PRODUCTION OF BENZYL ETHER FROM BENZYL ALCOHOL IN VAPOUR-PHASE

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The vapour-phase heterogeneous catalytic dehydration of benzyl alcohol in a continuous system on γ-aluminumoxyde catalyst may be performed if the reaction conditions are the following: temperature 220—300 C°; space velocity: 0,05—0,4 hour $^{-1}$. The yield of benzyl-ether is 50—66% in case of the above parameters.

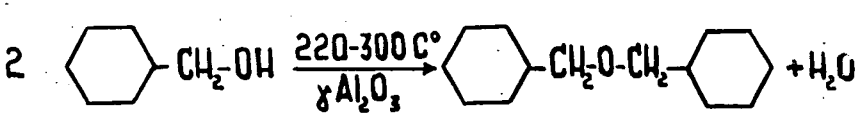
Regarding the production of benzyl-ether there are several references in the literature (1—27). One part of these publications accounts on the formation of benzyl-ether in connection with a reaction way, a considerable part, however, summarizes the methods worked out for the production of benzyl ether.

For the production of prim. symmetric ether the best and the most economic method seems to be the vapour-phase heterogeneous catalytic dehydration in a continuous system.

This process was first applied by P. SABATIER *et al.* (28—29) for dehydration of benzyl alcohol. They carried out experiments on various dehydration catalyst (Al_2O_3, TiO_2, *etc.*), but in each case they gained a resin like product. V. K. TETERIN (30) studied the dehydration of benzyl alcohol on activated clay. He observed the formation of benzyl ether only together with p-amino-benzolsulfonic acid.

We studied the dehydration of benzylalcohol on the effect of γ-aluminumoxyde catalyst.

The formation of benzyl ether was examined as a function of temperature and space velocity in continuous system. The temperature was varied between 200° and 500° and the values of space velocity between 0,05—0,4 hr^{-1}. The transformation is shown by the following reaction equation:



It was found that benzyl ether may be produced with good yield between 220 and 300 C°. Between the aforementioned temperature the yield was 50—66%, while the reaction took place without by-products, thus the unconversed 34—50% benzyl

alcohol might be regained and reacted. The dominating by-reactions above 300 C° are being studied.

At this process the changes of activity of catalyst was examined in connection with the function of time. It was proved that during the conversion of benzyl alcohol to benzyl ether the activity of γ-aluminumoxyd catalyst did not decrease. When preparing 500 g benzyl ether in 50 ml reaction space at 270 C° the activity of catalyst remains practically unchanged at 0,2 hr^{-1} space velocity. It was therefore uncessary to reactivate the catalyst under 100 hr functioning time.

Evaluating our experiments graphically the $H = f(t)_v$ function is shown in fig. 1. and $H = f(v)_t$ in fig. 2. where:

H: benzyl ether yield (%)

t: temperature (C°)

v: space velocity of benzyl alcohol (hr^{-1})

and the gained values are summarized in table 1.

Table I

	Benzyl alcohol		Temperature C°	Benzyl-ether yield %	Regained benzyl alcohol %	By-product %
	dosing velocity	space velocity				
	ml/hr	hr^{-1}				
1.	10,0	0,2	220	41	59	0
2.	10,0	0,2	230	50	50	0
3.	10,0	0,2	250	60	40	0
4.	10,0	0,2	270	66	34	0
5.	10,0	0,2	300	48	18	34
6.	10,0	0,2	350	10	0	90
7.	10,0	0,2	400	0	0	100
8.	10,0	0,2	500	0	0	100
9.	2,5	0,05	230	50	50	0
10.	5,0	0,1	230	50	50	0
11.	15,0	0,3	230	40	60	0
12.	20,0	0,4	230	30	70	0
13.	20,0	0,4	250	60	40	0
14.	20,0	0,4	270	65	35	0
15.	20,0	0,4	280	55	20	25
16.	20,0	0,4	300	45	20	35
17.	5,0	0,1	270	63	37	0
18.	10,0	0,2	200	10	90	0

Fig. 1. shows the known facts at the heterogenous catalytic dehydration reaction in vapour-phase that the yield of the forming compound changes along the maximum curve in the function of temperature.

Experimental

Starting substances:

1. Benzyl alcohol: b. p. 205 C°; D_{15}^{15}: 1,050 g/cm³; n_D^{20}: 1,5396.

2. The preparation of γ-aluminumoxyde catalyst took place from the watery solution of aluminium nitrate precipitated with ammonium hydroxyde. The washing

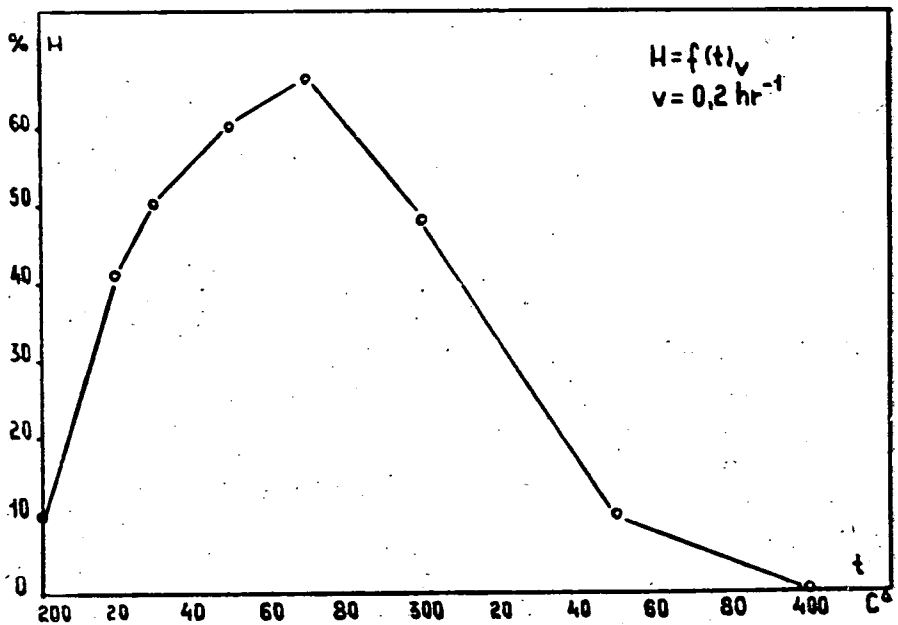

% H
H=f(t)v
v=0,2 hr-1
60
50
40
30
20
10
0
t
200 20 40 60 80 300 20 40 60 80 400 C°

Fig. 1

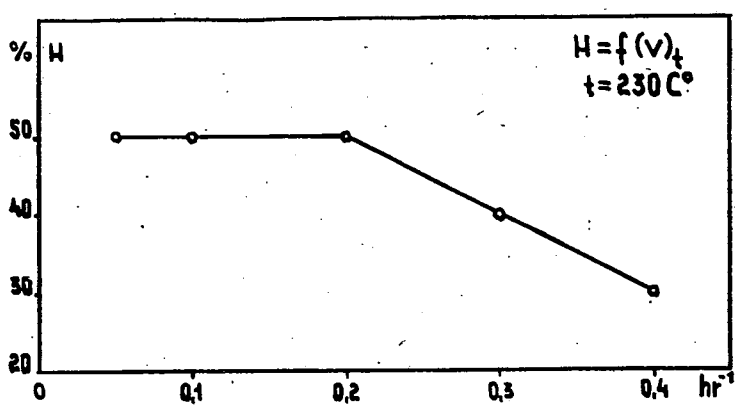

% H
H=f(v)t
t=230 C°
50
40
30
20
0 0,1 0,2 0,3 0,4 hr-1

Fig. 2

was followed by slow drying then by thermic dehydration at 500 C° and activation of the catalyst with air at 400 C°.

Description of the experiments

The process was studied at 200—500 C° in a vertical Rasotherm glass tube reactor. The volume of the reaction space was 50 ml ($1{,}2^2 \cdot \pi \cdot 11 \sim 50$ ml). The temperature was measured on iron constantan thermoelement controlled by mercurial thermometer and regulated with a drop-bridle thermoregulator. The sensitive point of the thermoelement was placed in a tube which was in the middle of the reaction space. The dosing was done with a syringe driven by a clockwork, thus securing the regular feeding of the reactors. At one experiment 50 ml benzyl alcohol was used and every experiment was repeated twice.

The isolation of the product

The products after the dehydration reaction ware separated from water, dried and fractionated by distillation. Owing to the great difference of the boiling point of the two substances the separation was easily carried out by a simple distillation. Benzyl-ether: b. p. 170 C° (16 Hgmm); D_4^{20}: 1,043 g/cm^3; n_D^{20}: 1,5614; C: 85,12; H: 6,98%; calculated from $C_{14}H_{14}O$: C: 84,81; H: 7,12%.

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ИЗГОТОВЛЕНИЕ БЕНЗИЛОВОГО ЭФИРА ИЗ БЕНЗИЛОВОГО СПИРТА В ПАРОВОЙ ФАЗЕ

М. Барток

На катализаторе γ-Al_2O_3 можно осуществлять дегидратацию бензилового спирта с методом парофазного гетерогенного катализа в проточной системе, если условия реакции следующие: температура: 220—300 C°; объёмная скорость: 0,05—0,4 час$^{-1}$. Выход безилового эфира, при этих условиях, 50—66%.