

## Hydrogen Pressure and Temperature Effect on the Rate of Nitrobenzene Hydrogenation over Skeleton Nickel in a Liquid Phase

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**Abstract:** The dependence of nitrobenzene hydrogenation rate upon hydrogen pressure and temperature in 2-propanol-water-aniline three component solvent over skeleton nickel has been studied. The investigation of the effect of pressure on the rate of the reaction where done in the region is corresponding to the zero reaction order. The temperature dependence of rate constants has two linear plots with a bending at temperature equal 298 K. An optimum set of conditions for reaction occurrence is established

**Key words:** Raney nickel, hydrogen pressure, zero order kinetics, adsorption

### INTRODUCTION

The catalytic hydrogenation of nitrocompounds and compounds containing nitrogroup with different substituents was investigated in liquid phase and gas phase over different types of catalysts with using a solvents of different nature and composition<sup>[1-4]</sup>.

A nitrogroup catalytic hydrogenation in substituted nitrobenzenes is the base for synthesizing a number of products of thin organic synthesis, aromatic amines in particular. It is well known that nitrobenzene hydrogenation product-aniline is widely used in synthesis of various dyes<sup>[4-6]</sup>.

The rate and the selectivity of aromatic nitro-compounds hydrogenation depend upon different factors such as temperature, hydrogen pressure and concentrations of catalyst and a hydrated compound. It is known that if hydrogen pressure is increased hydrogenation rates of nitro compounds is increased well<sup>[7]</sup>. when hydrogen adsorption is not a limiting stage of the process and the reaction proceeds at low concentration of a hydrated compound the nature of reaction rate dependence upon the pressure of hydrogen will be determined by the isotherm form of hydrogen adsorption<sup>[8]</sup>. Different authors showed that the degree of diffusion retarding influence significantly the character of hydrogenation rate-hydrogen pressure dependence<sup>[9-11]</sup>.

The main purpose of this study was to evaluate the effects of hydrogen pressure and temperature on the rate of nitrobenzene hydrogenation over a skeleton nickel catalyst taking into account the diffusion retarding kinetic region and adsorption factors in 2-propanol-water-aniline three components solvent.

### MATERIALS AND METHODS

**Solvents:** The reaction of nitrobenzene hydrogenation over skeleton nickel in a three-component solvent of 2-propanol-water-aniline with mass relationship of solvent components equal 50:12:38, respectively was chosen as the main object of the study. While choosing the composition of a solvent to carry out the nitrobenzene hydrogenation it is established that the change of water and aniline concentration in the limits of  $\pm 10\%$  from the composition of solvent chosen for the reaction did not effect the observed rate of hydrogen adsorption (Fig. 1).

**Preparation of a skeleton nickel catalyst:** Skeleton nickel catalysts are obtained by the treatment of dispersed nickel alloys with an inert component-aluminum, magnesium, silicon etc. with aqueous of hydroxides and carbonates of alkaline metals.

In the research industrial nickel-aluminum alloy of Ni:Al:Fe = 49.85:50.2:0.3 mass % was used. The alloy was grinded on a disk dispergator of impact-reflective action and it was separated to the fraction of different dispersity in an air separator of Gonnell. Skeleton nickel was obtained by the treatment of some fractions of nickel-aluminum alloy by 25% aqueous solution of sodium hydroxide during 1 h at 273-278 K and during 4 h at 368-373 K. After 2 h of treatment hydroxide solution saturated with sodium aluminate was changed by freshly prepared solution. After the treatment the catalyst was washed from the admixtures of hydroxide and aluminate with distilled water till neutral reaction on phenolphthaluene (ph.ph) and it was kept under the layer of water not more than two days.

The active skeleton nickel obtained according to this method had specific gravity equal to  $90+2 \text{ m}^2 \text{ g}^{-1}$ , the porosity is  $0.5+0.05 \text{ cm}^3/\text{cm}^3$  of a catalyst and maximum function of pores distribution along radii corresponding to the average radius of pores equal to  $20 \text{ \AA}^{[12,13]}$ .

**Kinetic experiment:** Previously the quantity of a catalyst and the intensity of mixing the liquid phase were chosen in such a way so as to exclude the effect of hydrogen dissolution process in a liquid medium on nitrobenzene hydrogenation rate.

To carry out the experiment 0.625-1.0 g of catalyst and 100 g of solvent were loaded into the reactor, Vishnevskiy Autoclave of a special design constructed on the department of physical chemistry in Ivanovo State University of Chemistry and Technology, Russia, system was hermetized, blown with hydrogen and thermostated at the temperature of the experiment. Further the catalyst during stirring was saturated with hydrogen from a gas phase for 15-30 min. Then a calibrated volume of nitrobenzene solution of a prepared concentration was introduced into the reactor by means of a syringe.

The observed nitrobenzene hydrogenation rates were calculated according to the data of volumetric measurements and the concentration of nitrobenzene in the samples of hydrogenate depending on the time of the reaction. The concentration of nitrobenzene were calculated on the base of the polarographic analysis using polarograph OH-104. The analysis was done in a citrate-phosphate buffer in the presence of aniline at pH equal to 10.0<sup>[1]</sup>.

For calculating the nitrobenzene hydrogenation rate, the values of hydrogen solubility which was determined according to the data given in literature were used<sup>[14]</sup>. The solubility of hydrogen in 2-propanol-water-aniline three component solvent was taken equal  $0.04 \text{ cm}^3 \text{ H}_2/\text{cm}^3$  liquid phase, in aniline the solubility of hydrogen is  $0.03 \text{ cm}^3 \text{ H}_2/\text{cm}^3$  liquid phase and in 2-propanol-water it is  $0.045-0.055 \text{ cm}^3 \text{ H}_2/\text{cm}^3$  of a liquid phase, respectively.

## RESULTS AND DISCUSSION

Figure 1 shows that on the kinetic curves two characteristic plots can be underlined. The first plot corresponds to the constant nitrobenzene hydrogenation rate and the second one corresponds to the directly proportional change of hydrogenation rate upon the nitrobenzene concentration. Constant nitrobenzene hydrogenation rate corresponds to the zero reaction order with respect to the hydrated compound and its decrease corresponds to the first order reaction with respect to nitrobenzene (Fig. 2).

The region of the changing of the reaction order with respect to nitrobenzene corresponds exactly to the region of deviation from the linear dependence of nitrobenzene concentration upon the time (Fig. 2).

**The effect of hydrogen pressure:** The study of the effect of pressure changing upon the rate of nitrobenzene hydrogenation was done in a region corresponding to the zero order reaction for the majority of hydrogenation reaction proceeding in region of a zero-order with respect to the hydrated compound there was an observed diffusion retarding the reaction on hydrogen. In these studies the conditions of nitrobenzene hydrogenation were chosen so that reaction corresponded to the kinetic region. It is seen from the comparison of Till parameter values calculated according to the data of the kinetic experiment<sup>[2]</sup>.

The observed rate of nitrobenzene hydrogenation was  $110 \text{ cm}^3 \text{ H}_2/\text{min g Ni}$  taking into account the catalyst rate it will correspond to the hydrogenation rate on the surface of a catalyst equal to  $495 \text{ cm}^3 \text{ H}_2/\text{min cm}^3 \text{ Ni}$  (Fig. 2). The value of the rate constant for nitrobenzene hydrogenation reaction taking into consideration the solubility of hydrogen will be:

$$K_s^0 = w_g^0/C_{\text{H}_2}^0 = 495/(60.4 \times 10^{-2}) = 195 \text{ c}^{-1}.$$

And the value of Till modules in this case will be:

$$F = k_s^0 R^2/D^* = 195.(2.4 \times 10^{-4})^2/2.10^{-5} = 0.35$$

Where,  $D^*$  is the effective hydrogen diffusion coefficient on the catalyst pores,  $R$  is the radius of the particles for skeleton nickel.

The value of the Till modules obtained corresponds to the kinetic region of the hydrogenation reaction and it is evidence of the absence of diffusion retarding.

The results of kinetic study shown in Fig. 3 confirm the fact that nitrobenzene hydrogenation in the conditions chosen proceeds in the kinetic region.

When hydrogen pressure increases to 1.5 atm the rate of nitrobenzene hydrogenation rate increases linearly (Fig. 4), then this linearity is destroyed and when the pressure reaches 11.5 atm the rate of nitrobenzene hydrogenation ceases to be dependent upon hydrogen pressure. Similar character of the dependence of nitro compounds hydrogenation rate upon hydrogen pressure has been discussed by Petrov *et al.*<sup>[3]</sup> and Borah *et al.*<sup>[11]</sup>.

The treatment of the data in Fig. 4 in linear coordinates corresponding to the dependence  $P/W = f(P)$  allows to find the limited value of observed rate of nitrobenzene hydrogenation reaction and the value of the adsorption hydrogen coefficient- $b_{\text{H}_2}$ .

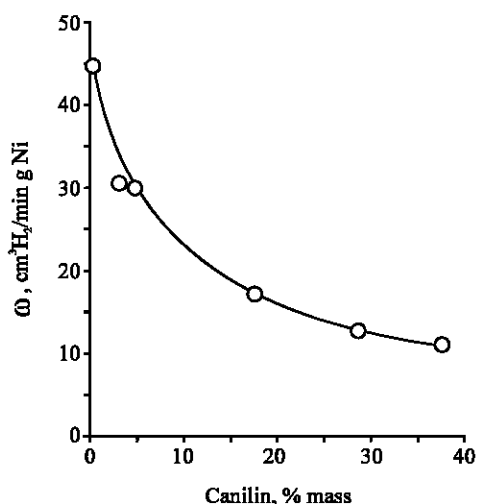


Fig. 1: Dependence of the observed rate of nitrobenzene hydrogenation upon the content of Aniline: temperature-398 K, the catalyst quantity is 1 g, hydrogen pressure is 1 atm., the size of catalyst particles is 4.5  $\mu\text{m}$ ., solvent is 2-propanol-water-80:20 mass %

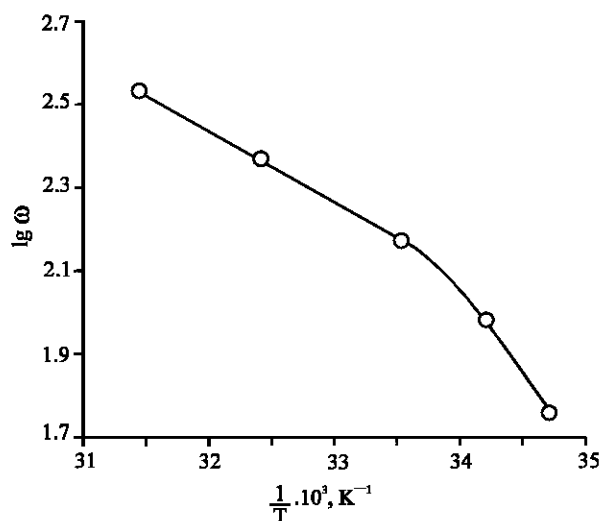


Fig. 3: The dependence of nitrobenzene hydrogenation rate upon the reaction temperature in the coordinates of Arrhenius equation. Solvent is 2-propanol-water-aniline-50:12:38 mass %, catalyst particles size is 4.5  $\mu\text{m}$ , catalyst amount is 1 g, nitrobenzene quantity is 1 g

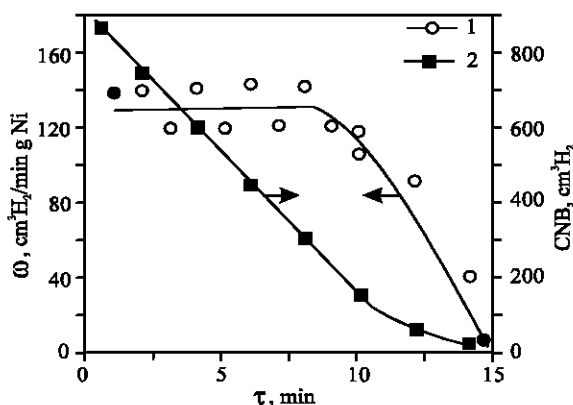


Fig. 2: The dependence of the observed rate of hydrogenation and concentration of nitrobenzene upon the reaction time. Solvent is 2-propanol-water-aniline-50:12:38 mass %, temperature is 298 K, catalyst quantity is 0.625 g, hydrogen pressure is 1 atm., catalyst particles size is 2.3  $\mu\text{m}$

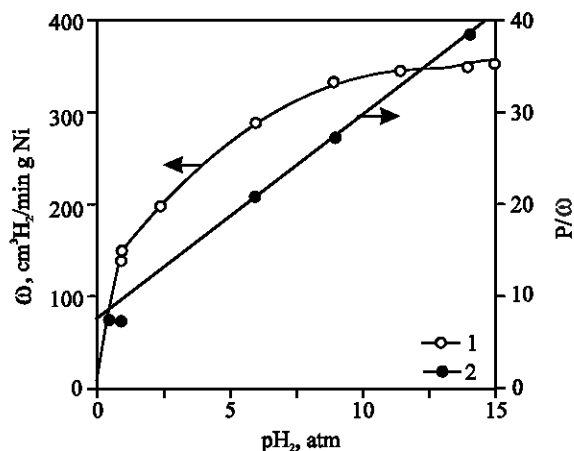


Fig. 4: The dependence of the observed rate of nitrobenzene hydrogenation reaction upon hydrogen pressure (N1) and Langmuir equation in linear coordinates. The (N2) experimental conditions correspond to the conditions in Fig. 1

The values of nitrobenzene hydrogenation rate calculated according to the data in Fig. 4 have the deviation not more than  $\pm 8\%$  from the values of nitrobenzene hydrogenation rate found experimentally. The deviation calculated does not exceed the usual error value in the rate of hydrogenation reaction for the kinetic experiment. The value of hydrogen adsorption coefficient found (Fig. 4) is  $8.2 \text{ atm}^{-1}$  which is in a good agreement

with Melius *et al.*<sup>[8]</sup>. Thus, the value of hydrogen adsorption coefficient found according to the data of a kinetic experiment in studying the hydrogenation reaction of 4-nitrophenol on Raney nickel in 2-propanol-water is  $6 \text{ atm}^{-1}$  and in studying the hydrogenation reaction of 4-nitrophenol on Raney nickel in 0.01 M aqueous solution of sodium hydroxide it is  $20 \text{ atm}^{-1}$  <sup>[15]</sup>.

**The effect of temperature:** The temperature dependence of rate constant for nitrobenzene hydrogenation has two

linear plots with the bending in the region of temperature equal 298 K (Fig. 3). The values of the activation energy calculated according to the data in Fig. 3 for the first and the second plots are 23 and 54 kJ mole<sup>-1</sup>, respectively. The latter value which corresponds to the kinetic field of the hydrogenation reaction nitrobenzene is in a good agreement with<sup>[6,16]</sup>.

Thus the kinetic field of nitrobenzene hydrogenation will conform to the following condition of carrying out the process: the reaction temperature should be not higher than 298 K, the hydrogen pressure should be about 11.5 atm, the size of the particles of catalyst should be not more than 3 μm and the reaction rate on the catalyst surface is 490–500 cm<sup>3</sup> H<sub>2</sub>/min cm<sup>3</sup> l ph g Ni.

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