

CATALYTIC HYDROGENATION OF ACETOPHENONE OVER RUTHENIUM CATALYSTS

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Catalytic hydrogenation of acetophenone in ethanol was studied by using 5 wt.% Ru supported on active carbon, alumina, and titania. Parameters of kinetic equations (reaction rate constants and adsorption coefficients) were evaluated and the influence of the support on the reaction course was discussed. An enhanced selectivity of Ru/TiO₂ towards carbonyl group hydrogenation with respect to the hydrogenation of the aromatic ring was confirmed.

Key words: Ruthenium catalysts; TiO₂ supported catalysts; Hydrogenation of acetophenone.

Ruthenium catalysts are attractive due to their high activity in hydrogenation of aromatic compounds. Some of them, specifically modified, exhibit outstanding selectivity for formation of cycloalkenes¹⁻⁵. Ruthenium supported on TiO₂ is especially suitable for selective hydrogenation of a carbonyl group in the presence of an aromatic system or a double bond⁶⁻¹¹. In the present work, the course of acetophenone hydrogenation over Ru catalysts prepared in our laboratory was compared with that over commercial catalysts.

EXPERIMENTAL

Chemicals

Ethanol (Kolin Distillery, Czech Republic) of analytical grade (azeotropic 4 vol.% H₂O) was used as a solvent. Acetophenone (Aroma Decin, Czech Republic) was used as a substrate. Hydrogen (grade 3.0) was supplied by Linde-Technoplyn Prague, Czech Republic. The substrate was purified by distillation before use and was chromatographically pure. The commercial hydrogenation catalysts were from Engelhard Co.: 5% Ru/C No. 1797 type Escat 40 ($S_{\text{BET}} = 850 \text{ m}^2/\text{g}$) and 5% Ru/Al₂O₃ No. LA 9359 Escat 44 ($S_{\text{BET}} = 125 \text{ m}^2/\text{g}$). Titania supported catalysts were prepared as described below. Ruthenium(III) chloride (Fluka AG, Germany) was utilized as the active component precursor, and the supports were titanium(IV) oxide No. 7702 (anatase, $S_{\text{BET}} = 40 \text{ m}^2/\text{g}$) and No. 7701 (rutile, $S_{\text{BET}} = 21 \text{ m}^2/\text{g}$), both from Degussa (Germany).

Catalysts Prepared and Kinetic Measurements

The 5 wt.% Ru/TiO₂ catalysts were prepared by impregnation of the titania supports with an ethanol solution of RuCl₃ having the appropriate metal concentration. Then, the solvent was slowly distilled off during intensive mixing of the mixture until a thick slurry was formed. The paste was dried in a nitrogen atmosphere in a furnace at 373 K. After 1 h drying, nitrogen was replaced by hydrogen, and the precursor was partly reduced for two hours. The final reduction was performed in hydrogen in a furnace heated up to 673 K for 12.5 h.

All the catalysts were fully activated in a furnace in a hydrogen atmosphere before their use at 363 K for 3.5 h, or at 453 K in the case of the carbon-supported catalyst. After activation, the catalysts were covered by ethanol, avoiding a contact with air, and transferred into the reactor where the final activation step took place (10 min, H₂).

Kinetic measurements were carried out in a semi-batch, stirred, isothermal reactor connected to gasometric burettes. All the experiments were performed at atmospheric pressure and 303 K. Typically, experimental batch was 15 ml of ethanol, 0.2 ml of a substrate, and the catalyst weight ranged from 0.3 to 1.0 g. The measurements were carried out in a kinetic regime excluding mass transfer effects. Samples, withdrawn at suitable time intervals, were analyzed chromatographically. A detailed description of a typical experiment was published elsewhere¹².

Time dependences of the concentrations of the reaction mixture components were treated by the least square fitting with random search and gradient optimization (Random Walk method terminated by the Gauss–Newton method).

Analytical Method

A gas chromatograph Hewlett–Packard, 5890 Series II Plus, equipped with FID and a capillary column HP-20 M (25 m × 0.2 mm × 0.35 μm) was used to analyse the samples. The analyses were carried out with a temperature program (373 K to 463 K) and a split ratio 1 : 25.

RESULTS AND DISCUSSION

Acetophenone hydrogenation¹³ can proceed through two reaction pathways (Fig. 1). Besides the compounds given in the scheme, also benzene, cyclohexene, cyclohexane, and ethylbenzene were found in the reaction mixture. Because only small amounts of

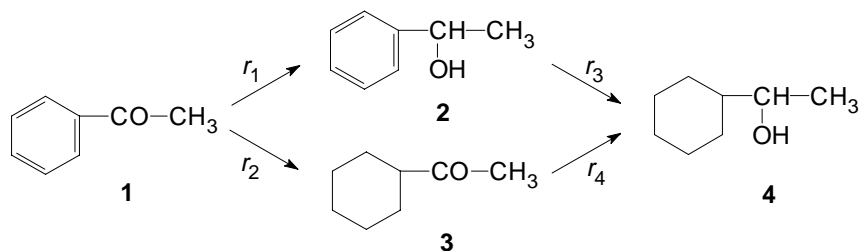


FIG. 1

The reaction scheme of acetophenone hydrogenation. **1** Acetophenone, **2** 1-phenylethanol, **3** methyl cyclohexyl ketone, **4** 1-cyclohexylethanol

these side products were detected, their formation was not included into the reaction scheme (Fig. 2).

The experimental data were described by using the simplified form of Langmuir-Hinshelwood equations¹⁴:

$$V dc_A/W dt = (-k_1 K_A c_A - k_2 K_A c_A - k_5 K_A c_A)/\phi$$

$$V dc_B/W dt = (k_1 K_A c_A - k_3 K_B c_B)/\phi$$

$$V dc_C/W dt = (k_2 K_A c_A - k_4 K_C c_C)/\phi$$

$$V dc_D/W dt = (k_3 K_B c_B + k_4 K_C c_C)/\phi$$

$$V dc_E/W dt = (k_5 K_A c_A)/\phi$$

$$\phi = K_A c_A + K_B c_B + K_C c_C + K_D c_D + K_E c_E ,$$

with initial conditions $t = 0$, $c_A = c_{A0} = 1.0$, $c_{B0} = c_{C0} = c_{D0} = c_{E0} = 0$. Symbols c_X and K_X denote concentration and adsorption coefficient of individual reaction mixture components, respectively, k denotes a rate constant, t refers to time, V denotes a reaction volume, and W denotes weight of a catalyst. The real initial concentration of acetophenone was $c'_{A0} = 0.1140$ mol/l. A typical course of the acetophenone hydrogenation is given in Fig. 3.

The kinetic data obtained are collected in Tables I and II. The confidential interval of the evaluated parameters is somewhat limited with respect to the big standard deviation and a large number of kinetic parameters in the proposed mathematical model. For adsorption coefficients, only the relative values are significant because arbitrarily multiplied absolute values of the adsorption coefficients also fit the proposed mathematical model¹⁴. During the course of the reactions, the activity of the catalysts usually

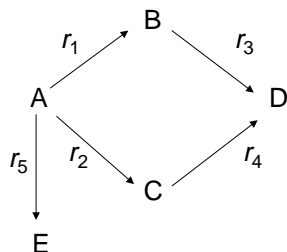


FIG. 2

The generic scheme of parallel-consecutive reactions. A Acetophenone, B 1-phenylethanol, C methyl cyclohexyl ketone, D 1-cyclohexylethanol, E minor substances, r_1 to r_5 particular reaction rates

decreased. Since the rate of the catalyst deactivation was not incorporated into the kinetic model, the activity decrease was reflected in high values of the adsorption coefficients of the hydrogenation products (predominantly of 1-cyclohexylethanol).

TABLE I
Acetophenone hydrogenation (k 's in mmol/g_{cat} min)

Catalyst	Rate constants				
	k_1	k_2	k_3	k_4	k_5
Ru/TiO ₂ (rutile)	150.0	19.8	13.5	110.3	43.4
Ru/TiO ₂ (anatase)	49.2	14.6	77.7	301.8	60.2
Ru/Al ₂ O ₃	65.5	28.7	61.7	105.3	11.0
Ru/C	102.2	10.4	28.2	59.1	10.8

TABLE II
Adsorption coefficients K , selectivities S and maximum concentrations c_{\max} in acetophenone hydrogenation

Catalyst	K_A	K_B	K_C	$S_R(B)$	$S_R(C)$	$c_{\max}(B)$	c_{\max}
Ru/TiO ₂ (rutile)	96.1	42.4	117.1	0.665	0.057	0.62	0.05
Ru/TiO ₂ (anatase)	281.1	68.4	176.6	0.326	0.056	0.21	0.05
Ru/Al ₂ O ₃	597.7	186.2	35.4	0.254	0.207	0.49	0.23
Ru/C	146.4	78.2	37.5	0.389	0.027	0.69	0.09

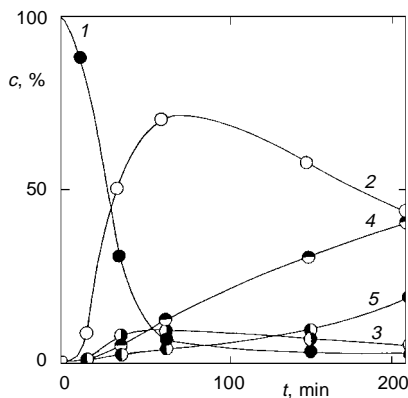


FIG. 3
Time course of acetophenone hydrogenation over Ru/C catalyst. c Concentration (%), t time (min). 1 Acetophenone, 2 1-phenylethanol, 3 methyl cyclohexyl ketone, 4 1-cyclohexylethanol, 5 minor substances

Selectivity to each intermediate (S_R) was determined at 99.9% conversion of the substrate. Its value means the ratio of an immediate intermediate concentration and a total concentration of all the compounds in the reaction mixture (Table II).

It follows (Table II) that the maximum concentration of 1-phenylethanol in experiments with the catalysts supported on TiO_2 and on the active carbon is substantially higher than that of methyl cyclohexyl ketone. When using $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst, the concentrations of both compounds are essentially of the same magnitude. The reasons for the different effects of the catalysts are not the same. The values of the rate constants for 1-phenylethanol formation were higher than that for methyl cyclohexyl ketone in all cases. The lower rates of formation of 1-cyclohexylethanol from 1-phenylethanol than from methyl cyclohexyl ketone were observed. Table II demonstrates that the surface sorption of methyl cyclohexyl ketone on TiO_2 is more favourable than the sorption of 1-cyclohexylethanol. On the contrary, the catalysts supported on Al_2O_3 and on the active carbon demonstrate opposite adsorption preferences. The high adsorptivity of a carbonyl group on Ru/TiO_2 catalysts is in agreement with already published data⁶⁻¹¹ where the catalysts showed higher selectivity for a carbonyl group hydrogenation in the presence of carbon double bond. The explanation might be sought in terms of a possible activation effect of the carbon double bond by Ti^{3+} cations. These ions are present in the TiO_2 support depending on the catalyst preparation^{6,11,13}.

The high adsorptivity of methyl cyclohexyl ketone was most likely the reason of the lower selectivity of the Ru/TiO_2 type catalysts in the hydrogenation of acetophenone to methyl cyclohexyl ketone. On $\text{Ru}/\text{Al}_2\text{O}_3$ and Ru/C catalysts, the adsorption of 1-phenylethanol was, conversely, much stronger. The fact that the selectivity to methyl cyclohexyl ketone on Ru/C was close to that determined on Ru/TiO_2 might be explained by combinations of k_1/k_2 , k_3/k_4 , and K_B/K_C ratios. In this case, their values had the same effect on the selectivity. On the other hand, the lower values of k_1/k_2 and the higher values of k_3/k_4 and K_B/K_C for the $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst resulted in the selectivity to methyl cyclohexyl ketone comparable to that to 1-phenylethanol.

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SYMBOLS

c_{A0}	initial concentration of acetophenone, mol/l
c_X	concentration of an intermediate X, mol/l
$c_{\max}(X)$	dimensionless concentration = (instantaneous concentration of a compound X / initial concentration of acetophenone)
K_X	adsorption coefficient of compound X
k_n	reaction rate constant, mmol/g _{cat} min
S_{BET}	specific surface area of catalyst determined by BET method, m ² /g
S_R	reaction selectivity
t	time, min

V	volume of reaction mixture, ml
W	catalyst weight, g
ϕ	surface coverage

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