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Colloidal and Nanosized Catalysts in Organic Synthesis: XV.[1] Gas-Phase Hydrogenation of Alkenes Catalyzed by Supported Nickel Nanoparticles

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Abstract—Gas-phase hydrogenation of alkenes and their derivatives, catalyzed by nickel nanoparticles supported on zeolite or silica gel support occurs at 150–250°C and an atmospheric hydrogen pressure and results in a high conversion. The selectivity of the hydrogenation depends on the amount of hydrogen: at a low diene (triene)–hydrogen ratio, selective hydrogenation of one multiple bond in the substrate is possible.

Keywords: catalysis, nanoparticles, nickel, hydrogenation, alkenes, gas phase, zeolite

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The classical method of hydrogenation of carbon–carbon multiple bonds involves a heterogeneous nickel, platinum, palladium, rhodium, or ruthenium-catalyzed gas-phase reaction [2]. Widely used is an accessible nickel catalyst, but in this case a successful reaction requires elevated temperature and pressure. Hydrogenations under milder conditions gave good results with platinum and palladium catalysts. Rhodium and ruthenium showed a high selectivity in the reduction of unsaturated alcohols, halides, and esters without their hydrogenolysis [3].

In our recent works [4, 5] on the hydrogenation of carbon–carbon multiple bonds on nickel nanoparticles (NPs) as colloidal solutions of alkanols or THF we have demonstrated the promise nanocatalysis offers in this process. However, the long reaction time (3–10 h), labor-consuming catalyst regeneration, and batch nature of the process make it difficult to scale-up.

A number of gas-phase hydrogenations of alkenes on transition metal NPs have been reported. Deghedi et al. reported the reduction of styrene and its derivatives on nickel NPs at temperatures of up to 130°C and a pressure of about 30 atm [6]. Belykh et al. [7] showed that hydrogenation of nickel NPs can be accomplished under milder conditions. Iron NPs were used to catalyze alkene hydrogen at a hydrogenation pressure of 10–20 atm [8]. Vanyorek et al. studied the hydrogenation of but-1-ene on a carbon nanotube–supported Pt catalyst [9]. The but-1-ene conversion reached 98%. A series of alkenes were successfully hydrogenated zeolite-supported rhodium NPs [10]. The reaction occurred at room temperature and a hydrogen pressure of 10 atm for 0.25–2 h in an autoclave. It is interesting that the hydrogenation of crotonaldehyde with H_2 in the presence of gold and silver NPs supported on a SBA-15 substrate resulted in C=O reduction, whereas the C=C bond remained intact [11].

The goal of the present work was to explore the possibility of continuous gas-phase flow hydrogenation of alkenes on a supported nickel NP catalyst and to assess the selectivity of this reaction. As a support we used zeolite A (fraction 2–2.5 mm). Nickel NPs were applied on the substrate by a procedure analogous to that described in [12] and involving ion exchange between Ni(II) chloride and the calcium form of zeolite A and reduction of the resulting nickel form with sodium tetrahydroborate in isopropanol followed by drying in a flow of hydrogen at 170–220°C (reaction temperature). According to [13], this procedure gives rise to nickel NPs about 5 nm in size. Glavee et al. [14] reported the formation of both nickel and nickel boride Ni_2B nanoparticles, along with NiO, in the reduction of

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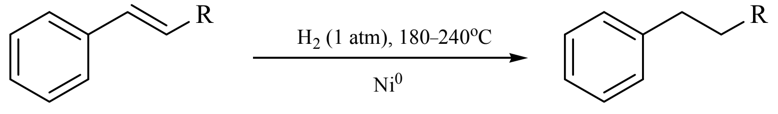
[1] For communication XIV, see [1].

nickel salts. However, we found that the formation of nickel NPs as a colloidal solution in isopropanol at $NaBH_4$–$NiCl_2$ ratios no higher than 2 : 1 is accompanied by deposition on the inner walls of the reaction vessel, when they were overheated, of a nickel metal mirror. This fact points to either exclusive formation of nickel NPs or the presence of quite a small fraction of nickel boride in the given colloidal system. In this connection, the formation in zeolite A pores of just nickel particles seems the most likely option. Indirect evidence for this suggestion is provided by the low resistance of the resulting catalysts to air and moisture, leading to its rapid deactivation, which is characteristic of metal nanoparticles [8].

In view of the low hydrolytic stability of the catalyst, special requirements are imposed for its application, specifically, water-proof conditions of loading to the reactor and dehydration of hydrogen and the substrate to be hydrogenated. We found that a similar hydrogenation catalyst can be prepared under conditions when nickel ions are reduced with sodium tetrahydroborate in an aqueous medium. The resulting catalyst is hydrolytically stable and shows fair stability on short contact with air. Such properties can be explained by the fact that the catalyst contains much more boron atoms in the crystal lattice, and this enhances the oxidative stability of nickel NPs.

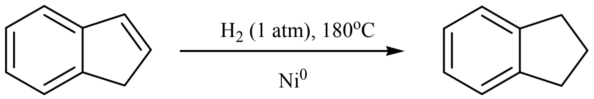
For the substrates for hydrogenation we chose cyclic and aromatic alkenes, including those containing functional groups. A Parr series 5400 continuous flow catalytic tubular reactor system was used. The reaction was performed in the gas phase at temperatures higher than the boiling points of the alkenes, at 1 atm on catalysts prepared both in isopropanol and in water.

It was found that zeolite-supported nickel NPs, irrespective of how they were prepared, exhibit a high catalytic activity in the hydrogenation of carbon–carbon multiple bonds. In particular, cinnamyl alcohol (**1**), methyl cinnamate (**3**), and indene (**5**) were successfully hydrogenated at 170–220°C, a 2–5-fold molar excess of hydrogen, and a 1-atm total pressure; therewith, neither the functional groups nor aromatic rings were involved in the reaction. The contact time calculated from the reactor volume, catalyst porosity, and volume of the gas phase under the reaction conditions was 2–7 s.



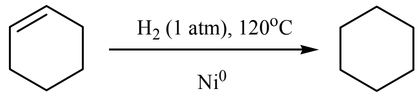
1, **3** **2**, **4**

R = CH_2OH (**1**, **2**), C(O)OMe (**3**, **4**).



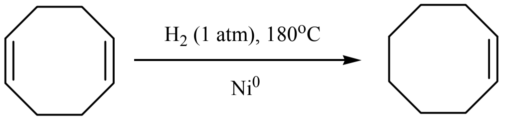
5 **6**

Cyclic alkenes are hydrogenated under the same conditions. Thus, cyclohexene **7** is hydrogenated to cyclohexane **8** within 2–3 s.

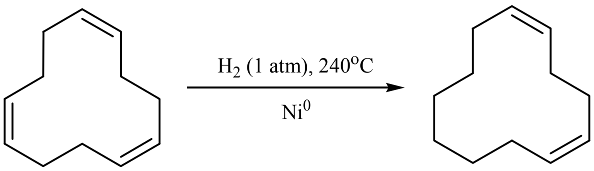


7 **8**

With a 6–7-fold molar excess of hydrogen, exhaustive hydrogenatione of cyclic dienes and trienes **9** and **11** takes place. However, with a 3-fold excess of hydrogen and the calculated contact time 2.5 s, diene **9** converts to cyclooctene **10** with the selectivity of 80%. In the same way, we could realize selective (96%) partial hydrogenation of triene **11** to cyclodeca-1,5-diene **12**. This result suggests that the process can be optimized for selective hydrogenation of one of several carbon–carbon multiple bonds.



9 **10**

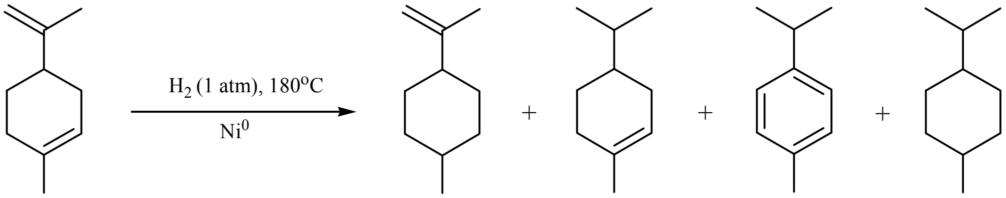


11 **12**

It was found that the contact time (volume feed rate of alkene) has a weaker effect of the selectivity of hydrogenation of dienes and trienes than the alkene–

hydrogen molar ratio. Thus, the hydrogenation of triene **11** for 2.3 s gave a mixture containing 26% of the hydrogenation product by one double bond (compound **12**) and 68% of cyclododecene. The triene could be selectively (up to 97%) hydrogenated to the diene on another substrate (on KSMG silica gel instead of zeolite). The hydrogenation of cyclooctadiene on silica gel–supported nickel NPs gave cyclooctene **10** in 78% yield (diene conversion 81%).

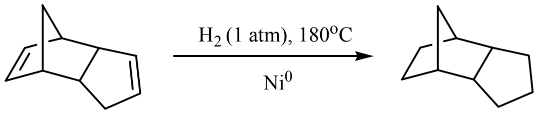
The hydrogenation of limonene **13** on a zeolite-supported nickel at a 3-fold excess of hydrogen and the contact time of 3.6 s occurred with a low selectivity. The following products were identified: the hydrogenation product of the cyclohexene double bond **14** (30%), hydrogenation product of the isopropenyl group **15** (44%), exhaustive hydrogenation product **17**, as well as limonene aromatization product 1-isopropyl-4-methylbenzene (**16**) (ca. 21%).



13 **14** **15** **16** **17**

The formation of compound **16** can be explained by the reversible dehydrogenation of the cyclohexene ring that takes place at a 3-fold excess of hydrogen, as well as by the high thermodynamic stability of the benzene ring in this product. It should be noted that benzene was not found among the hydrogenation products of cyclohexene. The reaction with a 5-fold excess of hydrogen gave less dehydroaromatization product **16** (6%), but the selectivity of hydrogenation of the multiple bonds in limonene was still low.

The prepared catalyst proved to be effective in the hydrogenation of dicyclopentadiene (**18**). We could obtain the exhaustive hydrogenation product tetrahydrodicyclopentadiene (**19**) (180°C, 2.5–4 s, 5–6-fold molar excess of H_2). Note that to hydrogenate dicyclopentadiene on a commercial nickel catalyst requires a pressure of 3.5 atm [15].

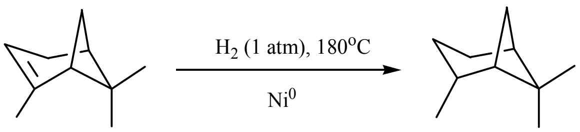


18 **19**

We also studied the effect of reaction conditions on the composition and yields of the hydrogenation products of diene **18**. Thus, with a 5-fold molar excess of hydrogen, the diene undergoes exhaustive hydrogenation within 2–2.5 s in the temperature range 180–210°C. With a 3 : 1 hydrogen:diene ratio (1.5-fold molar excess per one double bond), both the hydrogenation product of the norbornene ring and alkane **19** form, but their ratio depends on conditions. For example, in 4.4 s at 180°C the yield of compound **19** reaches 91%, whereas in 2.4 s under the same conditions the highest yield (77%) is characteristic of the hydrogenation half-product dihydrodicyclopentadiene, whereas the yield of alkane **19** is as low as 20%.

Diene **18** was also hydrogenated at a 2 : 1 hydrogen : diene ratio. The reaction within 5.2 s at 200°C gave 8% dihydrodicyclopentadiene and 87% tetrahydrodicyclopentadiene **19**. The reaction at a higher temperature resulted in a lower conversion of the starting compounds, probably, on account of a weaker interaction between the substrate and catalyst. Even though hydrogenation can be performed not using an excess of hydrogen, this approach is undesirable in view of the rapid deac-tivation of the catalyst because of the higher rate of adsorption of hydrocarbons on the catalytic centers compared to hydrogen.

Earlier we could not hydrogenate camphene and pinenes in the liquid phase with a high conversion [4]. In the gas phase at 170°C α-pinene (**20**) was exhaustively hydrogenated to form pinane **21**.



20 **21**

Thus, zeolite A–supported nickel NPs showed a high catalytic activity in the hydrogenation of alkenes of different structures. The use of KSMG silica gel as a substrate gave worse results in terms of the activity and durability of the resulting catalyst. Varying the hydrogen–alkene ratio and contact time allows, in some cases, selective hydrogenation one of several double bonds in unsaturated compounds. The catalyst exhibits a high activity in the absence of contact with air and moisture and at a high excess of hydrogen. The present research gave evidence showing that gas-phase hydrogenation of carbon–carbon multiple bonds with hydrogen on nanosized catalysts without using high pressures and temperatures deserves further research

EXPERIMENTAL

Gas chromatography–mass spectrometry analysis was performed on a Saturn 2100 T/GC3900 instrument (electron impact, 70 eV).

The catalyst was prepared by impregnating zeolite A (fraction 2–2.5 mm) with aqueous nickel(II) chloride hexahydrate for 5–6 h. The resulting material was filtered off, dried in air, and then treated with a suspension of sodium tetrahydroborate in isopropanol at 40–50°C or in water at 20–25°C for 1–2 h. The wet catalyst was loaded into the reactor and then dried from isopropanol or water in a flow of hydrogen immediately before reaction.

Catalytic hydrogenation was performed in a Parr series 5400 continuous flow catalytic tubular reactor system (reactor volume 20 cm^3, tube length 0.5 m, catalyst weight 6–8 g depending on porosity). The reactor is designed as a steel tube (inner diameter 7 mm, heating zone height 300 mm) embedded in an electric oven. The catalyst bed is placed in the central part of the reactor, and an inert packing (quartz) are placed before and after the catalyst bed. The source of hydrogen is a GV-7 generated with controlled gas feed.

General hydrogenation procedure. A steel reactor was loaded with 6.5 g of a wet catalyst (porosity 0.5), a 100-mm layer of a quartz packing (fraction 2–2.5 mm) was then poured on top, and a flow of hydrogen was then passed through the system for 0.5–1 h; as this took place, the temperature was gradually raised to 180°C. After the catalyst was ready, a liquid alkene and the required quantity of hydrogen were dosed to the reactor. Hydrogen was fed simultaneously with alkene.

Hydrogenation of cinnamyl alcohol (1). Alkene : hydrogen molar ratio 1:6, reaction time 2.6 s, reaction temperature 260° C. Yield of 3-phenylporpan-1-ol (**2**) 62%. Mass spectrum, *m*/*e* (I_{rel}, %): 136 (5) $[M]^+$, 117 (100), 91 (71), 77 (12), 65 (2).

Hydrogenation of methyl cinnamate (3). Alkene:hydrogen molar ratio 1 : 6, reaction time 2.3 s, reaction temperature 260° C. Yield of methyl phenylpropionate (**4**) 74%. Mass spectrum, *m*/*e* (I_{rel}, %): 164 (5) $[M]^+$, 131 (3), 117 (7), 104 (100), 91 (47), 77 (19), 51 (12).

Hydrogenation of indene (5). Alkene:hydrogen molar ratio 7 : 1, reaction time 2.8 s, reaction temperature 190°C. Yield of indane (**6**) 57%. Mass spectrum, *m*/*e* (I_{rel}, %): 118 (43) $[M]^+$, 117 (100), 91 (15), 63 (10).

Hydrogenation of cyclohexene (7). Alkene : hydrogen molar ratio 5 : 1, reaction time 2.44 s, reaction temperature 120°C. Yield of cyclohexane (**8**) 71%. Mass spectrum, *m*/*e* (I_{rel}, %): 85(7), 84 (100) $[M]^+$.

Hydrogenation of cycloocta-1,5-diene (9). *a*. Alkene : hydrogen molar ratio 3 : 1, reaction time 2.5 s, reaction temperature 180°C. Yield of cyclooctene (**10**) 78%. Mass spectrum, *m*/*e* (I_{rel}, %): 110 (21) $[M]^+$, 96 (70), 82 (81), 69 (93), 55 (100), 41 (100).

b. Alkene:hydrogen molar ratio 5 : 1, reaction time 1.8 s, reaction temperature 175°C. Yield of cyclooctene (**10**) 65%. Mass spectrum, *m*/*e* (I_{rel}, %): (21) $[M]^+$, 96 (70), 82 (81), 69 (93), 55 (100), 41 (100). Yield of cyclooctane 15%. Mass spectrum, *m*/*e* (I_{rel}, %): 112 (1) $[M]^+$, 97 (6), 84 (26), 70 (46), 57 (100), 41 (62).

Hydrogenation of cyclododeca-1,5,9-triene (11). *a*. Alkene:hydrogen molar ratio 3 : 1, reaction time 3.3 s, reaction temperature 240°C. Yield of cyclododeca-1,5-diene (**12**) 96%. Mass spectrum, *m*/*e* (I_{rel}, %): 164 (3) $[M]^+$, 134 (18), 120 (60), 92 (58), 79 (100), 65 (24), 41 (35).

b. Alkene:hydrogen molar ratio 5 : 1, reaction time 2.3 s, reaction temperature 240°C. Yield of cyclododeca-1,5-diene (**12**) 25%. Mass spectrum, *m*/*e* (I_{rel}, %): 164 (3) $[M]^+$, 134 (18), 120 (60), 92 (58), 79 (100), 65 (24), 41 (35). Yield of cyclododecene 65%. Mass spectrum, *m*/*e* (I_{rel}, %): 166 (3) $[M]^+$, 134 (17), 120 (43), 106 (15), 93 (44), 81 (70), 67 (100), 54 (23), 41 (39).

Hydrogenation of limonene (13). Alkene : hydrogen molar ratio 1:3, reaction time 3.6 s, reaction temperature 180°C. Yield of 1-isopropyl-4-methylcyclohexane (**14**) 30%. Mass spectrum, *m*/*e* (I_{rel}, %):

138 (10) $[M]^+$, 123 (20), 95 (100), 81 (35), 69 (78), 41 (76). Yield of 1-methyl-4-isopropylcyclohex-1-ene (**15**) 44%. Mass spectrum, *m*/*e* (I_{rel}, %): 138 (4) $[M]^+$, 123 (18), 95 (100), 81 (70), 67 (100), 41 (19). Yield of 1-isopropyl-4-methylbenzene (**16**) 23%. Mass spectrum, *m*/*e* (I_{rel}, %): 134 (4) $[M]^+$, 133 (32), 119 (100), 117 (15). Yield of 1-isopropyl-4-methylcyclohexane (**17**) 5%. Mass spectrum, *m*/*e* (I_{rel}, %): 140 (2) $[M]^+$, 96 (77), 68 (29), 55 (100).

Hydrogenation of dicyclopentadiene (18). Alkene : hydrogen molar ratio 3 : 1, reaction time 6.88 s, reaction temperature 180°C. Yield of tetrahydrodicyclopentadiene (**19**) 98%. ^{1}H NMR spectrum, δ, ppm: 1.20 t (2H, CH_2, $J = 8.4$ Hz), 1.25–1.58 m (10H, CH_2), 2.02 s (2H, CH), 2.27 s (2H, CH).

Hydrogenation of α-pinene (20). Alkene : hydrogen molar ratio, reaction time 2.6 s, reaction temperature 170°C. Yield of pinane (**21**) 97%. Mass spectrum, *m*/*e* (I_{rel}, %): 138 (3) $[M]^+$, 95 (91), 81 (93), 67(100), 55 (58), 41 (34).

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