S	Good A Good S

[a] Activity is indicated by A and S means selectivity.

parent that the two types of compounds behave entirely differently in several dehydrogenation systems.

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