Colloid and Nanosized Catalysts in Organic Synthesis: XXII.[1] Hydrogenation of Cycloolefins Catalyzed by Immobilized Transition Metals Nanoparticles in a Three-Phase System

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Abstract—The processes of unsaturated cyclic hydrocarbons hydrogenation in a three-phase gas–liquid–solid catalyst system in the presence of nanostructured nickel, cobalt, or iron catalysts in a flow reactor at 130°C and atmospheric pressure have studied. RX3Extra activated carbon, γ-Al$_2$O$_3$, NaX zeolite, and Purolite CT-175 cation-exchange resin have been used as supports; NaBH$_4$ and NH$_2$NH$_2$·H$_2$O were used as reducing agents. The catalytic activity of supported nanoparticles and their selectivity with respect to the product of exhaustive hydrogenation have been investigated.

Keywords: nanoparticles, nickel, cobalt, iron, hydrogenation, zeolite

Cyclic hydrocarbons are widely applied in different branches of chemical industry: fuel and energetics, oil processing, perfumery, pharmaceutics, and polymer production. For example, tetrahydrodicyclopentadiene is a component of high-energy propellant and an intermediate in the production of adamantane-based drugs; cyclooctane is the most efficient precursor of suberic acid which is used in the production of synthetic fibers, plastics, and drugs; pinane is used in the synthesis of pinane hydroperoxide which can serve as initiator of butadiene copolymerization with styrene.

The mentioned compounds can be obtained via catalytic hydrogenation of the corresponding unsaturated cyclic hydrocarbons (Scheme 1). In industry, these processes are mainly performed in a batch reactor, under relatively harsh conditions in a liquid phase. For example, dicyclopentadiene **1** can be hydrogenated at temperature 120–130°C and pressure 15 atm [2]. Hydrogenation of 1,5-cyclooctadiene **4** occurs at 70°C and 10 atm on suspended Pd/Al$_2$O$_3$ catalyst [3].

The use of nanocatalysts which allow significant acceleration of these processes is among modern trends in hydrogenation industry development. Metal nanoparticles can be applied as stabilized colloid solutions in liquid-phase processes [4] or as supported nanoparticles in gas-phase processes [5–10]. For example, a mixture of cyclooctene **5** and cyclooctane **6** has been obtained with selectivity 24 and 76%, respectively, at complete conversion of starting compound **4** using PEGylated palladium nanoparticles in an autoclave (liquid phase) at 90°C and 30 atm during 50 min [11]. Palladium nanoparticles have been used for hydrogenation of dicyclopentadiene **1** at 50°C and 10 atm during 2 h, the yield of exhaustive hydrogenation product **3** being 76% at conversion of starting dicyclopentadiene **1** 86% [12].

We have earlier studied gas-phase hydrogenation of unsaturated cyclic hydrocarbons at 140–240°C in the presence of nickel nanoparticles on different supports [13]. However, scaling of the process under these conditions can lead to enhancement of side reactions related to cycle rupture and rearrangement which in its turn results in the catalyst deactivation with the increase in the inter-regeneration period. Therefore, in this study we investigated hydrogenation of the corresponding cycloolefins in a three-phase system (under conditions of hydrogen diffusion through a liquid fild of hydrogenated olefin to active sites of the catalyst).

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[1] For communication XXI, see [1]

Scheme 1.
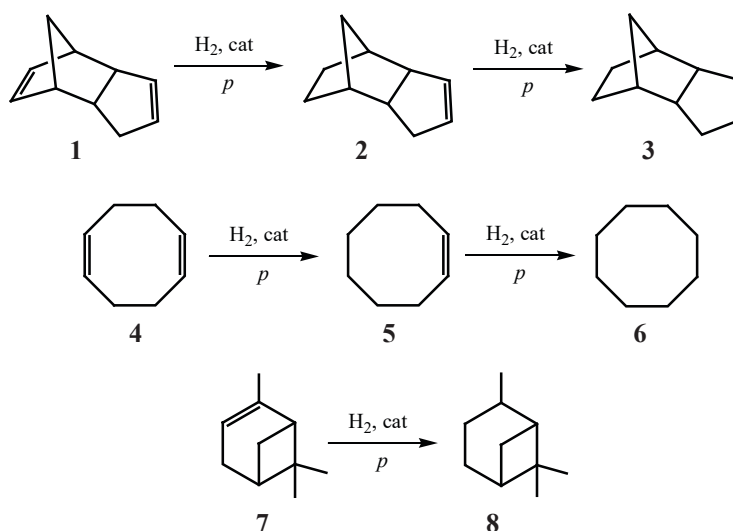
The experiments were performed in a Parr 5400 TubularReactorSystem flow reactor in the presence of transition metal nanoparticles (nickel, cobalt, or iron) immobilized at different supports: RX3Extra activated carbon, γ-Al_2O_3, NaX zeolite, or Purolite CT-175 cation-exchange resin. The efficiency of the probed catalysts was compared under identical conditions: temperature 130°C, atmospheric pressure, 2-fold molar excess of hydrogen with respect to a carbon–carbon double bond, catalyst loading 2 g, and liquid reagent supply 0.0036 L/h without any solvent. The reaction mixture composition was analyzed by means of ^{1}H NNR spectroscopy, GLC, and chromato–mass spectrometry.

The catalysts were prepared via impregnation of the support with an aqueous solution of the corresponding metal salt during 24 h, followed by the reduction with sodium borohydride in water at 20–25°C (method *a*) [14] or with hydrazine monohydrate in the presence of NaOH at 80–100°C (method *b*) [15]. Surface morphology of the obtained catalysts was different in terms of shape and size of the particles and their aggregates. Depending on the support and the reduction method, 40 to 140 nm metal particles and their aggregates with size up to 250 nm were formed at the surface.

Hydrogenation of dicyclopentadiene **1** was studied at 4-fold excess of hydrogen and conditional residence time of the substrate 0.074 h kg_{cat}/mol. The highest efficiency was revealed in the cases of cobalt (method *a*) and nickel (methods *a* and *b*) nanoparticles. Hydrogenation of dicyclopentadiene **1** occurred with sufficiently high selectivity with respect to the product of exhaustive hydrogenation

3 (Table 1, Exp. 5–12). The highest conversion of diene **1** was observed in the presence of nickel nanoparticles on γ-Al_2O_3 (Table 1, Exp. 7) (99.6%), the selectivity with respect to product **3** being 99.2%. It should be noted that direct reduction of cobalt at the support surface with hydrazine monohydrate was impossible, and the catalyst preparation demanded additional heating at 400°C during 4 h; yet the obtained catalyst exhibited low activity under the probed conditions.

Comparison of the nickel catalysts immobilized on γ-Al_2O_3, NaX zeolite, or the cation-exchange resin revealed no significant difference in activity and selectivity, in contrast to the catalysts prepared using the RX3 Extra activated carbon (Table 1, Exp. 4 and 8).

Iron nanoparticles did not exhibit significant catalytic activity. The highest conversion of dicyclopentadiene **1** was 15.2% in the presence of iron nanoparticles reduced with hydrazine monohydrate on γ-Al_2O_3.

It is interesting to notice that hydrogenation of 1,5-cyclooctadiene **4** at 4-fold excess of hydrogen and conditional residence time of the substrate 0.068 h kg_{cat}/mol yielded the product of partial hydrogenation **5** with selectivity up to 100% when using any of the studied catalysts (Table 2); that fact could be explained by low rate of compound **4** hydrogenation due to transannular interactions [16]. The nickel- and cobalt-containing catalysts were found the most efficient, yet in no case did we observe complete conversion of the substrate (Table 2).

Hydrogenation of α-pinene **7** was studied at 2-fold excess of hydrogen and conditional residence time of

Table 1. Conversion of dicyclopentadiene **1** and yield of the hydrogenation products

Exp. no.	Catalyst	Support	Reducer	Conversion, %	Yield, %	
					2	**3**
1	Ni	Purolite CT-175	$NaBH_4$	98.9	1.9	97.0
2	Ni	Zeolite NaX	$NaBH_4$	98.7	1.0	97.7
3	Ni	$\gamma\text{-Al}_2O_3$	$NaBH_4$	98.9	1.1	97.8
4	Ni	RX3Extra	$NaBH_4$	97.8	1.1	96.7
5	Ni	Purolite CT-175	$NH_2NH_2 \cdot H_2O$	98.6	1.0	97.6
6	Ni	Zeolite NaX	$NH_2NH_2 \cdot H_2O$	98.3	1.0	97.3
7	Ni	$\gamma\text{-Al}_2O_3$	$NH_2NH_2 \cdot H_2O$	99.6	0.8	98.8
8	Ni	RX3Extra	$NH_2NH_2 \cdot H_2O$	11.7	11.1	0.6
9	Co	Purolite CT-175	$NaBH_4$	98.5	3.7	94.8
10	Co	Zeolite NaX	$NaBH_4$	97.7	3.35	94.35
11	Co	$\gamma\text{-Al}_2O_3$	$NaBH_4$	97.5	1.3	96.2
12	Co	RX3Extra	$NaBH_4$	5.3	4.6	0.7
15	Fe	$\gamma\text{-Al}_2O_3$	$NH_2NH_2 \cdot H_2O$	15.2	12.2	3.0

the substrate 0.087 h kg_{cat}/mol. α-Pinene hydrogenation could be accompanied by side isomerization reactions, depending on the support acidity. Those processes were less pronounced in the cased of the nickel and cobalt catalysts, the selectivity with respect to product **8** reaching 99.7% (Table 3), except for cobalt nanoparticles on NaX zeolite (Table 3, Exp. 9), the content of the isomeriza-

tion products being up to 38.7% in the latter case. In the case of iron nanoparticles, the isomerization processes were more prominent, and the content of pinane **8** in the products did not exceed 18.6%.

We further investigated the stability of the most active catalysts. It was shown that the nickel catalysts immobilized on the cation-exchange resin and $\gamma\text{-Al}_2O_3$ were

Table 2. Conversion of cyclooctadiene **4** and yield of the hydrogenation products

Exp. no.	Catalyst	Support	Reducer	Conversion, %	Yield, %	
					5	**6**
1	Ni	Purolite CT-175	$NaBH_4$	96.5	96.5	0
2	Ni	Zeolite NaX	$NaBH_4$	97.2	97.2	0
3	Ni	$\gamma\text{-Al}_2O_3$	$NaBH_4$	96.8	96.8	0
4	Ni	RX3Extra	$NaBH_4$	82.1	82.1	0
5	Ni	Purolite CT-175	$NH_2NH_2 \cdot H_2O$	94.7	94.7	0
6	Ni	Zeolite NaX	$NH_2NH_2 \cdot H_2O$	96.6	96.6	0
7	Ni	$\gamma\text{-Al}_2O_3$	$NH_2NH_2 \cdot H_2O$	96.1	96.1	0
8	Ni	RX3Extra	$NH_2NH_2 \cdot H_2O$	31.3	31.3	0
9	Co	Purolite CT-175	$NaBH_4$	92.5	92.5	0
10	Co	Zeolite NaX	$NaBH_4$	93.6	93.6	0
11	Co	$\gamma\text{-Al}_2O_3$	$NaBH_4$	96.2	96.2	0

Table 3. Conversion of α-pinene **7** and yield of the hydrogenation products

Exp no.	Catalyst	Support	Reducer	Conversion, %	Yield, %	
					8	other[a]
1	Ni	Purolite CT-175	$NaBH_4$	99.7	98.6	1.1
2	Ni	Zeolite NaX	$NaBH_4$	81.5	75.0	6.5
3	Ni	$\gamma\text{-}Al_2O_3$	$NaBH_4$	99.9	99.6	0.3
4	Ni	RX3Extra	$NaBH_4$	99.7	99.5	0.2
5	Ni	Purolite CT-175	$NH_2NH_2 \cdot H_2O$	99.9	99.2	0.7
6	Ni	Zeolite NaX	$NH_2NH_2 \cdot H_2O$	99.5	96.6	2.9
7	Ni	$\gamma\text{-}Al_2O_3$	$NH_2NH_2 \cdot H_2O$	99.7	98,6	1.1
8	Co	Purolite CT-175	$NaBH_4$	97.7	71.9	25.8
9	Co	Zeolite NaX	$NaBH_4$	98.5	59.8	38.7
10	Co	$\gamma\text{-}Al_2O_3$	$NaBH_4$	97.8	96.4	1.4
11	Fe	Purolite CT-175	$NaBH_4$	95.3	16.7	78.6
12	Fe	Zeolite NaX	$NaBH_4$	85.2	0.1	85.1
13	Fe	Zeolite NaX	$NH_2NH_2 \cdot H_2O$	96.5	18.6	77.9

[a] Products of isomerization and subsequent hydrogenation

the most stable: the substrate conversion and the target products yield were not reduced over 10 h. Other nickel and cobalt catalysts exhibited the 10–15% decrease in the products yield during 10 h, but the catalytic activity was restored upon 1 h purging with hydrogen.

In summary, nickel nanoparticles (prepared via reduction with sodium borohydride or hydrazine monohydrate) revealed the highest catalytic activity and stability in the three-phase hydrogenation of unsaturated cyclic hydrocarbons. The studied nanoparticles could be arranged in the following series of decreasing catalytic activity: Ni > Co > Fe. The Purolite CT-175 cation-exchange resin and $\gamma\text{-}Al_2O_3$ were found the optimal supports for the nickel nanoparticles.

EXPERIMENTAL

The catalyzates were analyzed by means of chromato–mass spectrometry using a Saturn 2100 T/GC3900 instrument (EI, 70 eV). The ^1H NMR spectra were obtained using a Varian Mercury-300 spectrometer operating at 300 MHz. Quantitative GLC analysis of the reaction mass was performed using a Kristallyuks-4000M instrument (t_{start} = 100–210°C, t_{evap} = 250°C, polar column HP-5, l_{col} = 50 m, d_{col} = 0.52 μm, carrier gas: nitrogen, flame ionization detector, t_{det} = 250°C, solvent: n-hexane). Morphology of the catalysts was analyzed by means

of scanning electron microscopy using a FEI Versa 3D DualBeam instrument.

Catalysts preparation. The catalysts were prepared via impregnation of 2 g of the support (fraction 1–1.5 mm) with aqueous solution of nickel(II) chloride hexahydrate, cobalt(II) chloride hexahydrate, or iron(II) sulfate heptahydrate (2 g in 5 mL of water) during 24 h. After the impregnation, filtering off, and washing with distilled water, the catalyst was reduced with sodium borohydride (0.1 g in 10 mL of water) at 20–25°C during 20–30 min (method *a*) or with hydrazine monohydrate (10 mL in 10 mL of water) in the presence of 0.5 g of NaOH at 80–100°C during 50–60 min (method *b*).

Hydrogenation (*general procedure*). The reaction was performed in a Parr 5400 Tubular Reactor System laboratory device: reactor – steel tube (volume 20 cm³, length 0.5 m, inner diameter 7 mm) in an electric oven (heating zone height 300 mm). GV-7 hydrogen generator with adjustable gas feed served as hydrogen supply.

Humid catalyst was loaded in the reactor, 100 mm layer of inert carrier (quartz, same fraction) was applied from above, and the catalyst was dried in a hydrogen stream at 130°C prior to the reaction during 1–1.5 h. After that, the required amounts of the substrate and hydrogen were fed in the reactor at the desired temperature from above. The obtained data are collected in Tables 1–3

(the experiments with the substrate conversion below 5% were omitted).

Hydrogenation of dicyclopentadiene 1 was performed using 2 g of a catalyst at 130°C, hydrogen to alkene molar ratio 4 : 1; reagents feed 0.027 mol/h (alkene) and 0.108 mol/h (hydrogen); conditional reaction duration: 0.074 h kg_{cat}/mol.

endo-**Tetrahydrodicyclopentadiene (3).** Mass spectrum, m/e (I_{rel}, %): 136.9 (3.4) $[M+1]^+$, 136 (30.9), 120.9 (45.9), 95.0 (66.6), 67.0 (99.9).

Dihydrodicyclopentadiene (2). ^{1}H NMR spectrum, δ, ppm: 1.11–1.23 m (4H, CH_2), 1.35 q (2H, CH_2, J = 22.3 Hz), 2.03–2.18 m (4H, CH_2 + 2CH), 2.42 m (1H, CH). 2.89 m (1H, CH), 5.41 m (1H, CH=), 5.51 m (1H, CH=).

Hydrogenation of cyclooctadiene (4) was performed using 2 g of a catalyst at 130°C, hydrogen to alkene molar ratio 4 : 1; reagents feed 0.029 mol/h (alkene) and 0.116 mol/h (hydrogen); conditional reaction duration: 0.068 h kg_{cat}/mol.

Cyclooctene (5). Mass spectrum, m/e (I_{rel}, %): 109.8 (5.0) $[M+1]^+$, 109.0 (3.4) $[M]^+$, 95 (11.3), 81.8 (26.0), 67.0 (86.4), 54.0 (46.4), 41.0 (19.4).

Hydrogenation of α-pinene (7) was performed using 2 g of a catalyst at 130°C, hydrogen to alkene molar ratio 2 : 1; reagents feed 0.023 mol/h (alkene) and 0.046 mol/h (hydrogen); conditional reaction duration: 0.087 h kg_{cat}/mol.

Pinane (8). Mass spectrum, m/e (I_{rel}, %): 138 (3) $[M]^+$, 95 (91), 81 (93), 67(100), 55 (58), 41 (34).

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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