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Pt CATALYST FOR THE LIQUID-PHASE EPOXIDATION OF CYCLOHEXENE WITH AN O_2/H_2 MIXTURE

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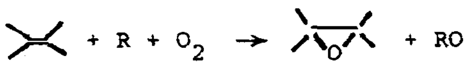
Conditions are found for the preparation of Pt catalysts providing the formation of epoxy-derivative in the reaction of cyclohexene with an O_2/H_2 mixture.

Найдены условия приготовления Pt катализатора для реакции окисления циклогексена кислородом в присутствии водорода с образованием эпоксида.

The simultaneous oxidation of olefins and various reducing agents with oxygen



(1)

is intensively studied at present. The reaction allows one to obtain the olefin epoxide as one of the products in the presence of porphyrin complexes of Fe, Mn and some other metals as catalysts, and ascorbic acid, metallic zinc, hydrogen, etc. as additional reductants (R). When R is H_2, a binary catalytic system is used. It consists of metal porphyrins in solution and colloidal or supported platinum [1-3]. Here we report on the possibility of obtaining epoxide on Pt catalysts in the absence of porphyrin complexes.

EXPERIMENTAL

The catalytic reaction was carried out in a static reactor at 295 K, under a total pressure of 1 atm, in the absence of internal and external diffusion limitations. The reaction started when a stirred suspension of previously ground catalyst in 1 ml of freshly distilled acetonitrile with 10 μl of c-hexene was put into contact with an equimolar O_2/H_2 gas mixture. Identification of products was performed on a CV-2091 chrommass-spectrometer with a searching system 2130. For quantitative analysis, a LHM-8MD chromatograph with flame-ionization detectors and a 0.8 % OV225/graphitized carbon black column was used.

Catalysts contained 2.0 wt.% Pt and were prepared by the incipient wetness technique using an aqueous solution of H_2PtCl_6 and silica (BET surface 200 m^2/g) as support. After drying in air at 330 K for 5 h, the samples were treated with a hydrogen flow (1 ml/g/s). When treated at ambient temperature, the samples changed their color only slightly, but with increasing temperature they acquired a grey color which indicates the reduction of Pt up to the metallic state, especially at 373 and 423 K.

RESULTS AND DISCUSSION

c-Hexane, c-hexenole, c-hexenone and epoxide of c-hexene were identified in the reaction mixture during catalytic testing. On a converted c-hexene basis they made up not less than 80 % of all products; selectivity of oxygen uptake at forming the organic oxygen-containing products reached 30 %, thus being higher than that reported for Pt systems with porphyrin complexes as co-catalysts.

Formation of c-hexane took place in the initial period of the experiments and about 0.5 h after the beginning of the process practically stopped. In a fraction of oxygen-containing organic products the ratio of the c-hexene epoxide to other compounds did not alter much from run to run; however a subsequent transformation of the former was found possible.

At the same time, the total activity of the catalyst and the proportion of the c-hexene epoxide formed depended critically on the temperature of catalyst pretreatment in hydrogen (see Table). Without such pretreatment, the catalysts turned out to be inactive, but small activity was shown by the slightly

Table 1

Catalytic properties of 2.0% Pt/SiO_2 samples reduced in H_2 at different temperatures in simultaneous oxidation of c-hexene and hydrogen (1.1×10^{-4} M c-hexene in 1 ml of acetonitrile, O_2/H_2 = 1 v/v, amount of catalyst 20 mg, 295 K)

Temperature of catalyst pretreatment in H_2 (K)	Time of reaction, (h)	c-Hexene conversion (%)	Selectivity, % of converted c-hexene	
			c-hexene oxide	c-hexane
295	2	12	15	23
323	1	55	17	17
323	2	83	23	14
373	1	61	18	14
373	2	68	23	11
423	1	37	7	60

reduced sample 1. On the other hand, the catalysts obtained at 423 K directed the catalytic process mainly toward the production of c-hexane. Most valuable properties with respect to the formation of c-hexene epoxide were displayed by catalysts 2 and 3 reduced at medium temperatures (323 and 373 K).

Formation of the epoxide is not excluded to occur on a particular active site where Pt is in an appropriate oxidation state and ligand environment. It might explain the regularities observed. However, a bifunctional action of the catalyst seems to be more probable when the products are formed in the presence of two types of active sites. Pt^o states might serve for the reduction of O_2 up to H_2O_2 (as is known from Refs [4,5]), but Pt ions facilitate the epoxide formation during the reaction of peroxide with olefins (as was observed with Pd^{2+} complexes [6,7]).

The fact that the effect reported here has not been found earlier is accounted for, presumably, by the too severe conditions used for the reduction of Pt catalysts. Some types of active sites disappear in this case, and the addition of co-catalysts, e.g., porphyrin complexes, becomes necessary.

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