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Partial hydrogenation of benzene to cyclohexene in a continuously operated slurry reactor

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A method has been developed for direct measurement of reaction rates in a continuously operated slurry (CST-) reactor. In contrast to the usual procedure in a two-liquid-phase system the reactor contains only one liquid phase, an aqueous zinc chloride solution in which a ruthenium lanthanoxide catalyst is suspended. The selectivity of benzene hydrogenation with respect to cyclohexene is higher when the new one-liquid-phase procedure is applied. With decreasing degree of benzene conversion the selectivity with respect to cyclohexene approaches 100%. The conclusion is that cyclohexane is formed only by consecutive hydrogenation of cyclohexene.

Keywords: partial hydrogenation of benzene; production of cyclohexene; kinetics; reaction mechanism; ruthenium catalyst

1. Introduction

The partial hydrogenation of benzene to cyclohexene is of great industrial interest. The high reactivity of the double bond makes cyclohexene very useful as a raw material for the production of cyclohexanol [1,2]. Therefore, this reaction has been extensively studied [3]. The hydrogenation of benzene to cyclohexene is typically performed in a stirred autoclave at about 425 K under hydrogen pressure of about 5 MPa in a system of two liquid phases, an aqueous salt solution and a benzene/cyclohexene phase, using a ruthenium catalyst which is suspended in the aqueous phase, fig. 1a. Cyclohexene yields of approximately 25–50% are achieved [4,5].

Because of various mass-transfer processes in this system, the knowledge about the kinetics and the mechanism of the partial hydrogenation of benzene is still unsatisfactory. Up to now kinetic studies were only carried out in a discontinuous manner. Therefore, a new method has been developed for direct measurements of reaction rates in a continuously operated slurry reactor in absence of a liquid benzene/cyclohexene phase, fig. 1b. Therefore, the vapor pressure of the hydrocarbon mixture is kept below the saturation vapor pressure. Calculations of mass-transfer have shown that the concentrations of hydrocarbons in the aqueous phase are

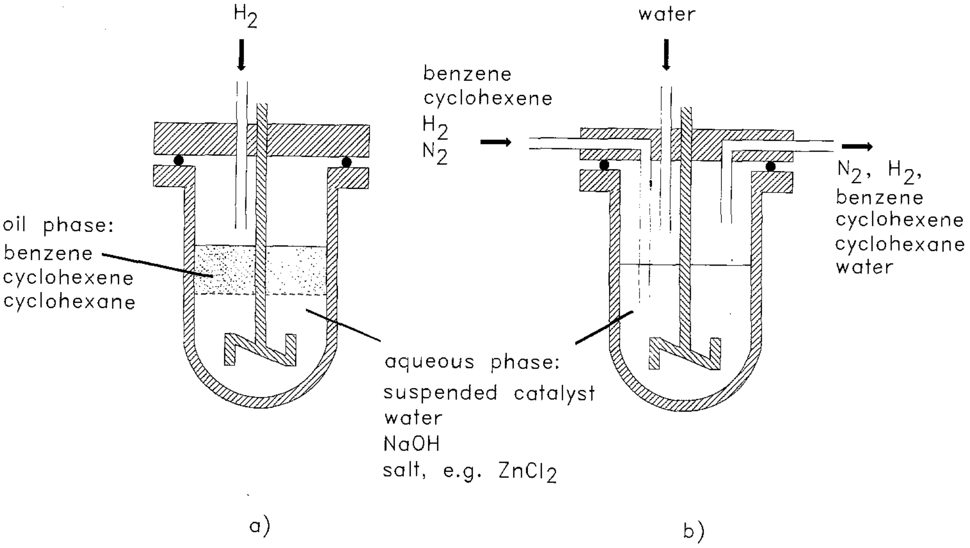

Fig. 1. (a) Batch reactor with a two-liquid-phase system, (b) one-liquid-phase system for measurements of reaction rates in a continuously operated reactor.

determined by vapor–liquid equilibria. This method allows to study the kinetics of the benzene hydrogenation by independent variation of the concentrations of hydrogen, benzene and cyclohexene via their partial pressures.

2. Experimental

A flow diagram of the experimental unit is shown in fig. 2. Dosing of benzene and cyclohexene is carried out by saturation of nitrogen flows. In the first stage of the saturator the gas flow is approximately saturated. In the second stage, which is kept at a lower temperature, the gas becomes supersaturated and the substances are partly condensed, resulting in an exactly saturated gas flow. The flows of hydrogen and nitrogen are controlled by thermal sensors and magnetic valves. The mixed gas stream is conducted to the reactor. The stainless steel reactor has a volume of 650 cm^3 (max. pressure 20 MPa, max. temperature 200°C). The temperature of the reactor is measured by a thermocouple and is kept constant by a temperature controller. The inner walls of the autoclave, the stirrer and the inlet pipes are coated with Teflon. The mean residence time of the gas stream can be varied between 10 and 200 min. The level of the water phase is kept constant by adding water using a piston pump. The gas phase of the reactor is mixed by an external circulating pump in order to avoid concentration gradients. The gas leaving the reactor is conducted to the UNIVAP precision gas sampling system of the on-line gas chromatograph for analysis of the hydrocarbons using a FID detector. The pressure which is generally kept at 5 MPa is controlled by a pressure gauge and a magnetic valve.

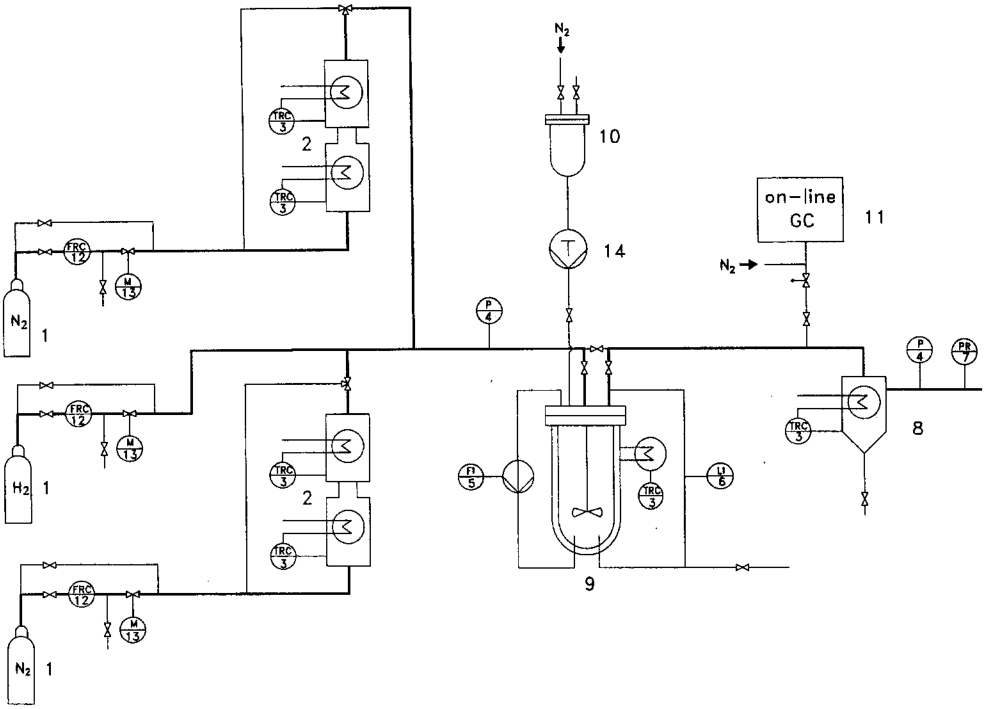

Fig. 2. Flow diagram of the experimental unit. (1) gas supply; (2) two-stage gas saturator; (3) temperature control; (4) pressure gauge; (5) circulating pump; (6) level indicator; (7) pressure controller; (8) condenser; (9) CST-reactor; (10) water reservoir; (11) on-line FID gas chromatograph; (12) flowmeter; (13) magnetic valve; (14) piston pump.

It is important to remark, that high selectivities towards cyclohexene can only be achieved, if any contact of catalyst particles with the vapor-phase is avoided. On a catalyst particle which is not completely covered by a water layer the readsorption of cyclohexene is not hindered so that hydrogenation to cyclohexane occurs in a fast reaction.

3. Results

3.1. SELECTIVITY TOWARDS CYCLOHEXENE

Usually the partial hydrogenation of benzene is carried out in a liquid-phase hydrogenation reaction with an aqueous solution of salt as stationary phase and a dispersed oil phase composed of benzene, cyclohexene and cyclohexane. The ruthenium catalyst is suspended in the aqueous phase. Benzene is continuously dissolved in the aqueous solution from the dispersed oil phase. Cyclohexene and cyclohexane formed in hydrogenation are extracted into the oil phase. It is believed, that this extraction of produced cyclohexene from the aqueous phase into the oil phase is indispensable for achieving high selectivities with respect to cyclohexene [5]. In order to prove this statement this usual two-liquid phase and the new one-liquid-phase procedure are compared under the same reaction conditions.

For these experiments a 1% Ru on La_2O_3 catalyst was used, which has been prepared following the description of Mitsui and Fukuoka [6]. Also the reaction conditions were chosen as described by these authors. The composition of the reaction mixture is characterized by the total pressure of all hydrocarbons, by the degree of benzene conversion and by the selectivity towards cyclohexene. The selectivity is usually defined as the ratio of the rate of cyclohexene formation and the rate of benzene composition. If we define r_1 as the rate of hydrogenation of benzene and r_2 as the rate of hydrogenation of cyclohexene,

$$r_1 = -\frac{1}{m_K}\frac{dn_{BEN}}{dt}, \tag{1}$$

$$r_2 = \frac{1}{m_K}\frac{dn_{CHA}}{dt}, \tag{2}$$

and

$$r_1 - r_2 = \frac{1}{m_K}\frac{dn_{CHE}}{dt}, \tag{3}$$

the selectivity is given by

$$S = \frac{r_1 - r_2}{r_1} = -\frac{dn_{CHE}}{dn_{BEN}}. \tag{4}$$

In the batch process with two liquid phases the reactants are initially charged into the vessel and left to react for a certain period t. During this unsteady-state operation the composition of the oil phase changes with time. For this procedure the selectivity towards cyclohexene is usually calculated by the ratio of the yield of cyclohexene Y and the degree of benzene conversion X,

$$Y(t) = \frac{n_{CHE}(t) - n_{CHE}(t=0)}{n_{BEN}(t=0)}, \tag{5}$$

$$X(t) = \frac{n_{BEN}(t=0) - n_{BEN}(t)}{n_{BEN}(t=0)}. \tag{6}$$

The selectivity defined in such a manner is called integral selectivity,

$$S'(t) = \frac{Y(t)}{X(t)} = \frac{n_{CHE}(t) - n_{CHE}(t=0)}{n_{BEN}(t=0) - n_{BEN}(t)}. \tag{7}$$

The relation between this integral selectivity S' and the selectivity S, which is called differential selectivity, can be derived from the equations (4) and (6),

$$S'(t) = \frac{1}{X(t)} \int_{X(t=0)}^{X(t)} S(X)\,\mathrm{d}X\,. \tag{8}$$

In order to calculate the integral selectivity the function $S(X)$ must be given for constant total amount of substances of hydrocarbons (benzene + cyclohexene + cyclohexane). Correspondingly, the selectivities obtained from CST (continuous stirred tank)-reactor must be given for constant total pressure of hydrocarbons.

The selectivities S' and S with respect to cyclohexene are shown as a function of the degree of benzene conversion in fig. 3.

For the two-liquid-phase batch experiment the selectivities observed in this study (open circles) are slightly higher than that reported by Mitsui and Fukuoka (open triangles). The new one-liquid-phase procedure is carried out in a CST-reactor. In this case differential selectivities are measured. For comparison with the batch experiment the integral selectivities for the one-liquid-phase experiment are calculated using equation (8). The CSTR experiments were carried out for a total pressure of hydrocarbons of 60 kPa which is about 20% of saturation pressure. The dependence of $S(X)$ on the degree of benzene conversion X has been expressed by the polynomial function

$$S(X) = 0.926 - 4.06 \times 10^{-3} X - 4.12 \times 10^{-6} X^2\,, \tag{9}$$

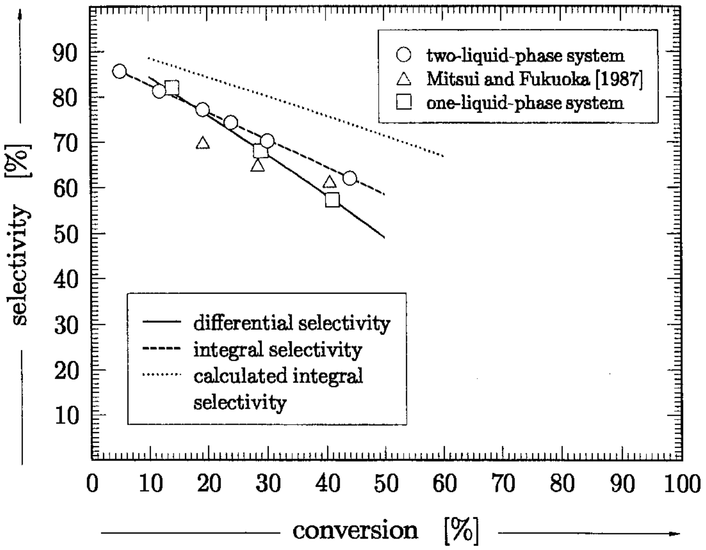

Fig. 3. Comparison of selectivities obtained with the two-liquid-phase system in a batch reactor and the one-liquid-phase system in a CST-reactor. Experimental conditions: (a) batch experiment: 250 ml water, 10 g NaOH, 1.0 g $ZnCl_2$, 4.9 g catalyst and 85 ml benzene, hydrogen pressure $P_{H_2} = 2.9$ MPa, temperature 403 K, total pressure 5.0 MPa; (b) CSTR experiment: 250 ml water, 10 g NaOH, 1.0 g $ZnCl_2$, 5.0 g catalyst, hydrogen pressure $P_{H_2} = 2.6$ MPa, pressure of hydrocarbons $P = 60$ kPa, temperature 403 K, total pressure 5.0 MPa.

which has been obtained by fitting to the experimental data of the one-liquid-phase procedure. The dotted line in fig. 3 gives these calculated integral selectivities, which are markedly higher than the selectivities of the batch experiment.

3.2. INFLUENCE OF THE SALT CONCENTRATION ON REACTION RATE AND SELECTIVITY

Fig. 4 shows the reaction rate of benzene conversion r_1 and the selectivity with respect to cyclohexene as a function of the $ZnCl_2$ concentration. The highest selectivity is achieved for $ZnCl_2$ concentrations larger than 0.04 mol ℓ^{-1}.

The influence of the salt concentration on the reaction rate and on the selectivity has been explained by Soede et al. [7] by an increase of the hydrophilicity of the catalyst particles due to the adsorption of ions on the catalyst surface. Therefore, the ruthenium particles are surrounded by a stable water layer. Furthermore, adsorbed ions cause a reduction of the reaction rate so that the catalytic reaction becomes the rate determining step. The kinetic study of partial hydrogenation of benzene in the CST-reactor has shown that by adding $ZnCl_2$ the reaction order with respect to hydrogen changes from 1.0 to 0.5, which probably indicates a change of the rate determining step from diffusional mass transport to a hydrogenation step.

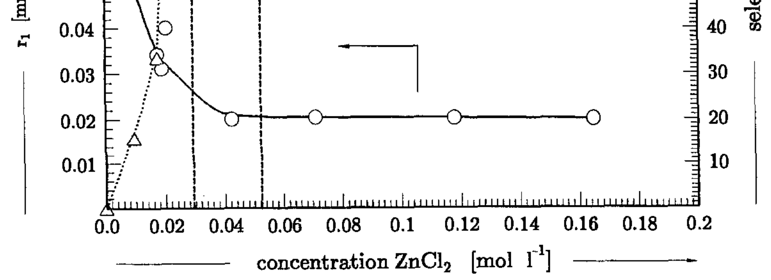

Fig. 4. Dependence of reaction rate of benzene conversion r_1 and selectivity towards cyclohexene on $ZnCl_2$-concentration. Experimental conditions: 250 ml water, 6.3 g NaOH, 5.1 g catalyst, hydrogen pressure $P_{H_2} = 690$ kPa, benzene pressure $P_{BEN} = 180$ kPa, temperature 403 K, total pressure 5.0 MPa.

3.3. REACTION MECHANISM

Struijk et al. [3] proposed a consecutive reaction mechanism of the benzene hydrogenation via cyclohexadienes and cyclohexene to cyclohexane. Fukuoka et al. [8], on the contrary, have also considered the shunt reaction benzene to cyclohexane. The experiments of this work have shown that the selectivity with respect to cyclohexene approaches one with decreasing degree of benzene conversion as shown in fig. 5.

The selectivity with respect to cyclohexene of one shown in fig. 5 seems to be contradictory to the extrapolated value of 0.93 obtained for the experiment shown in fig. 3. The reason for this discrepancy is that the concentration of $ZnCl_2$ is lower than that in the experiment of fig. 5 and thus below the value for optimum selectivity (see fig. 4). This lower concentration was chosen in order to compare the results of this work with the data of Mitsui and Fukuoka [6].

The conclusion is that cyclohexane is produced only by the consecutive hydrogenation of readsorbed cyclohexene according to the step-wise Horiuti–Polanyi mechanism favoured by Struijk et al. [3]. This hypothesis is supported by another experiment carried out at constant hydrogen pressure and at constant benzene pressure by variation of the cyclohexene concentration. Fig. 6 shows that the cyclohexene selectivity increases strongly as the cyclohexene concentration is reduced.

The most important advantage of the continuously operated CST-reactor is the direct measurement of reaction rates and the independent setting of hydrogen, ben-

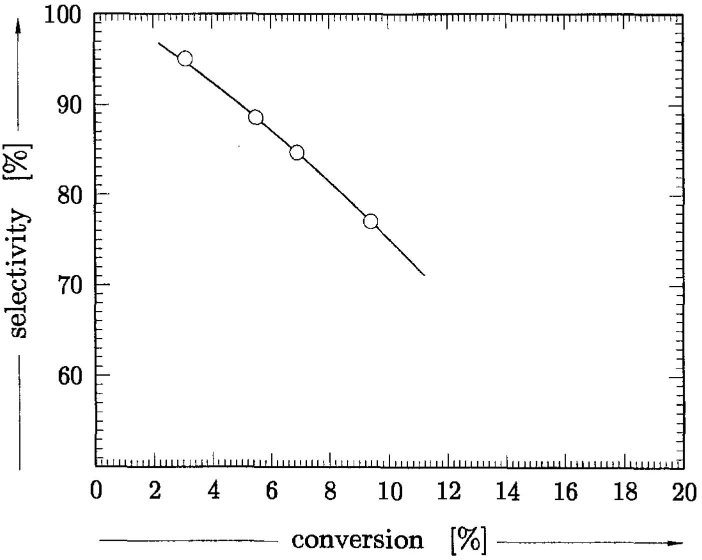

Fig. 5. Selectivity towards cyclohexene versus degree of benzene conversion. Experimental conditions: 250 ml water, 6.4 g NaOH, 1.77 g $ZnCl_2$, 5.0 g catalyst, hydrogen pressure $P_{H_2} = 1.2$ MPa, benzene pressure $P_{BEN} = 100$ kPa, temperature 403 K, total pressure 5.0 MPa.

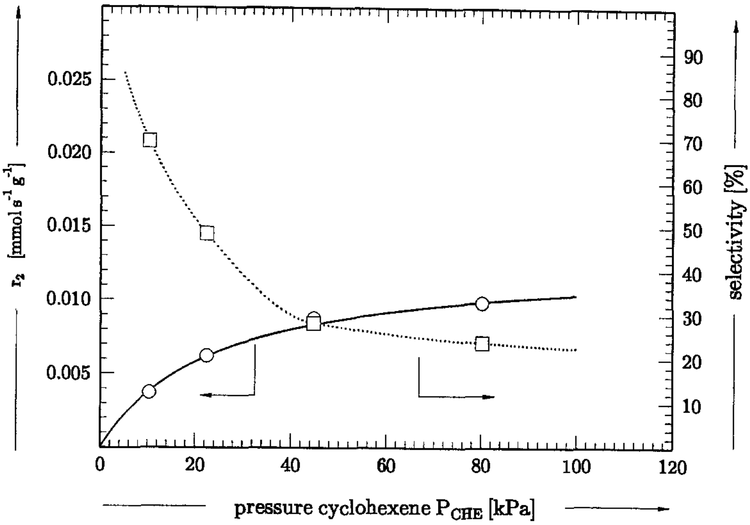

Fig. 6. Dependence of reaction rate of cyclohexene hydrogenation r_2 and selectivity towards cyclohexene on cyclohexene pressure. Experimental conditions: 250 ml water, 6.3 g NaOH, 5.0 g catalyst, 1.51 g $ZnCl_2$, temperature 403 K, total pressure 5.0 MPa.

zene and cyclohexene pressures as demonstrated for the experiment shown in fig. 6.

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