

CARBONYLATION OF 1-HEXENE IN THE PRESENCE OF
PALLADIUM-ANION-EXCHANGE RESIN CATALYSTS

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Activated charcoal, silica gel, and zeolites [1, 2] containing palladium are active in the carbonylation of lower olefins by carbon monoxide. In the present work, we studied the carbonylation of 1-hexene in the presence of a series of palladium catalysts containing AN-221, AN-251, and AN-511 anion-exchange catalysts produced in the Soviet Union as the supports.

RESULTS AND DISCUSSION

The following supports were used: 1) AN-211, obtained from the copolymer of styrene with 8% divinylbenzene (DBV) by animation of a copolymer of chloromethylated styrene (CMS) with DBV using ethylenediamine; 2) AN-511, which was obtained by the animation of a copolymer of CMS with DBV using diethylenetriamine; 3) AN-251, which was obtained by the copolymerization of 2-methyl-5-vinylpyridine with DBV [3].

At 170°C and 100 atm CO, 0.75 Pd/AN-221 (Ct-1), 0.5% Pd/AN-251 (Ct-2), and 0.75% Pd/AN-511 (Ct-3) all display activity in the carbonylation of 1-hexene. The carboxylic acid (CA) yields ranged from 45% to 85%. 1-Hexene was converted into a mixture of enanthoic and 2-methylcaproic acids. Stable olefin conversion was found upon repeated use of these Pd-anion-exchange resin catalysts. In the presence of palladium catalysts Ct-1 and Ct-3 with highest palladium content (0.75%), the curves for the conversion of olefin to CA pass through a maximum after five-fold or three-fold use, respectively. The finding of such maxima is apparently related to the transfer of a portion of the supported Pd which is unbound or only weakly bound to the support to the solution. The maxima on the conversion curves for 1-hexene to CA in the presence of Ct-1 and Ct-3 differ somewhat, perhaps due to differences in the structures of AN-221 and AN-511 anion-exchange resins.

Spectrophotometric measurements showed that Ct-1 and Ct-3 after 10-fold use contain 0.35-0.4% Pd. Thus, the adsorption capacity of AN-221 and AN-511 relative to Pd²⁺ ions is 0.04 meq/g anion-exchange resin, i.e., 100 times less than that relative to the Cu²⁺ ion, which is in accord with the difference in the radii of these ions (1.74 and 1.28 Å, respectively [4]). In the presence of Ct-2 which contains 0.5% Pd on anion-exchange resin AN-251, there is no maximum on the curve for the conversion of olefin to CA and the conversion of olefin to CA increases up to 47.5% with constant composition of the CA product mixture. The selectivity of the carbonylation of 1-hexene relative to the formation of enantoic acid (EA) was about 40% in the presence of Ct-1 and Ct-2 and about 60% in the presence of Ct-3. After 10-fold use, Ct-2 contained about 0.35% Pd.

We then studied the carbonylation of 1-hexene in the presence of Ct-4 (0.4% Pd/AN-221). Upon increasing the molecule/ratio of α -C₆H₁₂ to Pd(ψ) to 5000, the olefin conversion drops to 55%, although the selectivity relative to EA formation increases to 71.5% (Fig. 1). Neither the olefin conversion nor the selectivity relative to EA formation vary significantly in the range of ψ from 625 to 1875. The higher selectivity in the presence of Ct-4 ($\psi = 5000$) is apparently due to the favorable conditions for the coordination of the olefin at the palladium atom in the AN-211 matrix.

Ct-4 displayed high activity, selectivity, and stability; it does not decompose up to 230°C. The conversion of 1-hexene to CA is 67-69%. An increase in temperature from 90 to 170°C leads to an increase in the conversion of olefin to CA from 15% to 56% and further change is only slight.

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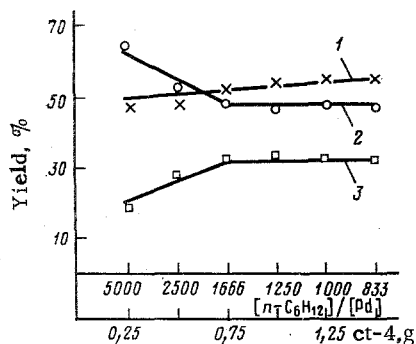


Fig. 1

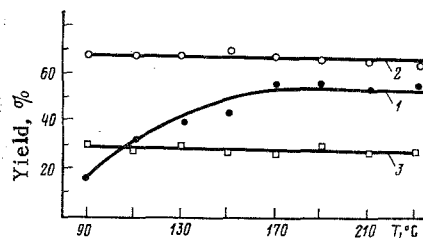
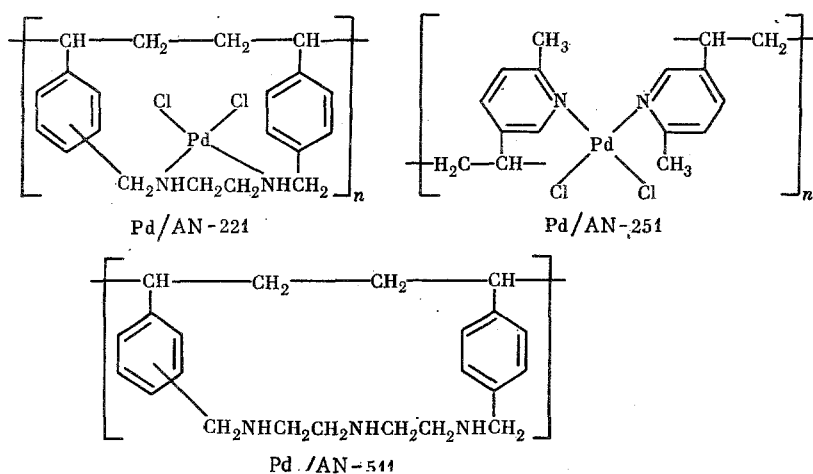


Fig. 2

Fig. 1. Effect of the α -C₆H₁₂/Pd mole ratio or amount of Ct-4 (0.4% Pd/AN-221) on the conversion of olefin to carboxylic acids (1) and the selectivity of the formation of enantoic (2) and 2-methylcaproic (3) acids at 170°C, pCO 100 atm at 20°C, τ 2 h, 1 g catalyst, 0.05 mole, α -C₆H₁₂, α -C₆H₁₂:AcOH:H₂O:HI mole ratio = 1:1:1:0.2.

Fig. 2. Effect of the temperature of the reaction in the presence of Ct-4 (0.4% Pd/AN-221) on the conversion of olefin to carboxylic acids (1) and the selectivity of the formation of enantoic (2) and 2-methylcaproic acids (3), 0.25 g Ct-4, 100 atm CO, τ 2 h, α -C₆H₁₂:AcOH:H₂O:HI mole ratio = 1:1:1:0.2.

An ESR study of Ct-1, Ct-2, and Ct-3 after 10-fold usage showed that their spectra have weak isotropic signals with $g_{\text{isot}} = 2.010$ and $\Delta H = 10$ e. The $\gamma_1:\gamma_2:\gamma_3$ signal intensity ratio is 1:7.5:5. The shape of these signals and their small width indicate that they are related to Pd⁺ ions. Apparently, the Pd²⁺ ions in the unit cell of the anion-exchange are active in the carbonylation of 1-hexene; some of these species without the DBV fragments may be given by the following schemes:



EXPERIMENTAL

The catalysts 0.75% Pd/AN-221 (Ct-1), 0.5% Pd/AN-251 (Ct-2), 0.75% Pd/AN-511 (Ct-3), and 0.4% Pd/AN-221 (Ct-4) were prepared by the adsorption of Na₂PdCl₄ from ethanolic solutions onto the ion-exchange supports in the OH form. The amount of adsorbed Pd²⁺ ion was determined relative to the difference in the content of this ion in the starting and equilibrium solutions by complexometric titration with Trilon. The 1-hexene sample had 99.5% purity, and CO was taken from cartridges with purity not less than 99.8%.

The ESR study was carried out on an ERS-200 spectrometer. The Pd content in the catalyst samples was found by atomic absorption spectrometry on a Saturn-2 spectrophotometer produced by the Severodonets Automation Experimental Design Bureau.

The carbonylation was carried out in glass ampules placed in a 0.15-liter steel autoclave at 170°C with 100 atm initial CO pressure (at 20°C) and α -C₆H₁₂:AcOH:H₂O:HI mole ratio = 1:1:1:0.2. In the experiment, we took 4.2 g (0.05 mole) 1-hexene, 3 ml o-xylene, 3 g acetic acid, 2.4 g (0.01 mole) 47% HI, and 0.9 g (0.05 mole) water. The reaction products were analyzed by gas-liquid chromatography on an LKhM-8MD chromatograph on 2.75 m x 3 mm steel column packed with 15% polyethylene glycol adipinate with 3% H₃PO₄ on Chromosorb G (60-80 mesh) at 175°C. The sample inlet temperature was 250°C. A flame ionization detector was used. The helium carrier gas flow velocity was 30 ml/min.

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CONCLUSIONS

A catalyst obtained by the deposition of palladium(II) on weakly basic anion-exchange resins displays high efficiency in the carbonylation of 1-hexene with the formation of a mixture of enanthoic and 2-methylcaproic acids.

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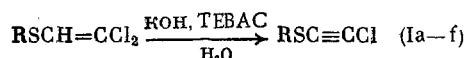
SYNTHESIS AND REACTIONS OF ORGANYL CHLOROETHYNYL SULFIDES WITH PHOSPHORUS-CONTAINING NUCLEOPHILES

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Organyl chloroethynyl sulfides RSC≡CCl (I) were previously obtained by the dehydrochlorination of organyl β,β -dichlorovinyl sulfides upon heating with KOH in vacuum without solvent in 40-50% yield [1] and in DMSO at 5-10°C and normal pressure with yields up to 80% [2].

In the present work, we used phase-transfer catalysis to simplify the preparation of these compounds and avoid the use of organic solvents. The yields were raised to 90-95%. The reaction was carried out in water using triethylbenzylammonium chloride (TEBAC) as the phase-transfer catalyst:



The optimal reaction conditions include a sulfide:alkali:TEBAC ratio of 1:2:0.1, 50% alkali concentration in water, 5-6 h reaction time, and 20-22°C. Heating to 30-35°C led to the partial polymerization of the desired product, while cooling to 10-15°C led to a marked decrease in the reaction rate.

The physicochemical characteristics and yields of (Ia)-(If) are given in Table 1. The IR spectra of the chloroacetylenes show a medium-intensity band at 2150-2170 cm⁻¹ in the

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