NOTES

Ion Exchange Resin-Catalyzed Transesterification Reaction

Use of synthetic ion exchange resins as catalysts is well established.[1]   The analytical methods adopted in following the course of reaction have generally been the conventional ones.   However, Juvete et al.[2] have used vapor-phase gas chromatography for following transesterification reactions with dry HCl gas catalyst.   Consequently, side reactions resulted, though to a minimum.

This note presents results obtained by using porous resins as catalysts, where no side reactions were noticed.   For most rate and equilibrium studies, it is necessary to chemically quench the reaction before analysis, whereas here a mere decantation of the resin was sufficient.

EXPERIMENTAL

The kinetics of liquid-phase transesterification of simple systems like ethyl acetate and methanol catalyzed by macroporous cation exchangers was followed by gas chromatography.   A literature survey revealed no prior information in this regard.   However, Beranek et al.[3] have reported gas-phase transesterification of simple esters on sulfonic acid resins at 120°C using a microflow reactor technique.   Kumar and Satyanarayana[4] have studied gas-phase transesterification of ethyl acetate with methanol using silica gel catalyst in a tubular reactor.

Materials

The resin used was syntheiszed in the laboratory[5] from a styrene–DVB copolymer and had a porosity of about 0.4 ml/g and total exchange capacity of 3.6 meq/g.   For comparison, Amberlyst 15 of Rohm and Haas Co. was used.[6]   AnalaR ethyl acetate, methanol, and methyl acetate were distilled prior to use.   Absolute alcohol was dried and distilled.

The gas-chromatographic apparatus used was a AIMIL-NCL dual-column chromatograph with an Elliot recorder arrangement.   Columns of Poropak Q were used, and N_2 was the carrier gas.   A Hamilton microliter syringe (10 μl capacity) was empolyed for injecting the reaction mixture.   For rate studies, the changes in component concentrations were followed by observing changes in the height of the peaks with time.   Initially, with pure products, a standard chromatogram was obtained.   The peak heights of the components were normalized to unit volume and taken as the standard.   From these, the concentrations of the components in the reaction mixtures were computed.   In this investigation, only changes in ethyl alcohol peak were followed since this peak was observed to be the most sharply resolved of the four components in the reaction mixture viz.,

$$\text{ethyl acetate} + \text{methanol} \rightleftharpoons \text{ethyl alcohol} + \text{methyl acetate}$$
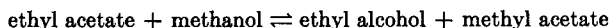
Analytical

Equilibrium studies were conducted by contacting a known weight of the H form of the resin (0.5 to 2 g) with 5 ml of the reaction mixture in a 10-ml glass ampoule. The ampoule was sealed and kept in a thermostat till equilibrium was established (usually about 24–48 hr).   The seal was then broken, contents filtered, and components estimated by gas-chromatographic technique.   The exchange capacities of the resin before and after were determined.[7]

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TABLE I
Equilibrium Constants[a]

[Alcohol]/ [ester] ratio	Temperature, °C	Catalyst, g	H^+ in solution, meq	Mean k value
1	60	0.5[b]	1.7370	1.359
1	60	2.0[c]	2.5850	1.357
1	60	0.5[c]	1.4925	1.350

Rate of methanolysis

				apparent first-order rate constant k_1' in sec^{-1}
10	30.6	0.5[b]	1.737	1.344×10^{-5}
10	40.0	0.5[b]	1.737	2.942×10^{-5}
			activation energy	15.83 kcal/mole
10	30.6	0.5[c]	1.730	1.467×10^{-5}
10	40	0.5[c]	1.731	3.298×10^{-5}
			activation energy	16.38 kcal/mole

[a] System: ethyl acetate + methyl alcohol $\rightleftharpoons$ methyl acetate + ethyl alcohol.
[b] Amberlyst 15.
[c] 0.6 (MARP) 30 x.

The rate of transesterification was followed by contacting a known volume (5 ml) of the reaction mixture with the resin for definite time intervals at constant temperature and determining the concentration of the components.

RESULTS AND DISCUSSION

The equilibrium constants, obtained and the data on pseudofirst-order rate studies are shown in Table I.

Reproducible results were obtained, and no interference was observed with the resin catalyst. As the resins used were macroporous, their efficiency in catalyzing non-aqueous medium reactions has also been confirmed.

Thus, the porous resin synthesized in the laboratory was found to be as good as Amberlyst 15 in catalyzing transesterification reactions. Further detailed work is in progress.

References

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