JOURNAL OF CATALYSIS **107**, 240–243 (1987)

NOTES

Indole Formation from *N*-Ethylaniline over a Poly(platinum phthalocyanine) Catalyst

1. INTRODUCTION

The syntheses, structures, and properties of poly(metal phthalocyanines) (Poly-*M*-Pcs) which possess a further expanded conjugated planar ring of metal phthalocyanine have been studied in recent years (*1*). Especially, Poly-*M*-Pcs as catalysts are expected to possess specific activities similar to those of metal phthalocyanines. However, few studies (*2*) have been carried out except for those on the oxidation in a liquid phase (*3–5*).

In the previous paper (*6*), dehydrocyclization of *o*-ethylaniline in a vapor phase was carried out over a poly(platinum phthalocyanine) catalyst (Poly-Pt-Pc) in a stream of hydrogen, and indole was obtained. The reaction mechanism and the role of hydrogen gas in the reaction were discussed in the paper. However, only a few studies have succeeded in the formation of heterocyclic compounds by the intramolecular dehydrocyclization of compounds containing a nitrogen atom in a chain such as diethylamine, *N*-ethylaniline, and diphenylamine (*7–10*).

In this work, the formation of indole from *N*-ethylaniline was tried over Poly-Pt-Pc, and indole was obtained in good yield, although the yield of aniline by hydrogenolysis exceeded that of indole. Thus the experiments were carried out under various conditions.

2. EXPERIMENTAL

Poly-Pt-Pc used as a catalyst was prepared according to the method of Epstein *et al.* (*11, 12*). Pyromellitonitrile (15.0 g) and $PtCl_2$ (11.2 g) were mixed, and urea (1.0 g) was added and ground sufficiently. Then, the mixture was heated at 310°C in a stream of nitrogen for 18 hr and heated at 360°C for 6 hr. In order to remove the monomer and oligomer, the resulting solid was ground and extracted with boiling pyridine using a Soxhlet extractor until the greenish color of the extract faded out. The residue was washed with acetone to remove the pyridine and then dried at 350°C for 3 hr *in vacuo*. Other Poly-*M*-Pcs (*M* is a central metal) were prepared from pyromellitonitrile and corresponding anhydrous metal chlorides in a preparation similar to that of Poly-Pt-Pc.

This Poly-Pt-Pc was a purplish black amorphous solid and was not dissolved in any organic solvents (*1, 12*). The molecular weight of the product may be large because of the removal of the monomer and oligomer with boiling pyridine. IR spectra were measured with a Hitachi 260-50 IR spectrophotometer using a KBr disk. The absorption spectra observed at about 1615, 1510, 1390, 1310, 1115, 910, and 755 cm^{-1} were broad. The data of elementary analysis (C, 41.6; H, 0.53; N, 19.4) were close to the values of polymer $(M(C_6H_2(CN)_4)_2)_n$. These two results also indicate that this catalyst was polymer (*12*). Differential thermal analysis (DTA) of Poly-Pt-PC was measured under hydrogen gas using a DTA-20B (Shimadzu Co.). The result showed that neither decomposition nor variation of the catalyst occurred at less than 550°C.

Commercially available Pt-black and Pt-supported catalysts were used for the comparison. *N*-Ethylaniline was distilled under reduced pressure for purification before use.

The reaction was carried out with an ordinary fixed bed flow reactor under atmospheric pressure in a stream of hydrogen or

0021-9517/87 $3.00

nitrogen as carrier gas. The catalyst was pretreated for 30 min in the same carrier gas and at the same temperature just before the initiation of the reaction. The raw material was fed into a reaction tube with a microfeeder, and the products were trapped in a flask cooled with ice water.

The identification of products was carried out using a GC-MS (GCMS-QP1000, Shimadzu Co.). The products were quantitatively analyzed by a gas chromatograph with a TCD on the column packed with Silicone DC-550 at 200°C in helium carrier gas. These determinations were carried out by an internal standard method with anisole.

3. RESULTS AND DISCUSSION

The catalytic activities of five Poly-*M*-Pcs containing the group VIII elements as central metals, Pt-black, and Pt-supported catalysts are listed in Table 1. Here, the amounts of catalysts used in this experiment were as follows: each Poly-*M*-Pc was equal in weight, the weight of Pt-black was equal to that of the Pt contained in Poly-Pt-Pc, the weight of each Pt-supported catalyst was equal to that used for the reaction of *o*-ethylaniline (6), and the yield of indole over Pt-supported catalysts was comparable to that over Poly-Pt-Pc. The result showed that the Poly-Pt-Pc was the best catalyst of the Poly-*M*-Pcs with respect to the yield of indole and the formation ratio of indole/aniline. In the case of Pt-black and Pt-supported catalysts, Pt-black and Pt-SiO_2 showed a higher indole/aniline ratio than Poly-Pt-Pc, but the yield of indole was low.

TABLE 1

Catalytic Activities of Various Catalysts[a]

Catalyst[b]	Contact time (g cat · hr/mol)	Yield (mol%)		$\frac{\text{Indole}}{\text{Aniline}}$ ratio
		Aniline	Indole	
Poly-Co-Pc	5.765	19.34	2.28	0.118
Poly-Ni-Pc	5.765	24.80	2.29	0.092
Poly-Rh-Pc	5.765	17.05	1.69	0.099
Poly-Pd-Pc	5.765	12.69	0.75	0.059
Poly-Pt-Pc	5.765	33.60	10.90	0.325
Pt-black	2.306	0.94	0.53	0.562
Pt-Al_2O_3	1.729	35.44	3.03	0.086
Pt-carbon	1.729	17.02	1.28	0.075
Pt-SiO_2	1.729	6.02	2.03	0.338
Pt-TiO_2	1.729	10.69	0.29	0.027

[a] Reaction temperature, 500°C: partial pressure of raw material, 0.08 atm; carrier gas, H_2.

[b] Each Pt-supported catalyst contains 5% of Pt by weight.

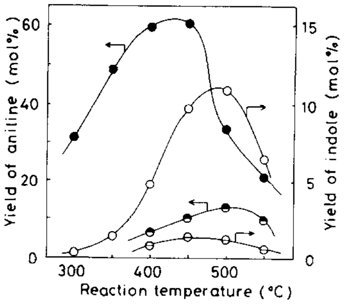


FIG. 1. Effect of reaction temperature. Yields of aniline (●) and indole (○) in H_2, and yields of aniline (◓) and indole (⊖) in N_2. Catalyst, Poly-Pt-Pc; contact time, 5.765 g cat · hr/mol; partial pressure of raw material, 0.08 atm.

Figure 1 shows the effect of reaction temperature on the yields of indole and aniline in hydrogen or nitrogen gas when Poly-Pt-Pc, with superior activity and selectivity, was used as a catalyst. The maximum yield of each case was obtained from about 400 to 500°C, and the yields decreased above these temperatures. The for-

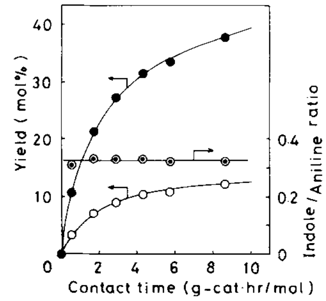


FIG. 2. Effect of contact time. Yield of aniline (●). Yield of indole (○). Indole/aniline ratio (⊙). Catalyst, Poly-Pt-Pc; reaction temperature, 500°C; partial pressure of raw material, 0.08 atm; carrier gas, H_2.

mation ratio of indole/aniline in hydrogen gas was a maximum at 500°C.

The effect of contact time on the reaction over Poly-Pt-Pc in hydrogen gas is shown in Fig. 2. In the case of no catalyst, aniline was scarcely formed and indole was not formed. The result showed that the catalyst was necessary for the progress of the reaction. Since the yield of aniline or indole indicated the typical curves observed over solid catalysts by a flow method, and the indole/aniline ratio was independent of contact time, the formation of indole and aniline appeared to occur without passing through stable free intermediates.

The time dependence of the yields over Poly-Pt-Pc is shown on the left side of Fig. 3. The yields were found to decrease with the passage of time on stream. Especially, though the decrease in yields was relatively small at 500°C, in a stream of hydrogen; it was larger in a stream of nitrogen.

The right side of Fig. 3 shows the restoration of catalytic activity due to feeding only hydrogen gas on the catalyst without reaction for an hour interval after 3 hr of reaction at 500°C in hydrogen gas. The initial yields of this reaction after the hydrogen treatment exceeded those just before the treatment. Especially, in the case of indole, the initial yield after the treatment was restored to the level at the beginning of the reaction.

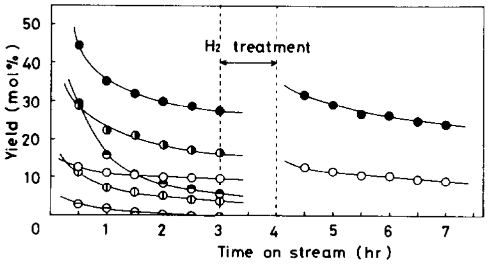
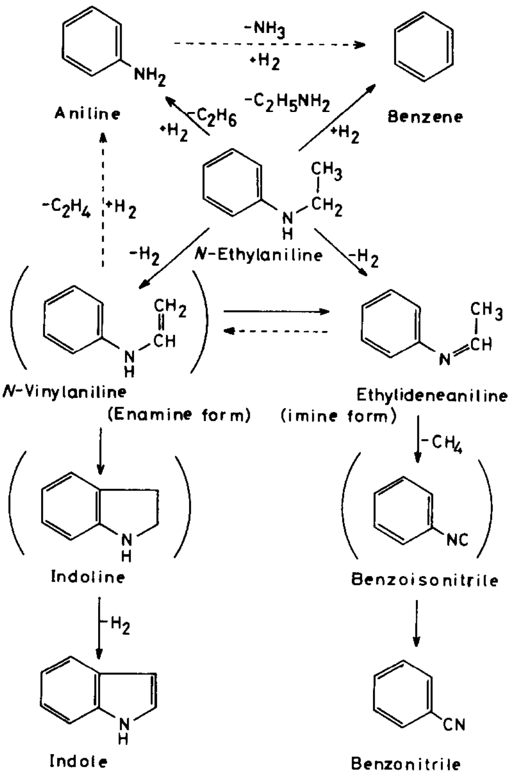


FIG. 3. Time dependence of the reaction and restoration of activity by hydrogen treatment. Yields of aniline (●) and indole (○) at 500°C, and yields of aniline (◓) and indole (⦶) at 550°C in H_2. Yields of aniline (◒) and indole (⊖) at 500°C in N_2. Catalyst, Poly-Pt-Pc; contact time, 5.765 g cat · hr/mol; partial pressure of raw material, 0.08 atm.

These facts probably suggest that hydrogen prevents the deposition of some chemical species which are difficult to remove from the catalyst during the reaction, such as the high-molecular-weight compounds formed by the reactions among more than two molecules, or the substances strongly adsorbed on the catalyst, and hydrogen makes active sites clean. Further, since the activity of the catalyst in hydrogen gas was much higher than that in nitrogen gas, as shown in Figs. 1 and 3, it is also suggested that the atomic hydrogen, which is made by the dissociation of hydrogen molecule on the catalyst, eliminates a hydrogen atom from the reactant and also assists in desorbing the products from the catalyst (*13*).

Finally, the products identified by GC-MS showed that benzene, benzonitrile, and ethylideneaniline were formed in addition to indole and aniline. Thus, aniline and benzene are probably formed by hydrogenolysis of *N*-ethylaniline, indole is formed by dehydrocyclization, and ethylideneaniline is formed by dehydrogenation of *N*-ethylaniline. Further, benzonitrile appears to be formed by demethanation of ethylideneaniline and rearrangement (*14*). But ethylideneaniline may not be an intermediate to indole, since Fig. 2 shows that the formation of indole seems to proceed without passing through stable intermediates.

In order to explain the reaction path to indole, it may be suitable to propose that an *N*-vinylaniline-form adsorbate is an intermediate state (*15–17*). This enamine-form adsorbate is immediately converted to ethylideneaniline in a free state. However, it is considered stable in the adsorbed state on the catalyst and converted to indole, and it seems that the electron transfer between a nitrogen atom in the adsorbate and Pt^{2+} of Poly-Pt-Pc by the coordination stabilizes the enamine form and accelerates the cyclization (*13*). The adsorbate appears not to be formed via ethylideneaniline, but formed



SCHEME 1. Reaction path from *N*-ethylaniline. Species in parentheses, which were not detected by analysis, are presumed compounds and adsorbates. The paths represented by dashed line are minor ones.

directly from *N*-ethylaniline. Indolines may be intermediates but were not detected by analysis. They are considered unstable under this experimental condition and immediately converted to indole.

Based on the above-mentioned matter, the reaction path is illustrated in Scheme 1.

REFERENCES

1. Wöhrle, D., *Adv. Polym. Sci.* **50,** 45 (1983).
2. Naito, S., and Tamari, K., *Z. Phys. Chem.* **94,** 150 (1975).
3. Hara, T., Ohkatsu, Y., and Osa, T., *Chem. Lett.*, 103 (1973).
4. Hara, T., Ohkatsu, Y., and Osa, T., *Bull. Chem. Soc. Japan* **50,** 696 (1977).
5. Ohkatsu, Y., Sekiguchi, O., and Osa, T., *Bull. Chem. Soc. Japan* **50,** 701 (1977).
6. Takamiya, N., Furuhata, K., and Onikubo, T., *Bull. Sci. Eng. Res. Lab., Waseda Univ.* **114,** 71 (1986).
7. Bell, W. H., and Rennie, R. A. C., *Brit.* **1,** 184, 242 (1970).
8. Polyakov, A. P., Erivanskaya, L. A., Fedotova, A. V., and Shuikin, N. I., *Vestn. Mosk. Univ. Ser. 2* **21,** 92 (1966). (C.A. 66-75827w)
9. Bragin, O. V., Preobrazhenskii, A. V., and Liberman, A. L., *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 2406 (1967). (C.A. 68-95414d)
10. Naito, M., Murayama, K., and Matsumoto, M., *Aromatikkusu* **32,** 39 (1980).
11. Epstein, A., and Wildi, B. S., *J. Chem. Phys.* **32,** 324 (1960).
12. Hara, T., Ohkatsu, Y., and Osa, T., *Bull. Chem. Soc. Japan* **48,** 85 (1975).
13. Mochida, I., Miyaishi, T., Goshi, H., Fujitsu, H., and Takeshita, K., *Appl. Catal.* **7,** 199 (1983).
14. Nagiev, T. M., Mamed'yarov, G. M., Kasimov, R. M., Mamedov, E. M., and Salakhov, V. A., *Azerb. Khim. Zh.*, 20 (1978). (C.A. 91-20077n)
15. Hickmott, R. W., *Tetrahedron* **38,** 3363 (1982).
16. Chapman, O. L., Eian, G. L., Bloom, A., and Clardy, J., *J. Amer. Chem. Soc.* **93,** 2918 (1971).
17. Wolff, T., and Waffenschmidt, R., *J. Amer. Chem. Soc.* **102,** 6098 (1980).

TOSHIKAZU ONIKUBO
NOBUKATSU NEMOTO
KOJI IKEDA
NOBUO TAKAMIYA

Department of Chemistry
Waseda University
3-4-1 Ohkubo, Shinjuku-ku,
Tokyo 160, Japan

Received October 23, 1986; revised April 8, 1987