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Hydrogenation of Ketones and Esters Catalyzed by Pd/C–SiO$_2$

T. I. Akchurin[a], **N. Z. Baibulatov**[a], **and V. A. Dokichev**[b]*

[a] *Ufa Institute of Chemistry, Russian Academy of Sciences, Ufa, Russia*
[b] *Ufa State Aviation Technical University, ul. K. Marksa 12, Ufa, 450008 Russia*
**e-mail: dokichev@anrb.ru*

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Abstract—Hydrogenation of unsaturated ketones and esters with molecular hydrogen on the 5%Pd/C–SiO$_2$ heterogeneous catalyst has been studied. The reaction direction and yield are determined by the starting compounds structure. Hydrogenation of unsaturated ketones containing phenyl group at the double carbon–carbon atom is accompanied by the reduction of the ketone group into the alcohol one. Hydrogenation of unsaturated esters is accompanied by transesterification.

Keywords: heterogeneous catalysis, carbon-silica carrier, hydrogenation, unsaturated ketones, unsaturated esters

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Hydrogenation of double carbon-carbon bonds in polyfunctional unsaturated compounds is important for synthetic organic chemistry. Heterogeneous palladium catalysts applied on various porous materials (active carbon, alumina, or zeolites) [1] or onto the Al$_2$O$_3$–SiO$_2$ composite [2] are most often used for hydrogenation. The carrier nature significantly affects the activity and selectivity of the catalyst. Hydrogenation of the C=C bond in unsaturated ketones on Pd/C can be accompanied by the reduction of carbonyl group [3] or elimination of a benzyl group in benzyl esters of unsaturated acids or the N-Cbz protective group in unsaturated amines [4].

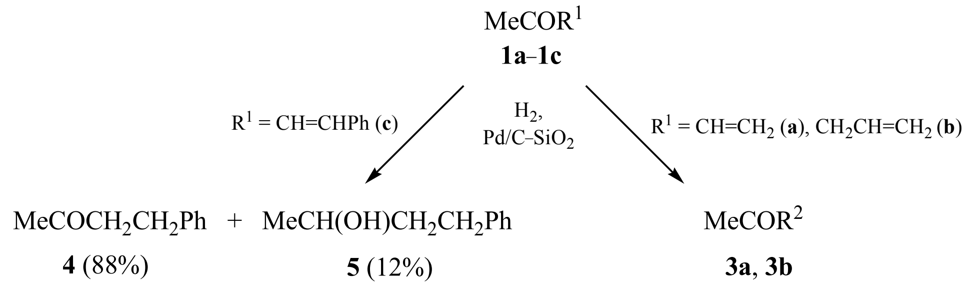
Modification of the Pd/C catalysts with MgBr$_2$ [5], tetramethylurea and quinoline [6], ethylenediamine [7], or dimethylsulfide [8] allows chemoselective hydrogenation preserving the carbonyl group. The catalysts prepared via application of palladium onto carbon nanotubes functionalized with ionic liquid [9], carboxylated carbon nanofibers [10], and ultradisperse diamond [11] are efficient towards selective hydrogenation of unsaturated carbonyl compounds.

Palladium catalyst on carbon-silica carrier (Pd/C–SiO$_2$) efficiently catalyzes hydrogenation of linear and cyclic olefins with molecular hydrogen [12]. We studied the catalytic properties of the Pd/C–SiO$_2$ system and the influence of the carbon-silica carrier on hydrogenation of unsaturated ketones and esters containing the C=C bonds in the alcohol and(or) acid part of the molecule with molecular hydrogen.

Physical and morphological properties of the carrier and the catalyst (statistical adsorption capacity, specific surface area, and the catalyst microstructure) have been reported earlier [12]. The following ketones and esters were used for the study of catalytical properties of Pd/C–SiO$_2$: but-3-en-2-one **1a**, pent-4-en-2-one **1b**, (3*E*)-4-phenylbut-3-en-2-one **1c**, (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one **1d**, methyl esters of acrylic (**2a**), 2-methacrylic (**2b**), (2*E*)-but-2-enoic (**2c**), and (2*E*)-3-phenylacrylic (**2d**) acids, allyl esters of propanoic (**2e**), methacrylic (**2f**), and (2*E*)-3-phenylacrylic (**2g**) acids, ethyl ester of oleic acid **2h**, and dimethyl esters of (2*Z*)-but-2-enoic (**2i**) and (2*E*)-but-2-enoic (**2j**) acids. The reaction was performed at 23°C in ethanol in the presence of 5% Pd/C–SiO$_2$ (molar ratio Pd : unsaturated compound = 1 : 100) using a volumetric device for hydrogenation at normal pressure.

Reduction of pent-4-en-2-one **1b** into methyl propyl ketone **3b** with quantitative yield and of but-3-en-2-one **1a** into methyl ethyl ketone **3a** with 60% yield revealed the higher reactivity of allyl double bond as compared to the vinyl one in the presence of Pd/C–SiO$_2$. Likely, that was caused by the conjugation of the vinyl bond with the carbonyl group. Selectivity of the reactions was up to 100%, and the ketones were not converted into alcohols (Scheme 1).

Scheme 1.



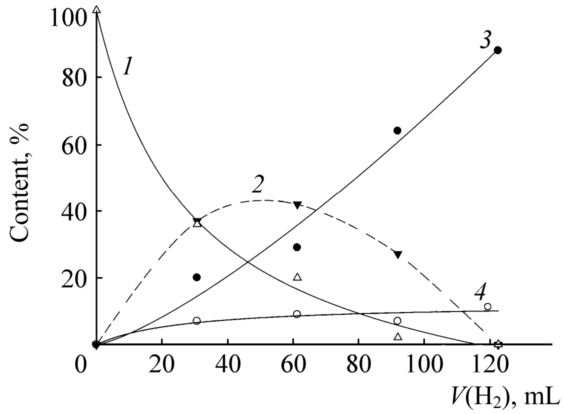
R^2 = Et (**a**, 60%), Pr (**b**, 100%).

Scheme 2.

$$\underset{\mathbf{1d}}{\mathrm{(PhCH{=}CH)_2CO}} \xrightarrow[100\%]{\mathrm{H_2,\ Pd/C{-}SiO_2}} \underset{\mathbf{6}\ (88\%)}{\mathrm{(PhCH_2CH_2)_2CO}} + \underset{\mathbf{7}\ (12\%)}{\mathrm{(PhCH_2CH_2)_2CH(OH)}} + \underset{\mathbf{8}}{\mathrm{[PhCH_2CH_2COCH{=}CHPh]}}$$

Hydrogenation of α,β-disubstituted double bond with phenyl substituent [(3*E*)-4-phenylbut-3-en-2-one **1c** and (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one **1d**] was accompanied by the reduction of the carbonyl group into the alcohol one, to form mixtures of saturated ketones **4**, **6** and alcohols **5**, **7** in quantitative yield and in the 88 : 12 ratio (Schemes 1 and 2).

The study of the composition of the reaction mass during hydrogenation of (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one **1d** as a function of the volume of consumed hydrogen (see the figure) revealed that the hydro-genation at the C=C and C=O occurred simultaneously, and the fraction of 1,5-diphenylpentan-3-ol **7** was independent of the amount of 1,5-diphenylpentan-3-one **6**.



Composition of the reaction products depending on the volume of hydrogen absorbed during hydrogenation of (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one **1d**: (*1*) **1d**, (*2*) (1*E*)-1,5-diphenylpent-1-en-3-one **8**, (*3*) 1,5-diphenylpentan-3-one **6**, and (*4*) 1,5-diphenylpentan-3-ol **7**.

Hydrogenation of esters **2a–j** containing the C=C bonds both in the alcohol and in the acid fragments was practically quantitative in the presence of 5%Pd/C–SiO_2. However, in contrast to the carbon carriers, the use of the C–SiO_2 composite induced the transesterification reaction. Hydrogenation of methyl acrylate **2a** in ethanol gave a mixture of methyl propionate **9a** and the product of its transesterification (ethyl propionate **10a**) in the 24 : 76 ratio. When the reaction was performed in isopropanol, the yield of isopropyl propionate was 25% (Scheme 3).

Scheme 3.

$$\underset{\mathbf{2a{-}2j}}{\mathrm{R^1CO_2R^2}} \xrightarrow[100\%]{\mathrm{H_2,\ Pd/C{-}SiO_2,\ EtOH}} \underset{\mathbf{9a{-}9j}}{\mathrm{R^3CO_2R^4}} + \underset{\mathbf{10a,\ 10c{-}10f,\ 10i,\ 10j}}{\mathrm{R^3CO_2Et}}$$

R^1 = CH=CH$_2$, R^2 = Me (**2a**); R^1 = C(Me)=CH$_2$, R^2 = Me (**2b**); R^1 = CH=CHMe, R^2 = Me (**2c**); R^1 = CH=CHPh, R^2 = Me (**2d**); R^1 = Et, R^2 = CH$_2$CH=CH$_2$ (**2e**); R^1 = C(Me)=CH$_2$, R^2 = CH$_2$CH=CH$_2$ (**2f**); R^1 = CH=CHPh, R^2 = CH$_2$CH=CH$_2$ (**2g**); R^1 = (9*Z*)-(CH$_2$)$_7$CH=CH(CH$_2$)$_7$CH$_3$, R^2 = Et (**2h**); R^1 = (*E*)-CH=CHCO$_2$Me, R^2 = Me (**2i**); R^1 = (*Z*)-CH=CHCO$_2$Me, R^2 = Me (**2j**); R^3 = Et, R^4 = Me (**9a**, 24%); R^3 = *i*-Pr, R^4 = Me (**9b**, 100%); R^3 = Pr, R^4 = Me (**9c**, 71%); R^3 = CH$_2$CH$_2$Ph, R^4 = Me (**9d**, 89%); R^3 = Et, R^4 = Pr (**9e**, 97%); R^3 = *i*-Pr, R^4 = Pr (**9f**, 58%); R^3 = CH$_2$CH$_2$Ph, R^4 = Pr (**9g**, 100%); R^3 = C$_{17}$H$_{35}$, R^4 = Et (**9h**, 96%); R^3 = CH$_2$CH$_2$CO$_2$Me, R^4 = Me (**9i**, 87%); R^3 = CH$_2$CH$_2$CO$_2$, R^4 = Me (**9j**, 98%); R^3 = Et (**10a**, 76%), Pr (**10c**, 29%), CH$_2$CH$_2$Ph (**10d**, 11%), Et (**10e**, 3%), *i*-Pr (**10f**, 42%), CH$_2$CH$_2$CO$_2$Me (**10i**, 13%), CH$_2$CH$_2$CO$_2$Me (**10j**, 2%).

Hydrogenation of other considered unsaturated esters with the C=C bond in the acid and(or) alcohol part of the molecule was performed in ethanol in the presence of 5% Pd/C–SiO_2. The experimental data showed that the composition and yield of the reaction products were determined by the ester structure. For example, for esters **2c** and **2d** it was observed that the introduction of methyl or phenyl substituent at the β-position with respect to the double bond led to the increase in the yield of the products of hydrogenation of methyl esters **9c** (71%) and **9d** (89%) and decrease in the yield of the ethyl esters **10c** and **10d** to 11 and 29%, respectively. In contrast to dimethyl fumarate **2i**, hydrogenation of dimethyl maleate **2j** afforded dimethyl succinate **9j** with practically quantitative yield and high selectivity. High selectivity of the reaction was observed during hydrogenation of methyl methacrylate **2b**, allyl esters of propanoic **2e** and (2*E*)-3-phenylacrylic acid **2g**, and ethyl ester of oleic acid **2h**.

The use of heterogeneous catalyst Pd/C–SiO_2 for hydrogenation of unsaturated esters allows single-stage preparation of methyl esters of saturated acids from ethyl esters of unsaturated acids or vice versa, ethyl esters of saturated acids from methyl esters of unsaturated acids.

In summary, hydrogenation of unsaturated ketones with a phenyl group at the double carbon-carbon bond in the presence of the 5%Pd/C–SiO_2 catalyst is accompanied by reduction of the ketone group into the alcohol one. Hydrogenation of the unsaturated carboxylic esters can be accompanied by transesterification, depending on the ester structure and the solvent.

EXPERIMENTAL

Spectral studies were performed using the equipment of Center for Collective Usage “Chemistry” of Ufa Institute of Chemistry, Russian Academy of Sciences. The reaction products were identified using a MAT 95 XP chromato–mass spectrometer (Thermo Finnigan, Germany) with a TRACE GC 2000 chromatograph, software XCALIBUR with NIST-05 mass spectra library (voltage 70 eV, ionizing chamber temperature 250°C, direct injection temperature 50–250°C, heating rate 15 deg/min, the spectra were recorded over *m*/*z* 14 to 550 Da at scan rate 2.5 scan/s).

Composition and yield of the products were determined by means of GLC using a GC-2014 chromatograph (Shimadzu, Japan); conditions: capillary column 30 m × 0.25 mm × 0.25 μm, (phase HP-1MS), temperature gradient from 50 to 250°C at 12 deg/min.

The reactants with purity of at least 98% were used: $PdCl_2$, but-3-en-2-one and pent-4-en-2-one, (3*E*)-4-phenylbut-3-en-2-one and (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one, methyl acrylate, methyl methacrylate (99%), butyl methacrylate (99%) (all from Aldrich), methyl-(2*E*)-but-2-enoate and methyl-(2*E*)-3-phenyl acrylate, allyl esters of propanoic, methacrylic, and cinnamic acid and dimethyl esters of maleic and fumaric acids with purity 98%, as well as ethyl ester of oleic acid prepared via conventional method from triglyceride of oleic acid [13].

Carbon-silica sorbent (InPTs Pilot, Ufa) was used as the carrier [14].

Catalyst preparation. Catalyst 5%Pd/C–SiO_2 was prepared as described elsewhere [12]. A mixture of 1.0 g $PdCl_2$, 2.4 mL of conc. HCl, and 6 mL of water was refluxed during 1.5 h until formation of transparent solution; 17 mL of water was then added and thoroughly stirred with 11.4 g of the carbon-silica carrier. The obtained mass was evaporated on a water bath and dried in an oven at 100°C. Yield 12.38 g.

Hydrogenation of unsaturated compounds. Volumetric setup for hydrogenation [15] consisted of thermostated glass reactor with a jacket and a gas burette. 10 mL of 95% ethanol, 50 mg of 5%Pd/C–SiO_2 containing 2.5 mg (0.024 mmol) of Pd, 2.34 mmol of ketone or ester were put in a 30 mL reactor. The reaction was performed with stirring at atmospheric pressure and 23±1°C. The volume of consumed hydrogen was measured at constant pressure by matching the levels of a liquid in the burette and in the equilibrating vessel. After the hydrogenation was complete (the volume of consumed hydrogen became constant), 0.20 g (2.34 mmol) of ethyl acetate was added to the mixture, and the catalyst was filtered off. The composition and yield of the products were determined by GLC. Physico-chemical properties of the prepared compounds coincided with the reference data [16–18].

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