HYDROGENATION AND HYDROGENOLYSIS OF ACETOPHENONE

Martina BEJBLOVÁ[a1], Petr ZÁMOSTNÝ[a2], Libor ČERVENÝ[a3,*] and Jiří ČEJKA[b]

[a] *Department of Organic Technology, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic; e-mail:* [1] *martina.bejblova@vscht.cz,* [2] *petr.zamostny@vscht.cz,* [3] *libor.cerveny@vscht.cz*
[b] *J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic; e-mail: jiri.cejka@jh-inst.cas.cz*

Catalytic hydrogenation and hydrogenolysis of acetophenone was investigated on supported palladium catalysts in liquid phase at temperatures 30–130 °C and pressures 1–10 MPa. A number of supports like active carbon, alumina and zeolites Beta and ZSM-5 were employed. The effects of solvent and support on the reaction mechanism of acetophenone transformation were studied. Catalysts with acid zeolite support showed a very high activity in transformation of acetophenone to ethylbenzene. Based on a kinetic model, the reaction rates of acetophenone transformation to ethylbenzene on Pd/C and Pd/Al$_2$O$_3$ catalysts were discussed. The kinetic model confirmed that the transformation of acetophenone to ethylbenzene proceeds primarily *via* a hydrogenation-dehydration mechanism and the effect of the direct hydrogenolysis of the C=O bond of acetophenone is insignificant.

Keywords: Hydrogenation; Hydrogenolysis; Carbonyl compounds; Acetophenone; Ketones; Reductions; Zeolites; Palladium; Active carbon; Heterogeneous catalysis; Solid support.

In a number of chemical reactions, carbonyl compounds are commonly reduced to corresponding alcohols; nevertheless, in some cases, it is desirable to transform the carbonyl group to methylene. The Clemmensen[1,2] and Wolff–Kizhner reduction[3,4] are the first procedures applied to the reduction of carbonyl compounds to corresponding hydrocarbons. Subsequently, a number of agents were utilized for these reductions, such as triisopropyl phosphite[5], lithium aluminium hydride[6,7] and sodium borohydride[8,9]. At present, heterogeneous catalytic hydrogenation and hydrogenolysis are the most commonly utilized procedures to perform these reactions.

The conversion of a carbonyl compounds to corresponding hydrocarbons in a hydrogenation environment can proceed by several mechanisms. The starting carbonyl compound can be first hydrogenated to alcohol, which is dehydrated in the following step to form the C=C bond, the latter being hydrogenated in the final step to the desired hydrocarbon. This mecha-

nism[10–14] operates *e.g.* on bifunctional catalysts with acid support (frequently zeolites) and a metal component. The metal hydrogenation component of the bifunctional catalyst initiates the hydrogenation steps (C=O → C–OH and C=C → C–C) while the acid component is responsible for dehydration of the alcohol produced. Hydrogenolysis, the second possible mechanism for the conversion of C=O group to CH_2 group, involves a direct splitting of the oxygen–carbon bond by hydrogen. Therefore, the carbonyl compound can be first hydrogenated to a corresponding alcohol, followed[15–18] by a hydrogenolytic splitting of the C–OH bond giving the desired hydrocarbon, or a direct hydrogenolysis of the C=O bond of the starting carbonyl compound takes place.

Palladium supported on active carbon[20–27], zeolites[11,12,16] or silica[28] is the most frequently employed catalyst for the conversion of carbonyl compounds to corresponding hydrocarbons. The conversion of a carbonyl group to methylene is facilitated by introduction of a small amount of an acid to the reaction mixture (hydrochloric and sulfuric acid[20–22,29] or more often acetic acid[15,23,24,30]).

Reduction of carbonyl compounds to hydrocarbons takes place also by using other hydrogenation catalysts based on *e.g.* copper(II)-chromium(III)[31], iron[32], nickel[33] or sulfides[34–36] and W, Mo, CoMo, NiMo. However, these catalysts are substantially less active for the conversion of C=O to CH_2 and hence require higher temperatures (200–300 °C) and pressures (up to 15 MPa).

The objective of this work is to describe the reaction mechanism of hydrogenation and hydrogenolysis of acetophenone on palladium catalysts. The effects of support and solvent on the kinetics of the system of these reactions were monitored. A detailed analysis of kinetic data made possible to describe the mechanism of oxygen removal from the molecule of acetophenone under the conditions of hydrogenation.

EXPERIMENTAL

Catalysts

Supported catalysts with 5 wt.% of palladium were used for hydrogenation of acetophenone. Zeolites ZSM-5 and Beta with different Si/Al ratios ranging from 12.5 to 140 were used as supports. The Pd/zeolite catalysts were prepared by impregnation of zeolites with a water solution of $PdCl_2$. A suspension of a zeolite (2.5 g) in 40% solution of $PdCl_2$ in HCl (0.6 ml) and distilled water (100 ml) was stirred for 9 h, followed by evaporation using a vacuum rotary evaporator, drying at 120 °C in a nitrogen atmosphere (2 h) and calcination at 400 °C (12–25 h) in a stream of nitrogen.

For comparison, a commercial 5% Pd/C catalyst from Doduco GmbH with dry matter content of 41.9% and 5% Pd/Al$_2$O$_3$ prepared at the Department of Organic Technology, were used[37]. No special activation was carried out prior to their use.

Apparatus and Kinetic Measurements

Catalytic tests were carried out in liquid phase in a 300 ml autoclave (Parr 4842) with a magnetic stirrer. An amount of 4.5 g of acetophenone (99%; Aldrich, U.S.A.), 10–80 mg of a catalyst, 150 ml of methanol p.a. or hexane p.a. (both Pliva–Lachema, Czech Republic) used as the solvent were charged to the autoclave. Then, the autoclave was heated to the reaction temperature (30–130 °C), followed by pressurizing with hydrogen (1–10 MPa) and stirring was started.

Analytical Methods

Analysis of the reaction products was carried out on a gas chromatograph (GC 17A Shimadzu) with the capillary column J&W Scientific (length 60 m, i.d. 0.32 mm, phase thickness 0.25 μm). The reaction intermediates were analyzed using GC-MS (Varian Saturn 2000).

RESULTS AND DISCUSSION

Figure 1 shows a typical time-on-stream dependence (T-O-S) of acetophenone conversions on Pd/C catalyst.

Using GC-MS, the following intermediates of acetophenone (**1**) transformation to ethylbenzene (**4**) were determined, namely 1-phenylethan-1-ol (**2**) and styrene (**3**). Based on the literature data and the results of our kinetic experiments, the following reaction scheme of the acetophenone
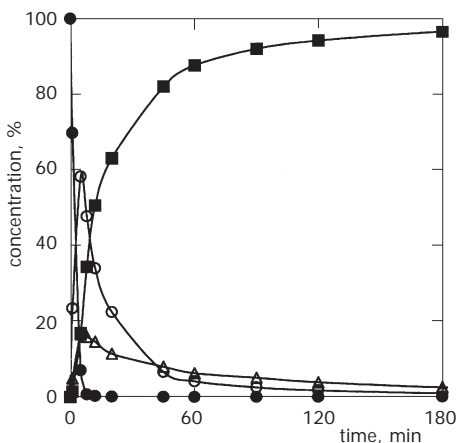

Fɪɢ. 1

Acetophenone hydrogenation on Pd/C catalyst in methanol (130 °C, 6 MPa): ● acetophenone, ■ ethylbenzene, ○ 1-phenylethan-1-ol, △ styrene)

transformation to ethylbenzene including possible hydrogenation, dehydration and hydrogenolysis steps can be proposed:

Ethylbenzene can be produced from acetophenone by a series reactions, in which acetophenone is first hydrogenated to 1-phenylethan-1-ol ($1 \rightarrow 2$), then consecutively dehydrated to styrene ($2 \rightarrow 3$), the double bond of which is finally hydrogenated to give ethylbenzene ($3 \rightarrow 4$).

Hydrogenolysis may also take part in the transformation of acetophenone to ethylbenzene, including a splitting of the C=O bond of acetophenone ($1 \rightarrow 4$) or the C–OH bond of 1-phenylethan-1-ol with hydrogen ($2 \rightarrow 4$).

To verify the proposed reaction mechanism, the kinetic data of acetophenone transformation to ethylbenzene on the Pd/C and Pd/Al_2O_3 catalysts were processed by regression analysis[38] using the program ERA 3.0. For the zeolite-based catalysts, the analysis of kinetic data will be published elsewhere[39]. Two alternative mathematical models formally corresponding to Scheme 1 were proposed to describe the kinetics of the Langmuir–Hinshelwood model and the model of non-stationary kinetics.

The Langmuir–Hinshelwood model was based on a common assumption[40] that the rate of a catalyzed reaction is controlled by the surface reaction as the rate-determining step and the reaction rate was described in the model by the following Eq. (*1*):

$$ r_i = \frac{k_i K_A c_A}{1 + K_1 c_1 + K_2 c_2 + K_3 c_3 + K_4 c_4} , \qquad (1) $$
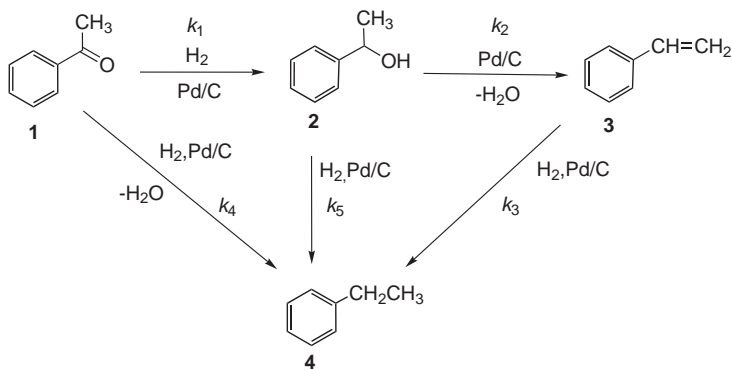
SCHEME 1
Reaction scheme of acetophenone transformation to ethylbenzene

where r_i is the rate of the i-th reaction according to Scheme 1, k_i its rate constant, K the formal adsorption coefficient and c the concentration of compounds **1–4** in the reaction mixture. Subscript A refers to a substance, which is a reactant in the i-th reaction.

The model of non-stationary kinetics has not used any assumption of the existence of the rate-determining step. All elementary steps in the systems of catalyzed reactions were described by kinetic equations of the following form:

$$\text{adsorption} \qquad r_{j,\text{ads}} = k_{j,\text{ads}} c_j c_{\text{L}} \,, \tag{2}$$

$$\text{surface reaction} \quad r_i = k_i c_{j\text{L}} \,, \tag{3}$$

$$\text{desorption} \qquad r_{j,\text{des}} = k_{j,\text{des}} c_{j\text{L}} \,, \tag{4}$$

where r_i and k_i are the rate and the rate constant of the i-th surface reaction, $r_{j,\text{ads}}$ and $k_{j,\text{ads}}$ the rate and the rate constant of adsorption of j-th reaction component and $r_{j,\text{des}}$ and $k_{j,\text{des}}$ the rate and the rate constant of its desorption. The symbol c_j refers to a concentration of a j substance in the reaction mixture, $c_{j\text{L}}$ the concentration of a j substance adsorbed on the catalyst surface relative to the volume of the reaction mixture and c_{L} the concentration of free active sites on the catalyst surface. All concentrations are defined as dimensionless quantities by Eq. (5).

$$c_j = \frac{c_j \,[\text{mol m}^{-3}]}{\left(\sum_j c_j \,[\text{mol m}^{-3}] \right)_{\hat{o}=0}} \tag{5}$$

The results of the regression analysis clearly show that the model of non-stationary kinetics made possible to satisfactorily describe the measured data, while the Langmuir–Hinshelwood model failed under certain reaction conditions (Fig. 2). The limited applicability of the Langmuir– Hinshelwood model can be explained by the erroneous assumption on the rate-determining reaction step[41]. For this reason, we have used the non-stationary kinetic model for further evaluation of the kinetic data.

Since mathematic modeling was also used to compare the reaction course in various solvents and in dependence on a catalyst support, an assumption was introduced into the model, postulating that an alteration of a solvent

itself affects only the rate constants of the sorption processes and does not significantly influence the value of the rate constant of the surface reaction. This assumption made it possible to assess all the experimental data in various solvents together, without any occurrence of an intolerable increase in the number of kinetic parameters. Figure 3 shows a comparison of the measured data and the data calculated from the model for optimal values of parameters.
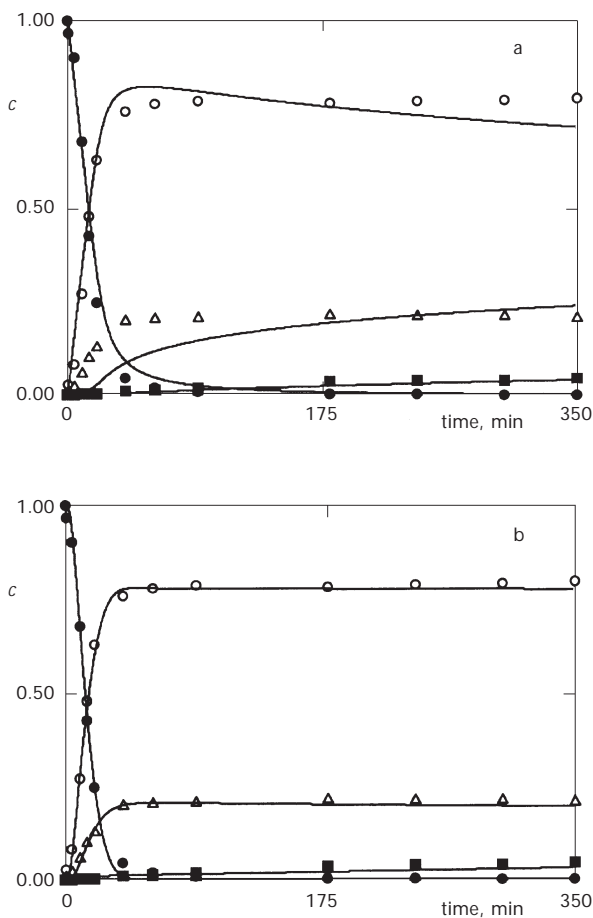

FIG. 2

Comparison of the measured and calculated data of acetophenone hydrogenation catalyzed by Pd/Al$_2$O$_3$ in methanol (130 °C, 6 MPa) using the Langmuir–Hinshelwood model (a) and the non-stationary kinetics model (b): ● acetophenone, ■ ethylbenzene, ○ 1-phenylethan-1-ol, △ styrene

Table I shows the estimated parameters and their reliability given by the range of confidence limits[42]. The test of statistical significance for the estimated values was performed at a reliability level of 95%. The statistically insignificant parameters were excluded from the model. Based on the values of the rate constants of the surface reactions (parameters k_1–k_5), it could be concluded that the transformation of acetophenone to ethylbenzene proceeds primarily through a system of hydrogenation-dehydration reactions with the following intermediates: 1-phenylethan-1-ol (**2**) and styrene (**3**) (reaction pathway: **1** → **2** → **3** → **4**). A minor effect of a direct hydrogenolytic splitting of acetophenone to ethylbenzene (reaction **1** → **4**) takes also part on catalysts with active carbon as a support. A similar splitting of 1-phenylethan-1-ol (**2** → **4**) is negligible. A relatively low reliability of the rate constant k_1 (a broad interval of the confidence limits) is caused
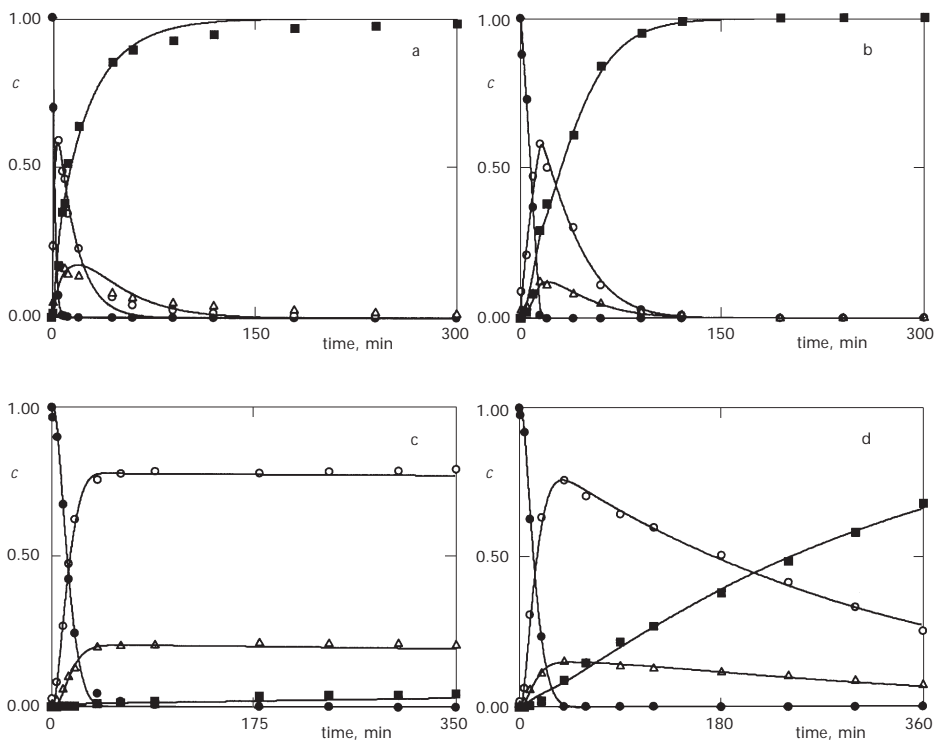

FIG. 3
Comparison of the measured and calculated data for Pd/C catalyst (a, b) and Pd/Al$_2$O$_3$ catalyst (c, d) in methanol (a, c) and hexane (b, d) (130 °C, 6 MPa): ● acetophenone, ■ ethylbenzene, ○ 1-phenylethan-1-ol, △ styrene

by the rapid conversion of acetophenone in the reaction mixture. The value of this rate constant is particularly projected in the solution of the model only if the concentration of acetophenone differs from zero and thus only several points at the beginning of each measurement are effective for the estimation of the value of this constant. Therefore, the reliability of estimation of the rate constants k_2 and k_3 is much higher.

The different rates of acetophenone concentration decrease in various solvents and on different catalysts are mainly caused by different rates of acetophenone sorption on the catalysts. In all cases, the rate of surface reaction was almost identical and always much higher compared to the rate of adsorption. The rates of consecutive reactions differed for various catalysts, which was apparently caused by the type and acidity of the support used. Using the Pd/C catalyst, the rate constants of dehydration of 1-phenyl-ethan-1-ol and hydrogenation of styrene were substantially higher than those over the Pd/Al$_2$O$_3$ catalyst.

TABLE I
Optimum values of kinetic parameters and their 95% confidence limits (in parentheses) estimated by regression analysis for Pd/C and Pd/Al$_2$O$_3$ catalysts in methanol and hexane at 130 °C and 6 Mpa, (≈0 indicates statistically insignificant parameters)

Rate constants	Pd/C, methanol	Pd/C, hexane	Pd/Al$_2$O$_3$, methanol	Pd/Al$_2$O$_3$, hexane
k_1	8.3 (6.7–300)	8.3 (6.7–300)	8.3 (1.7–32)	8.3 (1.7–32)
k_2	0.56 (0.52–0.76)	0.56 (0.52–0.76)	0.029 (0.028–0.030)	0.029 (0.028–0.030)
k_3	0.9 (0.7–1.4)	0.9 (0.7–1.4)	0.08 (0.07–0.09)	0.08 (0.07–0.09)
k_4	1.0 (0.03–4.8)	1.0 (0.03–4.8)	≈0	≈0
k_5	≈0	≈0	≈0	≈0
$k_{1,ads}$	1.8 (1.1–2.4)	0.27 (0.22–0.33)	0.25 (0.22–0.31)	0.30 (0.26–0.41)
$k_{2,ads}$	0.5 (0.3–6.4)	0.5 (0.2–7.1)	≈0	0.04 (0.03–0.05)
$k_{3,ads}$	0.3 (0.1–3.7)	≈0	≈0	0.5 (0.2–110)
$k_{4,ads}$	≈0	≈0	≈0	≈0
$k_{1,des}$	≈0	≈0	≈0	≈0
$k_{2,des}$	1.7 (1.1–3.7)	3.4 (1.6–48)	0.12 (0.10–0.13)	0.11 (0.08–0.13)
$k_{3,des}$	1.0 (0.3–7.5)	≈0	2.7 (0.5–972)	0.8 (0.2–170)
$k_{4,des}$	$\gg k_3$	$\gg k_3$	$\gg k_3$	$\gg k_3$

Table I shows that certain estimations of the sorption-desorption processes are less reliable, which is caused by a strong correlation between individual parameters. The insignificance of the rate constants of some of the sorption processes can be interpreted by assuming that a certain sorption process is much slower than the competitive surface reaction or the reverse sorption process. The value of the rate constant of ethylbenzene desorption ($k_{4,des}$) was such high compared to the rate constants of its production that an additional assumption was introduced in the model assuming that the produced ethylbenzene is, immediately after its production by the surface reaction, quantitatively desorbed from the catalyst surface.

Support Effect

The role of various supported catalysts with 5 wt.% of palladium in the reaction mechanism was investigated. Figure 4 depicts the T-O-S dependence of acetophenone conversion to ethylbenzene over individual catalysts. Figure 4 infers that acetophenone transformation to ethylbenzene in methanol easily proceeds on catalysts supported on active carbon and zeolites, whereas using alumina, acetophenone is hydrogenated only to 1-phenylethan-1-ol (Fig. 4b), not undergoing further transformation.

The Pd/zeolite catalysts are the most active in the acetophenone transformation to ethylbenzene. Acid properties of zeolites apparently procure water elimination from 1-phenylethan-1-ol as well as the consecutive formation of styrene. Török et al.[10] described the same reaction mechanism employing Pt/K-10 montmorillonite as the catalyst for a broad range of conversions of various ketones to corresponding hydrocarbons.

Nevertheless, styrene as a reaction intermediate was described even when an inert support like active carbon was used (Fig. 4a). In these systems, acid properties of the catalyst are due probably to palladium-activated hydrogen as it was described by, e.g., Červený[43,44].

As it is apparent from the presented data, a significantly low concentration of styrene is produced over the Pd/zeolite catalyst. Therefore, it can be assumed that hydrogenolysis, i.e. the direct splitting of the C=O bond of acetophenone or the C–OH bond of 1-phenylethan-1-ol by hydrogen, is significant in these transformations of acetophenone to ethylbenzene.

During hydrogenation of acetophenone catalyzed by palladium on zeolite support, another intermediate – methyl (1-phenylethyl) ether (**5**) (□ in Fig. 4c) – was found. Its formation is assumed to proceed, owing to the acid properties of a zeolite, via intermolecular dehydration of 1-phenylethan-1-ol with methanol.
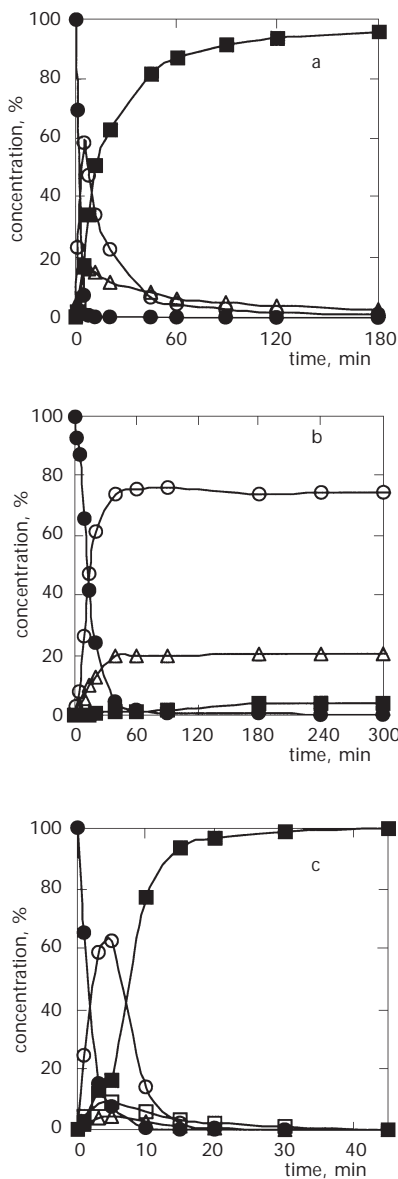
FIG. 4
The course of hydrogenation and hydrogenolysis of acetophenone on Pd/C (a), Pd/Al$_2$O$_3$ (b) and Pd/Beta (c) catalysts (50 mg) with various supports in methanol (130 °C, 6 MPa): ● acetophenone, ■ ethylbenzene, ○ 1-phenylethanol, △ styrene, □ methyl (1-phenylethyl) ether

Effect of Support Acidity

The extent of acidity of zeolite supports affects the initial rate of acetophenone conversion ($k_1 + k_4$). The effect of acidity of zeolites on the rate of acetophenone transformation is apparent from comparison of the initial rates of reactions catalyzed by palladium on zeolites Beta and ZSM-5 employed as supports (Table II). Four types of zeolite Beta, differing in their Si/Al ratio, *i.e.* in the concentration of their acid sites, and two types of ZSM-5 zeolite having also different Si/Al ratios were utilized as a support for hydrogenation catalysts. The initial rates of acetophenone transformation are significantly influenced by the support acidity; with decreasing Si/Al ratio, the initial reaction rates increase. On the other side, it is necessary to emphasize that the channel diameter of the zeolite used obviously does not play a key role in the reaction rate. For both zeolite ZSM-5 (with channel size of 0.53×0.55 nm) and zeolite Beta (large-pore zeolite, 0.76×0.64 nm)[45], the initial rates of acetophenone transformation are similar and seemingly more dependent on the concentration of aluminum than on the channel size of the particular zeolite.

Solvent Effect

The course of acetophenone hydrogenation can be also affected by solvent[23]. Therefore, the effect of solvent (polar methanol and non-polar hexane) on the initial rate of acetophenone transformation, r_0, was investi-

TABLE II
Effect of support acidity on the initial reaction rates of acetophenone conversion in methanol (130 °C, 6 MPa, 15 mg of catalyst)

Catalyst	Si/Al of the zeolite support	r_0, mmol min^{-1} g$_{cat}^{-1}$ [a]
Pd/Beta (1)	70	40.7
Pd/Beta (2)	35	55.6
Pd/Beta (3)	13.5	66.0
Pd/Beta (4)	12.5	220.9
Pd/ZSM-5 (1)	140	38.3
Pd/ZSM-5 (2)	15	102.2

[a] r_0 is the sum of the rate of acetophenone hydrogenation to 1-phenylethan-1-ol and that of hydrogenolysis of acetophenone to ethylbenzene.

gated (Fig. 5) as well as on the selectivity of 1-phenylethan-1-ol production (Fig. 6). In all cases, the selectivity was determined at 50% conversion of the reactant and defined as follows:

$$S_{50} = [\text{conc. } \mathbf{2} \text{ (\%)}/\text{conc. } \mathbf{2} \text{ (\%)} + \text{conc. } \mathbf{3} \text{ (\%)} + \text{conc. } \mathbf{4} \text{ (\%)} + \text{conc. } \mathbf{5} \text{ (\%)}] \times 100,$$

where S_{50} is the selectivity at 50% conversion of acetophenone (**1**), 1-phenylethan-1-ol (**2**), styrene (**3**), ethylbenzene (**4**), methyl (1-phenylethyl) ether (**5**).
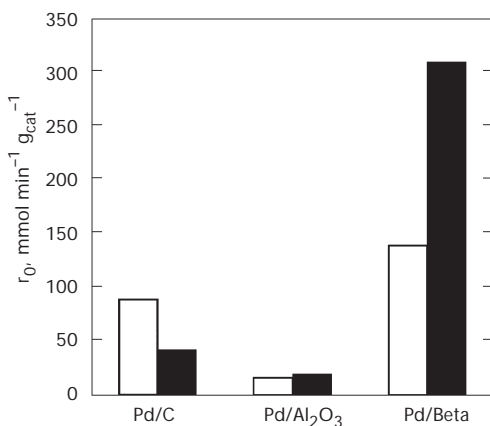

FIG. 5
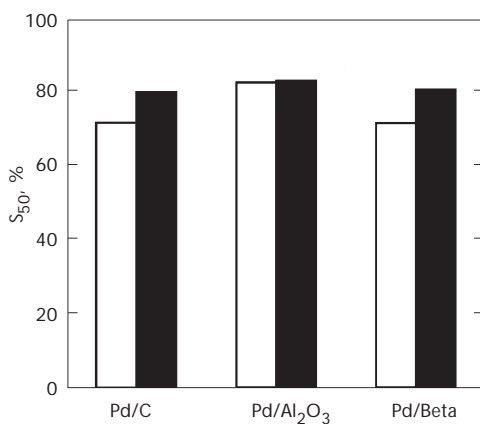Effect of the solvent (□ methanol, ■ hexane) on the initial reaction rate of acetophenone

FIG. 6
Effect of the solvent (□ methanol, ■ hexane) on the selectivity to 1-phenylethan-1-ol at 50% acetophenone conversion

As Fig. 5 shows, the effect of solvent on the initial reaction rate is not straightforward. Using the Pd/C catalyst, the initial rate in methanol was twice as high as in hexane. In contrast, for Pd/Al_2O_3 the initial rates did not significantly differ and using Pd/zeolite catalysts (*e.g.* zeolite Beta (2)), the rate was significantly higher in hexane. The presented results imply that the acidity of different supports obviously affects the initial rate of aceto-phenone decomposition in dependence on the type of the solvent used. With acid forms of zeolites, competitive adsorption of polar methanol to-
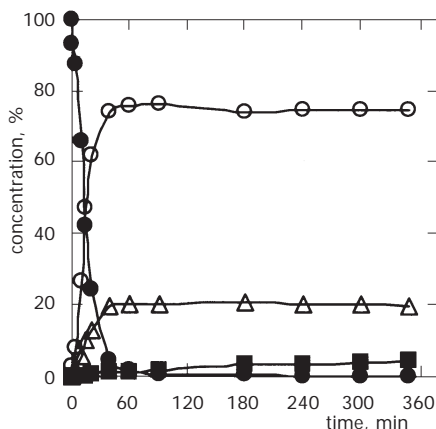

FIG. 7
Hydrogenation of acetophenone on Pd/Al_2O_3 in methanol: ● acetophenone, ■ ethylbenzene, ○ 1-phenylethan-1-ol, △ styrene
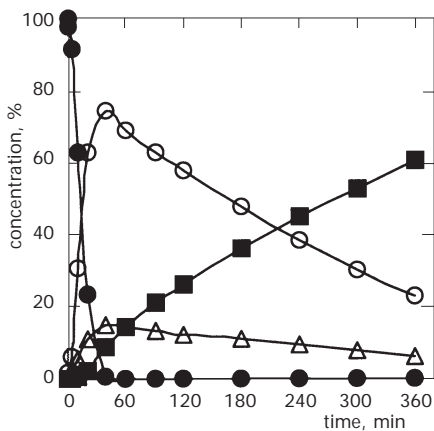

FIG. 8
Hydrogenation of acetophenone on Pd/Al_2O_3 in hexane: ● acetophenone, ■ ethylbenzene, ○ 1-phenylethan-1-ol, △ styrene

gether with acetophenone appears, whereas using hexane, acetophenone adsorption is preferentially adsorbed.

The selectivity to 1-phenylethan-1-ol at 50% acetophenone conversion was slightly higher in hexane with all types of the catalysts.

The most apparent effect of solvent was observed with 5 wt.% Pd/Al_2O_3. In methanol, the final product of acetophenone hydrogenation led to 1-phenylethan-1-ol (selectivity *ca* 75%), whereas after 6 h, the reaction mixture contained only 4% of ethylbenzene and the rest was styrene (Fig. 7), which was not further hydrogenated under the reaction conditions used. This unambiguously demonstrated that catalyst deactivation occurred. On the other hand, when hexane was used as solvent under the same reaction conditions, 1-phenylethan-1-ol reacted further as an intermediate and after the same time period (6 h), the reaction mixture consisted of 65% of ethylbenzene and 23% of 1-phenylethan-1-ol (Fig. 8).

CONCLUSIONS

Transformation of acetophenone to ethylbenzene successfully proceeds on palladium catalysts supported on active carbon and zeolites in methanol and hexane as solvents. Whereas on Pd/C, the initial rate of acetophenone reaction is higher in methanol, on the Pd/zeolite catalyst, the rate is higher in hexane. On Pd/Al_2O_3 catalyst, the reaction proceeds in methanol only giving 1-phenylethan-1-ol, which does not undergo any further reactions, whereas in hexane, the conversion to ethylbenzene continues. Palladium catalysts with zeolite supports were very active in these transformations. The acidity of the supports affected the hydrogenation rate and also contributed to a large extent to direct hydrogenolysis during the reaction.

The kinetic model describing the reaction system showed that, on the Pd/C catalyst, hydrogenation-dehydration mechanisms with intermediates of 1-phenylethan-1-ol and styrene took place in the transformation of acetophenone to ethylbenzene ($k_1 = 8.3$ s^{-1}), whereas direct hydrogenolytic splitting of the C=O bond of acetophenone has only a minor effect ($k_4 = 1.0$ s^{-1}). For the reactions catalyzed with Pd/Al_2O_3, the rate constants k_4 was zero and, thus, no direct hydrogenolysis of the C=O bond in acetophenone occurred. In addition, the kinetic model excluded the splitting of the C–OH bond of 1-phenylethan-1-ol to ethylbenzene ($k_5 \approx 0$) on the Pd/C as well as Pd/Al_2O_3 catalysts in methanol and in hexane.

REFERENCES

1. Risinger G. E., Mach E. E., Barnett K. W.: *Chem. Ind. (London)* **1965**, *16*, 679.
2. Reeves W. P., Murry J. A., Willoughby D. W., Friedrich W. J.: *Synth. Commun.* **1988**, *18(16–17)*, 1961.
3. March J.: *Advanced Organic Chemistry*. Wiley, New York 1992.
4. Gadhwal S., Baruah M., Sandhu J. S.: *Synlett* **1999**, *10*, 1573.
5. Olah G. A., Wu A.: *Synlett* **1990**, *1*, 54.
6. Zhang Y., Wu S., Wang X.: *Huaxue Shiji* **1992**, *14*, 365; *Chem. Abstr.* **1993**, *119*, 72309.
7. Suzuki H., Masuda R., Kubota H., Osuka A.: *Chem. Lett.* **1983**, *6*, 909.
8. Ono A., Maruyama T., Suzuki N.: *Synth. Commun.* **1987**, *17*, 1001.
9. Ono A., Suzuki N., Kamimura J.: *Synthesis* **1987**, *8, 736*.
10. Torok B., London G., Bartók M.: *Synlett* **2000**, *5*, 631.
11. Magnoux P., Lavaud N., Guisnet M.: *Top. Catal.* **2000**, *13, 291*.
12. Lavaud N., Magnoux P., Alvarez F., Melo L., Giannetto G., Guisnet M.: *J. Mol. Catal. A: Chem.* **1999**, *142, 223*.
13. Alvarez F., Magnoux P., Ribeiro F. R., Guisnet M.: *J. Mol. Catal.* **1994**, *92, 67*.
14. Melo L., Magnoux P., Giannetto G., Alvarez F., Guisnet M.: *J. Mol. Catal. A: Chem.* **1997**, *124*, 155.
15. Ofosu-Asante K., Stock L. M.: *J. Org. Chem.* **1987**, *52*, 2938.
16. Lansink-Rotgerink: U.S. 5 773 677, 1998; *Chem. Abstr.* **1997**, *126*, 263926.
17. Chihara T., Teratani S., Hasegawa-Ohotoma M., Amemiya T., Taya K.: *J. Catal.* **1984**, *90*, 221.
18. Chihara T., Shinzawa M., Yokoyama Y., Taya K., Ogawa H.: *React. Kinet. Catal. Lett.* **1989**, *39*, 181.
19. Mosby W. L.: *J. Org. Chem.* **1953**, *18*, 485.
20. Cromwell N. H., Cook K. E.: *J. Org. Chem.* **1958**, *23*, 1327.
21. Wilt J. W., Scheider Ch. A.: *J. Org. Chem.* **1961**, *26*, 4196.
22. Kindler K., Scharfe E., Henrich P.: *Justus Liebigs Ann. Chem.* **1949**, *565*, 51.
23. Horning E. C., Reisner D. B.: *J. Am. Chem. Soc.* **1949**, *71*, 1036.
24. Hartung W. H., Crossley F. S.: *J. Am. Chem. Soc.* **1934**, *56*, 158.
25. Levine M., Temin S. C.: *J. Org. Chem.* **1957**, *22*, 85.
26. Abu-Reziq R., Avnir D., Blum J.: *J. Mol. Catal. A: Chem.* **2002**, *187, 277*.
27. Freifelder M.: *Practical Catalytic Hydrogenation*. Wiley, New York 1971.
28. Chen H. W., Chen C. S.: *Catal. Lett.* **1996**, *39*, 39.
29. Breitner E., Roginski E., Rylander P. N.: *J. Org. Chem.* **1959**, *24*, 1855.
30. Baltzly R.: *J. Org. Chem.* **1976**, *41*, 920.
31. Nightingale D., Radford H. D.: *J. Org. Chem.* **1949**, *14*, 1089.
32. Glebov L. S., Mikaya A. I., Yatsenko A. E., Zaikin V. G., Kliger G. A., Loktev S. M.: *Tetrahedron Lett.* **1985**, *26, 3337*.
33. Maier W. F., Bergmann K., Bleicher W., Schleyer P. v. R.: *Tetrahedron Lett.* **1981**, *22, 4227*.
34. Landa S., Weisser O.: *Chem. Listy* **1956**, *50*, 569.
35. Landa S., Mostecký J.: *Chem. Listy* **1955**, *49*, 67.
36. Laurent E., Delmon B.: *Appl. Catal., A* **1994**, *109*, 77.
37. Fialová E.: *M.S. Thesis*. Institute of Chemical Technology, Prague 1985.
38. Zámostný P., Bělohlav Z.: *Comput. Chem.* **1999**, *23*, 479.

39. Bejblová M. *et al.*: Unpublished results.
40. Froment G. F., Bischoff K. B.: *Chemical Reactor Analysis and Design*, p. 89. John Wiley, New York 1979.
41. Zámostný P., Bělohlav Z.: *Appl. Catal., A* **2002**, *225*, 291.
42. Bělohlav Z., Zámostný P., Klusoň P., Volf J.: *Can. J. Chem. Eng.* **1997**, *75*, 735.
43. Červený L.: *Chem. Eng. Commun.* **1989**, *83*, 31.
44. Červený L., Růžička V.: *Sb. Vys. Sk. Chem.-Technol Praze, C* **1981**, *27*, 61.
45. Čejka J., Wichterlová B.: *Catal. Rev.–Sci. Eng.* **2002**, *44*, 375.