Evaluation of Nitrobenzene Hydrogenation Kinetic Particularities Over Mono and Bimetallic Ni Containing Hypercrosslinked Polystyrene

Roman V. Brovko[a,b,], Lev S. Mushinsky[b], Adel R. Latypova[a], Mikhail G. Sulman[b], Valentina G. Matveeva[b], Valentin Yu. Doluda[a,b*]

[a]Russia, 153000, Ivanovo, Sheremetievskiy Avenue 7, Ivanovo state university of chemistry and technology, department of physical and colloidal chemistry
[b]170026, Tver, Nab. A. Nikitina 22, Tver state technical university, department of chemical technology
doludav@yandex.ru

Nitrobenzene hydrogenation is a widely used process applied for aniline production. Nitrobenzene hydrogenation kinetics greatly depends on catalyst properties and structure therefore, its study can shed light on process particularities and catalyst properties. The article is devoted to study of nitrobenzene hydrogenation kinetics for monometallic Ni (18.4 wt.%) containing hypercrosslinked polystyrene and bimetallic Pd(0.5 wt.%), Ni(17.9 wt.%) containing hypercrosslinked polystyrene. Nitrobenzene concentration and hydrogen partial pressure influence was studied in a variety of conditions. Nitrobenzene hydrogenation over monometallic sample shows the formation of essential amounts of side products - nitrozobenzene and phenylhydroxylamine while for bimetallic sample direct formation of aniline was noticed. Langmuir–Hinshelwood model was used to study reaction kinetics. A complex model including azobenzene, phenylhydrohylamine and aniline formation steps was developed for monometallic catalyst. The reaction model for bimetallic Ni, Pd catalyst contains only direct aniline formation reaction due to high process selectivity. Values of adsorption and reaction constants are higher for bimetallic catalyst that can explain its enhanced nitrobenzene hydrogenation rate.

1. Introduction

Aniline is an important organic synthesis product a widely used to produce of aniline-formaldehyde resins, rubber additives, dyes (Li, 2018), additives for motor fuels and oils, and pharmaceuticals (Jagannath, 2018). At present, the world production of aniline has reached 8 million tons/year. In comparison, by 2027 it is planned to increase production to 10 million tons/year, which may contribute to the development of new, more efficient technical solutions in the synthesis of aniline. The sequence of reactions occurring in the hydrogenation process (Figure 1) determines many intermediates and by-products, which negatively affects the target product's yield. There are various methods for aniline production including catalytic hydrogenation of nitrobenzene (NB) over different catalysts and the non-catalytic route during metals treatment by acids (Jagannath, 2018).

Nitrobenzene hydrogenation using an acidic dissolution of Zn, Fe or Al was the first method for aniline production. This method is characterized by simple technical implementation and operation. However, this method accompanies a high amount of chemical waste, making it unapplicable for green chemistry conception.

Aniline synthesis using Raney nickel is one of the most applied industrial method. This method main advantages are the relatively high yield of aniline - 70-93% (Jagannath 2018), the possibility of catalyst recovery after deactivation, and low cost of a catalyst compared to the platinum group metals. Among the main disadvantages of this method are Ni catalyst synthesis before reaction, high nickel leaching during the reaction, and Raney type nickel deactivation. Raney type Nickel is pyrophoric, and contact with air can cause incidents. Nitrobenzene hydrogenation over platinum group metals (Pt, Pd, Rh, Ru) catalyst has a significant

advantage over acid accompanied hydrogenation or hydrogenation over Raney type Ni. Typically nitrobenzene hydrogenation rate is twofold higher, and process selectivity is higher for 10-15% (Jagannath, 2018).
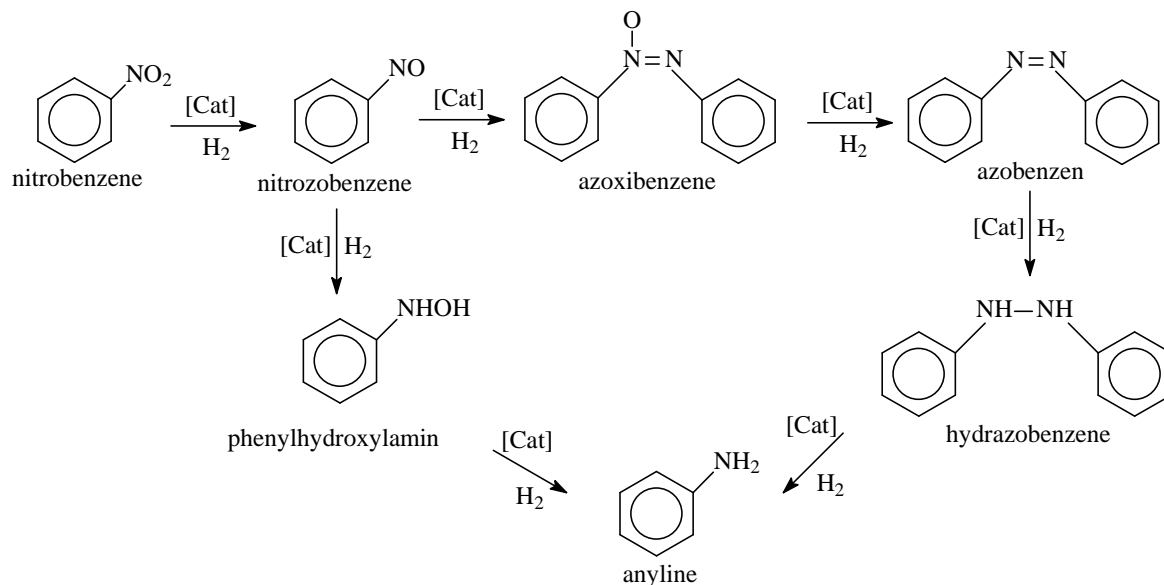

Figure 1: Reaction scheme of nitrobenzene to the aniline hydrogenation process

These advantages are accompanied by a considerable high cost of platinum group metals, therefore to be competitive to this parameter with Ranay type Ni significant decrease of platinum group metal loading in catalyst is needed. However, a decrease of active metal loading lower than 1 wt.% can significantly decrease the reaction rate.

One possible solution for the synthesis of an active catalyst with low loading of platinum group metal is to develop bimetallic catalysts(Cárdenas-Lizana et al. 2014; Chen et al. 2009) with core-shell structure where Ni nanoparticles are covered with platinum group metal (Pd, Pt, Ru) layer. However, the synthesis of bimetallic catalysts accompanies the possibility of obtaining two separate metal phases, without coverage of each other, especially in particle formation in rigid polymers such as hypercrosslinked polystyrene. The study of nitrobenzene hydrogenation kinetics gives additional insight in the understanding of bimetallic catalysts structure and reaction behavior (Petrov et al. 1990). The article is focused on nitrobenzene kinetics study over mono and bimetallic Pd, Ni containing hypercrosslinked polystyrene.

2. Materials and methods

2.1 Materials

Ni(Ac)$_2$ of chemical grade purity (99.1 wt. %), NaAc of chemical grade purity (99.4 wt. %), and Pd(Ac)$_2$ chemical-grade purity (99.0 wt. %) were purchased from Aurat (Russia). Chemical grade purity methanol (99.8 wt.%) was purchased from Vektron (Russia), hypercrosslinked polystyrene HPS MN-270 (Purolite inc., Great Britan) was purchased from a local supplier. To increase HPS hydrophilic surface properties polymer samples were modified using hydrogen peroxide. HPS sample was suspended in 5 wt. % hydrogen peroxide solution in water at 80°C in a round bottom flask equipped with reflux for three hours. Then the suspension was filtered through a Shott filter, washed with deionized water, and dried under vacuum.

2.2 Catalyst synthesis

Ni-based catalyst with theoretical 25 wt.% Ni loading was synthesized using modified HPS. Ni(Ac)$_2$ was dissolved in 1M water solution of NaAc, and a sample of HPS was added to the solution under stirring 300 rpm. The suspension was slowly evaporated under vacuum in rotax and dried under air. After drying, samples were reduced using hydrogen in a glass tube at 300°C for six hours, cooled to ambient temperature under nitrogen, and stored under nitrogen. Ni concentration was determined by X-ray fluorescence analysis (XFA) was found to be 18.4 wt.% of Ni. The sample was designated as Ni(18.4)-HPS.

For the synthesis of bimetallic Pd-Ni catalysts Pd(Ac)$_2$ was dissolved in 1M water solution of NaAc and a sample of Ni-HPS was added to solution under stirring 300 rpm. The suspension was mixed at 80°C for three

hours. The suspension was filtered, the residue was washed with water, dried, and reduced with hydrogen in the glass tube at 300°C for six hours, cooled to ambient temperature under nitrogen, and stored under nitrogen. The synthesized bimetallic sample contains 0.5 wt.% of Pd and 17.9 wt.% of Ni. The sample was designated as Pd(0.5)-Ni(17.9)-HPS.

2.3 Nitrobenzene hydrogenation

The catalytic hydrogenation of nitrobenzene was carried out on a Parr Series 5000 Multiple Reactor System. It consists of a steel thermo-controlled reactor with connections for purging, inert gas supply, and sampling line. Stirring was carried out with a magnetic drive by an electric motor (maximum revolutions per minute - 1600). Pressure control was carried out using a pressure sensor and gas pressure reducer. The accuracy of maintaining the temperature was 0.1°C.

A standard experiment was carried out following way. The reactor with weighed portions of the catalyst, nitrobenzene, and methanol was purged three times with nitrogen, then heated to the required temperature in a nitrogen atmosphere. Then the reactor was purged with hydrogen, constant reaction pressure was maintained by a pressure reducer. Hydrogenation of nitrobenzene was provided in methanol under the following conditions: catalyst weight from 0.2 g/l, reaction time 60 minutes, the temperature of 120 ℃, stirrer rotation frequency 1100 rpm. The products analysis was carried out by gas chromatography using a Kristalluks-4000M gas chromatograph (Russia, Meta-Khrom), equipped with a flame ionization detector and thermal conductive detector connected in series.

2.4 Hydrogen chemosorption study

Determination of hydrogen chemosorption for synthesized catalysts was provided using Chemosorber 4580 (Micromerics, USA). In typical analysis 0.1 g of catalyst sample was placed in quartz cuvette, then the sample was heated up to 300°C under helium with gas volumetric flow 10 ml/min, after the sample was cooled to ambient temperature and gas flow was switched to hydrogen (10 v.%) in helium for one hour. Subsequently, the gas flow was switched to helium, and the sample was again heated up to 300 °C. Hydrogen desorption curves were recorded by thermal conductivity detector, which data was converted to desorbed gas volume by preliminary made calibration curves.

3. Results and discussions

Nitrobenzene hydrogenation over monometallic Ni(18.4)-HPS sample (Figure 2a) results in low nitrobenzene hydrogenation reaction rate compare to bimetallic sample Pd(0.5)-Ni(17.9)-HPS (Figure 2b). Considerable differences in hydrogenation rate can be attributed to Pd presence in the bimetallic sample.
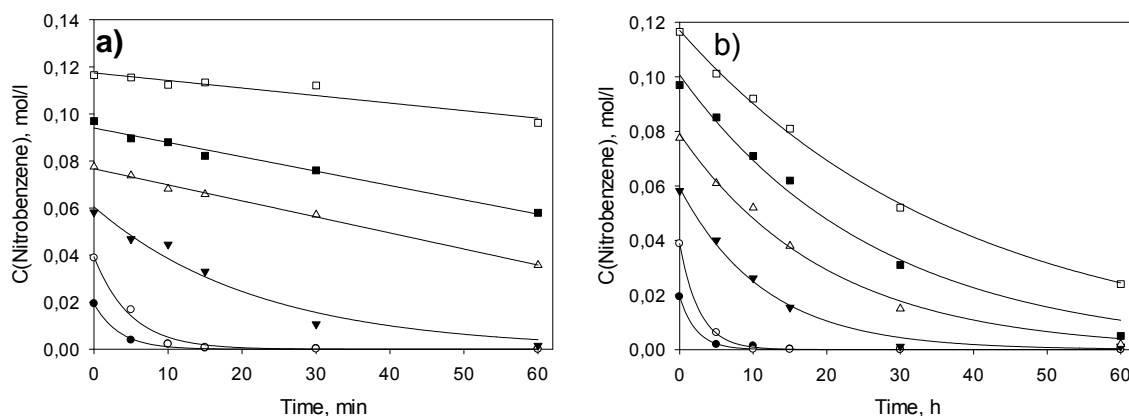

Figure 2. Effect of the initial nitrobenzene concentration on reaction rate for a) Ni(18.4)-HPS b) Pd(0.5)-Ni(17.9)-HPS (T = 120°C, p(H₂) = 23.5 bar, C(Cat)= 2 g/l, C(Ni) = 0.007 mol/L). Lines are calculated according to model equations 1-6 and kinetic parameter presents in table 1.

The main particularity of nitrobenzene hydrogenation over monometallic Ni(18.4)-HPS is the formation of an essential amount of nitrozobenzene and phenylhydroxylamine (Figure 3a). Nitrozobenzene can be considered as the first semi-product in consecutive reaction route (Figure 1) of aniline formation. Phenylhydroxylamine (Figure 3b) forms from nitrozobenzene during its catalytic hydrogenation and can be considered the last semi-product before aniline formation.
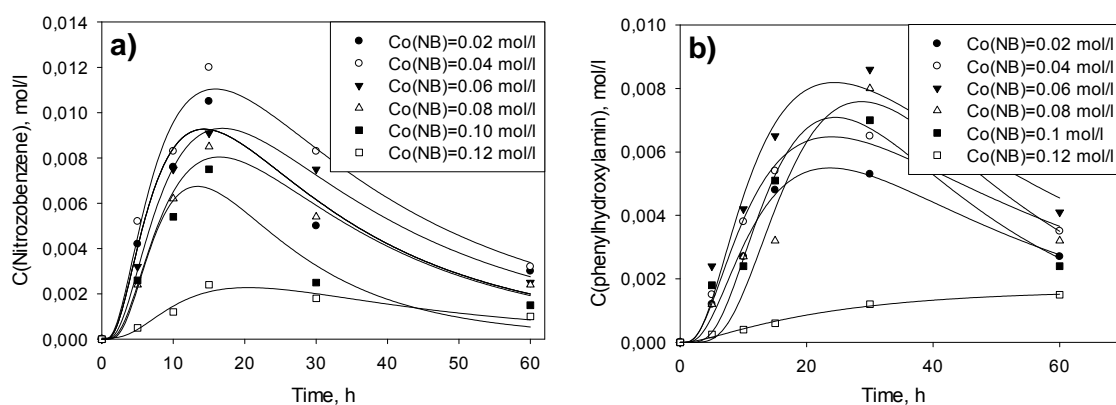
Figure 3. Effect of the initial nitrobenzene concentration on a) nitrozobenzene formation b) phenylhydroxylamine formation for Ni(18.4)-HPS (T = 120°C, p(H₂) = 23.5 bar, C(Cat)= 2 g/l, C(Ni) = 0.007 mol/L). Lines are calculated according to model equations 1-6 and kinetic parameter presents in table 1.

In the contradiction to the monometallic Ni(18.4)-HPS catalyst, formation of intermediate products was not noticed for the bimetallic Pd(0.5)-Ni(17.9)-HPS sample. Therefore the addition of Pd has a positive effect on hydrogenation process. Aniline as a target product forms on the final stage of nitrobenzene hydrogenation process (Figure 4 a and b). Aniline formation rate drastically differs for mono and bimetallic catalysts samples. For monometallic Ni(18.4)-HPS sample aniline formation rate 4-8 times lower compared to Pd(0.5)-Ni(17.9)-HPS sample. High aniline formation rate for bimetallic Pd(0.5)-Ni(17.9)-HPS sample can be attributed to higher hydrogen adsorption 7.8 g(H₂)/kg(Cat) compare to 2.6 g(H₂)/kg(Cat) for Ni(18.4)-HPS sample.
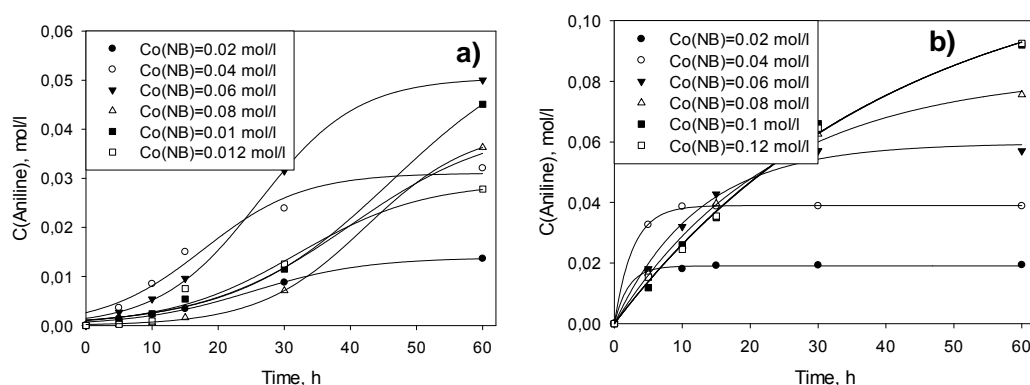

Figure 4. Effect of the initial nitrobenzene concentration on aniline concentration for a) Ni(18.4)-HPS and b) Pd(0.5)-Ni(17.9)-HPS samples (T = 120°C, p(H₂) = 23.5 bar, C(Cat)= 2 g/l, C(Ni) = 0.007 mol/L). Lines are calculated according to model equations 1-6 and kinetic parameter presents in table 1.

Study of hydrogen pressure influence over nitrobenzene hydrogenation rate (Figure 5) shows a considerable increase of reaction rate as for monometallic and bimetallic Ni(18.4)-HPS and Pd(0.5)-Ni(17.9)-HPS samples in case of hydrogen pressure increase from 23.5 Bar up to 50.1 Bar.
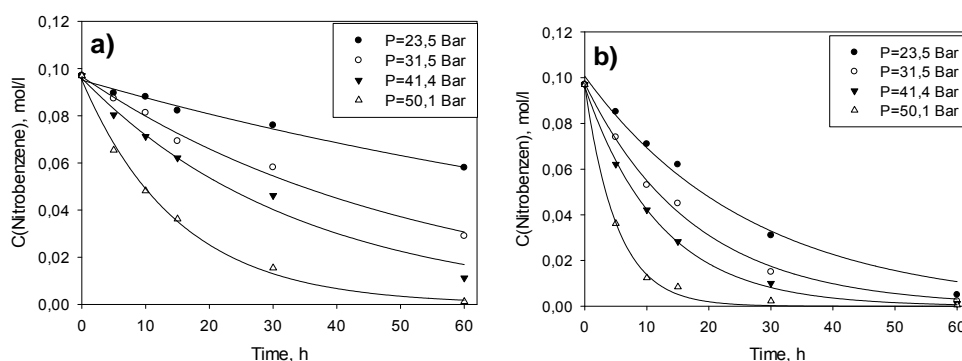
Figure 5. Effect of the hydrogen pressure over nitrobenzene hydrogenation process a) Ni(18.4)-HPS and b) Pd(0.5)-Ni(17.9)-HPS (T = 120°C, C(Cat)= 2 g/l, C(Ni) = 0.007 mol/L). Lines are calculated according to model equations 1-6 and kinetic parameter presents in table 1.

Hydrogen pressure has a significant influence over reaction intermediates - nitrozobenzene and phenylhydroxylamine formation rate and hydrogenation rates (Figure 6). Increasing in hydrogen pressure result in an appropriate increase in formation and hydrogenation rates of nitrozobenzene and phenylhydroxylamine.
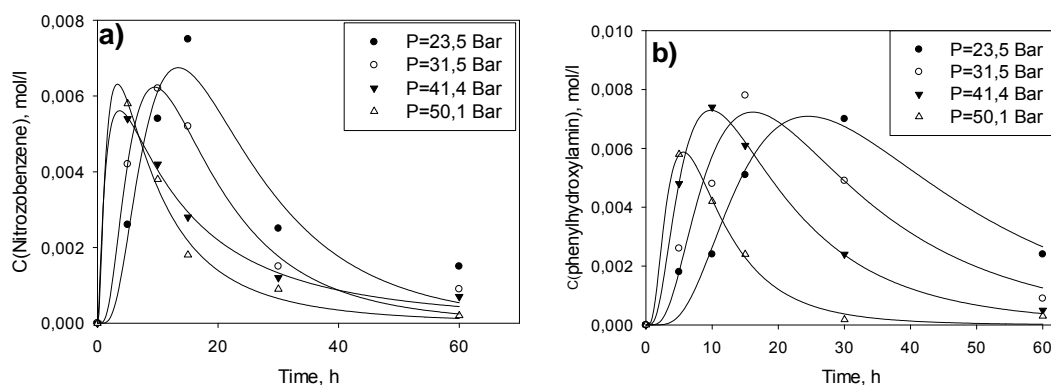

Figure 6. Effect of the hydrogen pressure over a)nitrozobenzene hydrogenation b) phenylhydroxylamine reaction rate for Ni(18.4)-HPS (T = 120°C, C(Cat)= 2 g/l, C(Ni) = 0.007 mol/L, C(NB)=0.1 mol/l). Lines are calculated according to model equations 1-6 and kinetic parameter presents in table 1.

Using Langmuir–Hinshelwood model for studied monometallic catalyst Ni(18.4)-HPS allows to develop rather complex model for nitrobenzene hydrogenation (Equations 1-4) including stage of nitorzobenzene and phenylhydrohylamine formation. For bimetallic Pd(0.5)-Ni(17.9)-HPS sample model have only two equations 5-6 due to very high rates of aniline formation.

$$\frac{d(\text{NB})}{dt} = -k_1 \frac{K_1 C_{\text{NB}}{}^n K_2 p_{H_2}{}^m}{\left(1 + K_1 C_{\text{NB}}{}^n + K_2 p_{H_2}{}^m + K_3 C_{\text{NzB}}{}^l + K_4 C_{\text{PHA}}{}^k\right)^2} \tag{1}$$

$$\frac{d(\text{NzB})}{dt} = k_1 \frac{K_1 C_{\text{NB}}{}^n K_2 p_{H_2}{}^m}{\left(1 + K_1 C_{\text{NB}}{}^n + K_2 p_{H_2}{}^m + K_3 C_{\text{NzB}}{}^l + K_4 C_{\text{PHA}}{}^k\right)^2} - k_2 \frac{K_3 C_{\text{NzB}}{}^l K_2 p_{H_2}{}^m}{\left(1 + K_1 C_{\text{NB}}{}^n + K_2 p_{H_2}{}^m + K_3 C_{\text{NzB}}{}^l + K_4 C_{\text{PHA}}{}^k\right)^2} \tag{2}$$

$$\frac{d(\text{PHA})}{dt} = k_2 \frac{K_3 C_{\text{NzB}}{}^l K_2 p_{H_2}{}^m}{\left(1 + K_1 C_{\text{NB}}{}^n + K_2 p_{H_2}{}^m + K_3 C_{\text{NzB}}{}^l + K_4 C_{\text{PHA}}{}^k\right)^2} - k_3 \frac{K_4 C_{\text{PHA}}{}^k K_2 p_{H_2}{}^m}{\left(1 + K_1 C_{\text{NB}}{}^n + K_2 p_{H_2}{}^m + K_3 C_{\text{NzB}}{}^l + K_4 C_{\text{PHA}}{}^k\right)^2} \tag{3}$$

$$\frac{d(\text{An})}{dt} = k_3 \frac{K_4 C_{\text{PHA}}{}^k K_2 p_{H_2}{}^m}{\left(1 + K_1 C_{\text{NB}}{}^n + K_2 p_{H_2}{}^m + K_3 C_{\text{NzB}}{}^l + K_4 C_{\text{PHA}}{}^k\right)^2} \tag{4}$$

$$\frac{d(\text{NB})}{dt} = -k_1 \frac{K_1 C_{\text{NB}}{}^n K_2 p_{H_2}{}^m}{\left(1 + K_1 C_{\text{NB}}{}^n + K_2 p_{H_2}{}^m\right)^2} \tag{5}$$

$$\frac{d(\text{An})}{dt} = k_1 \frac{K_1 C_{\text{NB}}{}^n K_2 p_{H_2}{}^m}{\left(1 + K_1 C_{\text{NB}}{}^n + K_2 p_{H_2}{}^m\right)^2} \tag{6}$$

Numerical determination of adsorption constants K_1-K_4, reaction rate constants k_1-k_3 and reaction orders *n, m, l, k* was made in MatLab software using Levenberg-Marquardt algorithm allowed to get values (Table 1) of reaction, adsorption constants and reaction orders.

Table 1: Values of reaction, adsorption constants and reaction orders for nitrobenzene hydrogenation.

Catalyst	K_1 1/mol	K_2 1/bar	K_3 1/mol	K_4 1/mol	k_1 (l Bar)/(s mol)	k_2 (l Bar)/(s mol)	k_3 (l Bar)/(s mol)	n	m	l	k
Ni(18.4)-HPS	1287	524	576	718	30619	15274	29956	0.87	1.12	0.94	0.97
Pd(0.5)-Ni(17.9)-HPS	7563	9293	-	-	59496	-	-	1.05	1.18	-	-

Adsorption constants for nitrobenzene K1 and hydrogen K2 are higher for bimetallic catalyst compare to monometallic sample. Therefore nitrobenzene and hydrogen are strongly adsorbed over bimetallic catalysts active surface and can react directly on the catalysts surface without diffusion into reaction media. Besides reaction constant of direct nitrobenzene hydrogenation is two times higher for bimetallic catalysts than monometallic samples.

4. Conclusions

Provided nitrobenzene hydrogenation kinetics modeling shows the complex mechanism for monometallic nickel-containing sample Ni(18.4)-HPS, where hydrogen pressure plays a leading role in achieving a high aniline formation rate due to low hydrogen adsorption and low reaction rates of intermediates products. On the contrary, for bimetallic Pd(0.5)-Ni(17.9)-HPS sample reaction kinetics mechanism consists of only one reaction of aniline formation. The enhanced reaction rate for bimetallic Pd(0.5)-Ni(17.9)-HPS sample can be explained by higher values of reaction and adsorption constants. Adsorption constants for nitrobenzene K1 is 6 times higher for the bimetallic sample compares to the monometallic sample. Therefore nitrobenzene is strongly adsorbed over bimetallic catalyst active surface and can react directly without diffusion into reaction media. While for monometallic sample diffusion of reaction products in the reaction media is possible, resulting in lower reaction rate and formation of intermediate products.

References

Cárdenas-Lizana F., Gómez-Quero S., Amorim C., Keane M.A., 2014, Gas phase hydrogenation of p-chloronitrobenzene over Pd–Ni/Al$_2$O$_3$, Applied Catalysis A: General, 473, 41-50.

Chen Y.W., Sasirekha N., Liu Y.C., 2009, Hydrogenation of p-chloronitrobenzene over NiPtB nanoalloy catalysts, Journal of Non-Crystalline Solids, 355, 193-201.

Jagannath B.L., Aniline and its analogs, Notion Press, Chennai, India.

Li X., 2018, Preparation, properties and application of polyaniline nanocomposites, Chemical Engineering Transactions, 71, 889-894.

Petrov L., Kumbilieva K., Kirkov N., 1990, Kinetic model of nitrobenzene hydrogenation to aniline over industrial copper catalyst considering the effects of mass transfer and deactivation, Applied Catalysis, 59, 31-43.