

NOTES

Effect of Surface Acidity on Alcohol Dehydration Catalysis by Pyrolyzed Polyacrylonitrile

INTRODUCTION

The development of heat-stable polymers has promoted investigations into the use of these new materials as heterogeneous catalysts. Recent reviews have been given by Cutlip (1), Roginski (2), Hanke (3), and Manassen (4).

Pyrolyzed polyacrylonitrile has received much evaluation with respect to its catalytic activity. The first work by Topchiev (5) determined that this polymer catalytically decomposed hydrogen peroxide. Subsequent researchers have studied the dehydrogenation and dehydration of alcohols, the isomerization of olefins, and the decomposition of formic acid and nitrous oxide.

Explanation of the catalytic activity of pyrolyzed polyacrylonitrile has been based on the quinoid structure unit by Manassen (6, 7) for dehydrogenation catalysis and on the presence of unpaired electrons by Gallard *et al.* (8, 9) for nitrous oxide decomposition.

Cutlip (10) has made detailed rate measurements on tertiary butyl alcohol dehydration over pyrolyzed polyacrylonitrile. A differential reactor was used to show that both reaction products, isobutylene and water, reduced the reaction rate. It was concluded that the adsorption of both products must be included in any reaction mechanism.

The work reported here concerns how the acidity of this polymer catalyst affects the rate of the dehydration of tertiary butyl alcohol.

EXPERIMENTAL

Catalyst preparation. The polyacrylonitrile was polymerized in water solution from acrylonitrile monomer and heat treated in air and nitrogen according to the procedure given by Cutlip (10). The resulting pyrolyzed material had a surface area of 15.2 m²/g as measured by nitrogen adsorption.

Catalyst impregnation. Aqueous 0.1*N* sodium hydroxide was used to impregnate 1/16-in. catalyst

particles with the desired concentration of base. This process was accelerated with an ultrasonic bath which provided intense agitation for the beaker containing the catalyst and base. The pH was regularly noted by stopping the agitation and introducing electrodes into the catalyst slurry. Impregnation was considered to be complete when the pH reached 8.5 or less.

Experimental reactor system. The reactor and on-line gas chromatograph system were similar to those described by Cutlip (10). A fluidized sand bath was used to control the reactor at 250°C. Reactor pressure was maintained slightly above atmospheric so that reactant and product analysis could be obtained with a gas chromatograph equipped with a heated gas-sampling valve.

Reaction rate measurement. Feed to the reactor consisted of pure alcohol; thus, the reaction rate was calculated from the product analysis, the alcohol feed rate, and the catalyst weight. Conversion was kept below 10% to maintain the reactant concentration nearly constant. All reaction rates were corrected to an average reactant pressure of 1 atm by assuming first-order kinetics.

RESULTS AND DISCUSSION

The calculated rate of dehydration is plotted against time from the start of the alcohol feed in Fig. 1. Curves II-VII represent data for the polymer catalyst which had undergone impregnation with various amounts of aqueous sodium hydroxide. A nitrogen atmosphere was maintained in the reactor until initial time when the alcohol feed was started. Deactivation with time occurred for the more active catalyst, but the activity did attain a constant value. This observed deactivation could possibly be a result of polymerization of isobutylene on some of the more acidic active sites.

Curve I of Fig. 1 is for a batch of fresh catalyst which did not undergo ultrasonic agitation.

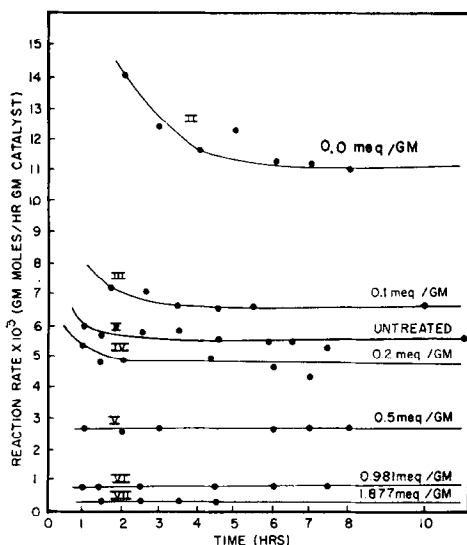


Fig. 1. Experimental reaction rate vs time.

The reaction rate for this catalyst sample was considerably less than for the fresh catalyst which was agitated with distilled water indicated by Curve II. The catalyst surface area increased upon agitation with water from 15.2 m²/g to 18.8 m²/g. This increase in surface area is not sufficient to account for the higher activity of the agitated catalyst. This indicates that the scrubbing and solvent action of the water may have removed some of the pyrolysis by-products

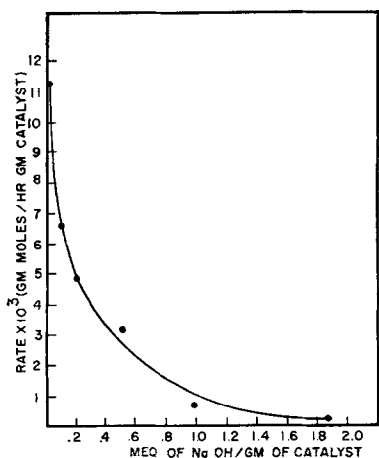


Fig. 2. Constant reaction rate vs amount of impregnated NaOH.

which covered a portion of the catalytically active surface. The surface area for the catalyst containing the maximum NaOH remained equal to that of the water-agitated sample.

Figure 2 shows the constant rate data as a function of the amount of base impregnated. For example, 0.981 meq of base per gram of catalyst decreased the rate to 7% of that of the untreated catalyst. This nonlinear decrease of catalyst activity indicates that the rate of reaction depends upon either the acid strength distribution of the catalyst or a multiple site mechanism.

These results indicate that the catalytic activity of pyrolyzed polyacrylonitrile for alcohol dehydration is probably due to the acidity of this polymer catalyst. The exact nature of these acidic sites remains unknown because of the yet uncertain structure of this pyrolyzed polymer.

REFERENCES

- CUTLIP, M. B., Ph.D. thesis, Univ. Colorado, Boulder, CO (1968).
- ROGINSKI, S. Z., AND SAKHAROV, M. M., *Zh. Fiz. Khim.* **42**, 1331 (1968).
- HANKE, W., *Z. Chem.* **9**, 1 (1969).
- MANASSEN, J., *Chim. Ind. (Milan)* **51**, 1058 (1969).
- TOPCHIEV, A. V., GEJDERIKH, M. A., DAUYDOV, B. E., KARGIN, V. A., KRENTSEL, B. A., KUSTANOVICH, M., AND POLAK, L. S., *Dokl. Akad. Nauk SSSR* **128**, 312 (1959).
- MANASSEN, J., AND WALLACH, J., *J. Amer. Chem. Soc.* **87**, 2671 (1965).
- MANASSEN, J., AND KHALIF, SH., *J. Amer. Chem. Soc.* **88**, 1943 (1966).
- GALLARD, J., NECHTSCHIEIN, M., SOUTIF, M., AND TRAYNARD, P., *Bull. Soc. Chim. Fr.* **10**, 2210 (1963).
- GALLARD, J., SALLE, R., TRAYNARD, P., AND TEYSSIE, P., "Proceedings of the Third International Congress on Catalysis," Vol. 2, p. 966. Wiley, New York, 1965.
- CUTLIP, M. B., AND PETERS, M. S., *Chem. Eng. Prog. Symp. Ser.* **64**, 1 (1968).

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