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CATALYSIS

Hydrogenation of *n*-Heptanal, Catalyzed by Cobalt Carbonyl Phosphine Complex

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Abstract—The use of the cobalt carbonyl phosphine complex $Co_2(CO)_6(PR_3)_2$ ($R = C_4H_9$) as catalyst precursor allows synthesis of *n*-heptanol from *n*-heptanal to be performed with high selectivity.

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Higher linear aliphatic aldehydes, in particular, *n*-heptanal, are intermediates in synthesis of higher linear alcohols, which are mainly used as surfactant components. In Russian, EU, and US industry, aldehydes are produced by hydroformylation (oxo synthesis):

$$RCH{=}CH_2 + CO + H_2 \xrightarrow{\text{Cat.}} RCH_2CH_2CHO. \qquad (1)$$

Reaction (1) is catalyzed by cobalt and rhodium carbonyl complexes. Hydrogenation of aldehydes into the corresponding alcohols in industrial oxo synthesis processes [Eq. (2)] is performed on heterogeneous catalysts and is characterized by high yields of target products and high productivity of reaction installations:

$$RCH_2CH_2CHO + H_2 \xrightarrow{\text{Cat.}} RCH_2CH_2CH_2OH. \qquad (2)$$

The drawback of the heterogeneous hydrogenation of aldehydes prepared by oxo synthesis is the need for performing, along with the distillation step, an additional power-consuming step of catalyst separation from the reaction products. Along with well-known heterogeneous hydrogenation catalysts, homogeneous catalysts of reaction (2), containing compounds of platinum [1], cobalt [2], rhodium [3, 4], and other Group VIII *d* elements [5, 6] are also known. They ensure the same output parameters of petrochemical processes as industrial heterogeneous catalysts do. Of particular interest among them are rhodium and cobalt carbonyl complexes, as they allow reactions (1) and (2) to be performed on one catalyst in one reactor and, correspondingly, the step of catalyst separation from the reaction products to be eliminated from the oxo synthesis process.

For the catalyst regeneration, an aqueous solution of cobalt acetate is added to the reaction product, and the resulting mixture after mixing is fed to fractional distillation for isolating commercial C_7 alcohols. The process is performed in the syngas atmosphere. Cobalt transforms into the compound $Co[Co(CO)_3P(C_4H_9)_3]_2$, from which the active form of the catalyst, $HCo(CO)_3P(C_4H_9)_3$, can be readily prepared. Among aldehydes, we chose *n*-heptanal, because it can be prepared by hydroformylation of 1-hexene in accordance with Eq. (1). 1-Hexene, in turn, is an intermediate product of polypropylene oligomerization process commercially implemented in Russia at OAO Nizhnekamskneftekhim. Cobalt carbonyl complexes were tested as catalysts, because specifically these complexes are used for oxo synthesis (propylene hydroformylation) of butanols and 2-ethylhexanol at plants in Perm (Russia) and Salavat (Bashkortostan, Russia).

Table 1. Influence of temperature on the rate and selectivity of *n*-heptanal hydrogenation. $P = 20.0$ MPa, [Co] = 0.1 wt %; CO : H_2 = 1 : 1 (by volume); Co : $P(C_4H_9)_3$ = 1 : 2; loaded amounts: 114.9 g (140×10^{-3} dm^3) of *n*-heptanal, 121.3 g (140×10^{-3} dm^3) of hexane (solvent)

T, °C	Reaction time, s	Content in reaction products, wt %			*n*-Heptanal conversion, %	Selectivity with respect to *n*-heptanol, %
		n-heptanal	*n*-heptanol	HBBPs		
160	0	48.6	–	–	–	–
	7.2×10^3	45.4	3.0	0.3	6.2	97.5
	1.08×10^4	42.0	6.0	0.8	12.7	95.3
180	0	48.6	–	–	–	–
	7.2×10^3	40.5	7.1	1.2	15.9	93.3
	1.08×10^4	28.5	17.7	3.7	40.3	87.7
200	0	48.6	–	–	–	–
	7.2×10^3	31.1	15.9	1.8	35.9	89.8
	1.08×10^4	7.6	34.1	7.4	84.3	82.1

EXPERIMENTAL

The *n*-heptanal hydrogenation was studied in a 0.5 dm^3 high-pressure batch reactor with airtight electric drive [7]. The kinetic control of the *n*-heptanal hydrogenation (3) was ensured by stirring the liquid phase at a high rate (~47 rps).

$$C_6H_{13}CHO + H_2 \xrightarrow{T,\ \text{cat.}} C_6H_{13}CH_2CH_2OH. \qquad (3)$$

The installation also included buffer vessels for carbon monoxide, hydrogen, and syngas, and also ~0.01 dm^3 high-pressure samplers that could be cut off. The reactor purged with carbon monoxide was charged with a solution of $Co_2(CO)_8$ in hexane and with a modifier, tributylphosphine $P(C_4H_9)_3$, after which syngas CO + H_2 was fed to a pressure of 10.0 MPa, and heating and stirring were switched on. *n*-Heptanal was charged into the high-pressure loading vessel purged with argon and syngas. On reaching the temperature of the experiment, *n*-heptanal was transferred into the reactor by the syngas pressure, and the pressure in the reactor was raised to 20.0 MPa. When studying the influence of the partial pressures of hydrogen (H_2) and carbon monoxide (CO), syngas of preset composition was prepared in the buffer vessels, was fed into the reactor, and was used for transferring *n*-heptanal from the loading vessel. Liquid phase samples were taken in the course of the experiment and were analyzed by gas–liquid chromatography under the following conditions: 3-m stainless steel column; Reoplex-400 liquid phase, 15 wt % on Chromaton N-AW-DMCS (fraction 0.16–0.20 mm); column temperature 140°C; flame ionization detector (FID), detector temperature 160°C; vaporizer temperature 200°C; carrier gas argon; flow rates, dm^3 s^{-1}: argon 5×10^{-4}, air 6.7×10^{-4}.

The hydroformylation is performed at increased syngas pressure, up to 30 MPa, which is necessary for ensuring the thermal stability of cobalt and rhodium carbonyl complexes at 110–180°C. Among cobalt complexes acting as catalyst precursors, dicobalt octacarbonyl $Co_2(CO)_8$ and the cobalt carbonyl phosphine complex $Co_2(CO)_6[P(C_4H_9)_3]_2$ are the most frequently used. Under the conditions of reaction (1), they form true hydroformylation catalysts: cobalt hydrocarbonyl $HCo(CO)_4$ and phosphine-substituted cobalt hydrocarbonyl $HCo(CO)_3[P(C_4H_9)_3]$, in accordance with the equations of activation of these catalyst precursors:

$$Co_2(CO)_8 + H_2 \xrightleftharpoons{T,\ \text{cat.}} 2HCo_2(CO)_4, \qquad (4)$$

$$Co_2(CO)_6[P(C_4H_9)_3]_2 \rightleftharpoons Co(CO)_3P(C_4H_9)_3, \qquad (5)$$

Performing reaction (1) in the presence of $HCo(CO)_3P(C_4H_9)_3$ allows the pressure to be decreased to 20.0 MPa, the yield of linear aldehydes to be

Table 2. Influence of the partial pressure of hydrogen on the rate and selectivity of *n*-heptanal hydrogenation. P_{CO} = 10.0 MPa; T = 180°C; reaction time 1.08 × 10^4 s; [Co] = 0.1 wt %; Co : $P(C_4H_9)_3$ = 1 : 2; loaded amounts: 114.9 g (140 × 10^{-3} dm^3) of *n*-heptanal, 121.3 g (140 × 10^{-3} dm^3) of hexane (solvent)

$P(H_2)$, MPa	Content in reaction products, wt %			*n*-Heptanal conversion, %	Selectivity with respect to *n*-heptanol, %
	n-heptanal	*n*-heptanol	HBBPs		
10.0	28.5	17.7	3.7	40.3	87.7
15.0	24.4	20.3	4.3	48.9	84.3
20.0	19.5	23.6	5.8	59.7	80.1

Table 3. Influence of the partial pressure of carbon monoxide on the rate and selectivity of *n*-heptanal hydrogenation. $P(H_2)$ = 7.0 MPa; T = 180°C; reaction time 1.08 × 10^4 s; [Co] = 0.1 wt %; Co : $P(C_4H_9)_3$ = 1 : 2; loaded amounts: 114.9 g (140 × 10^{-3} dm^3) of *n*-heptanal, 121.3 g (140 × 10^{-3} dm^3) of hexane (solvent)

P_{CO}, MPa	Content in reaction products, wt %			*n*-Heptanal conversion, %	Selectivity with respect to *n*-heptanol, %
	n-heptanal	*n*-heptanol	HBBPs		
6.0	30.8	16.4	1.6	36.4	91.3
10.0	34.1	13.2	1.5	29.7	90.1
14.0	38.3	9.6	0.9	21.1	92.2

increased, and the hydrogenating function of the catalyst to be considerably enhanced compared to $HCo(CO)_4$. Therefore, we chose $Co_2(CO)_6[P(C_4H_9)_3]_2$ as precursor. We examined the influence of temperature, contact time, and partial pressures of hydrogen and carbon monoxide on the rate and selectivity of the hydrogenation of *n*-heptanal into *n*-heptanol:

$$n\text{-}C_6H_{13}CHO + H_2 \xrightarrow[P = 20\text{ MPa},\ \text{cat } HCo(CO)_3P(C_4H_9)_3]{T = 60\text{–}200°C} C_6H_{13}CH_2CH_2OH. \qquad (3)$$

Preliminary experiments have shown that reaction (6) starts to occur at a noticeable rate at 160°C. Above 200°C, $Co_2(CO)_6[P(C_4H_9)_3]_2$ starts to decompose. Therefore, we chose for the study the temperature interval 160–200°C. The rate of reaction (6) increases with temperature. For example, whereas at 160°C and contact time of 1.08 × 10^4 s the *n*-heptanal conversion was 12.7%, at 200°C it was 84.3% in the same time (Table 1).

The selectivity with respect to *n*-heptanol decreases with increasing contact time because of the occurrence of side reactions such as crotonic condensation of *n*-heptanal and other transformations yielding high-boiling by-products (HBBPs). An increase in the hydrogen partial pressure from 10.0 to 20.0 MPa also leads to an increase in the *n*-heptanal conversion (from 40.3 to 59.7%, Table 2), i.e., accelerates reaction (6).

Carbon monoxide, on the contrary, inhibits the *n*-heptanal hydrogenation. For example, as the partial pressure P_{CO} is increased from 6.0 to 14.0 MPa (Table 3), the *n*-heptanal conversion decreases from 36.4 to 21.1%, with no appreciable changes in the selectivity with respect to *n*-heptanol.

Based on the results obtained, optimum conditions were found for performing reaction (6) to prepare *n*-heptanol from *n*-heptanal with high selectivity: T = 200°C, P = 20.0 MPa, CO : H_2 = 1 : 1 (by volume), contact time 1.08 × 10^4 s, [Co] = 0.1 wt %, Co : $P(C_4H_9)_3$ = 1 : 2.

CONCLUSIONS

(1) Effective catalyst for selective hydrogenation of *n*-heptanal to *n*-heptanol, generated in situ from $Co_2(CO)_6[P(C_4H_9)_3]_2$, was found.

(2) Optimum conditions were found for preparing *n*-heptanol from *n*-heptanal in the presence of $Co_2(CO)_6[P(C_4H_9)_3]_2$.

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