

Transformations of butyraldehyde in the presence of catalysts based on large-pore molecular sieves VPI-5 and $\text{AlPO}_4\text{-8}$

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It is found that zeolite-like crystalline aluminophosphates VPI-5, Si-VPI-5, and Mn-VPI-5 as well as those derived from them, $\text{AlPO}_4\text{-8}$, $\text{SAPO}_4\text{-8}$, and $\text{MnAPO}_4\text{-8}$, are capable of catalyzing aldol condensation and crotonization of butyraldehyde (BA). $\text{Pd}/\text{AlPO}_4\text{-8}$ is catalytically active in hydrocondensation of BA with H_2 at atmospheric pressure. The activities in BA conversion to 2-ethylhexane-3-ol-1-al increase in the following order: $\text{Mn-VPI-5} < \text{Si-VPI-5} < \text{VPI-5}$. The same order of activities is also found for $\text{AlPO}_4\text{-8}$, $\text{SAPO}_4\text{-8}$, and $\text{MnAPO}_4\text{-8}$. These catalysts are characterized by a lower initial activity in crotonization of BA than M^+NaX (CsNaX), but they are much more stable. $\text{Pd}/\text{AlPO}_4\text{-8}$ catalyzes BA conversion to 2-ethylhexanal even in the absence of H_2 feed to the reaction zone. The influence of catalyst pretreatments and experimental conditions on the catalyst structures and catalytic activities is discussed.

Key words: butyraldehyde; condensation; crystalline aluminophosphates; molecular sieves; VPI-5; $\text{AlPO}_4\text{-8}$; catalysis.

Earlier we have shown¹ that isomerization of *o*- and *m*-xylenes, alkylation of toluene with methanol, and dehydration of alcohols can proceed on the catalysts derived from crystalline aluminophosphate VPI-5 and its modification with silicon (Si-VPI-5) and manganese (Mn-VPI-5). VPI-5 is a zeolite-like molecular sieve of a new generation, which exhibits some specific structural and physicochemical properties.²⁻⁴ In this work, we have studied transformations of butyraldehyde (BA) in the presence of VPI-5, Si-VPI-5, Mn-VPI-5, $\text{AlPO}_4\text{-8}$, $\text{SAPO}_4\text{-8}$, $\text{MnAPO}_4\text{-8}$, and $\text{Pd}/\text{AlPO}_4\text{-8}$.

X-zeolites with exchangeable cations of alkali metals, which exhibit the properties of solid bases,^{5,6} are active catalysts for aldol condensation and crotonization of BA. In the presence of HNaX , HNaY , M^{n+}X , and M^{n+}Y , the process proceeds at a lower rate. In addition, the selectivity of the above-listed catalysts is somewhat lower than that of M^+NaX and M^+NaY .^{5,7}

When polyfunctional systems, in particular, compositions consisting of group VIII metals (Pt, Pd, Rh, Ni, or Co) and M^+NaX zeolites ($\text{M} = \text{Na}^+$, K^+ , or Rb^+) are used,^{5,8,9} the one-stage interaction of BA with H_2 yields two products — 2-ethylhexanal and 2-ethylhexanol-1. In this case, crotonization of BA and hydrogenation of carbonyl compounds are combined in a single process. The selectivity of the BA transformations is governed by the nature, state, and concentration of the metal that

plays the role of a hydrogenating component of the catalyst, as well as by the zeolite compositions and process conditions.^{8,9}

Experimental

The experiments were carried out either in a glass flask equipped with a reflux condenser and a magnetic stirrer under static conditions or in a flow system at atmospheric pressure using the procedure described in Ref. 5. H_2 was purified from O_2 and H_2O admixtures by passing through the columns filled with $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ and CaA zeolite; N_2 was purified by passing through the columns with $\text{Ni}/\text{Al}_2\text{O}_3$ and CaA zeolite.

The following catalysts were used in the experiments: (1) powder VPI-5 crystallites ($\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$ mole ratio was equal to one); (2) Si-VPI-5 synthesized as described earlier in Ref. 10; (3) Mn-VPI-5 prepared by VPI-5 treatment with a manganese salt, including the samples that were heated at 100–500 °C; this treatment resulted in the transformation of the VPI-5 structure to the $\text{AlPO}_4\text{-8}$ structure;¹¹⁻¹⁵ and (4) 0.2–0.5 % $\text{Pd}/\text{VPI-5}$ prepared by impregnation of powder VPI-5 with an aqueous $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ solution followed by thermal treatment.

Prior to carrying out catalytic reactions, granulated samples containing no binder (particle size 1–2 mm) were heated for 5 h in a flow of dry air at 500 °C. At this temperature, the organic reagent (di-*n*-propylamine), which was used for the synthesis of VPI-5,¹ was almost completely destroyed. The temperature was gradually raised at a rate of ~5 °C min^{-1} ; the samples were kept at 100 °C for 2 h and then at 200, 300, and

400 °C for 1 h at each temperature. Regeneration of the samples was performed under the same conditions.

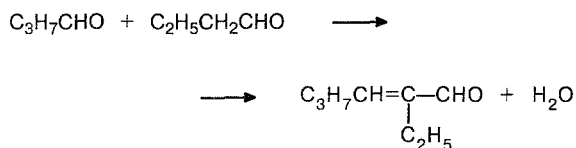
Reaction products were analyzed by gas-chromatography.⁵

The catalytic activities measured in the flow system varied with time during the reactions. The data given below in the tables refer to the maximum product yields in the experiments which lasted 5 h.

Variations in the crystalline structure of the molecular sieves studied were detected by X-ray diffraction analysis using a Dron-3 instrument.

Results and Discussion

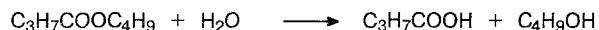
Crotonization of *n*-butyraldehyde



On the catalysts derived from VPI-5 and M-VPI-5 (M = Si, Mn), at 125–200 °C, BA is converted to 2-ethylhexenal (2-EH) and water with the selectivity (*S*) of 90.5–96.5 %. A 33.3 % yield of 2-EH is attained on VPI-5 at 200 °C and a volume velocity of the BA feed (*V*) 0.5 h⁻¹ (Table 1). The reaction products contain small amounts of 2-ethylhexane-3-ol-1-al, butyl butyrate (a product of the Tishchenko condensation of BA)



and *n*-butanol which appears to be formed by hydrolysis of the ester.



Another product of hydrolysis is butyric acid. At initial stages of the process, the acid is nearly completely adsorbed by the solid catalysts. BA partially decomposes, evolving gaseous products.

In contrast to the earlier studied reactions of xylene isomerization, toluene alkylation with methanol, and alcohol dehydration,¹ the catalyst derived from Mn-VPI-5 is least active in BA condensation, whereas the catalyst derived from Si-VPI-5 is somewhat less active than that derived from VPI-5.

It should be noted that VPI-5 heated at 200 °C, when di-*n*-propylamine is not yet completely removed,¹ exhibits a slightly higher activity than the sample treated in flowing dry air at 500 °C. Probably, the higher activity of the catalyst treated at 200 °C is associated with the presence of organic base, which contributes to its activity. However, during the thermal treatment, in addition to the removal of water and organic substances from the crystals of the molecular sieve, its structure can change.^{11–15}

According to the literature data,³ VPI-5 dehydrated in a vacuum retains the original topology of VPI. According to other data,^{11–13} during thermal dehydration,

Table 1. Condensation of butyraldehyde on various catalysts

Catalyst	<i>T</i> /°C	Aldehyde conversion (%)				<i>S</i> (A/B) (%)
		to butanol	to butylbutyrate	to 2-ethylhexenal (A)	total (B)	
VPI-5	150*	0.08	0.23	26.0	27.0	96.5
[AlPO ₄ -8]	175*	0.10	0.40	29.8	31.5	94.8
	200*	0.20	0.75	33.3	35.5	93.9
	125	0.05	0.15	12.0	12.5	96.0
	150	0.05	0.20	18.9	20.0	94.5
	175	0.10	0.40	23.5	25.0	94.0
	200	0.15	0.65	26.5	28.5	93.6
	200**	0.10	0.70	31.0	33.2	93.5
Si-VPI-5	125	0.03	0.10	10.0	10.8	93.5
[SAPO ₄ -8]	150	0.03	0.15	15.6	17.0	91.8
	175	0.05	0.40	20.8	23.0	90.5
	200	0.07	0.60	23.5	26.0	90.4
Mn-VPI-5						
[MnAPO ₄ -8]	150	0.05	0.05	6.5	6.8	95.5
	175	0.10	0.15	10.0	10.6	94.4
	200	0.15	0.25	12.5	13.4	93.2
0.65CsNaX***						
	100	—	—	41.0	41.3	99.2
	125	0.3	0.3	51.6	52.2	99.0
0.81CaNaX***						
	125	—	—	17.2	17.6	97.7
0.70RbNaY***						
	150	—	—	15.7	15.7	100
	200	—	0.7	35.3	36.0	98.0

Notes. The numbers preceding cations in the zeolite formulas indicate the fraction of Na⁺ ions exchanged with Mⁿ⁺; SiO₂/Al₂O₃ mole ratios are 2.5 and 4.4 for zeolites X and Y, respectively. *V* = 1 h⁻¹, *T*₀ = 500 °C, catalyzates contain 0–1.5 % of 2-ethylhexane-3-ol-1-al.

* *V* = 0.5 h⁻¹. ** *T*₀ = 200 °C. *** See Ref. 5.

VPI-5 undergoes a polymorphous transformation to AlPO₄-8, which results in the rearrangement of 18-membered rings of VPI-5 to 14-membered rings of AlPO₄-8. The extent of the rearrangement of VPI-5 to AlPO₄-8 is dependent on the conditions of thermal treatment (atmospheric pressure, a vacuum, heating rate, etc.)¹³ and on the procedure of the VPI-5 production.^{14–15} It is found¹⁵ that, depending on the conditions of the synthesis, in particular, on the order in which the reagents are added, two forms of VPI-5 can be obtained. One product can be successfully dehydrated without marked structural changes, whereas another product is subjected to hydrolysis and transformation to AlPO₄-8. Therefore, the conditions of the material synthesis must be carefully controlled.¹⁵ The combined action of heating and water vapor can result in complete destruction of the VPI-5 structure.

Related information on the behavior of Si-VPI-5 and Mn-VPI-5 is still limited.

Table 2. The effect of various treatments on the structures of VPI-5, Si-VPI-5, and Mn-VPI-5

Sample	Treatment	Crystal-line phase from XRD data
VPI-5	Original, hydrated	VPI-5
	Evacuation, 20 °C, 0.1 Torr, 10 h	VPI-5
	Evacuation, 20 °C, 0.1 Torr, 10 h + 75 °C, 0.1 Torr, 10 h	VPI-5
	In air, 20–200 °C, 2 h, 200 °C, 5 h	AlPO ₄ -8
	In air, 20–400 °C, 5 h, 400 °C, 5 h	AlPO ₄ -8
	In air, 20–500 °C, 5 h, 500 °C, 5 h	AlPO ₄ -8
	In air, 20–200 °C, 5 h, 200 °C, 5 h + BA reaction, 200 °C, 5 h	AlPO ₄ -8
	In air, 20–500 °C, 5 h, 500 °C, 5 h + BA reaction, 200 °C, 5 h	AlPO ₄ -8
	In air, 20–500 °C, 5 h, 500 °C, 5 h + reaction (toluene + methanol), 500 °C, 5 h	AlPO ₄ -8
	Si-VPI-5	Original, hydrated
Evacuation, 20 °C, 0.1 Torr, 10 h + 75 °C, 0.1 Torr, 10 h		VPI-5
In air, 20–500 °C, 5 h, 500 °C, 5 h		SAPO ₄ -8
Mn-VPI-5	Original, hydrated	VPI-5
	Evacuation, 20 °C, 0.1 Torr, 10 h + 75 °C, 0.1 Torr, 10 h	VPI-5
	In air, 20–500 °C, 5 h, 500 °C, 5 h	AlPO ₄ -8

When VPI-5 and M-VPI-5 are used in catalysis, in addition to the above-indicated factors, one more factor, *i.e.*, the effect of a reaction medium, should be taken into account. Systematic studies in this direction are of great importance for determining the possibilities of using these solids and for elucidating the nature of the phase that is responsible for the activity of the developing catalysts.

Table 2 summarizes the data related to the effect of pretreatment on the structure of aluminophosphates. The following conclusions can be drawn.

(1) VPI-5 synthesized by the known procedure¹⁰ undergoes no structural changes after evacuation at 20 °C (weight loss is 7.9 %) and at 75 °C (21.9 %); this finding completely agrees with the literature data.¹⁴

(2) The thermal treatment in an air flow at 20–200 °C for 3 h and then at 200 °C for 5 h gives rise to the rearrangement of VPI-5 to AlPO₄-8. The same process occurs at 400 and 500 °C, when di-*n*-propylamine is completely removed from the aluminophosphate.¹

(3) No additional changes in the structure of the AlPO₄-8 molecular sieve are found for the samples that are used in the reactions of crotonization of BA (at 200 °C) and of toluene alkylation with methanol (at 500 °C), accompanied by H₂O evolution. Hence, there is no influence of both reaction media under these conditions.

Similar results are obtained for Si-VPI-5 and Mn-VPI-5 (see Table 2). Note that weight losses for Si-VPI-5 and Mn-VPI-5 are 9.8 and 8.0 % after evacuation at 20 °C and 18.0 and 16.8 % after evacuation at 75 °C, respectively.

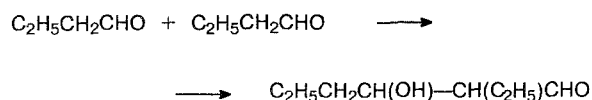
It follows from the data obtained that the values given in Table 1 and those reported earlier in Ref. 1 refer not to VPI-5, Si-VPI-5, and Mn-VPI-5, but to the catalysts having the AlPO₄-8 structure. To remove water and organic template from aluminophosphates and to avoid the transformation of VPI-5 to AlPO₄-8, it is necessary to employ another procedure for thermal pretreatment of the crystallites, which must differ from the procedures used earlier¹ and in this work.

Bearing in mind these general remarks, let us turn back to considering the data of Table 1, in which the literature data⁵ for CsNaX, CaNaX, and RbNaY zeolites are also presented for comparison. As one can see, the catalysts derived from VPI-5 (AlPO₄-8) and M-VPI-5 (MAPO₄-8) are inferior to 0.65CsNaX and comparable with 0.81CaNaX and 0.70RbNaY (SiO₂/Al₂O₃ = 4.4) with respect to the maximum activity, *i.e.*, to the initial rate in the experiments that lasted 5 h. However, BA transformations to 2-EH on AlPO₄-8, SAPO₄-8, and MnAPO₄-8 decrease only by 15–30 % within 5 h, while those on CsNaX and RbNaY diminish by a factor of 2–3.5 (Table 3), and after 5 h on stream, the order of catalytic activities changes. Thus, the aluminophosphate systems are much superior to faujasites with respect to catalytic "stability". This characteristic feature makes them very attractive for comprehensive studies.

Table 3. Variations in 2-ethylhexenal yields (% of theoretical yields) with time in the course of butyraldehyde condensation on various catalysts ($V = 1 \text{ h}^{-1}$)

Catalyst	$T/^\circ\text{C}$	t/h				
		1	2	3	4	5
AlPO ₄ -8	150*	26.0	25.0	24.0	23.0	22.5
	200*	33.3	31.5	30.0	29.0	28.5
	150	18.9	17.5	16.3	14.8	13.8
	200	26.5	24.0	23.0	21.0	20.5
SAPO ₄ -8	150	15.6	13.0	12.3	11.4	10.8
	200	23.5	22.6	21.5	20.5	20.0
MnAPO ₄ -8	150	6.5	6.4	6.3	5.9	5.7
	200	12.5	11.8	10.5	9.8	8.8
0.65CsNaX	100	41.0	21.5	18.5	15.0	12.0
	125	51.6	36.0	27.0	21.0	17.0
0.70RbNaY	150	15.7	10.5	6.5	5.5	4.5
	200	35.3	23.0	19.5	18.0	16.5

* $V = 0.5 \text{ h}^{-1}$.

Aldol condensation of butyraldehyde

This reaction proceeds at lower temperatures than other transformations of BA and, for this reason, is particularly suitable for studying the effect of pretreatment and related possible structural modifications on the activity and selectivity of the solid catalysts.

After evacuation at 20 °C for 10 h, *i.e.*, under the conditions that are used for XRD analyses, VPI-5 loses ~1/3 of the water content. Nevertheless, the structure of the aluminophosphate lattice persists after such treatment (see Table 2). The sample is active under static conditions already at room temperature (Table 4). The rise in temperature to 75 °C (b.p. of BA is 75.7 °C) makes it possible to reach a 24.5 % yield of 2-ethylhexane-3-ol-1-al for 5 h.

When the amount of the catalyst increases from 2.5 to 5 wt. %, the BA conversion grows insignificantly, and, at 10 wt. %, the conversion even decreases (see Table 4), and the yield of 2-ethylhexenal simultaneously increases. Apparently, the latter is adsorbed stronger on the active sites of VPI-5 than other compounds of the reaction mixture and, therefore, inhibits the process. This suggestion is confirmed by the time dependences of BA conversions at different amounts of the

aluminophosphate (Fig. 1, *a*): the linear dependences at 2.5 and 5 wt. % of the catalyst acquire another form at 15 wt. % and contact time 4–5 h. When a certain amount of unsaturated aldehyde is accumulated (>0.3 % in the reaction mixture), the rate of BA conversion decreases. The same dependence is also observed for AlPO₄-8 (Fig. 1, *b*).

The VPI-5 catalyst can be used in several runs without regeneration: the activity of the used catalyst in the second run is reduced only by ~25 % (see Table 4).

Evacuation of the molecular sieve at 0.1 Torr first at 20 °C and then at 75 °C and removal of ~90 % of the sorbed water (no structural change is found to occur during this treatment, see Table 2) makes almost no effect on the behavior of the developing catalytic system (see Table 4).

Si-VPI-5 pretreated under the same conditions is less active than VPI-5 (see Table 4). Mn-VPI-5 is even less active in BA condensation.

An analogous order of activities is found for the AlPO₄-8, SAPO₄-8, and MnAPO₄-8 molecular sieves, which are prepared from VPI-5, Si-VPI-5, and Mn-VPI-5, respectively, by thermal treatment under the conditions specified in Table 4.

Since the proton acidity of the samples¹ is antipate to their activities, we can draw the conclusion that the activity of the catalysts under consideration in aldol condensation of BA is not controlled by Brønsted acid sites, which interact with pyridine to yield PyH⁺ ions

Table 4. Aldol condensation of butyraldehyde under static conditions (75 °C, 5 h)

Catalyst	Pretreatment	Amount of catalyst (wt. %)	Yield of 2-ethylhexane-3-ol-1-al (% of theoretical yield) (A)	Total BA conversion* (% (B))	S(A/B) (%)
VPI-5	20 °C, 0.1 Torr, 10 h	10.0**	6.4	6.4	100
		2.5	22.0	22.0	100
		5.0	24.5	24.6	99.5
		10.0	20.6	20.9	98.5
		10.0***	15.6	15.9	98.0
		2.5	22.5	22.5	100
VPI-5	10 h + 75 °C, 0.1 Torr, 10 h	5.0	23.2	23.3	99.4
		15.0	20.8	21.2	98.1
		2.5	13.5	13.5	100
Si-VPI-5	10 h + 75 °C, 0.1 Torr, 10 h	5.0	15.7	15.8	99.4
		2.5	10.9	11.0	99.1
Mn-VPI-5	10 h + 75 °C, 0.1 Torr, 10 h	5.0	12.6	12.7	99.1
		2.5	18.8	18.8	100
AlPO ₄ -8	In air, 20–500 °C, 5 h + 500 °C, 5 h	5.0	20.0	20.1	99.5
		10.0	23.6	24.0	98.3
		15.0	20.3	20.8	97.6
SAPO ₄ -8	In air, 20–500 °C, 5 h + 500 °C, 5 h	2.5	11.5	11.5	100
		5.0	14.7	14.7	100
MnAlPO ₄ -8	In air, 20–500 °C, 5 h + 500 °C, 5 h	2.5	7.0	7.1	98.6
		5.0	10.9	11.0	99.1

* To 2-ethylhexane-3-ol-1-al + 2-ethylhexenal. ** At 20 °C. *** Reuse of the spent catalyst.

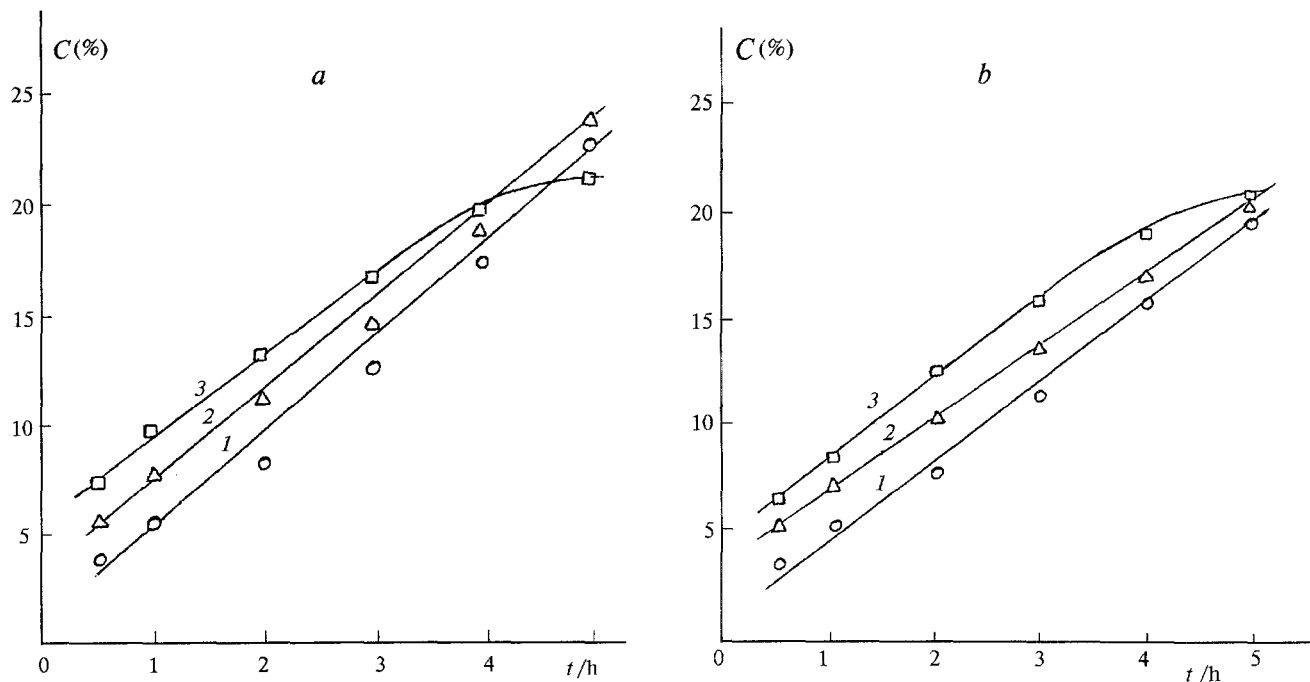
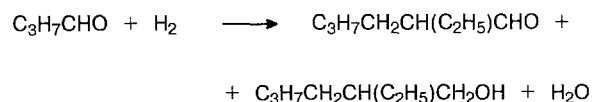


Fig. 1. Time dependences of butyraldehyde conversions (C) in the presence of VPI-5 evacuated at 75 °C (a) and of $\text{AlPO}_4\text{-8}$ at 75 °C and different amounts of the catalysts (%): 2.5 (1), 5 (2), and 15 (3).

(absorption band at 1548 cm^{-1} in the IR spectrum). There are strong grounds to suggest^{1,4} that this reaction involves weak H^+ sites, *i.e.*, apparently, P-OH groups, which are characterized by the IR band at 3675 cm^{-1} , and/or Lewis acid sites, which are detected by the IR band at 1448 cm^{-1} upon pyridine adsorption. In the case of VPI-5 and M-VPI-5, the organic base (di-*n*-propylamine), which is present in the samples pretreated at relatively low temperatures,¹ can also contribute to this reaction.

The above results can be considered as one of the first experimental proofs that VPI-5, Si-VPI-5, and Mn-VPI-5 as such and the incompletely dehydrated materials can be used as catalysts.

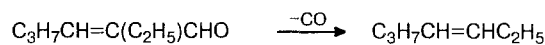
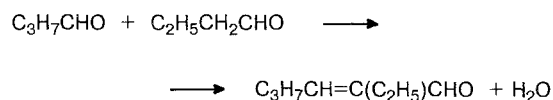
Hydrocondensation of *n*-butyraldehyde



Palladium-containing $\text{AlPO}_4\text{-8}$ exhibits the properties of a polyfunctional catalyst for BA conversions: when there is no H_2 feed, 2-ethylhexanal is still produced (Table 5). It is evident that the hydrogen formation is a result of partial decomposition of BA, for example, by the following scheme: $\text{C}_3\text{H}_7\text{CHO} \rightarrow \text{C}_3\text{H}_6 + \text{CO} + \text{H}_2$. The hydrogen is consumed both for reduction of Pd^{2+} and hydrogenation of 2-EH. A certain amount of Pd^0 can also arise from decomposition of

$\text{Pd}(\text{NH}_3)_4^{2+}$ cations in the course of thermal treatment of the catalyst.¹⁶

Two other products, *i.e.*, *n*-heptane and heptene, can be produced by the following reactions.



Pentene formation from propionaldehyde on RhY by the same reaction scheme (crotonization plus decarbonylation) was noted earlier.¹⁷

Decarbonylation and hydrogenation proceed slower on $\text{Pd}/\text{M}^+\text{NaX}$ than on $\text{Pd}/\text{AlPO}_4\text{-8}$. Probably, the state of palladium, the type of its interaction with the molecular-sieve support, and the contribution of adsorption factors (cation forms of faujasites are more polar solids) are different for these systems.

When passing a mixture of BA + H_2 over $\text{Pd}/\text{AlPO}_4\text{-8}$, yields of 2-EH sharply decrease, and BA conversion to 2-ethylhexanal and heptane simultaneously increases. At 175–200 °C, 2-ethylhexane-1-ol is produced (see Table 5). At $T > 175$ °C, BA hydrogenation to *n*-butanol becomes more intense. This appears to be related to the migration of Pd^0 particles, which are

Table 5. Hydrocondensation of butyraldehyde on Pd/AlPO₄-8 containing 0.5 % Pd, $V = 1 \text{ h}^{-1}$, $\text{C}_4\text{H}_8\text{O} : \text{H}_2 = 1 : 1.5$

Pretreatment	$T/^\circ\text{C}$	Aldehyde conversions (%)						total
		to heptane	to heptene	to butanol	to 2-ethyl-hexenal	to 2-ethyl-hexanal	to 2-ethyl-hexanol	
In air, 500 °C, 5 h	150*	3.5	0.05	0.05	10.0	3.3	—	22.4
	200*	15.0	0.1	0.35	6.1	6.3	—	40.0
	150**	3.5	0.2	0.07	2.1	3.4	—	14.4
	150***	6.0	0.1	0.10	9.7	2.8	—	27.0
	125	0.7	0.7	0.15	0.2	3.8	—	12.0
	150	5.0	3.0	0.35	0.1	7.7	—	28.0
	175	6.5	6.5	1.3	0.1	9.0	0.2	39.0
	200	9.0	14.5	7.0	0.2	5.6	4.0	59.0
In air, 500 °C, 5 h + + H ₂ , 400 °C, 5 h	150	2.5	1.5	4.0	0.2	14.0	0.5	25.6
	175	6.5	2.5	5.0	0.6	12.5	0.6	30.0
	200	9.5	7.5	8.0	0.7	7.5	2.5	45.0
H ₂ , 400 °C, 5 h + + in air, 500 °C, 5 h	150*	5.0	0.3	0.3	7.0	4.2	—	23.0
	175*	9.5	0.2	0.4	11.3	5.6	—	37.0
	200	12.0	0.1	0.6	6.5	6.6	—	39.0

* No carrier gas, no H₂ feed. ** In a N₂ flow, at a C₄H₈O to N₂ molar ratio of 1 : 1.5. *** No carrier gas, after the run with H₂ at 200 °C.

Table 6. Hydrocondensation of butyraldehyde on 0.2 % Pd/AlPO₄-8 ($\text{C}_4\text{H}_8\text{O} : \text{H}_2 = 1 : 1.5$)

V/h^{-1}	$T/^\circ\text{C}$	Aldehyde conversions (%)						total
		to heptane	to heptene	to butanol	to 2-ethyl-hexenal	to 2-ethyl-hexanal	to 2-ethyl-hexanol	
0.5	175*	8.0	0.1	0.1	0.1	3.7	—	38.0
	200*	23.0	0.1	0.1	3.5	4.5	—	51.0
	150	3.0	1.4	0.4	0.2	4.8	—	36.0
	175	5.5	1.6	0.6	0.2	5.8	0.2	46.0
	200	9.0	2.3	1.0	0.2	3.5	0.4	50.0
	150**	6.0	0.6	0.4	0.1	9.2	—	38.0
	175**	9.0	0.7	0.4	0.1	8.2	0.3	49.0
1	200*	9.7	0.3	0.1	5.5	4.0	—	34.0
	150	1.8	0.7	0.2	0.3	3.8	—	14.0
	175	6.0	1.0	0.4	0.3	8.6	—	30.0
	200	7.6	1.3	1.2	0.4	9.0	0.2	40.0

* No carrier gas, no H₂ feed. ** At a C₄H₈O to H₂ molar ratio of 1 : 0.8.

formed by H₂ interaction with the catalyst, toward the outer surface of the aluminophosphate crystals. Hydrogenation of BA on Pd⁰ particles can proceed prior to its condensation to 2-EH; the condensation can be catalyzed by the active sites located mainly inside the cavities of AlPO₄-8.

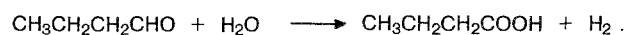
Prereduction of 0.5 % Pd/AlPO₄-8 in hydrogen at 400 °C sharply changes the selectivity of the developing catalyst: yields of saturated C₈ aldehyde and butanol increase, thus confirming the migration of the major part of Pd toward the outer surface of the molecular-sieve crystals, whereas heptene yields decrease (see Table 5).

Oxidation of the reduced sample in air at 500 °C yields a catalyst that is similar to Pd/AlPO₄-8, which is not subjected to the pretreatment in hydrogen.

It should be noted that the properties of the systems studied can be almost completely reproduced in repeated cycles consisting of the activation, run, and regeneration.

Similar results are obtained for the catalyst containing 0.2 % of Pd. However, decomposition of BA to gaseous products occurs to a lesser extent on this catalyst (Table 6).

In some cases, butyric acid is found among the reaction products of BA transformations in the presence of H₂ on Pd/AlPO₄-8 (yields up to 4 % of BA converted). Apparently, the acid is produced by the following reaction:



This reaction type is known for BA conversions on metal catalysts.¹⁸

Summarizing the results of this work, we can conclude that palladium-containing $\text{AlPO}_4\text{-8}$ exhibits some specific properties and can catalyze various reactions of organic substances. This finding opens new paths of scientific research.

The body of the experimental data obtained earlier¹ and in this work allow us to conclude that crystalline aluminophosphates VPI-5 and $\text{AlPO}_4\text{-8}$, which can be obtained by thermal treatment under specific conditions, can serve as a basis for the preparation of efficient catalysts for a number of chemical transformations. The modification of the molecular sieves by silicon or manganese makes it possible to expand the versatility of catalytic applications. The behavior of the developing catalytic systems is largely dependent on the procedure that is employed for water removal from the crystallites during their activation prior to use in catalysis.

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