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NOTES

Reaction of Phosphomolybdic Acid with Acrolein

Phosphomolybdic acid is one of the excellent catalysts for the synthesis of acrylic acid from acrolein and oxygen (*1, 2*), and acrylic acid is also formed by the reaction of acrolein with phosphomolybdic acid (*2*). In this note the reaction of phosphomolybdic acid with acrolein is investigated with a gas chromatographic pulse technique (*3*) to elucidate the catalysis of acrolein to acrylic acid.

EXPERIMENTAL

The apparatus consists essentially of a gas chromatograph and a microreactor which is inserted between a sample inlet and a chromatographic column of the former. The gas chromatograph was a Model 2B of Simazu Seisakusho Ltd. The microreactor was a U tube of glass with an inside diameter of 4 mm.

Phosphomolybdic acid of a guaranteed grade reagent was kneaded with a small amount of water, dried at 110°C, pulverized into ~32–50 mesh, and heat-treated at 540°C for 3 hr in an electric furnace. Acrolein of an industrial grade reagent was purified with a fractional distillation.

RESULTS

The reactor was charged with 1 g of phosphomolybdic acid, which was treated in a stream of air at 500°C for 20 min, and a sequence of 5-μl liquid acrolein slugs were injected into the reactor at 500°C with a stream of nitrogen or helium of 36 ml (NTP)/min in flow rate at intervals of 8 min. The amounts of acrylic acid and effluent acrolein were estimated. The results are shown in Fig. 1. The amounts of acrylic acid and effluent acrolein changed stepwise as at A, B, C, D, and E. After treatment with air for 30 min the experiment was repeated. The amounts of acrylic acid in the slugs after the treatment with

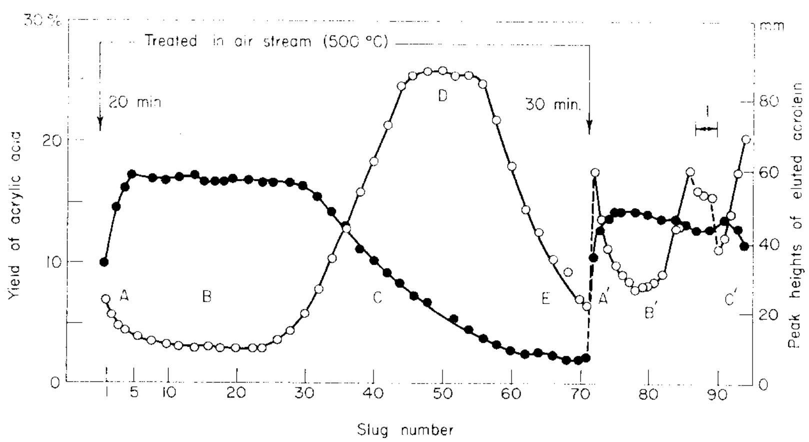

FIG. 1. Acrylic acid and effluent acrolein. Temperature, 500°C. Acrylic acid, ○; effluent acrolein, ●; *1, an air slug (10 ml) was injected 1 min before each acrolein slug.

air were about two times higher than those of corresponding slugs of a fresh specimen, although the duration of each step after the treatment was shorter than that of a fresh specimen. The amount of carbon dioxide was estimated in a separate run under the same conditions, and it changed stepwise in the same manner as that of acrylic acid.

Slugs of air of 10 ml were injected 1 min before the injection of several acrolein slugs in steps A, B, and C. In step A the injection of air interrupted the decrease of amounts of acrylic acid and carbon dioxide, in step B it increased both amounts, and in step C it interrupted the increase of both amounts.

The effects of temperature were estimated in a range from 450°C to 525°C. Results of similar tendencies were obtained at any temperature. The duration of each step was shorter as the temperature was higher, and the apparent activation energy in step B was 17 kcal/mole, which was estimated from the amounts of acrylic acid. The same amounts of acrylic acid were obtained, when slugs of acrolein were injected at different intervals of 4, 8, or 16 min in step B.

Vanadium pentoxide is also one of the excellent catalysts for the synthesis of acrylic acid (*4*). The reaction of vanadium pentoxide with acrolein was investigated with the same method. The formation of acrylic acid was also observed, but the amount of acrylic acid decreased monotonously with slug number.

Discussion

The experiments showed that the activity of phosphomolybdic acid toward acrolein increased after it had been reduced with acrolein to a fixed extent. The injection of slugs of air (or oxygen) interrupted those changes in the A and C steps, as it hindered the reduction of phosphomolybdic acid. A sufficient oxidation of the phosphomolybdic acid which had been reduced with acrolein restored its original activity, and even a little increase in the activity was observed, which might be due to the activation of the specimen with a successive reduction and oxidation.

The following speculation about the reason for the increase of the activity of a phosphomolybdic acid after the reaction has proceeded to some extent is proposed: A reduction of phosphomolybdic acid may favor the adsorption of acrolein and as a result the reaction may be accelerated.

In the vapor-phase catalytic oxidation of acrolein to acrylic acid over a phosphomolybdic acid catalyst the best results are obtained when the molar ratio of oxygen to acrolein is about one to one (*1*), and over a vanadium pentoxide catalyst the best results are obtained when the ratio is about seven, or higher, to one (*4*). It can be said that the former catalyst prefers a reductive atmosphere, and the latter catalyst, an oxidative atmosphere. The behavior of a phosphomolybdic acid and vanadium pentoxide in our experiments may correspond to these catalytic properties.

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