

A Novel Way for Hydroxyethylation by Using Clay Catalysts

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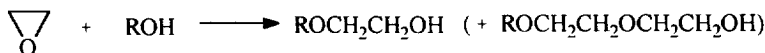
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Abstract: Hydroxyethylation of aralkyl alcohols (benzyl alcohol, 2-phenylethanol, 3-phenylpropanol) in the presence of a clay catalyst (K10) was successful. This method has some advantages in contrast with the conventional ones: effective, works at mild reaction conditions, easy the separation of catalyst from the reaction mixture. © 1997, Elsevier Science Ltd. All rights reserved.

Hydroxyethylation, the reaction of ethylene oxide with molecules containing active hydrogen atom is a catalytic process. The catalyst may be a base or an acid. In the case of oligo(poly)hydroxyethylation the character of the catalyst determines the concentrations of oligomers [the molar mass distribution (MMD)]¹ originated from the consecutive competitive reaction series. These reactions are usually homogeneous ones. One of the problems is the separation of the product from the catalyst. The second task is to achieve a narrow range MMD.

The opening of the oxirane ring with alcohols can be achieved with heterogeneous catalysts. The reaction with clay catalyst (both in liquid phase at 40-70°C and in gas phase at 120°C) gives good yield². This catalyst seems to be selective to monohydroxyethylation³ (the byproduct is dihydroxyethylated compound in small amount).



In our recent works^{4,5} some reactions catalyzed by an acidic clay (K10) are published. The insertion of various polyvalent transition metal ions into the clay increased the effectiveness of the catalyst⁵ acting as a Lewis-acid site.

The aim of this work is the application of an acidic clay type catalyst (K10) in the oligo(poly)hydroxyethylation reactions of various aralkyl alcohols (benzyl alcohol (**B**), 2-phenylethanol (**2-PE**), 3-phenylpropanol (**3-PP**)) to achieve a good hydroxyethylation rate, a good separation of the catalyst and a narrower **MMD** of the product.

RESULTS AND DISCUSSION

The starting aralkyl alcohols are Merck products, purity is >98% by HPLC. Purity of ethylene oxide (Fluka) > 99.8%.

K10 clay catalyst is a commercial product (Süd-Chemie, München), ion exchanged Cu^{2+} -K10 and Fe^{3+} -K10 are prepared and characterized according to reference⁴.

General reaction conditions: a semimicro apparatus based on the measurement of the volumetric flow⁶ of ethylene oxide was used. The composition of the products (MMD) was measured by HPLC (on a C18 reversed-phase column, eluent methanol-water 55/45 v/v, UV detection at 254 nm). The moles of ethylene oxide reacted with one mol starting compound (average degree of hydroxyethylation = ADE) was determined by weight-measuring and by spectrometric methods⁶ (^1H NMR, UV, IR). The separation of the catalyst from the reaction mixture was a simple filtration.

In the acetylation reactions the pure K10 was less effective⁵ than the metal ion modified clays, therefore the catalytic effect of various K10 derivatives was examined on the hydroxyethylation. According to the data of Table 1. all clays catalyzed the hydroxyethylation reaction, but the most effective was the unmodified K10, which has the highest Brønsted acidity⁷, therefore this was used in the following experiments.

Table 1. The effect of different clay catalysts on the hydroxyethylation of 3-PP (at 120°C, 30 min, 0.167g K10/0,02 mol substrate)

Catalyst	ADE
K10	2.99
Cu^{2+} -K10	2.31
Fe^{3+} -K10	1.30

An important factor is the amount of the catalyst. In Fig. 1. can be seen, that the efficiency of the catalyst (ADE/10 min) increases with its amount till a limit, from this value the uptake of ethylene oxide is constant.

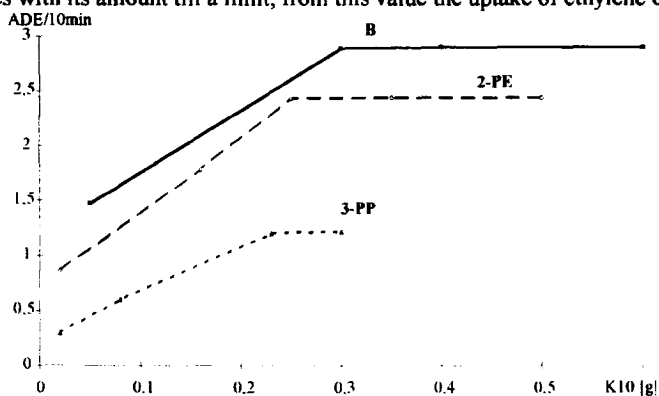


Figure 1. Effect of the amount of K10 on the hydroxyethylation of various aralkyl alcohols at 80°C (alcohol 0.02 mol)

The rate of the ethylene oxide uptake (ADE*100/min) decreases with increasing temperature (Fig. 2.). It means, that the adsorption of the reactants and the solubility of ethylene oxide have a great importance in this procedure. The rate of the chemical reaction increases, the adsorption decreases with increasing temperature. The result of these two processes makes a slight decrease in the overall reaction rate.

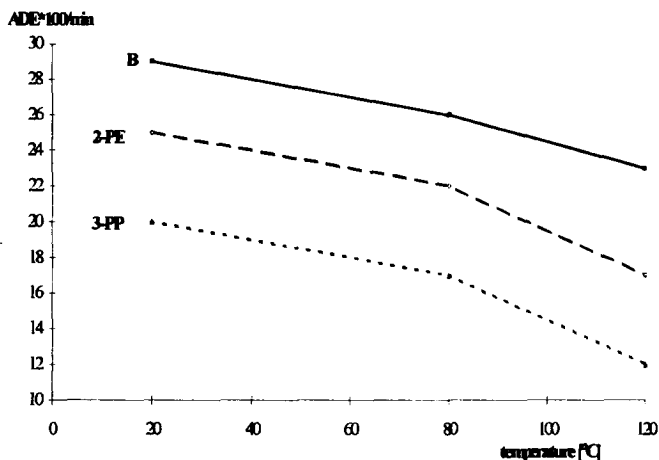


Figure 2. The effect of temperature on the ethylene oxide uptake

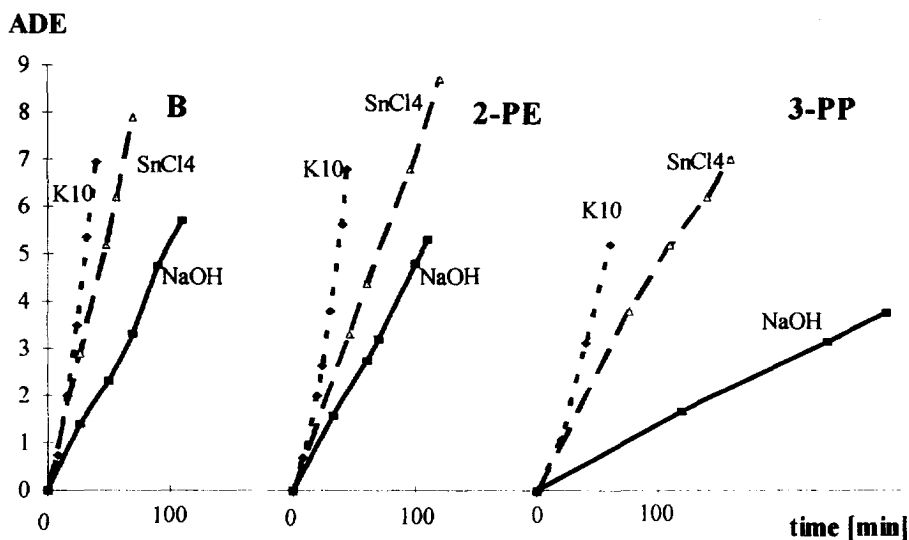
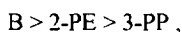


Figure 3. Hydroxyethylation with various catalysts (NaOH at 100°C, SnCl₄ at 50°C, K10 at 30°C)

On the other hand the hydroxyethylation depends on the aralkyl component of the reaction. The longer is the alkyl chain, the less the reaction rate. The order of the reactivity is as follows:



in accordance with the acidity of the alcoholic hydroxyl group.

The activity of the K10 catalyst is better than the common used ones (KOH, NaOH); e.g. it catalyses the hydroxyethylation at those temperatures where the alkaline catalysts are ineffective yet. Compared to SnCl_4 the reaction with K10 is faster (Fig. 3).

The MMD of the product prepared with K10 is different from the usual ones. While the MMD with bases is Weibull-Nycander-Gold type⁸ and with Lewis acids is Flory type⁹, the MMD with K10 is sharper than the Flory's one. It is demonstrated in Fig. 4. with hydroxyethylated B in the presence of various catalysts.

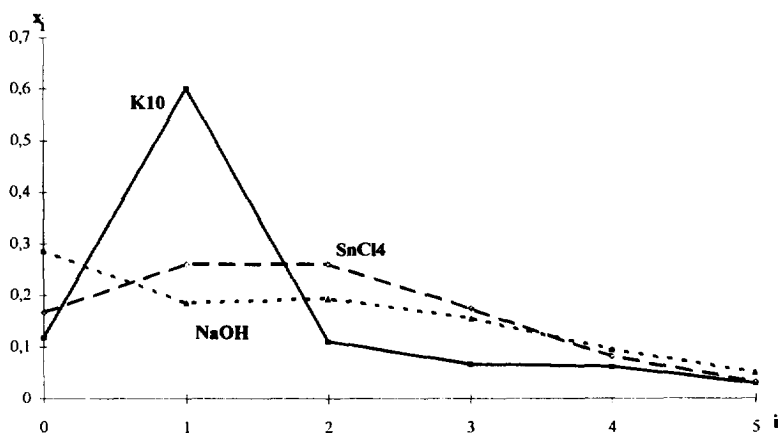


Figure 4. MMD of hydroxyethylated B in the presence of various catalysts (x_i = concentration of the i^{th} homologue)

Final conclusion: K10 catalyst seems to be useful for low temperature and heterogeneous oligo(poly)hydroxyethylation of aralkyl alcohols in order to achieve a narrow molar mass distribution.

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