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Abstract

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ON THE QUESTION OF THE USE OF RUTHENIUM CATALYSTS FOR THE HYDROGENATION OF FURAN COMPOUNDS

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As is known, one of the important directions in catalysis is the study of the catalytic properties of rare elements and of uninvestigated or little-investigated types and groups of solids (^{1}). The selection of new kinds of catalysts is of great practical and theoretical importance. In this respect ruthenium is of considerable interest, since its catalytic properties have so far been studied very little. Only a few works are known (see, for example, ($^{2-8}$)) in which the use of ruthenium for carrying out hydrogenation and dehydrogenation reactions of organic compounds is reported. At the same time, a number of features inherent in this metal (ionic radius, type of crystal lattice, magnetic, electronic, and adsorption (^{9}) properties) make it possible to suppose that ruthenium will prove to be a very active hydrogenation catalyst, in particular for nitrogen- and oxygen-containing compounds.

With the aim of investigating the behavior of ruthenium as a hydrogenation catalyst, on the one hand, and of finding active, stable, and selective catalysts, on the other, we have carried out the hydrogenation of a series of furan compounds on several types of ruthenium catalysts (^{10}).

It should be noted that the preparation of ruthenium catalysts is made difficult by the fact that the literature contains almost no procedures for preparing active ruthenium contacts, while the few works dealing with these questions (^{11,12,13}) contain only very general information. We developed methods for preparing the following ruthenium catalysts, arranged in order of activity: "active" ruthenium dioxide, ruthenium on activated carbon, ruthenium on silica gel, and others.

As the experiments showed, the support has a strong influence on the activity of the catalyst. Experiments on the hydrogenation of furan compounds were carried out in rotating autoclaves. The maximum initial hydrogen pressure was 120 atm. The amount of catalyst, calculated as metal, was from 1.5% to 0.5% and less relative to the weight of the substance being hydrogenated. Lower aliphatic alcohols were used as solvents. Preliminary data obtained in the hydrogenation of various groups of furan compounds with ruthenium catalysts are given below.

Hydrogenation of furfuryl alcohol and furylacrolein. In the hydrogenation of furfuryl alcohol on a catalyst containing 5% ruthenium on activated carbon, at room temperature and an initial pressure of 100 atm, furfuryl alcohol was obtained in yields up to 83%; at temperatures above 120°, a mixture of furfuryl and tetrahydrofurfuryl alcohols was obtained. The yield of the latter reached 62%. When "active" ruthenium dioxide was used as the catalyst, at temperatures around 100° tetrahydrofurfuryl alcohol was obtained in a yield of 89%. Both

the catalysts possessed high activity and retained it upon repeated use.

Hydrogenation of furylacrolein on one type of catalyst containing 5% ruthenium on activated carbon led to the formation of furylallyl alcohol (yield up to 27%); when furylacrolein was hydrogenated on ruthenium dioxide at temperatures of about 100°, tetrahydrofurylpropanol and 1,6-dioxaspiro-(4,4)-nonane were formed (the yields were 75.5 and 16.7%, respectively). Hydrogenation of furfurylideneacetone on a catalyst of 5% ruthenium on silica gel leads to the formation of 1-α-furylbutanone-3 (at temperatures up to 50°).

Hydrogenation of furan alcohols. Furfuryl and furylpropyl alcohols were hydrogenated at a high rate and in yields of up to 92% to the corresponding tetrahydrofuran alcohols on ruthenium dioxide. The process conditions depended on the type of catalyst; for example, when "active" ruthenium dioxide was used, the temperature was 80°.

Hydrogenation of furan ketones. Furfurylideneacetone and furylbutanone were very smoothly hydrogenated on a catalyst containing 5% ruthenium on activated carbon to tetrahydrofurylbutanol at room temperature. The yield of the alcohol reached 90%.

When furfurylideneacetone and furylhexadienone were hydrogenated on ruthenium dioxide at a temperature of about 110° and below, the corresponding tetrahydrofuran alcohols were formed in yields of up to 94%. When furfurylideneacetone was hydrogenated on the same catalyst at room temperature, along with tetrahydrofurylbutanol, 7-methyl-1,6-dioxaspiro-(4,4)-nonane was also formed (yield about 11%).

Hydrogenation of furan amines. In the hydrogenation of 1-(α-furyl)-3-aminobutane and 1-(α-furyl)-5-aminohexane on ruthenium catalysts, 1-(α-tetrahydrofuryl)-3-aminobutane and 1-(α-tetrahydrofuryl)-5-aminohexane were obtained. The yield of tetrahydrofuran amines reached 75%.

When a catalyst of 5% ruthenium on carbon was used, the furan ring was hydrogenated already at room temperature, although at a low rate. Hydrogenation proceeded rather rapidly on ruthenium dioxide; however, in this case the best yields were obtained at 100°.

We have established that, in the presence of a ruthenium catalyst, reductive amination of furan ketones can be combined with hydrogenation of the furan ring in a single operation, which is of great preparative interest. Thus, at a temperature of about 170°, under pressure, 1-(α-tetrahydrofuryl)-3-aminobutane and 1-(α-tetrahydrofuryl)-5-aminohexane were obtained from furfurylideneacetone and 1-(α-furyl)-hexadienone-5. The yields were 61% and 34%, respectively.

The data we obtained make it possible to state that ruthenium has considerable activity as a hydrogenation catalyst, which is retained during prolonged use of the catalyst. Noteworthy is the high activity of ruthenium catalysts, already noted earlier ([6,8]), with respect to the carbonyl group. In particular, in the hydrogenation of furylacrolein, the formation of furylallyl alcohol was observed.

An interesting feature of ruthenium catalysts also proves to be the possibility of using them for the one-stage preparation of tetrahydrofuran amines by reductive amination of furan ketones.

All this indicates the promising nature of work on the study of the properties of ruthenium catalysts and the development of methods for their preparation. There is also no doubt that the accumulation of experimental data in this field will make it possible to discover and theoretically explain the features inherent in ruthenium with respect to the sequence of reactions occurring on it, similar-

but on how this was at one time established for nickel catalysts (14). Furan compounds, owing to the presence in them of various types of bonds, constitute very favorable material for studying this question.

Research in this area is continuing.

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