Colloidal and Nanosized Catalysts in Organic Synthesis: XXIV.¹ Study of Hydrogenation of Furan and Its Derivatives in the Presence of MgO-Supported Nickel and Cobalt Nanoparticles

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Abstract—The processes of hydrogenation of furan and its derivatives (2-methylfuran, furfuryl alcohol, and furfural) in plug-flow type reactor under atmospheric hydrogen pressure at 20–220°C in the presence of supported nickel nanoparticles prepared via chemical reduction have been investigated. It has been found that nickel nanoparticles supported on magnesium oxide surface are the most reactive and stable under the considered conditions. This catalyst allows the corresponding hydrogenation products with 100% yield and complete conversion of the substrate.

Keywords: catalysis, nanoparticles, nickel, cobalt, furfural, furan

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Development of processes based on renewable sources has become an extremely important field of chemical engineering. One of the major products of biomass conversion is furfural [2] which is in its turn a precursor of a series of valuable organic compounds such as furfuryl alcohol, tetrahydrofurfuryl alcohol, 2-methylfuran, 2-methyltetrahydrofuran, furan, and tetrahydrofuran [3, 4].

Industrial hydrogenation of furfural is performed in the presence of copper-chromium catalysts at high pressure (up to 250 atm) and temperature 60–220°C, the yield with respect to furfuryl alcohol being 60–97% [5]. Hydrogenation of furfural with hydrogen can be also performed at pressure up to 20 atm and temperature up to 260°C when catalyzed with copper nanoparticles immobilized on various supports, the furfuryl alcohol being 96% [6–8].

Copper catalysts have been utilized in hydrogenolysis of furfural yielding 2-methylfuran (51.1–93.5%) at hydrogen pressure of 1–90 atm and temperature 150–280°C [9–11]. Hydrogenation of furfural with molecular hydrogen in the presence of NiO/SiO₂ at 200°C and

1 atm of hydrogen has allowed tetrahydrofurfuryl alcohol with 14.9% yield [12]. Hydrogenation of furfural in the presence of Ru/C in liquid 1-butanol (165°C and 25 atm of hydrogen) has afforded furfuryl alcohol, furfural conversion being 91% and the product yield being 42.4% [13].

Ruthenium catalysts have been utilized in the production of tetrahydrofurfuryl alcohol via hydrogenation if furfuryl alcohol [14–16]. The reaction occurs at 40–120°C and excessive pressure 20–60 atm. Nickel–palladium catalysts have also exhibited high efficiency in this reaction. For example, the yield of tetrahydrofurfuryl alcohol of 96% has been achieved in the presence of Ni–Pd/SiO₂ at 40°C and 40 atm, the reaction duration being 2 h [17].

2-Methyltetrahydrofuran has been obtained in 100% yield via hydrogenation of 2-methylfuran in the presence of Pd/C at 200°C and H_2 : 2-methylfuran molar ratio of (10–25): 1 [18].

Processes of furan hydrogenation in the presence of rhodium and rhenium catalysts at temperature up to 200°C and pressure 60 atm have been described [19–24]; the reactions have led to the formation of products of hydrogenolysis and ring opening.

¹ For communication XXIII, see [1].



Fig. 1. Composition of the catalysate as a function of temperature of furan hydrogenation at 1a: H₂ molar ratio 1 : 2.5 [specific substrate feeding rate 0.3 L/(kg_{cat} h), Ni⁰/ MgO]; (*1*) tetrahydrofuran and (*2*) furan.

We have earlier investigated the processes of hydrogenation of a series of unsaturated hydrocarbons in a plug-flow reactor at atmospheric pressure of hydrogen in the presence of nickel nanoparticles immobilized on various supports [25]. The nanostructured nickel catalysts have exhibited high efficiency in the said processes. The present study aimed to investigate the processes of hydrogenation of furan and its derivatives (2-methylfuran, furfural, and furfuryl alcohol) in a plug-flow reactor at atmospheric pressure of hydrogen using nickel and cobalt catalysts applied on various supports: γ -Al₂O₃, NaX zeolite, SiO₂, and MgO (Scheme 1).

The experiments were performed using a plugflow reactor (Parr 5400 Tubular Reactor System) at temperature 20–220°C, atmospheric pressure, 2.5-fold molar excess of hydrogen, specific feeding rate of the hydrogenated substrate 0.36 L/(kg_{cat} h), in bulk. The reaction mixtures were analyzed by means of ¹H NMR spectroscopy, GLC, and chromato–mass spectrometry.

The catalysts were prepared via impregnation of a support with an aqueous solution of the corresponding metal salt during 24 h, followed by filtration, washing with distilled water, and reduction with sodium borohydride in water at 20–25°C [26]. The obtained catalysts were analyzed by means of scanning electron microscopy using a FEI Versa 3D Dual Beam instrument (working distance 10 mm, secondary electrons detector: ETD, backscattered





Fig. 2. Composition of the catalysate as a function of temperature of 2-methylfuran hydrogenation at **1b** : H_2 molar ratio 1 : 2.5 [specific substrate feeding rate 0.3 L/(kg_{cat} h), Ni⁰/ MgO]; (*1*) 2-methyltetrahydrofuran, (*2*) 2-methylfuran, and (*3*) ring opening products.

electrons detector: CBS, elemental analysis method: EDS). The catalysts showed variable shape and size of the particles and their agglomerates. The particles with size starting from 70–100 nm were obtained, depending on the used support.

Preliminary assessment of the efficiency of the obtained catalysts (hydrogenation of furan **1a** at 100°C, other conditions also being identical) revealed that the yield of the target product **2a** was significantly dependent on the nature of the carrier. The yield of the hydrogenation product **2a** and the substrate **1a** conversion did not exceed 1–1.5% in the presence of Co^0/γ -Al₂O₃ or 13% in the presence of Ni^0/γ -Al₂O₃. When cobalt and nickel particles supported on NaX or SiO₂ were used in the same reaction, the yield of the product **2a** was below 4%. The use of MgO as the support significantly enhanced the yield of the product **2a** and the substrate **1a** conversion were achieved in the presence of Co^0/MgO .

Elucidation of the effect of the amount of nickel on MgO support on the hydrogenation product yield revealed that the optimal ratio between nickel(II) chloride and MgO, was 1.2 : 1. Hydrogenation of compound **1a** in the presence of Ni⁰/MgO afforded product **2a** in 68% yield at temperature as low as 25°C; the products of ring opening were not detected in the catalysate. The increase in temperature to 100°C allowed tetrahydrofuran **2a** with 100% yield (Fig. 1). Further increase in temperature led to the formation of the ring opening products (butan-1-ol, 26% at 160°C). It was found that the hydrogenation of furan **1a** in the presence of Ni⁰/MgO led to the product **2a** yield and the substrate **1a** conversion were 45–80% higher than in the presence of Co⁰/MgO, other conditions being the same.



Fig. 3. Composition of the catalysate as a function of temperature of furfuryl alcohol hydrogenation at $1c : H_2$ molar ratio 1 : 2.5 [specific substrate feeding rate 0.3 L/(kg_{cat}h), Ni⁰/ MgO]; (*1*) tetrahydrofurfuryl alcohol, (*2*) furfuryl alcohol, and (*3*) 2-methyltetrahydrofuran.

Similarly, 2-methylfuran **1b** was involved in the hydrogenation in the presence of Ni⁰/MgO. 2-Methyltetrahydrofuran **2b** was obtained with yield up to 94% and selectivity 100% at the specific feeding rate of the substrate **1b** 0.3 L/(kg_{cat} h), 2.5-fold molar excess of hydrogen, pressure 1 atm, and temperature (Fig. 2). Further increase in temperature also led to the formation of the furan ring opening products (16.6% at 140°C).

It should be noted that furan **1a** was more prone to hydrogenation under the considered conditions in comparison with 2-methylfuran **1b**, likely due to the steric effect of the substituent. For example, conversion of compound **1a** at 60°C (other conditions being identical) was found 15% higher in comparison with compound **1b**. Similar results have been earlier obtained in the presence of the Adams catalysts [27]. The rate constant of furan **1a** hydrogenation has been found 12% higher than that of 2-methylfuran **1b**.

Hydrogenation of furfuryl alcohol 1c in the presence of Ni⁰/MgO was performed at 100–200°C, specific feeding rate of alcohol 1a 0.36 L/(kg_{cat} h), and 2.5fold molar excess of hydrogen. The composition of catalysate obtained in that reaction as function of the process temperature is shown in Fig. 3. It should be noted that hydrogenation of the alcohol 1c occurred at higher temperature in comparison with compounds 1a and 1b. 94% yield of tetrahydrofurfuryl alcohol 2c 94%



Fig. 4. Composition of the catalysate as a function of temperature of furfural hydrogenation at **3** : H₂ molar ratio 1 : 2.5 [specific substrate feeding rate 0.3 L/(kg_{cat} h), Ni⁰/ MgO]; (1) tetrahydrofurfuryl alcohol, (2) furfuryl alcohol, (3) furfural, and (4) 2-methyltetrahydrofuran.

at complete conversion of the substrate was achieved at temperature as high as 200°C. The said effect was due to the influence of the steric and electron-accepting factors of the CH_2OH group on the ring stability [27].

Furfural **3** produced via biomass conversion is an important source for the synthesis of furan and its derivatives [28]. Hydrogenation of aldehyde **3** in the presence of Ni⁰/MgO was studied at temperature $120-200^{\circ}$ C, specific feeding rate of the substrate 0.36 L/(kg_{cat} h), and 2.5-foldmolar excess of hydrogen (Scheme 2, Fig. 4).

Analysis of the experimental data suggested that the decrease in the reactivity of the furan ring in the aldehyde **3** towards hydrogenation (the presence of the type 2 substituent, HC=O) led to a two-stage process: the hydrogenation of the ring affording product **2c** started only upon the reduction of the carbonyl group of the substrate **3** into the hydroxyl one (compound **1c**). The highest yield of the alcohol **2c** at 200°C was of 53% at complete conversion of aldehyde **3**. Further increase in temperature led to the increase in the fraction of the hydrogenolysis of the hydroxyl group of the alcohol **1c** yielding compound **1b**, its content in the catalysate being 13% at 240°C.

It should be noted that the attempt to hydrogenate the furan ring in ethyl 2-furoate under the conditions of hydrogenation of compound **3** failed, since the electron-



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accepting ethoxycarbonyl group was not involved in the hydrogenation.

In summary, we found that nickel nanoparticles stabilized on the MgO surface exhibited high catalytic activity towards hydrogenation of furan and its derivatives at pressure of 0.1 MPa and temperature 120–200°C, affording the hydrogenation products in up to 100% yield and selectivity in a plug-flow reactor. The obtained data (upon comprehensive investigation of the kinetic features and further optimization) can form a basis for the development of new efficient process for hydrogenation of furan and its derivatives.

EXPERIMENTAL

Chromato–mass spectroscopy analysis was performed using a Saturn 2100 T/GC3900 instrument (EI, 70 eV).

Catalysts preparation. The catalysts were prepared via impregnation of a solid support (MgO, SiO₂, γ -Al₂O₃, or NaX zeolite) with an aqueous solution of nickel(II) or cobalt(II) chloride hexahydrate (0.25–1.2 g of the salt per 1 g of the support) during 5–6 h, followed by filtration, washing with distilled water, and the treatment with an aqueous solution of sodium borohydride at 20–25°C during 20–30 min. The nickel particles size at the surface of the so obtained catalyst was of 70–100 nm [29]. The moist catalyst was loaded in the reactor and dried in a hydrogen stream at 120–300°C prior to the process.

General procedure for hydrogenation. The reactions were performed in a plug-flow reactor at atmospheric pressure and temperature 20-200°C. The reactions could occur either in a gas phase or in the gas-liquidsolid catalyst system, depending on the boiling point of the starting compounds. The laboratory-scale reactor consisted of a 12Kh18N10T steel tube with inner diameter 9 mm and the heating zone height 50 mm put in an electric oven. The catalyst was loaded in a middle part of the reactor, surrounded by inert filler (quartz attachment). Liquid furan or its derivatives were fed at rate of 0.3 L/(kg_{cat} h), hydrogen feeding rate being 190-230 L/(kg_{cat} h) (2.5-fold molar excess). The examples below are given for the catalyst prepared via impregnation of pressed MgO granules with nickel(II) chloride hexahydrate at the mass ratio 1.2:1, followed by reduction.

Tetrahydrofuran (2a). *a*. Compound 1a $[0.3 \text{ L/(kg}_{cat} \text{ h})]$ and hydrogen $[230 \text{ L/(kg}_{cat} \text{ h})]$ were fed to 6 g of the Ni⁰/MgO catalyst at 25°C. Conversion of furan 1a 63.5%. Selectivity with respect to product 2a 100%, yield 63.5%. Mass spectrum (EI), *m/e* (I_{rel} , %):

73.8 (71) $[M+1]^+$, 70.9 (100) [M-1], 70.0 (8), 69.0 (3), 55.0 (3), 42.9 (2), 42.0 (2), 41.0 (8), 40.1 (2).

b. Compound **1a** [0.3 L/(kg_{cat} h)] and hydrogen [230 L/(kg_{cat} h)] were fed to 6 g of the Ni⁰/MgO catalyst at 100°C. Conversion of furan **1a** 98.7%, selectivity with respect to product **2a** 100%, yield 98.7%.

c. Compound **1a** [0.3 L/(kg_{cat} h)] and hydrogen [230 L/(kg_{cat} h)] were fed to 6 g of the Co⁰/MgO catalyst at 25°C. Conversion of furan **1a** 20%, selectivity with respect to product **2a** 100%, yield 20%.

2-Methyltetrahydrofuran (2b). *a*. Compound **1b** [0.3 L/(kg_{cat} h)] and hydrogen [190 L/(kg_{cat} h)] were fed to 6 g of the Ni⁰/MgO catalyst at 20°C. Conversion of 2-methylfuran **1b** 56.5%, yield 56.5%. Mass spectrum (EI), *m/e* (I_{rel} , %): 86.7 (3) [M + 1]⁺, 72.7 (5), 56.8 (87), 55.8 (91), 54.9 (46), 43.0 (30), 41.0 (100), 40.2 (13).

b. Compound **1b** [0.3 L/(kg_{cat} h)] and hydrogen [190 L/(kg_{cat} h)] were fed to 6 g of the Ni⁰/MgO catalyst at 100°C. Conversion of 2-methylfuran **1b** 97.7%, selectivity with respect to product **2b** 96.6%, yield 94.4%.

Tetrahydrofurfuryl alcohol (2c). *a*. Compound **3** [0.3 L/(kg_{cat} h)] and hydrogen [210 L/(kg_{cat} h)] were fed to 6 g of the Ni⁰/MgO catalyst at 200°C. Conversion of aldehyde **3** 98.5%, yield 52.7%. Mass spectrum (EI), *m/e* (I_{rel} , %): 102.8 (5) [M + 1]⁺, 42.8 (14), 71.0 (100), 70.0 (11), 43.0 (52), 42.0 (12), 41.0 (50). Furfuryl alcohol (1c), yield 37.9%. Mass spectrum (EI), *m/e* (I_{rel} , %): 98.8 (4) [M+1]⁺, 97.8 (51) [M]⁺, 96.8 (10), 81.9 (9), 81.0 (100), 69.0 (11), 53.0 (10), 41.0 (4). **2-Methyltetrahydrofuran (2c)**, yield 3%.

b. Compound 1c $[0.3 \text{ L/(kg}_{cat} \text{ h})]$ and hydrogen $[210 \text{ L/(kg}_{cat} \text{ h})]$ were fed to 6 g of the Ni⁰/MgO catalyst at 200°C. Conversion of substrate 1c 98.9%, yield 94.5%. 2-Methyltetrahydrofuran (2b), yield 5.3%

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

- Mokhov, V.M., Popov, Yu.V., Paputina, A.N., Nebykov, D.N., and Shishkin, E.V., *Russ. J. Gen. Chem.*, 2019, vol. 89, no. 12, p. 2333. https://doi.org/10.1134/S1070363219120016
- Nakagawa, Y., Tamura, M., and Tomishige, K., ACS Catal., 2013, vol. 12, no. 3, p. 2655.

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https://doi.org/10.1021/cs400616p

- Nagaraja, B.M., Siva, K.V., Shasikala, V., Padmasri, A.H., Sreedhar, B., David, R.B., and Rama, R.K.S., *Catal. Commun.*, 2003, vol. 6, no. 4, p. 287. https://doi.org/10.1016/s1566-7367(03)00060-8
- Nagaraja, B.M., J. Mol. Catal. (A), 2007, vol. 265, nos. 1–2, p. 90. https://doi.org/10.1016/j.molcata.2006.09.037
- Stevens, J.G., Bourne, R.A., Twigg, M.V., and Poliakoff, M., *Angew. Chem. Int. Ed.*, 2010, vol. 49, no. 47, p. 8856.
 - https://doi.org/10.1002/anie.201005092
- Vetere, V., Merlo, A.B., Ruggera, J.F., and Casella, M.L., J. Br. Chem. Soc., 2010, vol. 21, no. 5, p. 914. https://doi.org/10.1590/s0103-50532010000500021
- Nagaraja, B.M., Siva Kumar, V., Shasikala, V., Padmasri, A.H., Sreedhar, B., David Raju, B., and Rama Rao, K.S., *Catal. Commun.*, 2003, vol. 4, no. 6, p. 287.
 - https://doi.org/10.1016/s1566-7367(03)00060-8
- Yan, K., Wu, X., An, X., and Xie, X., Chem. Eng. Commun., 2013, vol. 201, no. 4, p. 456. https://doi.org/10.1080/00986445.2013.775646
- Wettstein, S.G., Alonso, D.M., Gürbüz, E.I., and Dumesic, J.A., *Curr. Op. Chem. Eng.*, 2012, vol. 1, no. 3, p. 218.
 - https://doi.org/10.1016/j.coche.2012.04.002
- Geilen, F.M.A., vom Stein, T., Engendahl, B., Winterle, S., Liauw, M.A., Klankermayer, J., and Leitner, W., *Angew. Chem. Int. Ed.*, 2011, vol. 50, no. 30, p. 6831. doi10.1002/ anie.201007582
- Nakagawa, Y. and Tomishige, K., *Catal. Surveys Asia*, 2011, vol. 15, no. 2, p. 111. https://doi.org/10.1007/s10563-011-9114-z
- Seo, G. and Chon, H., J. Catal., 1981, vol. 67, no. 2, p. 424.
 - https://doi.org/10.1016/0021-9517(81)90302-x
- Ordomsky, V.V., Schouten, J.C., van der Schaaf, J., and Nijhuis, T.A., *Appl. Catal. (A)*, 2013, vol. 451, p. 6. https://doi.org/10.1016/j.apcata.2012.11.013
- Zhang, B., Zhu, Y., Ding, G., Zheng, H., and Li, Y., Gr. Chem., 2012, vol. 14, no. 12, p. 3402. https://doi.org/10.1039/c2gc36270h
- Khan, F.A., Vallat, A., and Süss-Fink, G., *Catal. Commun.*, 2011, vol. 12, no. 15, p. 1428. https://doi.org/10.1016/j.catcom.2011.05.024
- Tike, M.A. and Mahajani, V.V., *Ind. Eng. Chem. Res.*, 2007, vol. 46, no. 10, p. 3275.

https://doi.org/10.1021/ie061137m

- Nakagawa, Y. and Tomishige, K., *Catal. Commun.*, 2010, vol. 12, no. 3, p. 154. https://doi.org/10.1016/j.catcom.2010.09.003
- Xiu, S. and Shahbazi, A., *Ren. Sust. En. Rev.*, 2012, vol. 16, no. 7, p. 4406. https://doi.org/10.1016/j.rser.2012.04.028
- Aycock, D.F., Org. Proc. Res. Dev., 2007, vol. 11, no. 1, p. 156. https://doi.org/10.1021/op060155c
- Koso, S., Nakagawa, Y., and Tomishige, K., J. Catal., 2011, vol. 280, no. 2, p. 221. https://doi.org/10.1016/j.jcat.2011.03.018
- Koso, S., Watanabe, H., Okumura, K., Nakagawa, Y., and Tomishige, K., *Appl. Catal (B)*, 2012, vol. 111, p. 27. https://doi.org/10.1016/j.apcatb.2011.09.015
- Koso, S., Watanabe, H., Okumura, K., Nakagawa, Y., and Tomishige, K., *J. Ph. Chem. (C)*, 2012, vol. 116, no. 4, p. 3079. https://doi.org/10.1021/jp2114225
- Chen, K., Mori, K., Watanabe, H., Nakagawa, Y., and Tomishige, K., *J. Catal.*, 2012, vol. 294, p. 171. https://doi.org/10.1016/j.jcat.2012.07.015
- Amada, Y., Watanabe, H., Tamura, M., Nakagawa, Y., Okumura, K., and Tomishige, K., *J. Ph. Chem. (C)*, 2012, vol. 116, no. 44, p. 23503. https://doi.org/10.1021/jp308527f
- Popov, Yu.V., Mokhov, V.M., Nebykov, D.N., Shcherbakova, K.V., and Dontsova, A.A., *Russ. J. Gen. Chem.*, 2018, vol. 88, no. 1, p. 20. https://doi.org/10.1134/S1070363218010048
- 26. Popov, Yu.V., Mokhov, V.M., Latyshova, S.E., Nebykov, D.N., Panov, A.O., and Pletneva, M.Yu., *Russ. J. Gen. Chem.*, 2017, vol. 87, no. 10, p. 2276. https://doi.org/10.1134/S107036321710005X
- 27. Smith, H.A. and Fuzek, J.F., *J. Am. Chem. Soc.*, 1949, vol. 71, no. 2, p. 415. https://doi.org/10.1021/ja01170a013
- Koso, S., Ueda, N., Shinmi, Y., Okumura, K., Kizuka, T., and Tomishige, K., *J. Catal.*, 2009, vol. 267, no. 1, p. 89. https://doi.org/10.1016/j.jcat.2009.07.010
- Popov, Yu.V., Mokhov, V.M., Latyshova, S.E., Nebykov, D.N., Panov, A.O., and Davydova, T.M., *Russ. J. Gen. Chem.*, 2018, vol. 88, no. 10, p. 2035. https://doi.org/10.1134/S1070363218100018