

Selective hydrogenation of cinnamaldehyde over Ru/Y zeolite

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Abstract

The selectivity and activity of liquid-phase hydrogenation of cinnamaldehyde over 5%Ru/Y were strongly influenced by the solvent used. Other process parameters (temperature, substrate concentration and reduction mode) were also evaluated. An improved selectivity (from 30 to 70%) under optimised reaction conditions as well as higher activity were achieved.

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1. Introduction

Selective hydrogenation of α,β -unsaturated aldehydes gives unsaturated alcohols—industrially valuable products and intermediates for the synthesis of various fine chemicals. The sensory properties of unsaturated alcohols are typically applied in perfumery and food industries [1,2], while pharmaceutical industry processes unsaturated alcohols mainly as intermediates [3,4].

Conventional catalysts based on metals such as nickel, palladium or rhodium are almost unselective towards unsaturated alcohols in hydrogenation of α,β -unsaturated aldehydes [5]. Although, ruthenium itself is just moderately selective, and similar or better selectivities can be achieved with osmium, iridium or platinum catalysts, ruthenium has particular and interesting catalytic properties [6–8]. Furthermore, ruthenium itself is one of the most inexpensive platinum group metals.

Alumosilicates represent wide spectra of materials with specific catalytic properties. Zeolites, a subset of aluminosilicates can be defined as microporous crystalline structures [9]. Zeolites and zeolite-supported catalysts, the variety of their structures, shape selectivity, tunable acidity and other unique properties make them essentially indispensable in

crude-oil refinery applications [10] and advantageous for the synthesis of fine chemicals [11]. The FAU zeolite structure (Y zeolite) represents one of the most successfully employed aluminosilicate in petrochemistry [12]. The intrinsic properties of Y-zeolite supported catalysts in the hydrogenation of cinnamaldehyde, beneficial for the achievement of high yields of cinnamylalcohol, have been reported previously [13,14].

Our previous investigation [15] confirmed the fundamental suitability of the Ru/Y zeolite-supported catalyst for selective hydrogenation of cinnamaldehyde, however, the increase of catalyst activity and selectivity would be desirable. This work involves experimental evaluation of various reaction conditions on the hydrogenation of cinnamaldehyde over the 5%Ru/Y catalyst.

2. Experimental

2.1. Catalyst synthesis

The 5%Ru/Y catalyst was prepared by wet impregnation of Y-zeolite support (Zeolyst International, CBV 712) by aqueous solutions of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ($x \leq 1$, Sigma Aldrich). The impregnation was carried out in a rotary evaporator (Buchi Rotavapor R114) for a period of 24 h. The impregnated catalyst was dried at 383 K for 12 h in air.

An improved catalyst selectivity without any major impact on the activity was formerly observed during repeated experiments [J. Hájek et al. submitted to Chem. Eng. J.].

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Therefore, the entire batch of 5%Ru/Y (mean particles size 23 μm) underwent a 6 h run in cyclohexane (for conditions, see Section 2.3).

After the reaction, the catalyst was filtered, slowly and very carefully washed with small amounts (10–20 ml) of acetone (pro analysis quality, total amount of acetone ca 1.5 l). The washed catalyst was dried for 2 h in an oven at 378 K.

2.2. Chemical reduction

Two procedures were applied for the chemical reduction of the fresh catalyst e.g. reduction with NaBH_4 [16] and reduction with hydrazine [17].

NaBH_4 reduction: The catalyst was reduced by 10% solution of NaBH_4 (97%, Fluka) in distilled water ($n_{(\text{NaBH}_4)}(\text{mol})/n_{(\text{Ru})}(\text{mol}) = 10$). The solution was slowly, dropwise added to intensively stirred suspension of catalyst in ca 50 ml of distilled water. The reduction was terminated one hour after the whole amount of NaBH_4 was added. The reduced catalyst was filtered and carefully washed with small amounts (10–20 ml) first of distilled water and consequently with doses of acetone (ca 500 ml). The washed catalyst was dried in an oven for 2 h at 378 K.

Hydrazine reduction: Calculated amount ($n_{(\text{N}_2\text{H}_4\cdot\text{HCl})}/n_{(\text{Ru})} = 10$) of $\text{N}_2\text{H}_4\cdot\text{HCl}$ (98%, Aldrich) was dissolved in ca 30 ml of distilled water and the solution was dropwise added to stirred suspension of catalyst in water solution of Na_2CO_3 (99.5%, Merck) ($n_{(\text{Na}_2\text{CO}_3)}(\text{mol})/n_{(\text{N}_2\text{H}_4\cdot\text{HCl})}(\text{mol}) = 1$).

After the whole amount of hydrazine was added, the stirred suspension was left for 1 h at 323 K. Particular attention was paid to remove the excess of Na_2CO_3 from the catalyst. Therefore, higher amounts of water and acetone were used during the washing procedure, otherwise analogous conditions (to NaBH_4 reduction) during the washing and drying step were applied.

The further treatment of the reduced catalysts (run in cyclohexane, sieving, activation) was analogous to non-reduced catalyst.

2.3. Catalyst testing

Liquid-phase hydrogenation of cinnamaldehyde (98%, Aldrich) was carried out within the kinetic region under a total pressure of 50 bars at 373 K in a 500 ml stirred batch reactor (Autoclave Engineers, USA). Prior to hydrogenation each catalyst sample (mean particle size 23 μm) was activated under hydrogen flow (2 h, 573 K). A list of solvents and corresponding basic properties of the reactants and main products is provided in Tables 2 and 3.

The reaction products were identified with GC-MS and analysed by GC (HP-6890, Hewlett & Packard, USA). The content of individual components in the reaction mixture was determined by the Internal Standardisation Method (n-decane, Aldrich, USA).

Table 1
Properties of the 5%Ru/Y catalyst

Catalyst	Surface area (m^2/g)	Carbon content (%)
Fresh	900	0.0
Spent ^a	330	14.0

^a After one run in cyclohexane (as described in Section 2).

The selectivity with respect to unsaturated alcohol was calculated as the ratio of the product formed to reacted cinnamaldehyde. The evaluation of the catalyst activity was based on turnover frequency (TOF) and on the conversion achieved after 6 h of hydrogenation. Since the observed strong catalyst deactivation makes the one-point evaluation of selectivity and activity problematic, the complete reaction courses were discussed.

The metal loading of the catalyst was verified by the DCP analysis; surface area and carbon content of the catalyst are indicated in Table 1. More detailed characterisation results have been reported previously [15]. During this study, all of the reactions were performed with the so called “spent” catalyst prepared according to the procedure described in Section 2.

3. Results and discussion

In general, the reaction might give a broad spectrum of undesired products (aromatic ring hydrogenation, hydrogenolytic products). However, in the particular case of hydrogenation over zeolite supported catalysts the key problem is formation of condensation by-products (acetalisation) in lower alcohols due to acidic properties of aluminosilicates [15]. Aromatic ring hydrogenation and hydrogenolysis were completely restricted over the treated (“spent”) catalyst. Condensation by-products were detected just for reactions carried out in 2-propanol and 2-butanol. The complete reaction network involving condensation as well as formation of other undesired by-products has been reported earlier [15]. In the absence of such products, the reaction network is represented by the scheme shown on Fig. 1.

3.1. Solvent effect

Firmly established, the catalytic performance of heterogeneous catalysts might be considerably influenced by

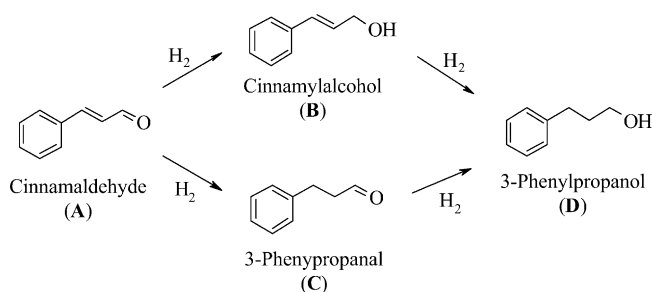


Fig. 1. Cinnamaldehyde hydrogenation network.

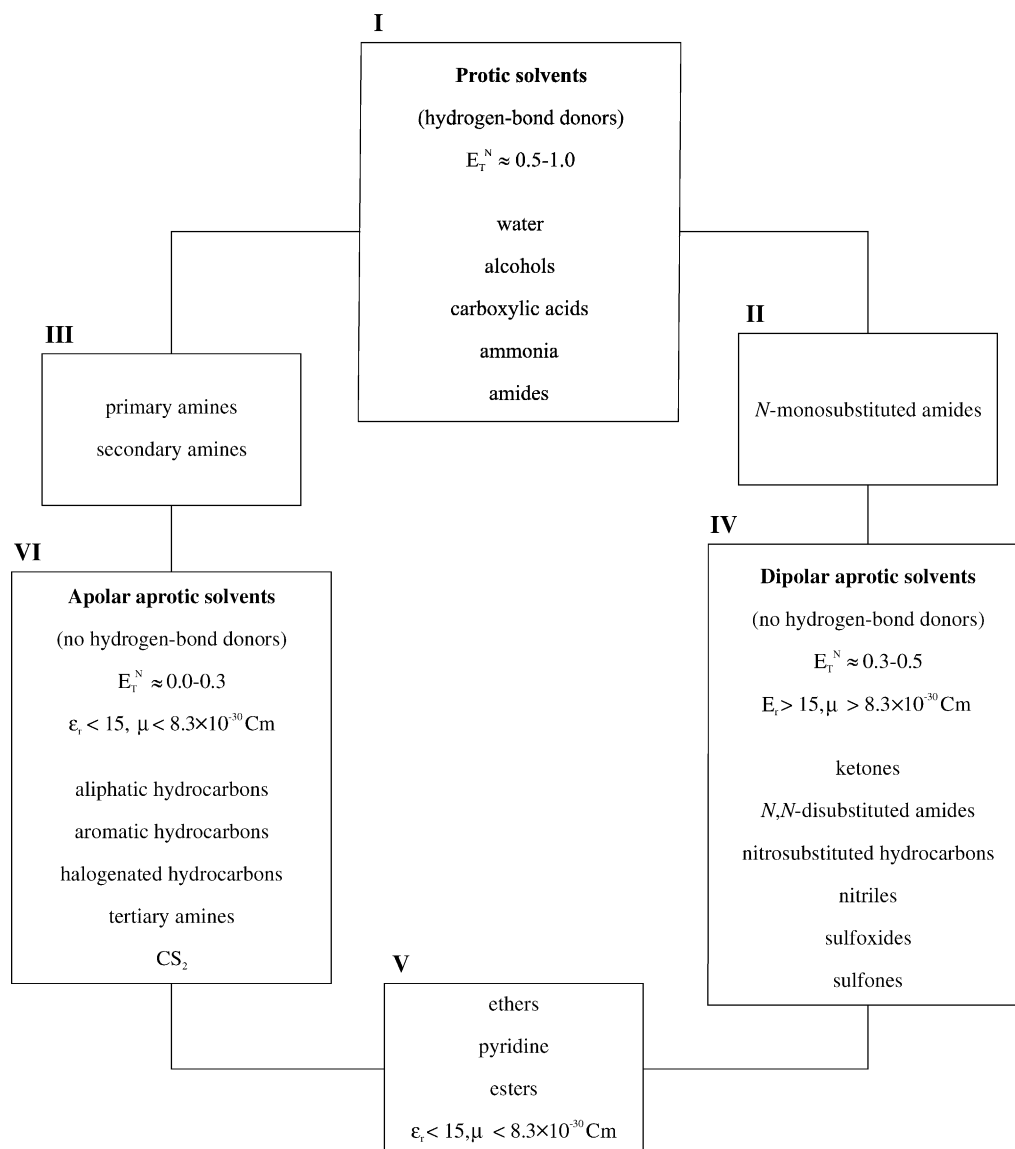


Fig. 2. Parker's classification of solvents according to solvent-solute interactions ([21], p. 82).

the applied solvent, however, it has been shown that it is hardly possible to abridge the results [18]. Typically, the effect of solvent varies with the whole set of its properties, from which, some may predominate in correlation to the tested substrate [19,20]. Commonly [21] the solvents can be classified²:

1. according to their chemical bonds;
2. using physical constants;
3. in terms of acid-base behaviour;
4. in terms of solute-solvent interactions;
5. using multivariate statistical methods.

The solvent effect in catalytic hydrogenations within the kinetic region comprises mainly interactions with substrate

² Due to large chemical and physical differences among solvents the complex solvent classifications including the presented one unavoidably overlap.

and catalyst. Solvent-solute interactions split solvents in terms of Parker's classification [22] (Fig. 2) into three main groups (**I**, **IV**, **VI**). Presented categorisation is not rigid, groups of solvents **II**, **III**, **V** are assigned as intermediate ones. The choice of $\epsilon_r = 15$ (**IV**, **V**) is arbitrary, reflecting the practical effect that in solvents with $\epsilon_r < 15$ freely solvated ions are no longer observable ([21], p. 84).

The solvents screened in this study represent the most conventional and easily available ones, covering the main groups of Parker's classification. To manage a comfortable separation from reaction products (b.p. ca. 493–533 K) the selected solvents should have boiling points optimally below 423 K (150 °C). An overview of used solvents with some of their basic properties is presented in Table 2. Table 3 summarises the basic properties of the reactant and the main products. Both tables report polar parameters. The experimental results presented in further text would be related

Table 2
Index of the used solvents

Group	Solvent	Supplier, purity	ϵ_r	b.p. (K)	μ ($\times 10^{-30}$ cm)	E_T^N
I	2-Propanol	Lab-Scan, 99.7%	19.92	355	5.5	0.546
	Cyclohexanol	J.T. Baker, 99%	15.00	434	6.2	0.509
	2-Butanol	J.T. Baker, 99%	16.56	372	5.5	0.506
	2-Pentanol	Merck, 98%	13.71	393	5.5	0.488
	3-Pentanol	Aldrich, 98%	13.35	388	5.5	0.463
	<i>t</i> -Butanol	J.T. Baker, 99%	12.47	355	5.5	0.389
IV	Acetone	Merck, 99.5%	20.56	329	9.0	0.355
V	Ethylacetate	Merck, 99%	6.02	350	5.9	0.228
	Tetrahydrofurane	Fluka, 99.8%	7.58	340	5.8	0.207
VI	Toluene	J.T. Baker, 99.5%	2.38	384	1.0	0.099
	Xylene ^a	Merck, 96%	2.37 ^b	413	0.4	0.074 ^c
	Triethylamine	Fluka, 99.5%	2.42 ^b	362	2.2	0.043
	Isooctane ^d	Merck, 99.5%	1.94 ^b	372	\times	0.012 ^e
	Cyclohexane	J.T. Baker, 99.5%	2.02	354	0.0	0.006

^a Mixture of isomers, the chief constituent of commercial xylene is usually the *m*-isomer.

^b 293 K.

^c For *p*-isomer.

^d 2,2,4-trimethylpentane.

^e *n*-octane.

to the solvent polarity in terms of Parker's classification of solvent–solute interactions.

The relative permittivity ϵ_r is given for the pure material at 298 K unless stated, b.p. is the normal boiling point of solvent (Merck Online Database), μ dipole moment, and E_T^N normalised empirical parameter for solvent polarity.

The dielectric constant (also called relative permittivity $\epsilon_r = \epsilon/\epsilon_0$ where ϵ_0 is the permittivity of vacuum) plays an important role in the characterisation of solvents, useful for the measurement of solvent polarity (i.e. the higher ϵ_r the higher is its polar character). The dipole moment μ provides information on the structure of solvent by expressing the electrical asymmetry of the molecule. The empirical parameter of solvent polarity (E_T) obtained from spectroscopic measurements provides complex and very accurate characterisation of solvent polarity. The collection of E_T values for organic solvents represents so far the most comprehensive solvent polarity scale ([21], p. 417). Normalised E_T^N values range from 0.000 for tetramethylsilane to 1.000 for water, the most polar solvent.

Table 3
Physical properties of the main reaction components

Material	ϵ_r^c	ϵ_r^d	b.p. (K)	μ ($\times 10^{-30}$ cm)
Cinnamaldehyde ^{a,b}	13.3	\times	524	12.3
Cinnamylalcohol ^e	14.5	19.2	531	6.0
3-Phenylpropanal ^f	4.8	4.8	496	7.8
3-Phenylpropanol ^e	11.1	9.4	511	5.7

^a Gramstad [23].

^b 293 K.

^c Zero approximation method.

^d Hedstrand method [24].

^e Goebel and Wenzke [25].

^f Goebel and Wenzke [26].

Permittivities in Table 3 were calculated from dipole moments [27] using the published experimental data. The ϵ_r value of 3-phenylpropanal (C) is apparently underestimated. The polarities of the main reaction compounds are very similar. Because of the polarity, reactants are poorly soluble in water, well soluble in alcohols and dipolar solvents and less soluble in saturated hydrocarbons such as cyclohexane.

The attempts to generalise results in heterogeneous catalysis in terms of solvent properties did not succeed. Nevertheless, some basic considerations ([20], p. 76) concerning the solvent effect can be indicated:

1. any solvent having exclusive electron pairs can be expected to interact with the catalyst to some extent;
2. protic solvents such as alcohols are the most commonly used solvents but they are hydrogen-bond donors and have been reported to interact with catalysts surfaces;
3. useful alternatives that apparently do not interact as much as alcohols with the catalyst include ketones, ethers and esters;
4. saturated hydrocarbons should be considered as the most inert solvents since they do not adsorb on the catalysts and they do not bond to substrate extensively under moderate conditions.

An overview of the hydrogenation results is presented in Tables 4–6 where the solvents are grouped according to Parker's classification. The conversion values (x_6) are related to the reaction time of 6 h. The S_{25} indicates the selectivity towards cinnamylalcohol at the conversion of 25%.

3.2. Protic solvents

Reactions carried out in alcohols exhibited relatively high rates and the selectivity varied significantly upon the solvent

Table 4
Hydrogenation of cinnamaldehyde in protic solvents (373 K, 50 bars)

Solvent	x_6 (%) ^a	TOF (s^{-1}) $\times 10^3$	S_{25} (%)	E_T^N
2-Pentanol	100	100	7	0.488
2-Propanol	100	31	4	0.546
2-Butanol	97	28	34	0.506
3-Pentanol	79	25	46	0.463
<i>t</i> -Butanol	71	22	50	0.389
Cyclohexanol	38	6	2	0.509

^a Conversion after 6 h.

Table 5
Hydrogenation of cinnamaldehyde in aprotic dipolar solvents (373 K, 50 bars)

Solvent	x_6 (%)	TOF (s^{-1}) $\times 10^3$	S_{25} (%)	E_T^N
Acetone	50	7	21	0.355
Ethylacetate	43	7	32	0.228
Tetrahydrofuran	40	5	43	0.207

used (Table 4). The hydrogenation patterns are presented by Fig. 3. The formation of undesired condensation products (acetalisation) was observed in 2-propanol and to minor extent also in 2-butanol.

Table 6
Hydrogenation of cinnamaldehyde in aprotic solvents (373 K, 50 bars)

Solvent	x_6 (%)	TOF (s^{-1}) $\times 10^{-3}$	S_{25} (%)	E_T^N
Triethylamine	48	13	54	0.043
Isooctane	40	12	46	0.012
Cyclohexane	40	8	49	0.006
Xylene	30	42	26	0.074
Toluene	24	6	72	0.099

Generally, the hydrogenation activity increased with the solvent polarity, whereas the selectivity decreased (Fig. 4). The two exceptions for 2-pentanol and cyclohexanol are discussed below.

The observed trends can be possibly, in accordance with literature ([20], p. 70), explained through hydrogen bonding of the carbonyl oxygen with hydroxy group of the alcohols. The smaller and more reactive was the alcohol the stronger and more effective was the bonding and the lower was selectivity towards C=O group hydrogenation product (cinnamylalcohol).

In 2-propanol the bonding was effective, thus the alcohol bond to the carbonyl group restricted hydrogenation of this bond while hydrogenation of the allylic group was

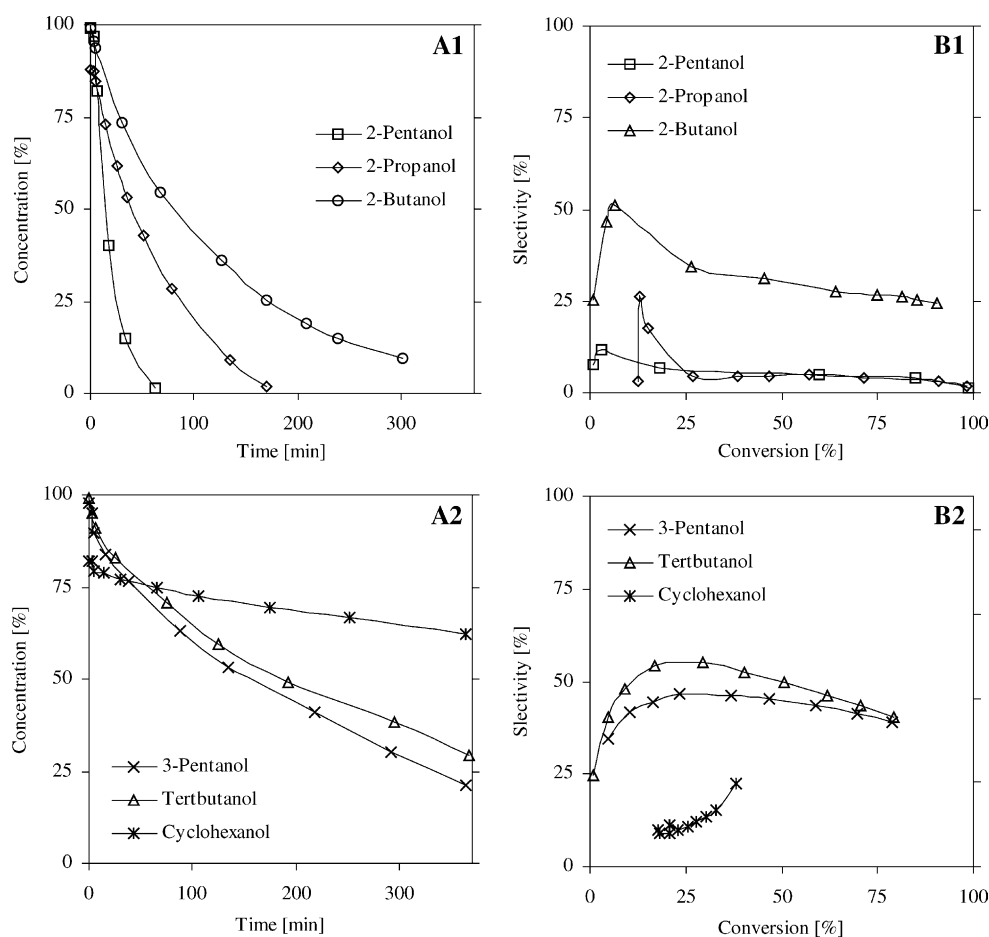


Fig. 3. Hydrogenation of cinnamaldehyde over 5%Ru/Y in protic solvents. A, activity; B, selectivity towards cinnamylalcohol.

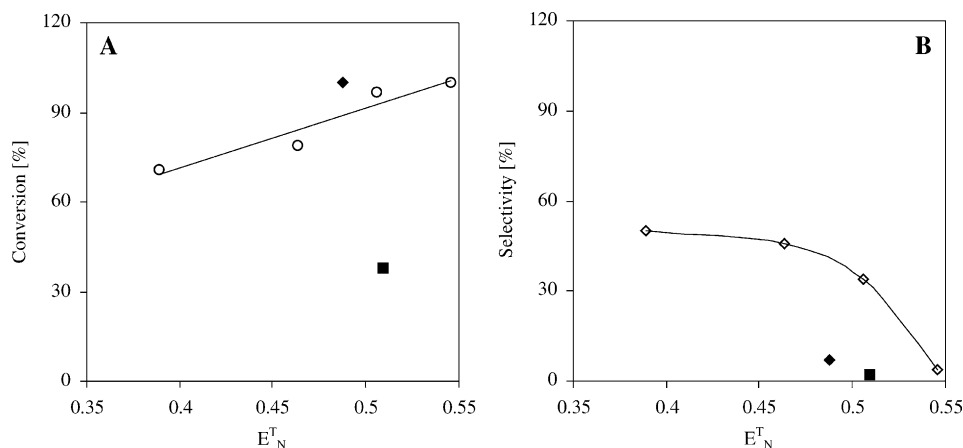


Fig. 4. Hydrogenation in alcohols. A, selectivity; B, activity trends; exceptions: (◆) 2-pentanol; (■) cyclohexanol.

predominant and thus the yield of cinnamylalcohol was low (lowered also by condensation). Thermodynamically preferred hydrogenation of C=C group can explain the high activity in 2-propanol. A less efficient hydrogen bonding in *t*-butanol yielded cinnamylalcohol, while the increased possibility for hydrogenation of the carbonyl group decreased the overall reaction rate (note that hydrogenation in inert hydrocarbons where hydrogen bonding does not exist was much slower than hydrogenation in *t*-butanol and more selective (Table 6). Evaluating the results, additional effects that possibly influence catalytic performance and difficult to quantify such as catalyst acidity and hydrogen donor abilities of solvents should be considered too.

There were two major exceptions: hydrogenations carried out in 2-pentanol and in cyclohexanol. Exceptionally fast reaction rate in 2-pentanol corresponds well with similar results obtained in hydrogenation of 1-phenyl-1,2-propanedione and citral [28,29]. Although, this observation does not correspond directly with the presented solvent-polarity trends, it is, however, consistent with the general assumption of hydrogen bonding. In this particular case, probably other effects such as hydrogen solubility, adsorption strength etc. are also involved.

Hydrogenation in cyclohexanol exhibited performance different from other alcohols. The used solvent was denoted as per analysis purity (+99%), however, a broad range of impurities has been revealed during the GC analysis. MS–GC proved the presence of cyclohexyl acetate, cyclohexyl hexanoate, cyclohexyl ester of hexanoic acid etc. Since the amount of solvent in the reactor was in large excess with respect to the amount of catalyst and substrate, minor impurities in the solvent can have a remarkable influence on the catalytic properties ([20], p. 78).

3.3. Dipolar aprotic solvents

Reaction rates in dipolar aprotic solvents were low compared to the rates in alcohols (Table 5). Selectivity-conversion trends were similar to those of higher alcohols, i.e. the cata-

lyst activity increased with solvent polarity whereas selectivity decreased, however, the shape of selectivity-conversion dependence was different (Fig. 5). Explanations for the reaction behaviour should be different from those for the polar solvents, since dipolar solvents are not hydrogen bond donors.

Dipolar aprotic solvents possess relatively high permittivities and dipole moments. These solvents do not act as hydrogen donors, however, they are good electron-pair donor (EPD) solvents. Characteristic for these solvents is the formation of EPD/electron-pair acceptor (EPA) complexes associated with an electron transfer from a donor to an acceptor molecule ([21], p. 19). Reported adsorption of tetrahydrofuran (THF) on metal surfaces [30,31] as well as possible adsorption of acetone and ethylacetate is therefore expected.

According to the obtained experimental data, the solvent–solute and solvent–catalyst interactions played a role in the catalytic performance since both, activity and selectivity were associated with solvent polarity (Table 5) i.e. with EPD/EPA complexation ability.

3.4. Apolar solvents

Catalyst activity in apolar solvents was low, at the same time selectivity towards (B) was higher compared to polar and dipolar solvents. Tested apolar solvents can be generally divided into two subsets e.g. so-called “saturated” solvents (triethylamine, isooctane, cyclohexane) and aromatics (xylene, toluene). The experimental results are shown in Table 6 and Fig. 6.

Apolar solvents typically do not interact with the solute since only non-specific forces can operate, however, some of these solvents, for instance aromatics, could be relatively strongly adsorbed on the catalyst surfaces. The competition between benzene (solvent) and 1-methylcyclohexene (substrate) adsorption was observed, during hydrogenation and the results were related to the aromatic character of benzene, i.e. to the presence of unshared electron pairs [32].

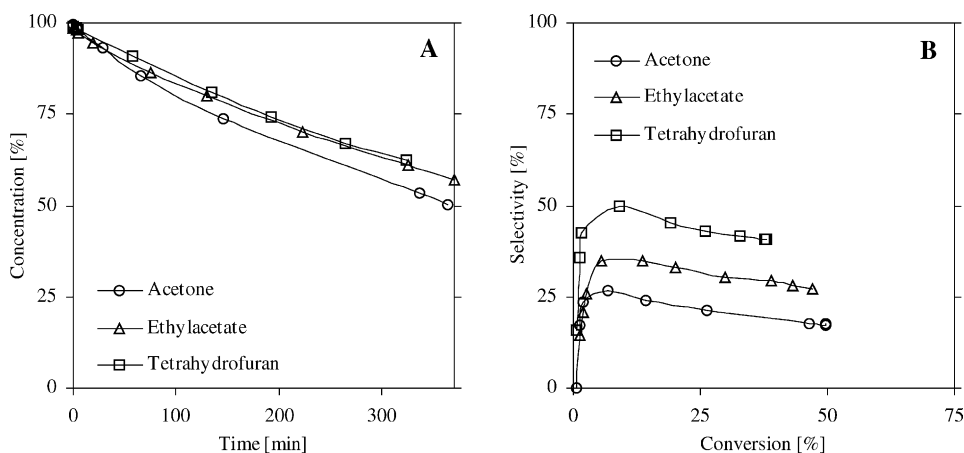


Fig. 5. Hydrogenation of cinnamaldehyde over Ru/Y in aprotic dipolar solvents. A, activity; B, selectivity towards cinnamylalcohol.

It can be concluded from the experiments, that the polarity factor plays a role also in the instance of apolar solvents.

Application of solvents containing aromatic ring (toluene, xylene) decreased the hydrogenation rates compared to other apolar solvents. The effect is plausibly associated with competitive adsorption of the solvent and substrate on the cata-

lyst surface. Hydrogenation carried out in more inert xylene shows higher TOF and conversion compared to the reaction carried out in toluene. The difference in the yields of (B) for xylene and toluene cannot be attributed to polarity, but it could be probably explained by the presence of impurities in xylene (purity 96%).

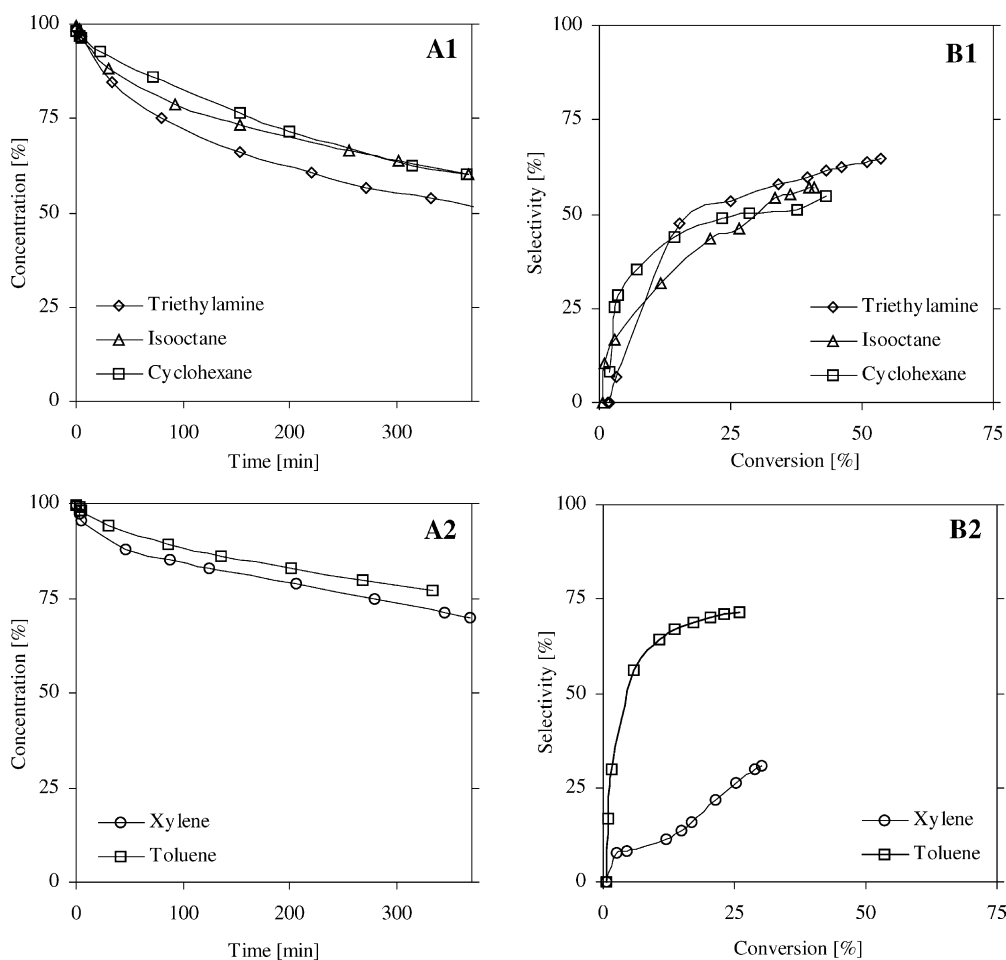


Fig. 6. Hydrogenation of cinnamaldehyde over 5%Ru/Y in aprotic solvents. A, activity; B, selectivity towards cinnamylalcohol.

Evaluation of the solvent effect showed that the highest selectivities (50–70%) towards cinnamylalcohol were obtained in apolar solvents (toluene, triethylamine, cyclohexane). At the same time reaction rates in these solvents were low, typically conversions of only 30–40% after 6 h (50 bars, 373 K) were achieved. Similar results, high activities in 2-propanol and low activity in hexane were observed in hydrogenation of cinnamaldehyde over a commercial Ru/C catalyst as reported by Cerveny et al. [33].

Solvent effects in heterogeneous catalysis comprise physical and chemical effects that control intrinsic catalysts performance. The main factors affecting the selectivity and activity of catalysts are reactant solubility, polarity or acido-basicity of solvents and competitive chemisorption of reactants and solvents. In the particular case of molecular sieves (including zeolites) diffusion and shape selectivity should be also considered [34].

Although the presented above results were discussed mainly in terms of polarity, adsorption and solvent–solute–catalyst interactions, the solvent effect is more complex and some other factors should be considered, too. One of the most important and apparent effect is reactant and hydrogen solubility. The effect of reactant solubility under the high solvent excess can be neglected. The reactants were clearly observed to be less soluble in apolar solvents but at the reaction temperature in the high excess of solvent certainly reactant solubility cannot play any significant role. The possible effect of hydrogen solubility is a well-known factor in the three-phase processes. The analysis of hydrogen solubility is not straightforward. There is no comprehensive data available on hydrogen solubility under the used reaction conditions (373 K, 50 bars) and involving the whole set of applied solvents. Some limited information is presented in the work of C.L. Young [35]. Furthermore, accurate estimation of solubilities is difficult since currently available methods give only very approximate results [36,37].

Based on the tabulated data [35] for two solvents 2-propanol (fast reaction) and cyclohexane (slow reaction) and on calculations previously performed in [38] it can be reasonably estimated that hydrogenation in 2-propanol was not limited by hydrogen solubility.

In order to further improve the catalyst selectivity the substrate concentration and the effect of temperature were tested.

3.5. Substrate concentration and temperature effect

The experiments were carried out in cyclohexane with the substrate to catalyst ratio ranging from 3 to 24. The influence of temperature was evaluated covering a broad interval of temperatures (293–373 K).

At the lowest substrate/catalyst ratio the reaction was unselective towards (**B**) and complete conversion was achieved in ca. 3 h (Table 7). At higher substrate/catalyst ratios enhanced selectivity was obtained, but the reaction rate decreased. The lowest activity was observed at the

Table 7

Activity and selectivity at different substrate/catalyst ratios (373 K, 50 bars)

Ratio	x_6 (%)	TOF (s^{-1}) $\times 10^{-3}$	S_{25} (%)	S_{40} (%)
3	100	26	1	1
6	40	8.0	49	53
24	11	4.6	44	53

Table 8

Activity and selectivity as a function of temperature (cyclohexane as a solvent)

Temperature (K)	x_6 (%)	TOF (s^{-1}) $\times 10^{-3}$	S_{10} (%)	S_{20} (%)	Pressure (bar)
293	9	0.11	44 ^a	×	80
323	21	3	32	48	80
373	40	8	40	47	50

^a 530 min.

highest substrate/catalyst ratio of 24 with 40% conversion achieved in about 23 h.

According to results presented in Table 7 the selectivity towards (**B**) was not clearly affected by the substrate/catalyst ratio higher than 3, at the same time, at higher ratios the reaction time was considerably prolonged. A reasonable substrate/catalyst ratio that gives a compromise between high yield of (**B**) and acceptable activity can be reached at the ratio of about 6 (40% conversion in 6 h). The decreased selectivity at the lowest substrate/catalysts ratio might be associated with the high reaction rate leading to the thermodynamically preferred product (unsaturated aldehyde).

High selectivity ($\approx 97\%$) to unsaturated alcohol (**B**) was earlier achieved over Pt/Y catalyst in a ternary solvent at 313 K (40 °C) by Gallezot et al. [39]. Temperature dependent selectivity was noticed during the hydrogenation of cinnamaldehyde over the sol–gel Ru–Sn/SiO₂ catalyst [38], when decrease of reaction temperature (433 → 373 K) increased the selectivity from 60 to 80%.

Results in the present study (Table 8) do not indicate any substantial increase of selectivity at temperatures lower than 373 K, while as expected, the catalyst activity increased with temperature.

The amount of substrate as well as the reaction temperature did not affect apparently the selectivity. The main problem in hydrogenation of cinnamaldehyde in cyclohexane was the substantial decrease of catalyst activity at

Table 9

Effect of chemical reduction on the catalyst activity and selectivity (cyclohexane, 373 K, 50 bar)

Catalyst	TOF (s^{-1}) $\times 10^{-3}$	x_6 (%)	Highest selectivity (%)
Non-reduced ^a	8	40	55
NaBH ₄ reduction	19	97	59
N ₂ H ₄ reduction	31	92	40

^a Without chemical reduction (all catalyst activated prior hydrogenation).

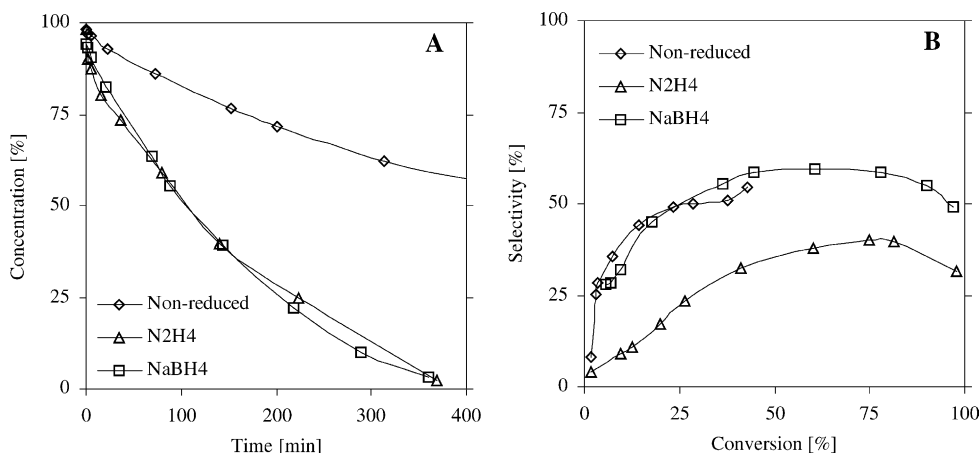


Fig. 7. Effect of chemical reduction on catalyst activity and selectivity. A, activity; B, selectivity towards cinnamylalcohol.

lower temperatures, especially with higher amounts of cinnamaldehyde. On the contrary low amounts of substrate lead to a complete loss of selectivity towards (B). In this particular case of cyclohexane as a solvent, temperature 373 K, pressure of 50 bars and the substrate/catalyst ratio of 6 were acceptable from both, selectivity and selectivity viewpoints.

3.6. Effect of chemical reduction

Chemical reduction was effective in improving the catalyst activity during the hydrogenation of cinnamaldehyde over Ru-Sn/SiO₂ catalysts [40]. The best results were obtained over the NaBH₄ reduced catalyst. Another possible chemical reducing agent is hydrazine [18]. In the following text activity and selectivity of a non-reduced catalyst were compared to catalysts reduced with NaBH₄ and hydrazine (N₂H₄) reduced ones (Table 9, Fig. 7).

Chemical reduction improved the catalysts activity by 2–4 times compared to the non-reduced catalyst. Chemically re-

Table 10
Solvent effect in hydrogenation over NaBH₄ reduced 5%Ru/Y catalysts (373 K, 50 bar)

Solvent	TOF (s ⁻¹) × 10 ⁻³	x ₆ (%)	S ₂₅ (%)	Highest selectivity (%)
Cyclohexane	19	97	49	59
Toluene	23	81	35	48
Triethylamine	20	72	52	68

duced catalysts exhibited similar activities, whereas the catalyst reduced with NaBH₄ was more selective.

Combination of the chemical reduction mode (NaBH₄) and the most promising solvents resulted in the data given in Table 10 and Fig. 8.

Compared to the previous experiments with the same catalyst but without chemical reduction, the increase of activity was confirmed, while selectivity remained at the same level, with an exception of toluene, where the selectivity decrease was observed.

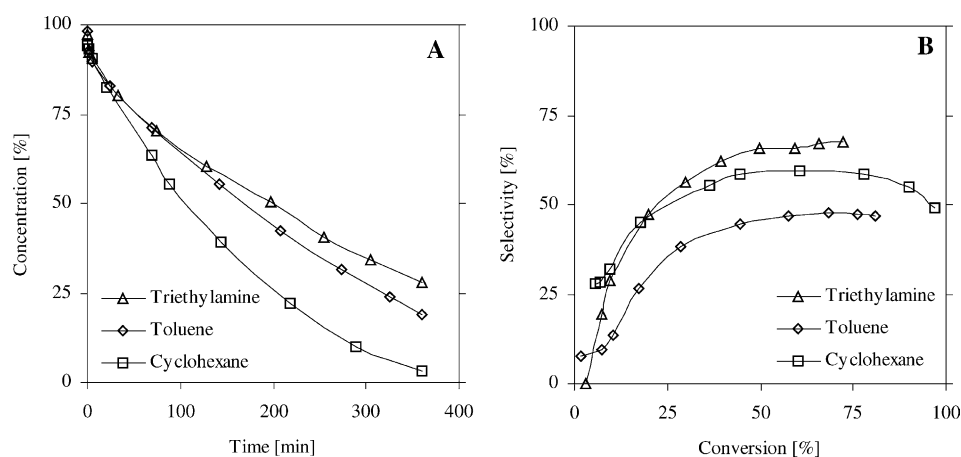


Fig. 8. Solvent effect in hydrogenation over NaBH₄ reduced 5%Ru/Y catalysts. A, activity; B, selectivity towards cinnamylalcohol.

4. Conclusions

Catalytic behaviour of 5% Ru/Y catalyst in the liquid-phase hydrogenation of cinnamaldehyde was strongly influenced by the used solvent. Catalytic performance was correlated to the solvent polarity in terms of Parker's classification.

The catalyst was the most active in alcohols, and relatively inactive in dipolar and apolar solvents. Undesired condensation reactions in the lower alcohols can be avoided by application of alcohols with longer chain length starting from *t*-butanol. Reasonable activity and selectivity of about 50% was reached in these alcohols, however, the highest selectivity towards cinnamylalcohol (up to 70%) was obtained in apolar solvents.

The reaction temperature as well as the substrate to catalyst ratio (6–24) did not apparently influence the selectivity. At the same time for the very low substrate to catalyst ratio of 3 the selectivity towards cinnamylalcohol was completely lost.

Chemical reduction of catalyst by NaBH₄ and N₂H₄ increased activity by 2–4 times for reactions carried out in the apolar solvents (cyclohexane). The NaBH₄ reduced catalyst exhibited selectivities equal to the non-reduced one, while hydrazine reduction had a negative effect on selectivity. The highest selectivity over the NaBH₄ reduced catalyst (≈70%) at reasonable conversion of ca 70% after 6 h of reaction was achieved in triethylamine (373 K, 50 bars, substrate/catalyst = 6).

Optimisation of reaction conditions as well as the catalyst preparation procedure considerably enhanced selectivity and activity of the tested Ru/Y zeolite supported catalyst. As a result, previously achieved the highest selectivity of 30% [15] towards cinnamylalcohol was substantially improved to 60%, while conversion increased from 40 to 100% after 6 h of reaction time at the same reaction conditions (cyclohexane, 373 K, 50 bars, substrate/catalyst ratio equal to 6).

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