CHANGE IN THE SELECTIVITY OF THE ACTION OF CATALYSTS DURING THE HYDROGENATION OF THE DIENE GROUP

COMMUNICATION 2. MODIFICATION OF A NICKEL CATALYST WITH CADMIUM


In the catalytic hydrogenation of 6-methylheptadiene-3,5-one-2 (dienone) under mild conditions, two unsaturated ketones are formed: 6-methylheptene-5-one-2 (methylheptenone) and 6-methylheptene-3-one-2 (isomeric ketone), capable of further hydrogenation to 6-methylheptanone-2 (methylheptanone).

The dienone can also be directly converted to methylheptanone by the addition of 2 moles of hydrogen without desorption of the intermediate product in the volume. In our previous work [1] it was established that on a skeletal nickel catalyst and in the presence of nickel catalysts on carriers, the hydrogenation of dienone proceeds nonselectively: from the very beginning of the process, hydrogen is added both at the 3,4-double bond, and at the 5,6-double bond. In contrast to this, on the catalyst Ni-ZnO, the process proceeds only in direction I: the isomeric ketone is not formed.

We proposed that for the selective hydrogenation of the 3,4-double bond, the dienone molecule should be adsorbed on the catalyst with its enone group (C= C-C= O). Here there may be a conjugated hydrogenation of its C=O and neighboring C= C bonds, occurring by 1,4-addition of hydrogen

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\begin{align*}
\text{C} = \text{C} - \text{C} = \text{C} - \text{O} + 2\text{H}_2 \rightarrow \text{C} = \text{C} - \text{C} - \text{C} = \text{O}
\end{align*}
\]

Such a mechanism of the selective hydrogenation of the 3,4-double bond explains the modifying action of ZnO, which is capable of intensifying the activation of the dienone by the C=O group.

The presence of similarity in the catalytic properties of cadmium and zinc is well known. The Cd\textsuperscript{2+} ion exerts an activating effect upon metallic...
catalysts in the hydrogenation of the C=C bond [2], even stronger than the Zn$^{+2}$. Like zinc [3], metallic cadmium is inert in the hydrogenation of the C=C double bond, but it is capable of catalyzing the reduction of the C=O group [4]. Cadmium chromite, like zinc chromite [5], catalyzes the selective reduction of the C=O group of $\alpha,\beta$-unsaturated ketones and aldehydes. In view of the indicated similarity, in this work we studied the possibility of changing the selectivity of the action of nickel catalysts on carriers in the hydrogenation of the dienone by modification with cadmium.

**EXPERIMENTAL**

Two samples of aluminum oxide, activated charcoal, and titanium dioxide were used as the carriers for the catalysts. To determine the structural-sorption characteristics of the carriers, we measured the sorption isotherms with respect to methanol vapors in a vacuum apparatus with a quartz spring balance. Table 1 presents the structural-sorption characteristics of samples of the carriers, while Fig. 1 presents the sorption isotherms of methanol vapors. As can be seen from Table 1 and Fig. 1, the aluminum oxide samples differ in values of the specific surface and pore radii. They both are large-pored sorbents. Activated charcoal is fine-pored. The hysteresis loop on its isotherm is negligible, which indicates a small volume of the transitional pores and a predominance of fine pores. Titanium dioxide is nonporous and has a negligible specific surface.

The carriers were impregnated with a solution of nickel (and cadmium) nitrate, calcined for 6 to 8 h at 425°, and reduced for 10-15 h at 350° with hydrogen, free of oxygen and moisture. The nickel content in the catalyst was 20%. The amount of cadmium is given always in % of the nickel.

Hydrogenation was conducted in a rotating stainless steel autoclave at an initial pressure of 50 atm. After absorption of approximately 1 mole of hydrogen, the reaction was interrupted. Methanol was used as the solvent; the dienone concentration in solution was 10%, that of pyridine 7%. The amount of the catalyst in the experiment was 10% (calculated on the basis of metallic nickel) of the weight of the dienone. In the catalyzates obtained we determined the content of the dienone, methylheptenone, methylheptanone, and the isomeric ketone by the method of gas-liquid chromatography, and in a parallel sample - the content of the dienone and isomeric ketone by a polarographic method. The total content of ketones was determined.