CATALYSIS IN CHEMICAL AND PETROCHEMICAL INDUSTRY

Studying the Three-Phase Hydrogenation of Nitrobenzene to Aniline in the Presence of a Ruthenium Catalyst

V. Yu. Doluda[a], A. E. Filatova[a], *, E. M. Sulman[a], V. G. Matveeva[a, b],
S. P. Mikhailov[b], A. I. Sidorov[a], and Yu. Yu. Kosivtsov[a]

[a]Tver' State Technical University, Tver', 170026 Russia
[b]Tver' State University, Tver', 170100 Russia
*e-mail: afilatowa@mail.ru
Received April 4, 2018; revised April 4, 2018; accepted April 9, 2018

Abstract—The results are presented from studying the catalytic properties of ruthenium catalyst 3% Ru/MN270 based on hypercrosslinked polystyrene in the reaction of three-phase hydrogenation of nitrobenzene to aniline. The following parameters are varied in the study: the NB concentration in the range from 0.12 to 0.24 mol/L, the catalyst concentration in the range from 1.11×10^{-4} to 11.12×10^{-4} mol/L, the temperature in the range from 160 to 190°C, and the partial hydrogen pressure in the range from 1.013 to 0.113 MPa. The optimum parameters of the process are determined, allowing 97% conversion of nitrobenzene and a selectivity of 98% towards aniline to be achieved.

INTRODUCTION

The catalytic hydrogenation of nitrobenzene (NB) is the most important chemical and technological process in the synthesis of aniline (AN), which is one of the most popular products and intermediates of the chemical industry. Aniline is of great importance in the manufacture of polyurethane, rubber, dyes, pharmaceuticals, pesticides, and herbicides. Aniline can be used as a corrosion inhibitor for, e.g., protecting metals in a carbon tetrachloride medium. Aniline phosphates added to solutions of strong electrolytes slow the corrosion of carbon steels. Various salts and reagents based on aniline are used as additives to fuels and lubricating oils in fuel purification processes [1−3].

A mechanism for the hydrogenation of nitrobenzene was proposed in 1898 by Haber [4]: the reduction of nitrobenzene to aniline occurs in three stages with the formation of intermediate compounds, such as nitrosobenzene and phenylhydroxyilamine (Fig. 1). In addition, it was assumed in [4] that the formation of the following by-products is possible: azoxybenzene, azobenzene, and hydrazobenzene.

In industry, the hydrogenation of nitrobenzene to aniline is conducted in the gas phase with copper or nickel catalysts at high temperatures (553−573 K) and an H_2 pressure of 0.1−0.5 MPa [5−9]. Fairly high conversion (97−98%) and selectivity (97−98%) values are achieved, though the gas-phase process is an energy-intensive procedure. The hydrogenation of NB in the liquid phase allows us to substantially reduce (to 323− 453 K) the temperature of the process. Homogeneous catalytic systems based on the complexes of transition metals (Pd, Pt, Ru, etc.) are used in classical means of the liquid-phase hydrogenation of nitrobenzenes [10−12]. Homogeneous catalysts are usually easily soluble in reaction media, providing access to catalytically active centers and resulting in a high selectivity when the process is conducted under mild conditions. However, the use of homogeneous catalysts is associated with problems in purifying products contaminated with metal complexes and the use of expensive catalysts [13].

In contrast to homogeneous catalysts, heterogeneous catalysts are easily separated from the reaction medium and can be reused [14−19]. Metallic contacts (Pt, Ru, Pd, Au, and Ni) deposited mainly on inorganic porous media are used as heterogeneous catalysts for the three-phase hydrogenation of NB to AN; bimetallic catalysts are often used as well. Hydrogenation in organic solvent media proceeds at higher hydrogen pressures (1−4 Mpa) than the homogeneous process at temperatures of 323−343 K. Nevertheless, these catalysts sometimes show poor selectivity toward aniline. In addition, their use results in the formation of by-products (see Fig. 1) whose accumulation is not environmentally friendly [20−23].

In the last decade, there have been many efforts to create metal complexes immobilized on various supports in order to combine the advantages of homogeneous and heterogeneous catalysts [24, 25]. Nanostructured catalysts based on noble metals and polymer matrices are of great importance for practical
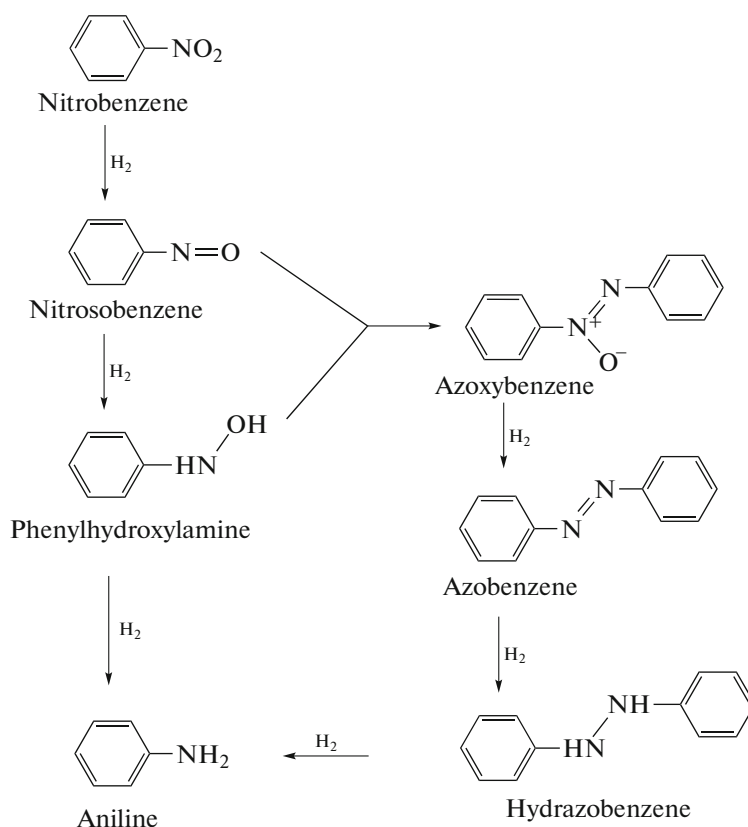
Fig. 1. Reaction scheme (Haber mechanism) of the selective hydrogenation of nitrobenzene to aniline.

application [26, 27]. Studies aimed at investigating the properties of hypercrosslinked polystyrene (HPS) as carriers and stabilizers of catalytically active nanoparticles (Ru, Pd, Pt, etc.) are currently of the highest interest [28–31]. The results from trial experiments on the hydrogenation of NB to AN in the presence of a ruthenium catalyst supported on HPS were published in [32]. It was shown that the ruthenium catalyst on HPS displays activity comparable to that of catalysts on other supports, but with higher selectivity towards the target product. In addition, the use of HPS as a support improves the stability of the catalytic system.

More detailed study is needed for the practical application of catalysts based on HPS, especially with regard to the kinetics of the hydrogenation of NB and determining the optimum parameters of the process. Results from studying the three-phase catalytic hydrogenation of nitrobenzene to aniline in the presence of a ruthenium catalyst based on hypercrosslinked polystyrene are presented in this work.

EXPERIMENTAL

Materials

A catalyst with a 3% content of Ru on hypercrosslinked polystyrene of the MN270 brand (Purolite Int., United Kingdom) was used in this work. The following reagents were used: nitrobenzene of analytical purity grade (Merck Schuchardt OHG, S 6568270 308); pure hydrogen gas (GOST P (Russian State Standard) 51673–2000), Class I; nitrogen (GOST (State Standard) 9293–74), Class I; isopropyl alcohol of reagent purity (TU (Technical Specifications) 2632-009-0027787–02; Base no. 1, Khimreaktiv, Russia); ruthenium(IV) hydroxychloride (TU 2625-038-00205067–2003; OAO Aurat, Russia); tetrahydrofuran of analytical purity grade (STP TU KOMP 1-174-10; mass fraction of tetrahydrofunan, no less than 99.5%); methanol (Sigma Aldrich); sodium hydroxide (GOST 4328–77); and hydrogen peroxide (2611-027-78119972–2011).

Synthesizing the Catalyst

The technique developed earlier [26] was used to synthesize a catalyst with a 3% content of Ru on hypercrosslinked polystyrene of MN270 grade. The synthesis had a number of steps:

1. Hypercrosslinked polystyrene (HPS) (a fraction with a particle size of <60 μm) was washed with water and dried under vacuum before use.

2. The prepared HPS was impregnated with an aqueous solution of ruthenium hydroxychloride ($Ru(OH)Cl_3$) in tetrahydrofuran + methanol + water complex solvent with a component ratio of 4 : 1 : 1 at room temperature.
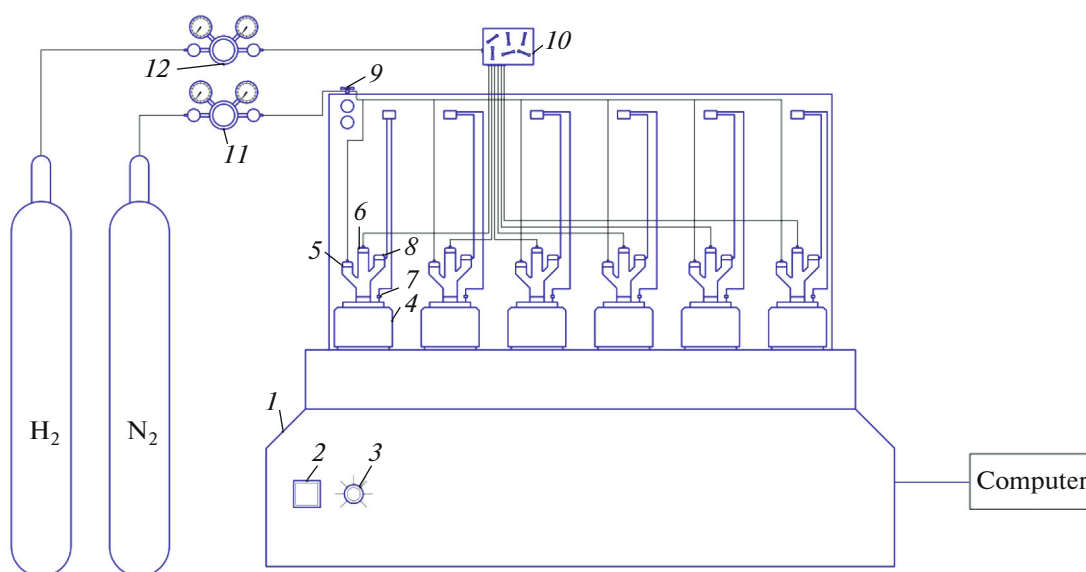
Fig. 2. Series 5000 Parr multiple reactor system (MRS) with main unit *1*, power switch *2*, knob *3* for adjusting the rotation speed of stirrers in reactor cells, reactor cell *4*, valve *5* for purging the reactor cells with nitrogen, valve *6* for supplying hydrogen and sampling, thermocouple *7*, pressure gauge *8*, valve *9* for controlling the nitrogen flow, valve *10* for controlling the hydrogen flow, and pressure reducers *11* and *12* for the gases supplied to the reactor.

3. The resulting catalyst was dried at 70°C, treated with solutions of NaOH and H_2O_2 at 80°C, and then washed with water to neutral pH and dried at 85°C.

4. The catalyst was reduced for 2 hin a hydrogen medium at atmospheric pressure and an average temperature of around 300°C.

The physicochemical characteristics of the 3%Ru/MN270 catalyst were studied in [26]. Results from transmission electron microscopy showed ruthenium nanoparticles were uniformly dispersed, and their average diameter was around 2 nm. According to X-ray photoelectron spectroscopy studies, the oxidation states of ruthenium are (0) and (+4) in the form of RuO_2 [26]. The concentration of active centers in the reduced catalyst was determined via chemisorption on an AutoChem 2950 HP high-pressure chemical adsorption analyzer. The concentration of active centers of the 3%Ru/MN270 catalyst was 0.00243 mmol/g.

Hydrogenation of Nitrobenzene

The catalytic hydrogenation of nitrobenzene was conducted with a Parr Series 5000 multiple reactor system (Fig. 2).

The setup consisted of six temperature-controlled steel reactors equipped with nozzles for flushing, supplying an inert gas, and sampling. Mixing was done with a magnetic stirrer driven from an electric motor (maximum number of revolutions per minute, 1600). The pressure was controlled using pressure sensors. The reactor was thermostatted with a programmable heating coil.

As in the standard experiment, the reactor with weighed amounts of catalyst, nitrobenzene, and isopropyl alcohol was purged three times with nitrogen at a pressure of 2 MPa and then heated to the required temperature in a nitrogen atmosphere. Upon reaching the operating temperature, the reactor was purged three times with gaseous hydrogen, which remained in the system at an overall pressure of 2 MPa. The partial pressure of hydrogen in the system was 0.987 MPa.

Analysis of the Reaction Mixture

A Kristalluks-4000M gas chromatograph (Mega-Khrom, Russia) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) connected in series was used to analyze the reaction medium. The reaction mixture was injected into the evaporating unit with a 1-µL Hamilton syringe. A ZB-1 column 30 m long and 0.32 mm in diameter was used to separate all components present in the mixture. The reaction mixture was separated in the programmed thermostat temperature mode: 50°C (5 min) → 40°C/min (200°C) → 200°C (3 min). The temperature of the evaporator was 120°C and the temperature of the detector was 200°C. Helium at a flow rate of 30 mL/min and a pressure of 3.5 atm was used as the carrier gas. Before sampling, the syringe dispenser was washed three times with a solvent to avoid contaminating the analyzed mixture with foreign substances.
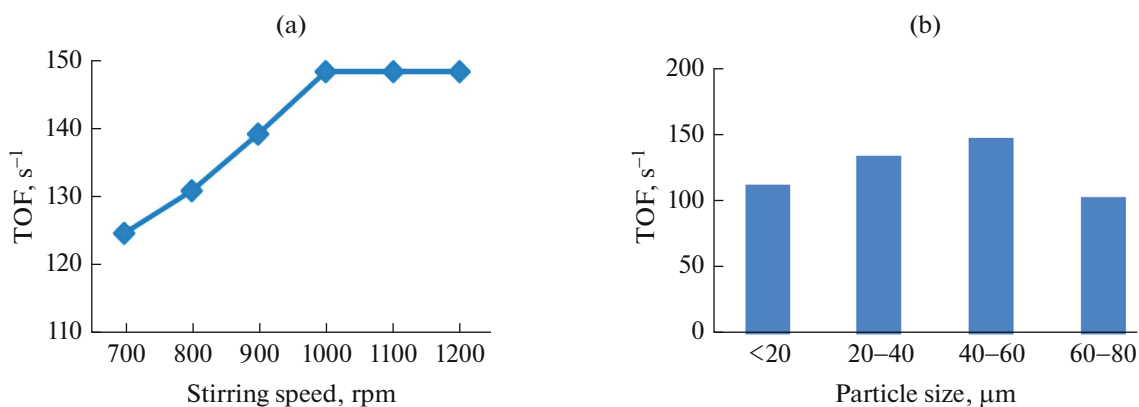
Fig. 3. TOF versus (a) stirring speed and (b) the used catalyst particle size ($C_0 = 0.24$ mol/L; $C_c = 7.42 \times 10^{-4}$ mol Ru/L; $\tau = 30$ min, $P_{\text{part H}_2} = 0.987$ MPa; $T = 180°C$).
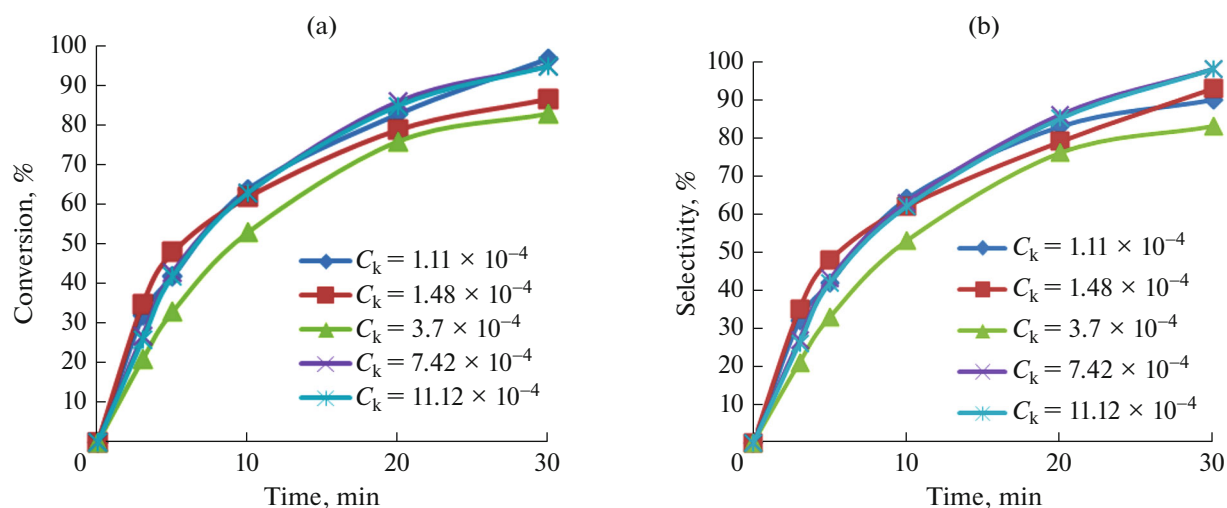

Fig. 4. (a) Nitrobenzene conversion and (b) selectivity towards aniline versus catalyst concentration ($C_0 = 0.24$ mol/L; $\tau = 30$ min; $P_{\text{part H}_2} = 0.987$ MPa; $T = 180°C$).

Determining the Concentration of Active Centers in the Catalyst

To calculate the catalytic activity, the concentration of activity active centers in the investigated catalyst was determined on an AutoChem HP 2950 analyzer by means of H_2 chemisorption. It was established that the concentration of active centers on the 3% Ru/MN270 catalyst was 0.00243 mmol Ru/g.

RESULTS AND DISCUSSION

Preliminary experiments on determining the kinetic region of the reaction were performed to study the kinetics of the three-phase hydrogenation of nitrobenzene to aniline in the presence of a 3% Ru/MN270 catalyst. The effect of the intensity of stirring was studied at rotation speeds of 700 to 1200 rpm. The activity of the catalyst (turnover frequency, TOF) was esti-

mated as the number of moles of the substrate converted to the product with reference to the duration of the process and the concentration of active centers in the weighed portion of the catalyst.

The dependence of TOF on the intensity of stirring is presented in Fig. 3a. The TOF value grows along with the intensity of stirring, reaches a maximum value of 148 s^{-1} at 1000 rpm, and then remains constant. Our results suggest the inhibition of external diffusion ends upon reaching 1000 rpm. The effect of the size of catalyst particles on the TOF value was investigated to exclude regions of the inhibition of internal diffusion during the hydrogenation of nitrobenzene. Based on the data given in Fig. 3b, the optimum size of the catalyst grains was 40–60 μ.

To determine the optimum concentration of the catalyst (C_c), NB was hydrogenated with values varied of 1.11×10^{-4} to 11.12×10^{-4} mol/L and an initial NB
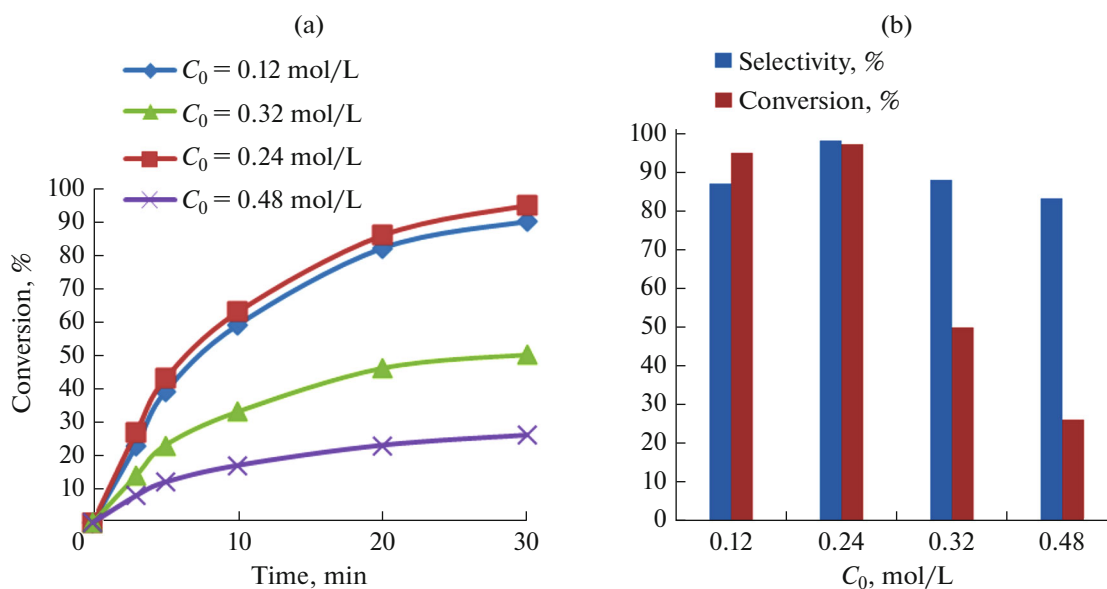
(a) (b)

Fig. 5. (a) Nitrobenzene conversion and (b) selectivity towards aniline versus initial concentration of nitrobenzene ($C_c = 7.42 \times 10^{-4}$ mol Ru/L; $T = 180°C$; $\tau = 30$ min; $P_{\text{part H}_2} = 0.987$ MPa).
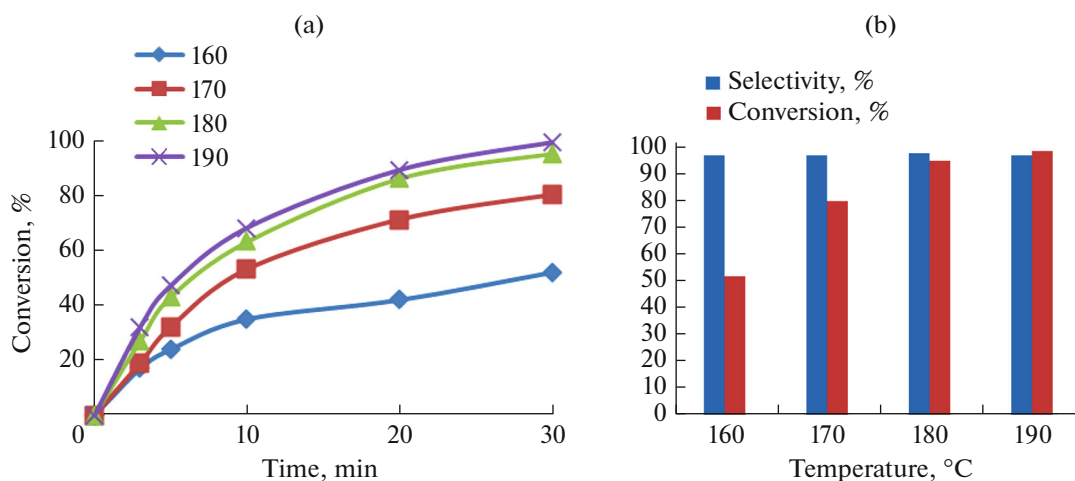
(a) (b)

Fig. 6. (a) Nitrobenzene conversion and (b) selectivity towards aniline versus temperature ($C_0 = 0.24$ mol/L; $C_c = 7.42 \times 10^{-4}$ mol Ru/L; $\tau = 30$ min; $P_{\text{part H}_2} = 0.987$ MPa).

concentration (C_0) of 0.24 mol/L. The dependences of the nitrobenzene conversion and the selectivity towards aniline on the period of the reaction at different C_c values are given in Figs. 4a and 4b, respectively. The maximum NB conversion (97%) and selectivity towards AN (98%) are achieved with a catalyst concentration of 7.42×10^{-4} mol/L. Raising the catalyst concentration further had no effect on conversion or selectivity.

The optimum value of the initial NB concentration was determined by varying the C_0 value from 0.12 to 0.48 mol/L. Upon raising the C_0 value from 0.12 to 0.24 mol/L, both the NB conversion (from 95 to 97%; see Fig. 5a) and the selectivity towards AN (from 87 to 98%; see Fig. 5b) increase. With a further increase in the C_0 value, the conversion falls to 26%; the selectivity, to 83% (see Fig. 5).

The temperature dependence of the conversion of nitrobenzene to aniline was investigated at temperatures ranging from 160 to 190°C (Fig. 6). As can be seen, the nitrobenzene conversion grew to 99% upon an increase in temperature (see Fig. 6a). As follows from the temperature dependence of the selectivity towards AN (see Fig. 6b), the highest value (98%) was achieved at a temperature of 180°C, and the NB conversion at this
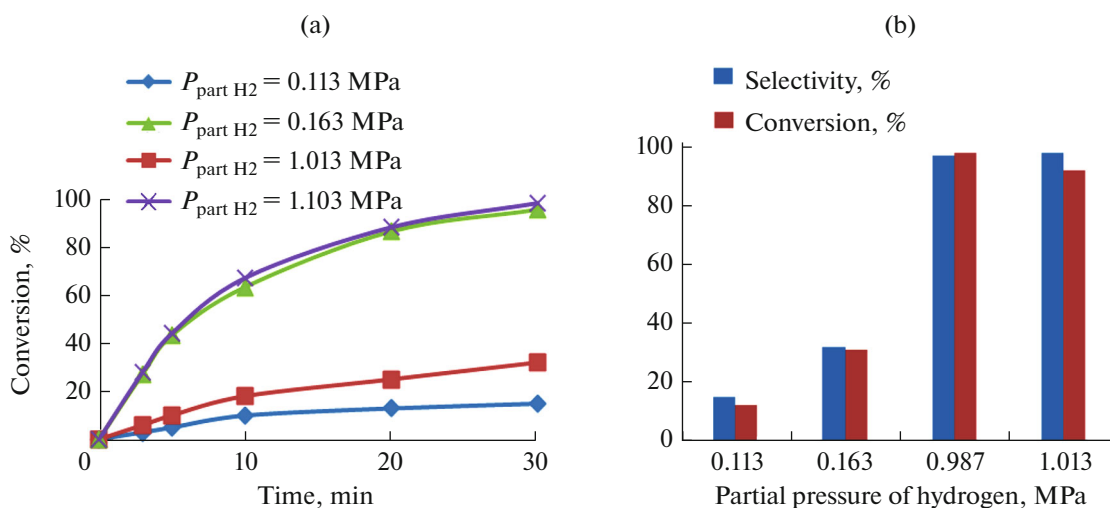
(a) (b)

Fig. 7. (a) Nitrobenzene conversion and (b) selectivity towards aniline versus partial pressure of hydrogen ($C_0 = 0.24$ mol/L; $C_c = 7.42 \times 10^{-4}$ mol Ru/L; $\tau = 30$ min; $T = 180°C$).

temperature was 97%. Selectivity fell upon a further increase in temperature.

In studying the influence of the partial pressure of hydrogen on the process of selective hydrogenation of NB to AN, experiments were performed while varying the $P_{\text{part H}_2}$ value from 0.113 to 1.013 MPa (Fig. 7). The hydrogen pressure had a considerable effect on the hydrogenation process: the process slowed at low pressures (0.113 and 0.163 MPa) and was characterized by low values of the NB conversion (15 and 32%, respectively) and low selectivity towards AN (12 and 31%, respectively). Raising the partial pressure of hydrogen to 0.987 MPa increased the selectivity toward AN to 98% and the NB conversion to 97%. A further increase in the $P_{\text{part H}_2}$ to 1.013 MPa had a negligible effect on

the selectivity toward AN and the NB conversion (see Fig. 7).

Based on our studies, the following conditions are optimum for use in the reaction of three-phase hydrogenation of nitrobenzene to aniline: isopropyl alcohol as a solvent; $C_0 = 0.24$ mol/L; $C_c = 7.42 \times 10^{-4}$ mol Ru/L; 30 min of the reaction; $P_{\text{part H}_2} = 0.987$ MPa; $T = 180°C$; and 1000 rpm of stirring. It should be noted that the three-phase hydrogenation of NB in the presence of a heterogeneous 3%Ru/MN270 catalyst proceeds under milder conditions than the gas-phase process [35, 36]. The maximum selectivity towards aniline under optimum conditions is 98% at 97% conversion of nitrobenzene. The stability of the 3%Ru/MN270 catalyst is an essential factor when using it in an industrial scale. The performance of one load of 3%Ru/MN270 catalyst over ten repeated cycles was therefore studied. The results from studying the stability of the ruthenium catalyst are presenetd in Fig. 8. According to these data, the NB conversion and the selectivity towards AN were virtually the same over 10 cycles, testifying to the stability of the 3%Ru/MN270 catalyst.
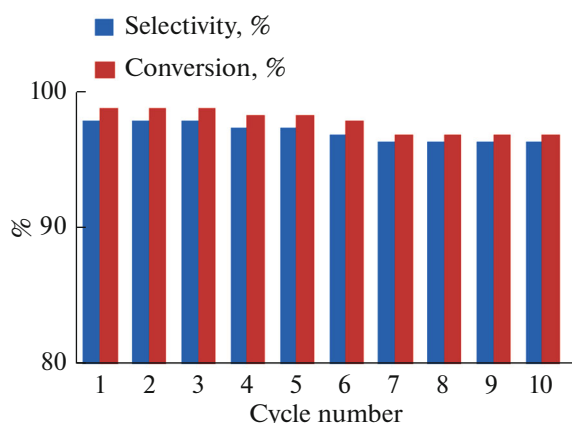

Fig. 8. Results from studying the stability of the 3%Ru/MN270 catalyst in ten repeated cycles ($C_0 = 0.24$ mol/L; $C_c = 7.42 \times 10^{-4}$ mol Ru/L; $T = 180°C$; $\tau = 30$ min; $P_{\text{part H}_2} = 0.987$ MPa).

CONCLUSIONS

A ruthenium catalyst based on hypercrosslinked polystyrene, 3%Ru/MN270, was studied. Optimum conditions for conducting the three-phase hydrogenation of nitrobenzene into aniline with 98% conversion and 97% selectivity were determined. The investigated 3%Ru/MN270 catalyst displayed high catalytic activity and stability, which is important for its application on an industrial scale.

FUNDING

REFERENCES

1. Shokouhimehr, M., *Catalysts,* 2015, vol. 5, no. 2, pp. 534−560.

2. Blaser, H.-U., Malan, C., Pugin, B., Spindler, F., Steiner, H., and Studer, M., *Adv. Synth. Catal.,* 2003, vol. 345, nos. 1−2, pp. 103−151.

3. Wu, H., Zhuo, L., He, Q., Liao, X., and Shi, B., *Appl. Catal., A,* 2009, vol. 366, no. 1, pp. 44−56.

4. Haber., F., Z. *Elektrochem.*, 1898, vol. 4, pp. 506−514.

5. Gelder, E.A., Jackson, S.D., and Lok, C.M., *Chem. Commun.,* 2005, no. 4, pp. 522−524.

6. Polotnyuk, O.-V.Ya., *Katal. Prom-sti*, 2013, no. 5, pp. 55−80.

7. Verho, O., Gustaffson, K.P.J., Nagendiran, A., Tai, C.-W., and Backvall, J.-E., *ChemCatChem,* 2014, vol. 6, no. 11, pp. 3153−3159.

8. Westerhaus, F.A., Jagadeesh, R.V., Wienhöfer, G., Pohl, M.-M., Radnik, J., Surkus, A.-E., Rabeah, J., Junge, K., Junge, H., Nielsen, M., Brückner, A., and Beller, M., *Nat. Chem.,* 2013, vol. 5, pp. 527−543.

9. Sangeetha, P., Seetharamulu, P., Shanthi, K., Narayanan, S., and Rama Rao, K.S., *J. Mol. Catal. A: Chem.,* 2007, vol. 273, nos. 1−2, pp. 244−249.

10. Rahaim, R.J. and Maleczka, R.E., *Org. Lett.,* 2005, vol. 7, no. 22, pp. 5087−5090.

11. Shil, A.K., Das, P., *Green Chem.,* 2013, vol. 15, no. 12, pp. 3421−3428.

12. Schabel, T., Belger, C., and Plietker, B., *Org. Lett.,* 2013, vol. 15, no. 11, pp. 2858−2861.

13. Copéret, C., Chabanas, M., Saint-Arroman, R.P., and Basset, J.M., *Angew. Chem., Int. Ed. Engl.,* 2003, vol. 42, no. 2, pp. 156−181.

14. Shokouhimehr, M., Kim, J.-H., and Lee, Y.-S., *Synlett,* 2006, no. 4, pp. 618−620.

15. Janssen, M., Müller, C., and Vogt, D., *Green Chem.,* 2011, vol. 13, no. 9, pp. 2247−2257.

16. Kim, J.-H., Kim, J.-W., Shokouhimehr, M., and Lee, Y.-S., *J. Org. Chem.,* 2005, vol. 70, no. 17, pp. 6714−6720.

17. Höller, V., Wegricht, D., Yuranov, I., Kiwi-Minsker, L., and Renken, A., *Chem. Eng. Technol.,* 2000, vol. 23, no. 3, pp. 251−255.

18. Rakitin, M.Yu., Doluda, V.Yu., Tereshchenkov, A.Yu., Demidenko, G.N., Lakina, N.V., Matveeva, V.G., Sul'man, M.G., and Sul'man, E.M., *Catal. Ind.,* 2015, vol. 7, no. 1, pp. 1−5.

19. Tobe, M.L. and Burgess, J., *Inorganic Reaction Mechanisms,* Harlow, UK: Longman, 1999.

20. Zhao, F., Ikushima, Y., and Arai, M., *J. Catal.,* 2004, vol. 224, no. 2, pp. 479−483.

21. Li, C.-H., Yu, Z.-X., Yao, K.-F., Ji, S.-F., and Liang, J., *J. Mol. Catal. A: Chem.,* 2005, vol. 226, no. 1, pp. 101−105.

22. Makosch, M., Hydrogenation over supported noble metal catalysts: from characterization to design, *Dr. Sc. ETH Zürich Dissertation,* Augsburg: ETH Zürich, 2012.

23. Evangelisti, C., Aronica, L.A., Botavina, M., Martra, G., Battocchio, C., and Polzonetti, G., *J. Mol. Catal. A: Chem.,* 2013, vol. 366, pp. 288−293.

24. Polshettiwar, V., Len, C., and Fihri, A., *Coord. Chem. Rev.,* 2009, vol. 253, nos. 21−22, pp. 2599−2626.

25. Toebes, L.M., van Dillen, J.A., and de Jong, K.P., *J. Mol. Catal. A: Chem.,* 2001, vol. 173, pp. 75−98.

26. Matveeva, V.G., Valetskii, P.M., Sulman, M.G., Bronshtein, L.M., Sidorov, A.I., Doluda, V.Yu., Gavrilenko, A.V., Nikoshvili, L.Zh., Bykov, A.V., Grigorjev, M.E., and Sulman, E.M., *Catal. Ind.,* 2011, vol. 3, no. 3, pp. 260−270.

27. Sulman, E., Matveeva, V., Doluda, V., L. Nikoshvili, L., Bykov, A., Demidenko, G., and Bronstein, L., *Stud. Surf. Sci. Catal.,* 2010, vol. 175, pp. 153−160.

28. Sulman, M., Doluda, V., Grigoryev, M., Manaenkov, O., Filatova, A., Molchanov, V., Sidorov, A., Bykov, A., Shkileva, I., Sulman, A., Stein, B., and Matveeva, V., *Bull. Chem. React. Eng. Catal.,* 2015, vol. 10, no. 3, pp. 313−323.

29. Tsyurupa, M.P., Tarabaeva, O.G., Pastukhov, A.V., and Davankov, V.A., *Int. J. Polym. Mater.,* 2003, vol. 52, no. 5, pp. 403−414.

30. Pavlova, L.A., Davankov, V.A, and Lependina, N.A., *Sorbtsionnye Khromatogr. Protsessy,* 2014, vol. 14, no. 1, pp. 75−85.

31. Qingquan, L., *Macromol. Chem. Phys.,* 2010, vol. 211, no. 9, pp. 1012−1017.

32. Rakitin, M.Yu., Doluda, V.Yu., Tyanina, A.A., Petrova, A.I., Sulman, E.M., and Matveeva, V.G., *Russ. J. Phys. Chem. B,* 2017, vol. 11, no. 7, pp 1113−1116.

33. Berezovskii, V.M., *Khimiya vitaminov* (Chemistry of Vitamins), Moscow: Pishchevaya promyshlennost', 1973.

34. Rajashekharam, M.V., Nikalje, D.D., Jaganathan, R., and Chaudhari, R.V., *Ind. Eng. Chem. Res.,* 1997, vol. 36, no. 3, pp. 592−604.

35. Sangeetha, P., Shanti, K., Rama Rao, K.S., Viswanathan, B., and Selvam, P., *Appl. Catal., A,* 2009, vol. 353, no. 2, pp. 160−165.

36. Deshmukh, A.A., Prashar, A.K., Kinage, A.K., Kumar, R., and Meijboom, R., *Ind. Eng. Chem. Res.,* 2010, vol. 49, no. 23, pp. 12180−12184.

Translated by O. Kadkin