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CATALYTIC PREPARATION OF MESITYL OXIDE FROM ACETONE

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In the process of the aldol condensation of acetone the preparation of mesityl oxide has been studied with respect to the temperature and the nature of catalyst. Strong basic ion exchangers Ionenaustauscher III (Merck III) and Lewatit MP 500 were used in the temperature range from 0 to 50°C. Better results are achieved with Merck III, as is evident from DAA/MO yields, rate constants and energy activation values. Empirical expressions for DAA/MO production are given.

Исследовали влияние температуры и природы катализатора на процесс альдольной конденсации ацетона при получении окиси мезитила (ОМ). Использовали сильные основные ионообменники марки Ionenaustauscher III (Merck III) и Lewatit MP 500 в интервале температур от 0 до 50°C. Исходя из выходов ДАС/ОМ (ДАС=диацетоновый спирт), величин констант скоростей и энергий активации, лучшие результаты достигнуты при использовании Merck III. Приводятся эмпирические выражения производства ДАС/ОМ.

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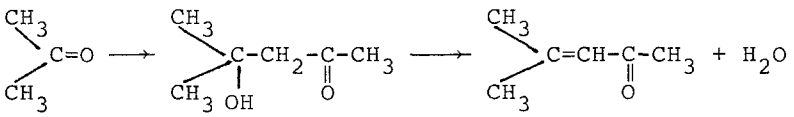
INTRODUCTION

In the aldol condensation of acetone into diacetone alcohol (DAA) numerous by-products, such as mesityl oxide, isophorone mesitylene, phorone and 3,5-xylenol are also obtained. Various catalysts are used for this purpose, especially basic catalysts like barium, calcium and magnesium hydroxide or alumina [1-3]. The application of strongly basic anion exchange resins is also known [4-6]. Mesityl oxide (MO) is one of the main by-products in the process of DAA synthesis. It is predominantely formed at higher temperatures according to the schematic equation:



acetone diacetone alcohol mesityl oxide

Thus in many studies of diacetone alcohol condensation from acetone the study of mesityl oxide formation is also included.

EXPERIMENTAL

In previous works the catalytic preparation of diacetone alcohol was studied [7,8]. Simultaneously the formation of mesityl oxide was also determined. In this work its production is studied with respect to the temperature and the catalyst nature. The experiments were carried out in the temperature range from 0 to 50°C, using strongly basic ion exchangers Lewatit MP 500 and Ionenaustauscher III (Merck III) as catalysts. All the experiments were performed in a laboratory set-up for batch production described earlier [7]. Preparation of catalyst was done by 24 h swelling in distilled water and 2 h immersion in 1 M NaOH, then rinsed with water and ethanol. A gas chromatography method was used to identify reaction products.

RESULTS AND DISCUSSION

Reaction courses of diacetone alcohol synthesis and mesityl oxide formation with Lewatit MP 500 as catalyst are shown in Figs 1 and 2, respectively. It is evident that the mesityl oxide yield increases with increasing temperature following the simultaneous decrease in diacetone alchol content. Concerning the yield values of both products, it is also clear that the quantities of other possible by products such as isophorone, mesitylene, phorone and 3,5-xylenol are negligible. Similar results are obtained with both catalysts used, as is given in Fig. 3. Better results are achieved by Ionenaustauscher III (Merck III) for both products. It is also evident that diacetone alcohol and mesityl oxide yields are exponential functions of the temperature. When plotting logarithmic values of DAA/MO yield vs. inverse temperature, a linear dependence is obtained as is seen in Fig. 4. The slopes of straight lines for DAA and MO preparation are of the same magnitude. A general empirical equation is of the type

$$\ln m = \ln m_o + A/T \qquad (1)$$

where m_o is the hypothetic yield at infinite temperature and A is the line slope. Calculating these individual constants from the experimental data the following specific equations are obtained:

$$\ln m = 2.482 + 550.95/T \quad \text{for DAA-1} \qquad (2)$$

$$\ln m = 2.182 + 550.95/T \quad \text{for DAA-2} \qquad (3)$$

$$\ln m = 20.793 - 5785.20/T \quad \text{for MO-1} \qquad (4)$$

$$\ln m = 20.293 - 5785.20/T \quad \text{for MO-2} \qquad (5)$$

In Table 1 the calculated rate constants of both reactions for all the experimental conditions are given. From the temperature dependence of the rate constant, i.e. from the ln k vs. 1/T dependence, an approximate activation energy is determined

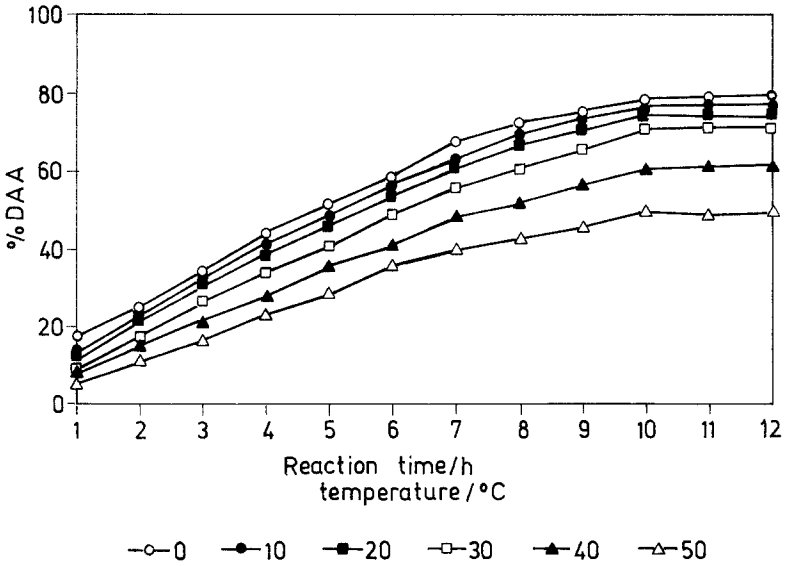


Fig. 1. Reaction course of DAA synthesis. Catalyst: Lewatil MP 500

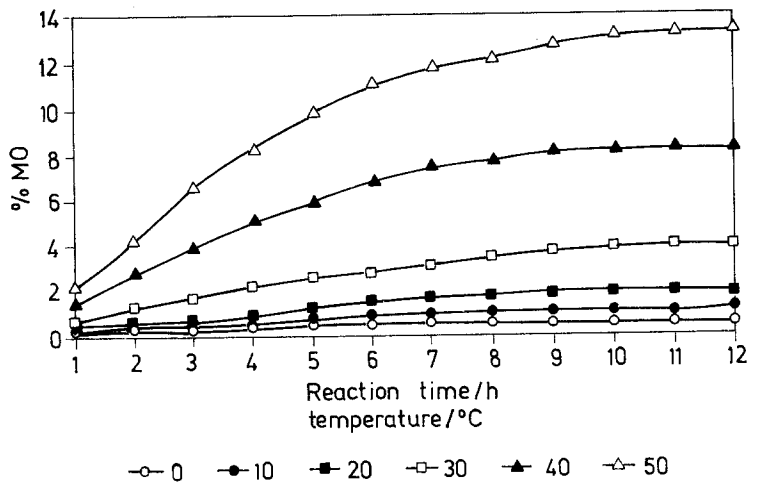


Fig. 2. Mesityl oxide formation during the reaction. Catalyst: Lewatit MP 500

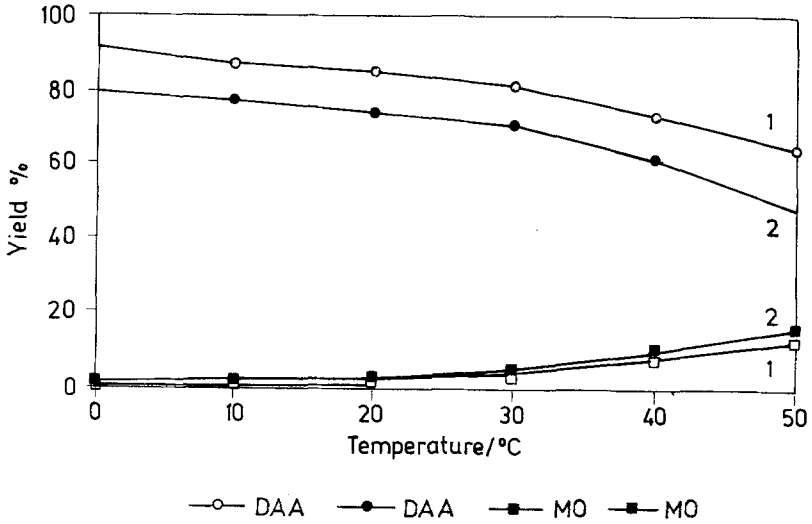


Fig. 3. Effect of temperature on the yield of DAA and MO. Catalysts: 1-Merck III, 2-Lewatit MP 500

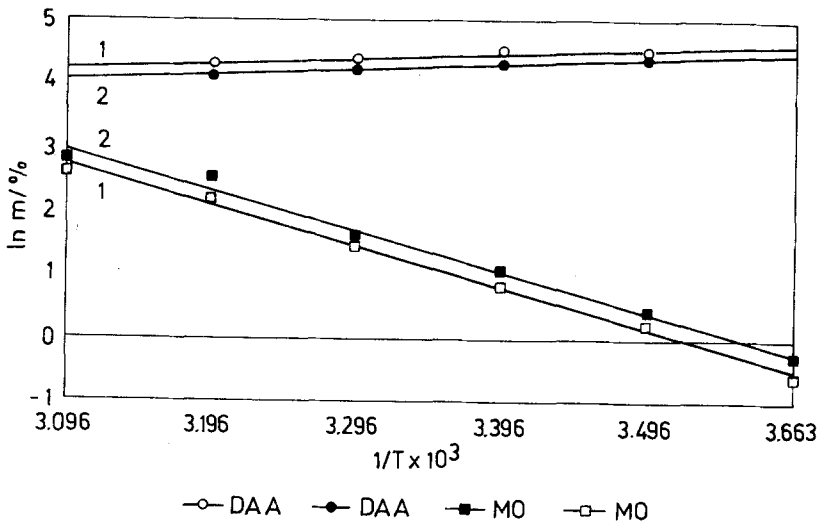


Fig. 4. Linear dependence of DAA/MO yield vs. 1/T Catalysts: 1-Merck III, 2-Lewatit MP 500

using the relation

$$\frac{(\ln k)}{(1/T)} = \frac{E_a}{R} \qquad (6)$$

The calculated values of E_a are also given in the Table.

Table 1

Rate constant and approximate activation energies of DAA synthesis and MO formation

t/°C	Rate constant, k/h^{-1} Ionenaustauscher III		Lewatit MP 500	
	DAA	MO	DAA	MO
10	0.2495	0.0004	0.1575	0.0004
10	0.2099	0.0010	0.1450	0.0010
20	0.1989	0.0018	0.1350	0.0018
30	0.1761	0.0051	0.1200	0.0042
40	0.1302	0.0117	0.0950	0.0110
50	0.1131	0.0231	0.0725	0.0200
$E_a/J\ mol^{-1}$	11640	-59860	12080	-57030

CONCLUSION

In the process of the aldol condensation the quantity of mesityl oxide is negligible at low temperatures, increasing significantly above 30°C. For each decade of increasing temperature, the velocity of the reaction is about two times higher. Simultaneously the DAA yield increases because of the exothermic character of the reaction.

Better results achieved by Merck III catalyst in comparison with Lewatit MP 500, ensuring higher MO yields of about 20%. Rate constants and E_a values confirm the results obtained.

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