HYDRATION OF 2-METHYLBUTENES ON ORGANIC ION EXCHANGE RESIN CATALYSTS

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The course of the hydration of a mixture of 2-methyl-1-butene and 2-methyl-2-butene in dependence on the structure of strongly acidic styrene–divinylbenzene ion exchange resin catalysts has been studied. The most efficient catalysts turned out to be macroporous ones. The reaction rate increased with increasing temperature, while the amount of the product (2-methyl-2-butanol) in the equilibrium reaction mixture decreased. Similarly, the hydration was strongly affected by the water to alkene molar ratio in the starting reaction mixture. Modification of ion exchange resin catalysts with 1-butylamine did not affect course of the hydration in the case of gel type catalysts, while with macroporous resin catalysts the addition of amine up to 0·5% of the total catalyst exchange capacity showed activating effect.

Hydration of alkenes to alcohols is catalysed by acid catalysts, and that both homogeneous and heterogeneous. The decisive aspect that affects the course of the hydration is contact of both reactants which are practically immiscible. This problem is eliminated by intense stirring, by the type of reactor, by the use of a substance being solvent for both components or by an emulsifier, by catalyst modification, *etc.*, *i.e.* by the methods, some of which are called phase transfer catalysis. The often used catalysts for hydration are strongly acidic organic ion exchange resins. It is the structure of their polymer gel which plays important role in ensuring optimal conditions for hydration reaction.

Considerable research effort has been devoted to the hydration of lower alkenes, and thus *e.g.* hydration of propene and of isobutylene is performed on industrial scale. Hydration of 1-pentene and 2-methylbutenes on gel-like ion exchanger Amberlite IR 120 was studied by Odioso and coworkers[1]. The broader series of ion exchangers was used by Osokin and coworkers[2] and by Polyanskii and coworkers[3]. Further investigated problems were the solvent effect on the course of the reaction[2,4,6] and the effect of hydrophobization of ion exchangers[5]. Hydration of the isoalkenes present in petrochemical C_5 fraction has been reported by Giles[6] who used acetone as a solvent and the set of three reactors in series and also by Polyanskii and coworkers[7] who utilized a hydrophobized ion exchange resin catalyst.

In the present work we have examined the effect of the structure of polymer gels

of strongly acidic organic ion exchange resin catalysts on the course of the liquid phase hydration of 2-methylbutenes to 2-methyl-2-butanol (tert.pentanol).

EXPERIMENTAL

Starting Compounds

2-Methylbutenes were prepared by dehydration of 2-methyl-2-butanol, using 85% phosphoric acid as the catalyst. The alkenes formed were distilled, dried over sodium sulphate and redistilled, giving the final mixture containing 21·4% of 2-methyl-1-butene and 78·2% of 2-methyl-2-butene (determined by GCL). 1-Butylamine was normal purity grade (Lachema Brno), *p*-toluenesulphonic acid was of analytical purity.

Petrochemical C_5 fraction (CHZ ČSSP Litvínov) was selectively hydrogenated to remove present dienes (especially isoprene and cyclopentadiene) and had the following composition: 3-methyl-1-butene 0·6, isopentane 9·5, 1-pentene 1·5, 1-pentane + *trans*-2-pentene 30·6, *cis*-2-pentene 5·2, 2-methyl-1-butene 5·5, 2-methyl-2-butene 20·4, cyclopentene 9·2, cyclopentane 12·7, 2-methylpentane 2·6, and 3-methylpentane 0·4 wt. %.

Catalysts

Basic properties of the ion exchangers used are given in Table I. The catalyst K1-66 is a linear polystyrene crosslinked with 1,4-bis(chloromethyl)benzene in solvent, *i.e.* in the swelled state[8]. A partial neutralization of ion exchangers with 1-butylamine was made such that 1 g of the dry ion exchanger was swelled in 50 ml of distilled water and then the calculated amount of the amine was added under intense stirring. After 1 h, the ion exchanger was decanted and dried at 105°C for 12 h. The swelling ability of ion exchangers and methods for determining this property were reported earlier[9].

Apparatus and Procedure

The reaction was carried out in a static, stirred glass 4 ml-reactor under nitrogen pressure of 0·45 MPa. The reactor was provided with a resin closure for sampling and was stirred by a mag-

TABLE I

Properties of ion exchange resin catalysts used

Catalyst	Cross-linking % DVB	Specific surface $m^2 g^{-1}$	Exchange capacity mequiv $H^+ g^{-1}$	Swelling degree, ml g^{-1}	
				2-methylbutenes	water
Amberlyst XN 1010	80	570	3·3	0·07	0·3
K1-66	66[a]	4·5	4·4	0·2	3·0
Lewatit SPC 118	18	35	4·65	0·2	0·76
Lewatit SC 102	2	0·1	5·1	0·0	5·96

[a] Value corresponds to the content of 1,4-bis(chloromethyl)benzene.

netic stirrer. The reactor was placed in a jacket of liquid temperature-controlled bath. It was charged with 0·12 g of dry ion exchanger, then the known amount of water was added and the mixture was allowed to swell for 0·5 h. Then 3 ml of a mixture of 2-methylbutenes were added, the reactor was closed and pressurized to 0·45 MPa by nitrogen. The moment of the immersion of the reactor to the thermostatted liquid was taken as the beginning of the reaction.

Analytical Methods

Reaction mixtures were analysed gas chromatographically with the use of 1 m-column packed with Poropak N (4 mm i.d., 170°C, thermal conductivity detector). The mixture of 2-methyl-butenes was analysed at room temperature on 10·3 m-column (3 mm i.d.) packed with 12% EDO (ethyl-N,N′-dimethyloxamate) on Chromosorb P (100—120 mesh), using thermal conductivity detector.

RESULTS AND DISCUSSION

Fig. 1 shows the course of the hydration of 2-methylbutenes to 2-methyl-2-butanol (tert.pentanol) on all the ion exchange resin catalysts studied as well as the course observed with the homogeneous catalyst, p-toluenesulphonic acid. The experiments were carried out at 60°C, at which temperature the differences in the reaction course were more distinct due to the higher conversions of the methylbutenes achieved.
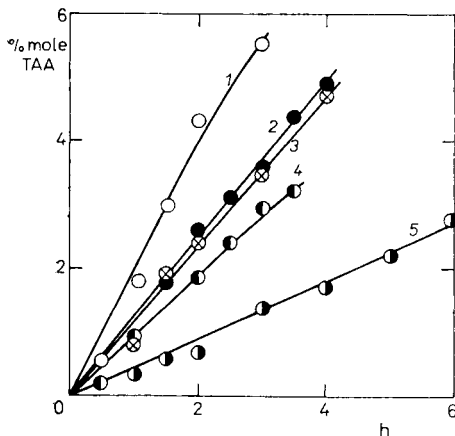

Fig. 1

Hydration of 2-methylbutenes to tert.pentanol (2-methyl-2-butanol) (TAA) on different ion exchange resin catalysts. Reaction conditions: 60°C, 0·45 MPa N_2, H_2O/C_5H_{10} mol. ratio = 1; 1 K1-66, 2 Lewatit SPC 118, 3 p-toluenesulphonic acid (0·1126 g), 4 Lewatit SC 102, 5 Amberlyst XN 1010
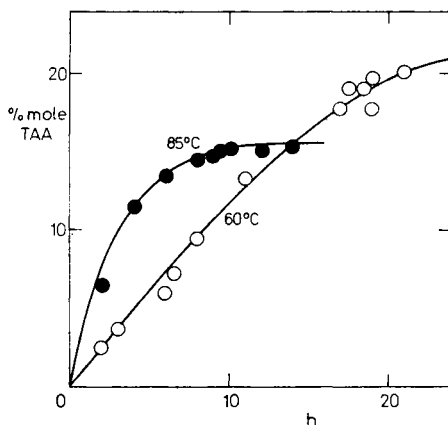
Fig. 2

Hydration of 2-methylbutenes on Lewatit SPC 118 catalyst. Reaction conditions: 0·45 MPa N_2, H_2O/C_5H_{10} mol. ratio = 1

It becomes evident that there are differences in the reaction course in dependence on individual catalysts. As we used identical reaction conditions for all the catalysts, the above mentioned differences can be ascribed to the different properties of the catalysts, especially to the differences in their polymer structure and consequences thereof, since exchange capacities of the catalysts differ only little from each other. All the catalysts are strongly hydrophilic and thus practically all the water of the reaction medium is contained in the polymer gel and the olefins form the non--aqueous phase in the reactor.

The most efficient catalyst has turned out to be the ion exchanger K1-66, *i.e.* the catalyst which was crosslinked only after linear polymer chains had been formed, using the medium ensuring high mobility of the chains[8]. This manifests itself also in the high specific surface of the swelled ion exchanger $(625 \text{ m}^2/\text{g})$ determined by the method reported by Jeřábek[10]. The homogeneous catalyst used in the amount corresponding to the number of sulphonic acid groups in the ion exchangers showed the same catalytic activity as macroporous ion exchanger Lewatit SPC 118. The other ion exchangers tested, *i.e.* the low-crosslinked gel type without apparent porosity, Lewatit SC 102, and the highly crosslinked type with maximal specific surface, Amberlyst XN 1010, were found to be less effective.

Fig. 2 shows kinetic curves of the hydration of 2-methylbutenes on commercial macroporous ion exchanger Lewatit SPC 118. They document the increase in the reaction rate at higher temperatures and the decrease in the equilibrium conversion of the reaction with increasing reaction temperature, in agreement with thermodynamic data on alkene hydration reported by Polyanskii and coworkers[5]. Hence, one has to choose such temperature at which the reaction rate of hydration of alkenes and the equilibrium of the reaction attain optimal values. Thus, for example, at room temperature, the equilibrium of the hydration is around 80% conversion, while the rate of the reaction is unmeasurable.

The effect of the molar ratio of water to the methylbutenes on the course of the hydration reaction is presented in Fig. 3*a,b*. The experiments were performed with representatives of common commercial ion exchangers, and that both macroporous and gel-like types. The results demonstrate the different effect of the parameter just examined on the reaction course, depending on the type of the ion exchanger used.

As the course of the hydration of methylbutenes is strongly affected by the properties of macromolecules of the resin catalysts used, we have made an attempt to change their hydrophilic character by adding an organic base. It is known that the gradual neutralization of strongly acidic styrene–divinylbenzene ion exchangers decreases their hydrophility, although even their complete neutralization does not make it possible to attain the hydrophobity of the starting hydrocarbon copolymer. We have used 1-butylamine for this purpose, assuming that its C_4-alkyl group can also contribute to the decrease of the polymer hydrophility. The results are shown in Fig. 4*a,b*.

All the experiments discussed above have been performed with the use of a mixture of both reactive 2-methylbutenes. As in the industrial process the starting material would be petrochemical C_5 fraction, we have made comparative experiments with this hydrocarbon mixture (for the composition see Experimental), using Lewatit SPC 118 as the catalyst and the reaction temperature 85°C. We found that at the molar ratio of water to 2-methylbutenes equal to 1, the conversion with the pure alkenes is 13·6 mol %, while with the C_5 fraction and at threefold molar excess of water to the reacting alkenes it is only 8·1 mol %. This difference indicates that the unreactive hydrocarbons retard the hydration reaction. Whether this rate decrease is caused by competitive chemisorption of the unreactive hydrocarbons on active sites or by the negative effect of the greater amount of the hydrocarbons in the reaction mixture on the contact of both phases in the gel region of the catalyst cannot be decided from these experiments.

The results show that the decisive factor that affects the hydration of 2-methylbutenes is the accessibility of strongly acidic functional groups of the ion exchanger catalyst with respect to the molecules of hydrated hydrocarbons. As even the homogeneous catalyst is dissolved preferentially in the aqueous phase and hydrocarbon molecules have thus to migrate to this phase, there is no significant difference between the action of the homogeneous catalyst and heterogeneous ion exchangers. The activity of the ion exchange resin catalysts studied is influenced above all by their swelling ability in both media of the reaction system — the aqueous and hydrocarbon phase. The degree of swelling in both media (Table I) follows the sequence of the catalyst activity. The ion exchanger K1-66 swells in both media to the extent
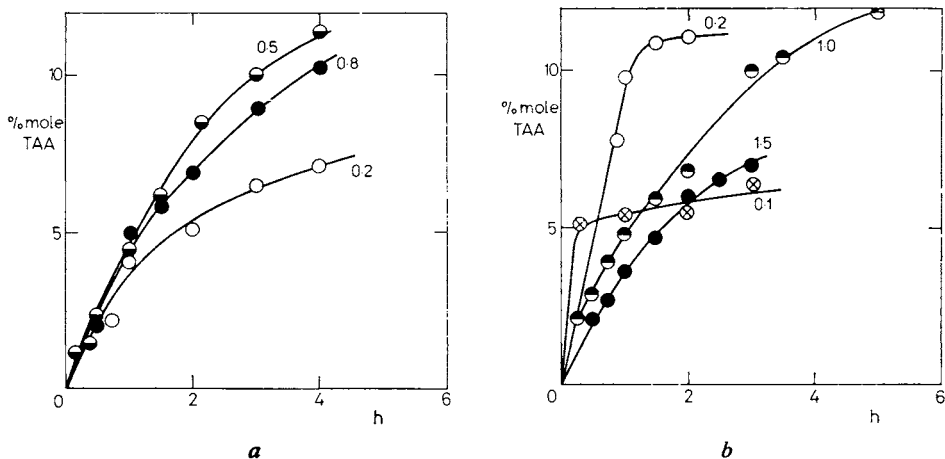

FIG. 3

Effect of the water to 2-methylbutenes molar ratio. Reaction conditions: 85°C, 0·45 MPa N_2; the molar ratios are given at the curves; *a* Lewatit SC 102, *b* Lewatit SPC 118

comparable to that found for ion exchanger Lewatit SPC 118. The swelling ability of the highly crosslinked ion exchanger Amberlyst XN 1010 is substantially smaller, and with the gel ion exchanger Lewatit SC 102, the decisive factor is the insensitivity of its gel structure to the hydrocarbon phase.
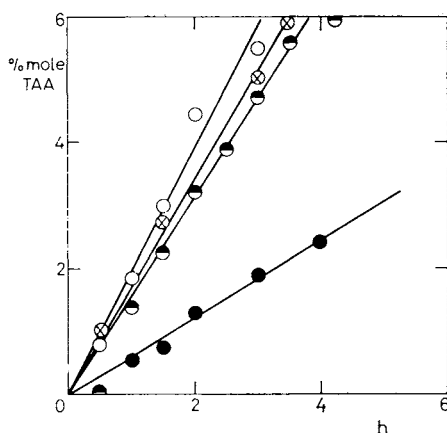
These conclusions are supported also by the results presented in Fig. 3a,b. In the case of the gel-like ion exchanger (Fig. 3a) the rate of the hydration decreases at the
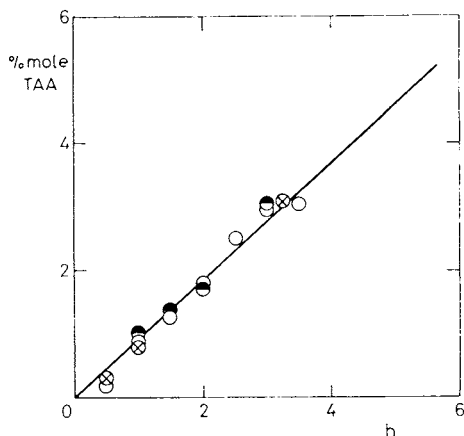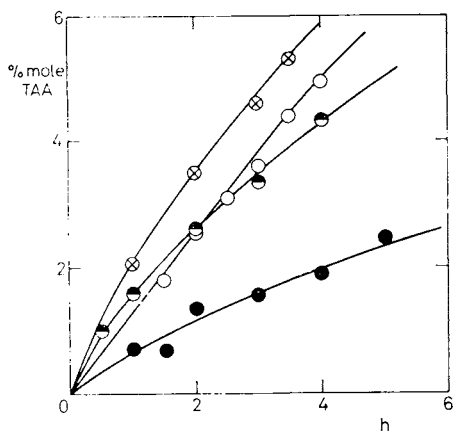
FIG. 4

Effect of treatment of ion exchange resin catalyst with 1-butylamine on hydration of 2-methyl-butenes. Reaction conditions: 60°C, 0·45 MPa N_2, H_2O/C_5H_{10} mol. ratio = 1; a Lewatit SC 102, b Lewatit SPC 118, c K1-66; ○ the starting, untreated catalyst, ⊗ 0·5% of the butylamine with respect to the ion exchanger capacity, ◓ 5% of the butylamine, ● 50% of the butylamine (both with respect to the total ion exchange capacity of the catalyst)

low molar ratio of water to the alkenes. This can be ascribed to the nearly complete absorption of water in the gel of the ion exchanger, while only very thin layer of the catalyst surface is available for the catalytic hydration. The effective concentration of water is thus very low on the sites on which the catalytic reaction is taking place. In the case of macroporous ion exchange resin catalyst, one finds opposite situation (Fig. 3b). Due to the high specific surface of the ion exchanger and the considerable crosslinking of its macromolecular skeleton, the polymer does not swell by water to a significant extent, by which the water is accumulated at the surface of the gel on which the hydration reaction proceeds. Hence, the reaction is thus fastest at low water to alkenes molar ratios, and in short period, the concentration regions close to the equilibrium of the reaction are achieved. On increasing water to alkenes molar ratios, the reaction system becomes three-phase one, and amount of water exerts no more any significant effect. The reaction rate thus decreases.

Similar assumptions can also be applied to the results obtained with the ion exchangers modified by addition of the strong organic base, 1-butylamine. In the case of the gel-like low crosslinked Lewatit SC 102 (Fig. 4a), the added butylamine does not affect the reaction rate. It is known that during chemisorption, strong bases occupy uniformly the acid groups of the low crosslinked gel. Therefore, most of the butylamine added is thus located within polymer gel and affects only negligibly the surface of the particles on which the catalytic reaction is taking place. In the case of macroporous ion exchanger Lewatit SPC 118 (Fig. 4b), the highest reaction rate is achieved with 0·5% of 1-butylamine. The addition of 5% of the amine gives nearly the same results as with the untreated catalyst, and the butylamine chemisorbed on half of the sulphonic acid groups of the ion exchanger leads to a marked decrease of catalytic activity. This shows that the addition of the amine in the amounts not exceeding 5 per cent affects positively contact of the reaction components with active sites of ion exchanger Lewatit SPC 118. At the greater amounts this positive effect is compensated by the decrease of the acid capacity of the ion exchanger, the net result being decrease in the rate of the hydration. The catalyst K1-66 acts in different way, likely due to the special structure of its polymer gel. This ion exchange resin catalyst is highly crosslinked but is possesses low specific surface. However, the crosslinking procedure applied for its synthesis (see Experimental) ensures its excellent swelling ability, at least in some parts of the polymer mass. These properties are responsible for the high catalytic activity of the resin in alkene hydration (Fig. 1). They are likely also the reason why the addition of butylamine does not result in increase of the catalyst activity, not even in the region of low butylamine concentrations, since the well swelled gel mass cannot be further positively affected. Hence, butylamine addition leads to the activity decrease which is proportional of the amount of the butylamine added.

The above results demonstrate that the rate of hydration of 2-methylbutenes catalysed by strongly acidic ion exchangers depends on a number of factors. Besides

reaction temperature, the very important parameter is the structure of the polymer mass of the ion exchanger used. The suitable catalysts are macroporous ones. Their specific surface can be increased only to such a degree which does not result in the decrease in pore diameter of the ion exchanger below a certain limit. This limit depends on dimensions of reaction components, especially of alkenes and formed alcohols. Gel-like styrene–divinylbenzene ion exchangers, even those very low crosslinked, are not suitable, since their strongly polar and thus hydrophilic gel mass is insensitive to the hydrocarbon phase of the reaction mixture. From this aspect, ion exchangers of the type K1-66 are catalysts of choice, but these are not still commercially available.

REFERENCES

1. Odioso R. C., Henke A. M., Stauffer H. C., Frech K. J.: Ind. Eng. Chem. *53*, 209 (1961).
2. Osokin J. G., Kryukov S. I., Feldblum V. Sh., Sirotina T. S.: Khim. Prom. *8*, 457 (1979).
3. Polyanskii N. G., Markevich S. M., Kozlova T. I., Potudina N. L.: Nefekhimiya *1*, 804 (1961).
4. Kryukov S. I., Kutin A. M., Osokin J. G., Feldblum Sh. V.: Neftekhimiya *6*, 753 (1966).
5. Laskorin B. N.: U.S.S.R. 143 555 (1961).
6. Giles J. H.: U.S. 4 182 920 (1980).
7. Polyanskii N. G., Kozlova T. I.: Zh. Prikl. Khim. *39*, 1788 (1966).
8. Tsurupa M. P., Volynskaya A. V., Belchich L. A., Davankov V. A.: J. Appl. Polym. Sci. *28*, 685 (1983).
9. Setínek K.: Chem. Prum. 26/51, 535 (1976).
10. Jeřábek K.: Anal. Chem. *57*, 1597 (1985).

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