Zeolites, in which the various cations have been reduced to the metal, accelerate both the hydrogenation—dehydrogenation and the isomerization of hydrocarbons, which reactions proceed on the acid—base and oxidation—reduction centers of these catalysts [1-3]. A study of the hydrogenating properties of metal—zeolite catalysts was started recently. It was shown that these catalysts exhibit a relatively high activity in reactions for the hydrogenation of hydrocarbons [4-6]. The effect of the structure of the zeolites, the nature of the metals and the techniques used to insert them into the zeolite, the conditions employed to reduce the cations, and the migration of the atoms on the hydrogenating properties of these catalysts has practically not been studied. In the present paper such a study was carried out on the model reaction of ethylene hydrogenation.

EXPERIMENTAL METHOD

The catalysts were prepared by cation exchange and by impregnation of the Na forms of the zeolites (faujasite and mordenite) and aluminosilicate using the complexes of Pt(NH₂)₄Cl₂, Pd(NH₄)₄Cl₂ and nickel acetate, and H₂PtCl₆. The Pt and Pd catalysts were reduced with hydrogen at 380°C, while the nickel catalysts...
were reduced at 450° [4, 7]. The ethylene hydrogenation was run in a flow apparatus, the hydrogen and ethylene were dried with zeolite, and the H₂ and C₂H₄ were freed of oxygen on a Ni–Cr catalyst.

The activity of the catalysts was expressed in g-mole of ethane, referred to per g-atom of metal. As the measure of the activity we adopted degrees of ethylene conversion that were quite remote from the equilibrium degrees of conversion, where a pseudzero order of the reaction was retained. The obtained results are given in Figs. 1-3.

DISCUSSION OF RESULTS

Figure 1 shows the activity of the Pt catalysts as a function of the nature of the support and the method used to insert the metal into it. Zeolites of the X and Y type with a faujasite structure, despite a variable SiO₂/Al₂O₃ ratio, have a close activity (curves 1 and 2). Synthetic mordenite has an activity that is one order of magnitude smaller (at 30°), which can be associated with a small effective diameter of the channels (~5 Å) and diffusion retardation (5). The catalytic activity is also noticeably affected by the method used to insert the metal into the zeolite. Thus, the hydrogenating activity of Pt/NaY, obtained by exchange (1), is higher than the activity of the Pt/NaY that was prepared by impregnation with chloroplatinic acid (3). A close activity is also possessed by the Pt/aluminosilicate catalyst that was obtained by the impregnation method (4). In this series of catalysts the changes in the activity are apparently associated with the degree of dispersion of the metal on the support. In the case of the catalysts obtained by impregnation the platinum that is contained in the union of the acid H₂PtCl₆ is found in the cavities and in the secondary porous structure of the zeolite and the pores of the aluminosilicate. During the drying and reduction of the catalyst the decomposition rate of the chloroplatinic acid and the aggregation rate of the platinum atoms can under certain conditions be higher than the rates of the corresponding processes for the cation-exchange form of platinum, which leads to a reduction in the activity. This is also corroborated by the practically same hydrogenating activity of Pt–zeolite and Pt/aluminosilicate catalysts that had been prepared by the impregnation method.

A study of the catalytic properties of the zeolites, containing Pd and Ni, disclosed that the rules for the hydrogenation of ethylene on the indicated catalysts are the same. Thus, the activities of the Na forms of zeolites of the X and Y type, containing palladium, differ only to a slight degree. The same relation also holds for the Ni–faujasite catalysts, while in its activity the Pd–mordenite catalyst is inferior to the Pd-faujasite catalysts, as is also observed for platinum. As regards the relation between the hydrogenating activity and the nature of the metal, then the catalysts, prepared on the basis of the Na form of faujasite, can be arranged in the following order: Pt/NaY > Pd/NaY >> Ni/NaY. Here the platinum catalyst is twice as active as the palladium catalyst, while the nickel catalyst lacks activity under the compared conditions (30°).

The catalytic activity of zeolites, containing metals, is determined to a large degree by the reduction conditions. From the activity of the Pt–zeolite catalyst in the hydrogenation of ethylene as a function of the reduction temperature (see Fig. 2), it follows that varying the temperature from 200 to 400° is without effect on the extent of hydrogenation. Further increase in the temperature leads to a sharp decrease in the ethylene conversion, while for all practical purposes the catalyst loses its activity completely at 550-600°. It should be mentioned that the indicated relation also holds for catalyst samples that prior to reduction had been treated with air at 250-380°. The activity of the catalysts that had been ignited at 550-650° is practically independent of the reduction temperature. A decrease in the catalytic activity with increase in the reduction temperature is apparently associated with an increase in the size of the platinum crystals, which was also observed by other authors. Thus, in the hydrogenation of ethylene on silica gel, containing platinum, a decrease in the catalytic activity was also observed at 500°; not only the total ethylene conversion decreased here, but also the specific activity [8]. An aggregation of the atoms and the formation of coarse crystals of the metal during the reduction of Ni–zeolite catalysts was also observed by us when studying the isomerization and hydrogenation of hydrocarbons [4]. The hydrogenating activity of the Pt–zeolite catalyst as a function of the temperature of its prior treatment with air is a most interesting fact (see Fig. 3). From the reduction isotherm it follows that heat treatment, the same as reduction at 450-600°, leads to a substantial decrease in the hydrogenating activity. We will mention that this effect cannot be related with the process of water removal from the zeolite, since the activity of the catalysts (for each reduction temperature) did not change at 250-400°. It is possible to assume that during heat activation a part of the platinum cations migrates to the s₅ sections, with a higher coordination in oxygen. The reduction of such cations by hydrogen is possible, since the s₅ sections are available for hydrogen molecules. However, the platinum in these