PARTIAL HYDROGENATION OF TOLUENE OVER A RUTHENIUM CATALYST - A MODEL TREATMENT OF A DEACTIVATION PROCESS

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Abstract--Hydrogenation of toluene to methylcyclohexene and methylcyclohexane was performed over a commercial 5% Ru/act. charcoal catalyst. The reaction was strongly affected by deactivation of the catalyst. The complete reaction model was examined together with a number of its simplified versions regarding their ability to fit experimental data. On the basis of the regression analysis results it was shown that methylcyclohexene could be thought as the main source of the strongly and irreversibly adsorbed surface deposits responsible for activity decrease of the catalyst. Direct transformation of toluene to methylcyclohexane was found to be insignificant. On the other hand substantial role of disproportionation of methylcyclohexene was proved.

INTRODUCTION

As published elsewhere in detail [1] ruthenium catalysts are effective in partial hydrogenation of aromatics to corresponding derivatives of cycloalkenes. Their positive action in this reaction is only possible either when suitable inorganic modifiers of the catalysts [1-4], organic additives to a reaction mixture [1,5,6] or catalysts prepared by the sol-gel method are used [1,7,8]. The low cost cyclohexene has a wide range of potential applications. The most prominent is converting it to cyclohexanol [1].

In these experiments considerable loss of activity of ruthenium catalysts is frequently observed. This phenomenon is usually assigned to slow reversible desorption of cycloalkenes or to strongly physically adsorbed surface species formed in alkylation reactions [1,9,10].

Although special attention of many authors has been paid to detail examination of various related problems [1], a model treatment of the deactivation process based on the formation of the unspecified surface deposits has been omitted.

In this paper we report on hydrogenation of toluene over a ruthenium catalyst strongly affected by activity decrease. We were seeking of expressing of the process in a form of a widely acceptable mathematical model.
EXPERIMENTAL

Catalyst
5% Ru/act. charcoal type Ru-19A (Batch No. 118017052) catalyst containing 47 wt % of water supplied by Johnson & Matthey was used. The total surface area of the catalyst attained a value of $S_{\text{tot}}=1170$ m$^2$/g$_{\text{cat}}$ (BET, Pulse Chemisorb 2700, Micrometrics, USA) and the specific surface area of ruthenium $S_{\text{Ru}}=52$ m$^2$/g$_{\text{Ru}}$ (titration method [11]). The catalysts (both the metal and the support) was rentgenoamorphous with elemental crystallites of ruthenium less than 1 nm (XRD 3000 P diffractometer, R. S eefert & Co., Germany). AAS analysis (Spectr AA 300, Varian, USA) detected a considerable amount of sodium ions (0.95 wt %) in the catalyst.

Chemicals

Analysis
Samples of a reaction mixture were analyzed on a H&P 5890 Series II Plus gas chromatograph (Hewlett Packard, USA) with FID detector and HP-20M capillary column (50m/0.32nm/0.32μm), temperature program $T_1$-$T_2 = 333-353$ K, pressure of a carrier gas $P(N_2) = 25$ kPa and a split ratio 1:50.

Experiments
Hydrogenations were carried out isothermally (303 K) at atmospheric pressure in a magnetically stirred batch reactor (15 ml). Typically an amount of 0.8 to 1.2 g of a wet catalyst was activated in a solvent system (12 ml) water (25 wt %)-methanol (75 wt %) directly in the reactor for 15 min in a stream of hydrogen (50 ml min$^{-1}$). The reaction was started by injection of a mixture water-methanol-toluene (3 ml) to the reactor.

RESULTS AND DISCUSSION

Experimental data obtained in consecutive hydrogenation of toluene to methylcyclohexene and methylcyclohexane were described by means of Langmuir-Hinshelwood's kinetic approach. The kinetic models were valid under strongly simplifying assumptions of an existence of one type of surface active sites, adsorption of each molecule of reactants on a single active site and the surface reaction as the rate determining step.