SULPHONATED POLYSTYRENE ON EXPANDED METAL SHEETS AS SOLID ACIDIC CATALYST FOR GAS-LIQUID REACTIONS

Z. ŽITNÝ and M. KRAUS

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchdol

Received May 15th, 1975

Supported acidic catalysts of the ion exchanger type were obtained by coating sheets made from expanded metal with polystyrene and by subsequent sulphonation. The catalysts were tested for reesterification of ethyl formiate by 1-butanol and for alkylation of phenol by isobutylene. In both cases they have shown good activity. The excellent hydrodynamic properties of expanded metal sheets for contacting liquids with gases were almost not changed by covering with a polymer.

Vertical packing of absorption and distillation columns made from sheets of expanded metal which was developed by Kolář and coworkers[1-5] has been used also as a catalyst support for reactions in systems gas-liquid-solid catalyst[6-8]. Mejstříková[8] has studied in detail the properties of a palladium catalyst supported on sheets of expanded aluminium for hydrogenation of liquid nitrobenzene at 60°C and at atmospheric pressure in a flow reactor. In the present paper we wish to show how this idea can be applied to the catalysts of the ion exchanger type, *i.e.* to sulphonated polystyrenes.

EXPERIMENTAL

Catalyst A. Polystyrene (10 g) was dissolved in benzene (60 – 120 ml) and expanded aluminium sheets 3 cm wide and 33 cm long were coated with this lacquer-like solution in order to cover completely the ribs and to form a film in the openings of the mesh. The expanded metal was of the same type as in the preceding work[8], *i.e.* its ribs were approx. 1 mm thick and the openings had the form of a rhombus with diagonals of 5 and 10 mm. The polystyrene solution was applied either by immersing the sheets into it or by a brush. The polystyrene film was dried on air under an infra-red lamp. The coating was repeated if necessary until a film of 0·1 – 0·2 mm thickness was obtained. Then polystyrene was sulphonated by immersing the sheets into hot concentrated sulphuric acid. The temperature and duration of sulphonation depended on required degree of substitution and on the properties of polystyrene sample. The conditions varied in the range of 80 to 180°C and of 5 min to 2 hours. A satisfactory catalyst was of light to dark brown colour and was obtained *e.g.* by 5 min sulphonation at 180°C. After withdrawing the sheets from sulphuric acid, the catalyst was washed several times by immersion into cold water or preferably ethanol in which the catalyst swells less and therefore is mechanically more stable during washing. The washed sheets were dried on air and then packed into the reactor. In the course of the sulphonation the smooth surface of the polymer was roughened and the film in some openings was destroyed. A sample of sulphonated polystyrene scraped from the carrier was titrated with sodium hydroxide solution and 2·5 to 3·0 mmol H^+/g were found according to the conditions of sulphonation.

Catalyst B. A mixture of styrene (50 ml), technical divinylbenzene (40%, 0·5 ml) and 0·25 g of benzoyl peroxide was heated to 80°C until the polymerization proceeded so far that the solution had the viscosity of 300 to 500 cSt. The mixture was cooled off, 0·5 ml of divinylbenzene, 0·5 g of benzoyl peroxide and, if necessary, up to 10 ml of benzene were added in order to obtain a lacquer suitable for application in the described way. The coated carrier was heated intensively by a infrared lamp to finish the polymerization and a hard, glassy layer was eventually formed. The sulphonation was easier than in case A, the suitable temperature range lay between 100 to 130°C, when the reaction time was 10 to 30 min. The content of sulphonic groups, found by titration, amounted to 2·5 to 3·8 mmol/g.

Chemicals. All compounds were commercial preparations which were distilled before use. 1-Butanol, b.p. 118°C; ethyl formate, b.p. 54—55°C; butyl formate, b.p. 107°C; phenol. b.p. 182°C. Isobutylene from a pressure bottle had the purity of 99%.

Analysis. The reaction mixture from reesterification experiments were analyzed by g.l.c. using an apparatus with thermal conductivity detection and 5% of poly(ethylene glycol)-methylether as the stationary phase at 75°C with hydrogen as the carrier gas. Phenols were separated on a column with 6% of Apiezone L at 140°C.

Aparatus. A similar equipment as in the preceding study[8] was used. The reactor consisted of a vertical glass tube (50 mm i.d.) with a mantle in which a liquid from a thermostat was circulated. In the reactor, suspended on a distributing head, three sheets of expanded metal (3 × 33 cm) were placed. The less volatile component (1-butanol) was fed by a pump through a pre-heater

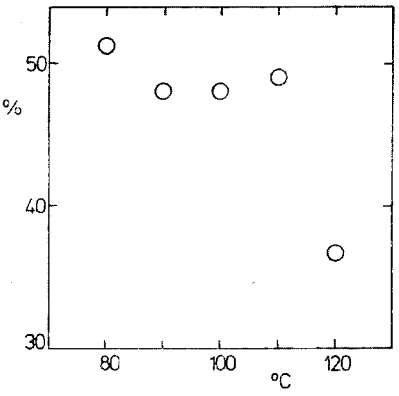

FIG. 1

Effect of Temperature on Ethyl Formate Conversion

Catalyst B, feed rate 0·055 mol/min of ethyl formate and 0·108 mol/min of 1-butanol.

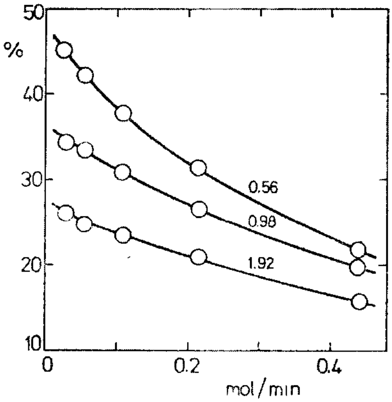

FIG. 2

Conversion of 1-Butanol in Dependence on Its Feed Rate at Different Component Ratio

Numbers at curves give molar ratio of 1-butanol to ethyl formate feed rates.

onto the head and trickled down the sheets. The more volatile component (ethyl formate) was pumped into a evaporator and its vapours went through a pre-heater into the bottom of the reactor. The arrangement was always counter-current and liquid and gaseous efluents were received separately. In the reaction of phenol with isobutylene the evaporator was not used and only the liquid efluent was collected. The measurements were conducted when the steady state was achieved.

RESULTS AND DISCUSSION

The purpose of this work was a general verification of applicability of sulphonated polystyrene supported on expanded metal for catalytic reactions in the system gas–liquid. Therefore the model reaction was selected mere on the basis of its suitability for a laboratory apparatus of a given size and its simplicity of analytical evaluation than on other criterions. The reesterification seemed to fulfil this conditions and preliminary experiments in a batch reactor with commercial ion exchangers at the boiling point of the reaction mixture indicated as sufficiently rapid the reaction of ethyl formate with 1-butanol

$$HCOOC_2H_5 + C_4H_9OH \rightleftharpoons HCOOC_4H_9 + C_2H_5OH\,. \qquad (1)$$

The first experiments with sulphonated polystyrene on the expanded metal carrier were intended for locating the temperature range. As Fig. 1 shows the conversion was temperature independent between 90 to 110°C. The reason is very probably a compensation of the increase of reaction rate and of the decrease of solubility of ethyl formiate in the liquid phase with increasing temperature. This finding allowed us to measure at 100°C and to neglect all possible temperature gradients inside the reactor. The next series of experiments confirmed a steady activity of the catalyst during many hours. In order to find out whether the coating of the expanded metal with a polymer

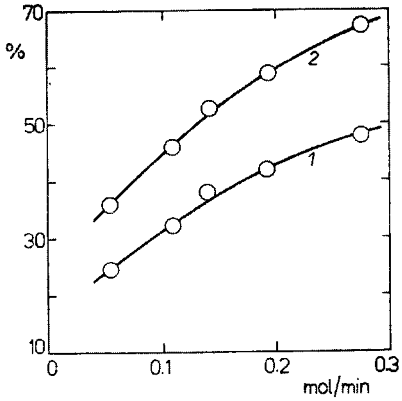

FIG. 3

Conversion of 1-Butanol in Dependence on Feed Rate of Ethyl Formate

1-Butanol feed rate: *1* 0·108 mol/min, *2* 0·043 mol/min.

changes its ability to enhance the mass transfer between the liquid and gaseous phase, several series of experiments were conducted with various coatings. Table I shows that covering the mesh with polystyrene or desactivated (by neutralization) catalyst does not change the mass transfer significantly.

For illustrating the observed course of reaction (*1*) Figs 2 and 3 were selected. Fig. 2 shows the change in conversion with the change of feed rate at constant ratio of reactants, Fig. 3 demonstrates the dependence of conversion on feed rate of the liquid component (1-butanol) at constant feed rate of the vaporized component (ethyl formate).

The process inside the reactor is quite complex; the gaseous component is partly dissolved in the liquid, the liquid component is partly vaporized, the reaction takes place on contact of the liquid with the solid catalyst and the products are partly vaporized. The function of the reactor as a distillation column is demonstrated by the data in Table I: the gaseous efluent contains more ethanol than the liquid. Mathematical modelling of simultaneous chemical reaction and separation would require a good knowledge of vapour–liquid equilibrium data for our four-component mixture which are not available; however, this was not the goal of this work. The simultaneous

TABLE I

Composition of the Liquid and Gaseous Efluents (in mol. %) after Contact of Ethyl Formate and 1-Butanol with the Reactor Packing of Expanded Metal Catalytically Inactive and Active

100°C, feed rate 0·055 mol/min of ethyl formiate and 0·108 mol/min of 1-butanol.

Efluent	Ethyl formate	Butyl formate	1-Butanol	Ethanol
		Uncoated sheets		
Liquid	19·0	—	81·0	—
Vapour	72·0	—	28·0	—
		Sheets coated with polystyrene		
Liquid	17·8	—	82·2	—
Vapour	75·7	—	24·5	
		Sheets coated with neutralized catalyst B		
Liquid	16·5	—	83·5	—
Vapour	74·0	—	26·0	—
		Sheets coated with active catalyst B		
Liquid	19·7	16·5	50·4	13·4
Vapour	23·0	10·1	25·6	41·3

processes could be of use in cases when the separation of products would shift the equilibrium conversion in the desirable direction. However, it is quite clear that the best application of the reactor type under study would be for reactions which involve two components differing strongly in volatility, as was the case with hydrogenation of nitrobenzene.

Therefore we have made a few experiments with the alkylation of phenol by isobutylene which yields tert-butyl phenols. At 70°C, feed rate 0·15 mol/min of phenol and 0·008 mol/min of isobutylene the conversion of phenol was around 4% giving approx. equal amounts of *o*- and *p*-tert-phenol. This reaction is much slower than the above reesterification and in order to obtain higher conversions longer catalyst sheets or elevated pressure would be necessary. However, the applicability of this form of acidic catalyst has been proved.

REFERENCES

1. Kolář V.: Czech. 163 411.
2. Kolář V.: Czech. 149 727.
3. Kolář V., Endršt M.: This Journal *37*, 3719 (1972).
4. Kolář V., Endršt M.: This Journal *38*, 359 (1973).
5. Kolář V., Endršt M.: This Journal *38*, 367 (1973).
6. Kraus M., Mejstříková M., Bažant V.: Czech. Appl. 3687-73.
7. Mejstříková M., Kraus M.: Czech. Appl. 3250-73.
8. Mejstříková M.: This Journal *39*, 2740 (1974).