Hydrogenation of nitrotoluenes controlled by the electrochemical potential of the catalyst

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The hydrogenation of 2-nitrotoluene, 2,4-dinitrotoluene and 2,4,6-trinitrotoluene on Pd/C, Pt/C and Ni/SiO_2 catalysts was investigated in a liquid phase batch reactor at pressures between 0.4 and 2.5 MPa. The reaction was controlled by regulating the substrate supply in such a way that the electrochemical potential of the catalyst and, consequently, the surface concentration of active hydrogen was kept at a constant level. The observed hydrogenation rate dependence on the concentration of active surface hydrogen shows that the hydrogen activation is at least one of the rate determining steps. Additionally, controlling the reaction by the potential of the catalyst allows one to prevent dangerous feed concentrations and fast deactivation, too.

Keywords: hydrogenation; electrochemical potential of the catalyst

1. Introduction

The hydrogenation of nitroaromatics is usually carried out on catalysts containing Ni, Pd, or Pt [1,2] as the active components. The main reaction products are the corresponding amines.

The high oxidation potential of the nitroaromatics as well as some assumed side-reactions between the intermediates and the amines to polymers can cause catalyst deactivation [3–5] and, in consequence, non-stationary conditions of the reaction. To be on the safe side, only low substrate concentrations in the reactor are allowed. With stationary concentrations of nitroaromatics in the ppm range causing catalyst potential values up to some hundreds of mV, the hydrogenation controlled by the electrochemical potential of the catalyst – the so-called potential controlled hydrogenation – can ensure safe operation conditions [6,7]. Additionally, this method can provide insight into the relation between the reaction rate and the surface concentration of active hydrogen.

This paper presents results of the hydrogenation of 2-nitrotoluene, 2,4-dinitrotoluene and 2,4,6-trinitrotoluene under the conditions of a feed-controlled electrochemical potential of the catalyst in a liquid phase batch reactor.

During hydrogenation occurring on metal catalysts, the metal component of the catalyst is directly involved in the charge transfer processes between substrate and hydrogen.

The redox reactions taking place on the metal surface lead to stationary concentrations of hydrogen, which generally deviate from equilibrium values. This is the reason for quasi-stationary potentials of the catalyst, which can differ from the equilibrium hydrogen potential by hundreds of mV. If the catalyst particles possess some conductivity, these potentials can be measured against a reference electrode. A hydrogen electrode is to be preferred, if hydrogen is used as the reducing agent. To measure the potential of suspended catalysts, a collector electrode has to be placed in the suspension.

By means of Nernst's equation (eq. (1)) one can calculate the relative surface concentration $[\mathrm{H^S}]_{\mathrm{rel}}$ of active hydrogen:

$$[\mathrm{H^S}]_{\mathrm{rel}} = \{[\mathrm{H^S}]/[\mathrm{H^S}]_0\}\mathrm{e}^{-\Delta E(F/RT)}, \tag{1}$$

where $[\mathrm{H^S}]_0$ means the equilibrium concentration of active hydrogen (in the absence of substrate), $[\mathrm{H^S}]$ is the actual stationary surface concentration, E is the electrochemical potential, F Faraday's constant, R the gas constant and T the temperature.

2. Experimental

The hydrogenation experiments were carried out at 368 K and at pressures ranging from 0.4 to 2.5 MPa. 2-nitrotoluene, 2,4-dinitrotoluene and 2,4,6,-trinitrotoluene were chosen as model substances.

The batch reactor used for these investigations is made from high-grade steel and has a volume of 0.8 ℓ. Fig. 1 shows an outline of the autoclave and the peripheral components. The turbine impeller (3000 $\mathrm{min^{-1}}$) in the lower part of the reactor causes an intensive mixing of the catalyst suspension and the gas phase. The hydrogen is supplied via a pressure transducer for operating and isobaric conditions. The solution of nitroaromatics is fed into the reactor by means of a plunger dosage pump. The amount of solution injected is measured by a volumetric burette. The feed injection is regulated by a control device equipped with a potential measuring head [7,12]. This measuring head combines the collecting electrode, accepting the electric potential of the catalyst, and the reference hydrogen electrode (fig. 2). The electrochemical potential of the collecting electrode is governed by the charge transfer from the catalyst particles to the electrode. Due to its small specific surface, the contribution of the collecting electrode (platinum cylinder) itself to the potential generation can be neglected. This was demonstrated by Gerischer's current/voltage measurements. With different amounts of catalyst in the reactor a high intensity of charge transfer was observed [9].

The collecting electrode is fixed on a PTFE tube. At its lower end this tube is

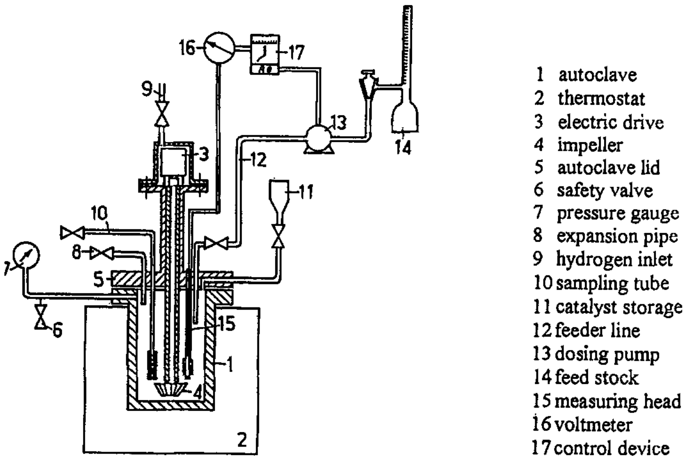

Fig. 1. Outline of the hydrogenation apparatus.

closed by a porous ceramic plug and includes the reference electrode as a platinum wire, surrounded with hydrogen-saturated Pd/C.

For the hydrogenation tests 1.5 g of commercial Ni/SiO_2 (Kt 6504V, Leuna-Werke), 0.5 g Pd/C (E 101 R/W, Degussa; Hanau) or 0.5 g Pt/C (F 101 R/W, Degussa; Hanau) catalysts were used. The Ni catalyst had a metal content of 67 wt% and was air-stabilised, the Pd as well as the Pt catalyst had metal contents of 5 wt%. The crushed catalysts were suspended in 150 ml of a mixture of toluene, ethanol and water (molar ratio = 2 : 6 : 3) in the reaction vessel. Before providing

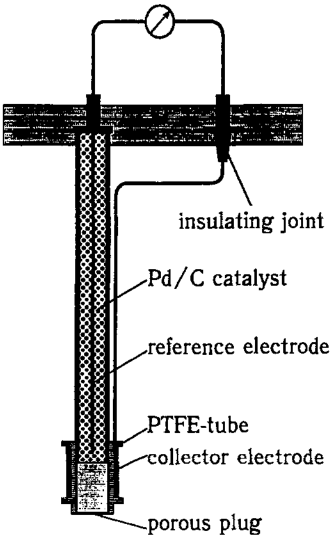

Fig. 2. Scheme of the potential measuring head.

the reaction at 368 K, the slurry was maintained at reaction temperature for 4 h under a hydrogen pressure of 2.5 MPa and, subsequently, left at room temperature overnight.

The nitro groups concentration was 1.7 val./ℓ in the substrate feed solutions. The nitro compounds were dissolved in the mixture of toluene, ethanol and water, mentioned above. Liquid samples were taken by means of a thin dip pipe that extended through the top lid to the bottom of the reactor. For the gas chromatographic analysis of the reaction products a HP 5890 II device equipped with a Pona (HP, cross-linked-methyl-silicone) capillary column and a FID as well as a dc/ac polarographic device were used. The sensitivity of the polarographic method for the nitro compounds analysis was better than 2.5×10^{-6} g/ℓ.

In all experiments the concentration of the substrate was so low that the detection limits of the analytical devices were not reached. That means, that, in spite of the high reaction rates under the chosen conditions, the stationary substrate concentrations were very low (lower than 1 ppm).

3. Results

The hydrogenation rates of 2,4,6-trinitrotoluene at pressures in the range of 0.4–2.5 MPa were determined on the Ni catalyst at a controlling potential of $E = 50$ mV. After a short induction period, the catalytic activity is relatively stable at this potential. Fig. 3 shows the catalytic activity. For the hydrogenation of 2-nitrotoluene, Pd/C, Pt/C and Ni/SiO_2 catalysts were used. By changing the controlling potential it was possible to measure the hydrogenation rate at different concentrations of the active surface hydrogen. The measurements were carried out at a temperature of 368 K and a pressure of 2.5 MPa.

In fig. 4, the catalytic activity versus surface concentration of the atomic hydrogen was plotted in logarithmic scales. Representing data in this way, the slope of lines corresponds to apparent reactions orders (n). Depending on the catalyst, these orders ranged from −0.6 to −1.5.

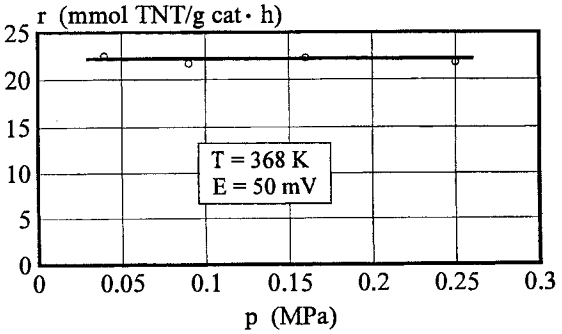

Fig. 3. Hydrogenation of 2,4,6-trinitrotoluene; reaction rate as a function of the pressure.

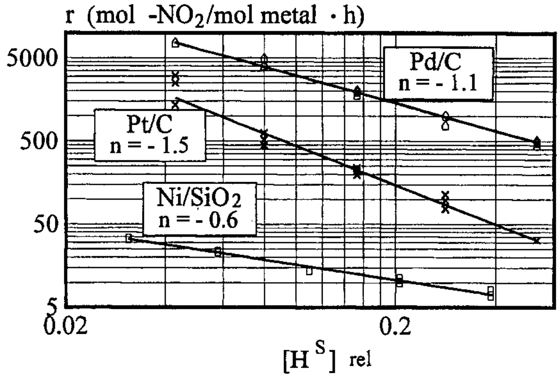

Fig. 4. Hydrogenation of 2-nitrotoluene on Pd/C, Pt/C and Ni/SiO_2 catalysts; the reaction rate as a function of the concentration of the active hydrogen.

The hydrogenation of 2-nitrotoluene (NT), 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT) was investigated under similar conditions on the Ni/SiO_2 catalyst.

Fig. 5 displays the hydrogenation rates of these three nitroaromatics as a function of the hydrogen surface concentration. The hydrogenation rates of the nitrotoluene and the dinitrotoluene nearly coincided, whereas the activity of trinitrotoluene was distinctly higher. The apparent reaction orders were found between −0.5 and −0.6. The deactivation behaviour of a Ni/SiO_2 catalyst during the hydrogenation of 2,4,6-trinitrotoluene was investigated in a solution buffered with Na_2CO_3/$NaHCO_3$ (300 mg/ℓ). To characterise the catalyst deactivation, the activity was measured twice (15 min each run) at every potential value. The average

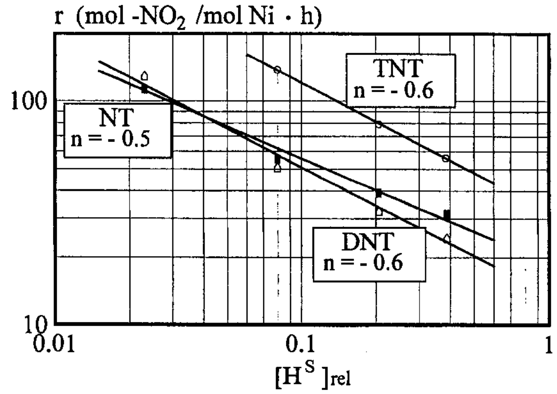

Fig. 5. Hydrogenation of 2-nitrotoluene (NT), 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT) on a Ni/SiO_2 catalyst; the reaction rate related to the nitro groups versus concentration of active hydrogen.

activities ratio of the second to the first period, denoted as D, was chosen to describe the deactivation process.

The relative surface concentration of active hydrogen was calculated from the catalyst potential, as already mentioned. The results (fig. 6) show that the decrease of the hydrogen concentration by two orders of magnitude does not cause fast deactivation, as indicated by values of D close to 1. In the case of its further decrease, however, drastic deactivation is observed, indicated by a value of D markedly lower than 1.

4. Discussion

As can be seen in fig. 4, the highest catalytic activity results for Pd/C and the lowest activity for the Ni/SiO$_2$ catalyst. The palladium catalyst is the most suitable with respect to the reaction conditions, which is in accordance with the results of others [1,13].

The results obtained in potential controlled hydrogenation provide information about the reaction mechanism.

As shown in fig. 7, under our conditions (gas–liquid–solid system) the hydrogenation of nitro compounds can be written as a sequence of steps. At first the gas phase hydrogen is dissolved in the liquid phase (reaction step R1), then the adsorption of hydrogen on the catalyst (R2) follows. On the metal the molecular hydrogen is converted into one-atomic species (R3). This active hydrogen reacts with the nitroaromatic on the surface (R4). In general, the rate of R4 is a function of both the concentrations of active hydrogen and of nitroaromatics. Under conditions of the potential controlled reaction the stationary concentration of the nitroaromatic governs the surface concentration of the active hydrogen.

As already mentioned, the hydrogen pressure in the examined region had no influence on the reaction rate (fig. 3). The dissolution (R1) and the adsorption (R2)

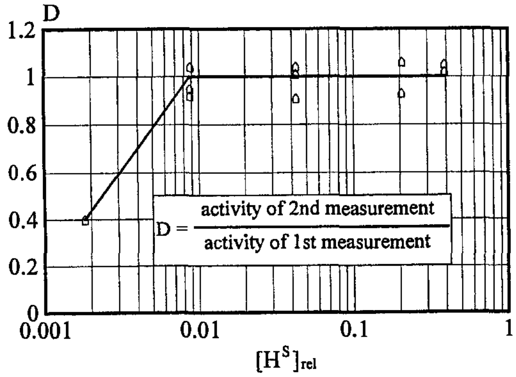

Fig. 6. Deactivation (D) of the Ni/SiO$_2$ catalyst as function of the concentration of active hydrogen.

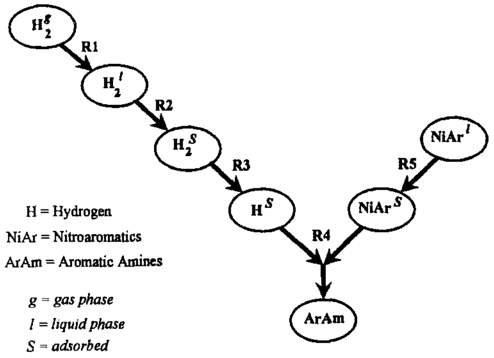

Fig. 7. Reaction scheme of the hydrogenation of nitrotoluenes. R_1–R_5: partial steps of reaction.

of molecular hydrogen depend on hydrogen pressure. They, therefore, cannot be rate determining.

The negative slope of the lines in the figs. 4 and 5 provides evidence that the activation of hydrogen on the surface (R3) is at least one of the rate determining steps.

Considering the concentration of active hydrogen as a function of its formation as well as of its consumption suggests that the apparent hydrogen reaction order should depend on the relationship of both these reaction steps. If the hydrogen activation (R3) proceeds much more facile than the hydrogenation step (R4), the concentration of the active hydrogen is nearly independent of the hydrogenation rate. One should expect great negative values of the apparent reaction order. Otherwise, if the formation of the atomic hydrogen (R3) was rate determining and its consumption (R4) took place much more facile, a strong influence of the hydrogenation rate on the surface concentration of the active hydrogen would be the consequence. In this case the hydrogen reaction order can approach zero.

The steeper slope ($n = -1.5$) observed for platinum catalyst (fig. 4) indicates a more facile hydrogen activation step compared with the hydrogenation. In opposite, the nickel catalyst shows a more flat correlation ($n = -0.5$), revealing a favoured hydrogenation with regard to the hydrogenation activation step.

On this catalyst, the dependence of the hydrogenation rate on the surface concentration of active hydrogen is similar for the three different nitrotoluenes, as shown in fig. 5.

However, the hydrogenation rate of trinitrotoluene is markedly higher than that of its both homologues. The reason for their lower activities could be a smaller effective surface area of the catalyst, caused by adsorption of the reactant, by-products or products. An effect of the reaction products can be excluded because their enrichment does not influence the hydrogenation rate, as established by recent experiments [12,14]. An effect of reactants is more likely to occur and will be discussed in a forth coming paper.

For many catalytic processes, the decay of activity during the reaction is a serious problem. The experiments regarding the deactivation of the nickel catalyst show a rapid decrease of activity in the region of low concentrations of active surface hydrogen ($< 1\%$ of the equilibrium value). At higher concentrations stable activities are observed (fig. 6). Performing the hydrogenation at those high surface concentrations of hydrogen (at low values of the catalyst's potential), one can avoid deactivation.

We suppose that in the region of low hydrogen concentrations the intermediates on the surface of the catalyst react with each other or with the amines instead of reacting with the hydrogen. The products of this reaction are higher molecular substances which are unsoluble and unable to leave the surface. By blocking of the active sites they cause the decline of catalytic activity. This assumption is supported by the results of Westerterp and co-workers [4,5], who succeeded in reactivating the catalyst by oxygen treatment after hydrogenation of nitroaromatics.

5. Conclusions

(1) Controlling the electrochemical potential of the catalyst by the substrate feeding rate is a suitable way to carry out hydrogenation of nitro compounds under definite reaction conditions.

(2) This method allows conclusions about the rate determining steps of the reaction.

(3) Moreover, this method allows to prevent high substrate concentrations in the reaction solution, to maintain high catalytic activity and to prevent fast deactivation.

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