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Abstract

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LIQUID-PHASE HYDROGENATION

OF CERTAIN MONONUCLEAR AROMATIC COMPOUNDS

IN THE PRESENCE OF RUTHENIUM CATALYSTS

(Presented by Academician A. A. Balandin, 9 XI 1964)

Recently ruthenium has increasingly attracted attention as a catalyst for the hydrogenation of organic compounds. Nevertheless, only fragmentary information is available in the literature on the hydrogenation of aromatic substances with the aid of such contacts (1–8).

The high efficiency of ruthenium catalysts was established by the authors in a successive study of the hydrogenation of furan compounds (9–13). This was manifested especially clearly in the hydrogenation of furan amines (13). In order to continue the systematic study of the catalytic properties of ruthenium, on the one hand, and to search for active and stable catalysts for the hydrogenation of aromatic compounds, on the other, we carried out experiments on the liquid-phase hydrogenation of a number of aromatic substances (14). The catalysts used were ruthenium dioxide, 5% ruthenium on activated carbon, and 5% ruthenium on silica gel. The methods of preparation and reduction, as well as the reproducibility of these catalysts, have already been described by the authors (11,13,15). Ruthenium dioxide proved to be the most active contact in the hydrogenation of the aromatic ring (see Fig. 1).

Hydrogenation was carried out in rotating autoclaves. The initial hydrogen pressure was 100 atm. The amount of catalyst, calculated as metal, was from 1 to 0.5% by weight of the substance being hydrogenated.

Hydrogenation of benzene and toluene. On RuO_2 and 5% Ru/C catalysts, preliminarily reduced in an autoclave at 100° and a hydrogen pressure of 50 atm, benzene and toluene are smoothly hydrogenated to cyclohexane and methylcyclohexane with quantitative yield up to temperatures of about 250°. At appreciable rates, at a hydrogen pressure of 100 atm, benzene is hydrogenated at 60°, and toluene at 90°. This fact once again confirms the known proposition

Fig. 1

Figure 1: Fig. 1

that the rate of hydrogenation decreases when alkyl substituents are introduced into the aromatic nucleus.

Fig. 1. *I*—rate of hydrogenation on RuO_2; *II*, *III*—rate of hydrogenation of phenol on 5% Ru/C and 5% Ru/silica gel; $t = 20°$, solvent—methanol

Hydrogenation of phenol and cresols. As is known, hydrogenation of phenol is carried out on an industrial scale. Therefore, the search for effective catalysts for this process is of special interest. Recently a number of works have appeared on the hydrogenation of phenol at temperatures close to room temperature on platinum-group catalysts $^{(17-19)}$. Our experiments with preliminarily reduced ruthenium catalysts showed that phenol and cresols are smoothly hyd —

are hydrogenated to cyclohexanol and the corresponding homologues. Hydrogenation of phenol proceeds at room temperature.

The yield of cyclohexanol is almost quantitative. However, to achieve high hydrogenation rates it is advisable to carry out the process at 50-60°. Cresols require a higher temperature for hydrogenation than phenol (90°).

The results obtained in the hydrogenation of phenols are given in Table 1.

Table 1

Hydrogenation of phenols

Starting substance	Catalyst	Solvent	Hydrogenation conditions: t, °C	Hydrogenation conditions: initial hydrogen pressure, atm	Reaction product	Yield, %
Phenol	5% Ru/silica gel	Water	20	100	Cyclohexanol	96
Phenol	RuO_2	Water	20	100	Cyclohexanol	97.3
m-Cresol	RuO_2	CH_3OH	90	120	3-Methylcyclohexanol	76.4

According to our data, phenols are hydrogenated more readily than benzene and its homologues. An analogous phenomenon is also observed when platinum is used as the catalyst (^{19}).

Hydrogenation of aromatic acids and their derivatives. Hydrogenation of the benzene ring in aromatic acids over ruthenium catalysts proceeds slowly even at 115-125°, and at 150° is complicated by side processes. The yield of hexahydrobenzoic and hexahydrophthalic acids did not exceed 65%. Figure 2 shows the dependence of the yield of hexahydrobenzoic acid on temperature.

Fig. 2. Effect of temperature on the yield of hexahydrobenzoic acid: **I** —RuC_2 catalyst; **II** —5% Ru/silica gel catalyst.

Hydrogenation of salts of aromatic acids over ruthenium contacts proceeds smoothly and at high rates, as has already been noted by other authors ([3]).

As follows from the data in Table 2, aqueous solutions of salts of phthalic acids are hydrogenated over RuO_2 and 5% Ru/C catalysts at 120° and elevated hydrogen pressure. The yield of free hexahydrophthalic acids approaches quantitative.

It should be noted that increasing the pH of aqueous solutions of salts of aromatic acids to 10-12 or higher has a favorable effect on the hydrogenation process. Apparently, in general, carrying out hydrogenation over ruthenium catalysts in alkaline media is preferable. These facts can be explained using concepts concerning the influence of pH on the strength of the hydrogen bond with the catalyst surface (see, for example, ([20])).

As a result of hydrogenation of dimethyl terephthalate, carried out over an RuO_2 catalyst without solvent at 180°, dimethyl hexahydroterephthalate was obtained in 95% yield.

Hydrogenation of nitrobenzene. Nitrobenzene is hydrogenated over RuO_2 and 5% Ru/C stepwise. At 70-90° aniline is formed in 85% yield, and at 100-130° cyclohexylamine. The yield of the latter reaches 76%.

Table 2

Hydrogenation of salts of aromatic acids (solvent—water)

Starting substance	Catalyst	Hydrogenation conditions: t, °C	Hydrogenation conditions: initial hydrogen pressure, atm	Reaction product	Yield, %
$KOOC-C_6H_4-COOK$	RuO_2	120	105	$KOOC-C_6H_{10}-COOK$	99
$NaOOC-C_6H_4-COONa$	RuO_2	120	95	$NaOOC-C_6H_{10}-COONa$	98

Starting substance	Catalyst	Hydrogenation conditions: t, °C	Hydrogenation conditions: initial hydrogen pressure, atm	Reaction product	Yield, %
$NaOOC-C_6H_4-COONa$	5% Ru/C	150	95	$NaOOC-C_6H_{10}-COONa$	96
$NaOOC-C_6H_4-COONa$	RuO_2	80	130	$NaOOC-C_6H_{10}-COONa$	80

Hydrogenation of aromatic amines*. As follows from the data in Table 3, aromatic amines and diamines are smoothly hydrogenated in high yields to the corresponding amines of the cyclohexane series in the presence of ruthenium contacts.

Table 3

Hydrogenation of aromatic amines and diamines (solvent–methanol)

Starting substance	Catalyst	Hydrogenation conditions: t, °C	Hydrogenation conditions: initial hydrogen pressure, atm	Reaction product	Yield, %
$H_2N-C_6H_5$	RuO_2	100	105	$H_2N-C_6H_{11}$	90
$H_2N-C_6H_4-NH_2$	RuO_2	100	110	$H_2N-C_6H_{10}-NH_2$	74.6
$H_2N-C_6H_4-NH_2$	RuO_2	180	110	$H_2N-C_6H_{10}-NH_2$	80
$H_2N-C_6H_4-NH_2$	Ru/C	180	105	$H_2N-C_6H_{10}-NH_2$	88.2
$H_2N-C_6H_4-NH_2$	Ru/C	160	120	$H_2N-C_6H_{10}-NH_2$	77.3

We note that it is not possible to hydrogenate aromatic diamines successfully on ordinary hydrogenation catalysts (nickel, platinum, palladium).

Thus, ruthenium catalysts proved to be especially effective in the preparation of cyclohexyl diamines, which is very important, since the latter are used for the production of heat-resistant polyamides ([21]). In the hydrogenation of 1,4-phenylenediamine on ruthenium catalysts, yet another very valuable feature was found: hydrogenation at a temperature of about 170° proceeds with high stereospecificity, and the reaction product consists almost entirely of trans-1,4-diaminocyclohexa-

* With the participation of B. I. Zhizdyuk.

Further study of such "morphological" properties of ruthenium-based catalysts appears to be of considerable interest.

The study showed that ruthenium contacts can be widely used for processes of liquid-phase hydrogenation of various aromatic compounds. Of particular interest for industry, apparently, are the results obtained in the hydrogenation of phenol and aromatic diamines.

It should be emphasized that ruthenium catalysts can be used for long periods without any noticeable decrease in activity.

All this suggests that industrial hydrogenation catalysts can be developed on the basis of ruthenium.

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