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Solvent and substituent effects in hydrogenation of aromatic ketones over Ru/polymer catalyst under very mild conditions

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ABSTRACT

The paper reports on the solvent and the substituent effects in hydrogenation of aromatic ketones (acetophenone and its derivatives) in the presence of Ru catalyst supported on functionalized gel-type methacrylate-styrene resin under very mild conditions (1 bar H_2, 40 °C). The investigated solvents included methanol, 2-propanol, tetrahydrofuran, toluene, isooctane, and cyclohexane, with and without addition of water. The best catalytic activity was obtained in biphasic solvent system consisting of isooctane/water (1:1). In methanol and 2-propanol the beneficial role of water was observed. The effects are discussed in terms of solvent protic/aprotic and polar/apolar properties. The impact of substituents depended on their electron-donating/withdrawing character, and on the position on the aromatic ring of acetophenone. The presence of electron donating substituents tended to increase the reaction rate, and the electron withdrawing group slowed down the process. Steric effect was observed for methylacetophenone isomers with CH_3 group at ortho, meta and para positions.

1. Introduction

Catalytic hydrogenation of aromatic ketones constitutes an important aspect of organic synthesis, enabling the preparation of a great number of secondary alcohols widely used in pharmaceutical, cosmetic, food and chemical industries as solvents, intermediates, flavor additivities, fragrances, etc. The hydrogenation of acetophenone and its substituted derivatives are typical examples of this type of reactions. Since formation of side products is possible during the multistep reactions (for example via hydrogenation of phenyl ring and hydrogenolysis of produced alcohols) (Scheme 1), the development of highly active and selective catalysts working preferably under mild conditions is still a challenging task that requires thorough consideration of various factors. In addition, the heterogeneous character of a catalyst combined with its stability would be a very desirable feature of a catalyst of choice.

There are not many studies directed at the hydrogenation of acetophenone and its derivatives using supported monometallic (Ni, Pt, Pd, Cu, Ir, Rh) and bimetallic (Ni-Pt, Pt-Sn) catalysts [1–9]. Among them, only few addressed the effect of substituents, their positions on aromatic ring or their electron-donating/withdrawing character. Thus, Vetere et al. [7] showed that the presence of electron donating group such as $-OCH_3$ on aromatic ring tends to increase the initial reaction rate, while the presence of –Cl– substituent (electron withdrawing group) slows down the process as compared to the hydrogenation of the parent acetophenone.

The authors also observed a decrease of the initial reaction rate when the $-CH_3$ group was located at ortho position of aromatic ring, most likely due to the steric effect. Similar trend was observed by F. Zaccheria et al. [4]. On the other hand, Hess et al. [6] noticed an opposite tendency, i.e., the relative rates were higher in the presence of electron-withdrawing substituents and lower with electron-donating groups. Moreover, the authors pointed out to the influence of chiral modifier on hydrogenation rates. However, all these studies were performed under different conditions, with temperature ranging from ambient to 90 °C, hydrogen pressure from 1 to 10 bar, using various solvents and catalysts. Therefore, it is difficult to determine which factors have a decisive influence on the observed reaction rates and trends. To shed some light on this phenomenon we have decided to investigate first the impact of solvent on the catalytic activity and selectivity of the studied catalyst, 2 wt.%Ru supported on functionalized gel-type methacrylate-styrene resin (referred to as FCN, where FCN means "functionalized"), and then the impact of electron-donating/withdrawing character of substituents and their positions on aromatic

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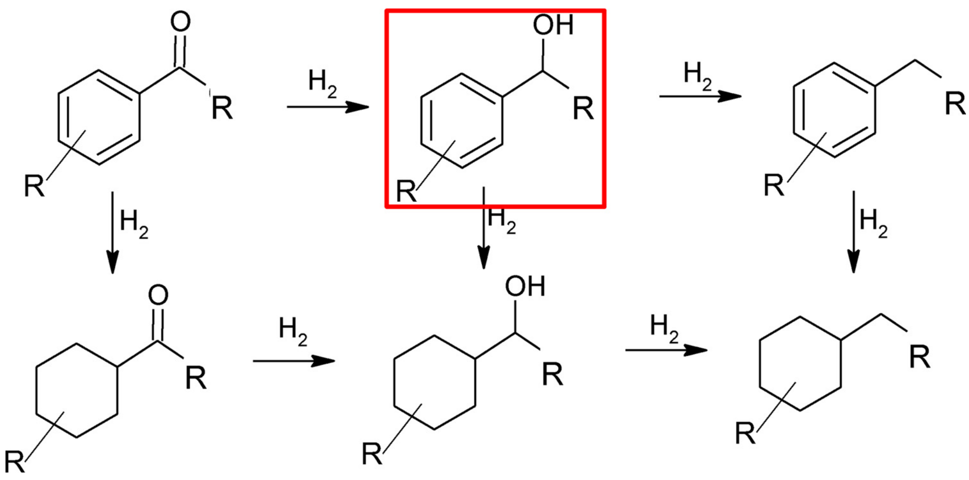


Scheme 1. Hydrogenation of acetophenone and its derivatives.

ring of acetophenone. Our previous studies [10,11] revealed that ruthenium catalysts (1–4 wt% Ru) supported on gel-type methacrylate-styrene resin functionalized with C═O, −OH, –NH, and $–NH_2$ groups showed a very promising catalytic behavior in hydrogenation of acetophenone. Specific properties of this polymer, e.g. hydrophobic/hydrophilic character, the ability to coordinate to Ru via functional groups and the swelling ability, make this polymer very attractive as a carrier. FCN resin contains both apolar (styrene) and polar (O- and N-containing groups) constituents. The ability to swell is a very important feature since it effectively separates polymeric chains thus greatly enhancing the accessibility of active centers inside the polymer matrix [12]. This support was also successfully used for Pd catalyst in hydrogenation of 2-butyne-1,4-diol and phenylacetylene [13]. In addition, ruthenium catalysts are known to be active and selective in hydrogenation of C═O group containing compounds. For example, the hydrogenation of levulinic acid and alkyl-levulinates have been thoroughly investigated in the presence of a range of Ru supported catalysts [14,15]. Ru/Y zeolite catalyst was successfully applied in the hydrogenation of cinnamaldehyde [16]. Ruthenium catalysts supported on metal oxides exhibited high activity and selectivity in the stereoselective hydrogenation of paracetamol [17].

It is well known that the solvent nature may influence both the activity and the selectivity of the catalyst, and the solvent effect must be considered when optimizing reaction conditions. Bertero et al. [18], as well as Trasarti et al. [19], studied this aspect for the liquid-phase hydrogenation of acetophenone over SiO_2 supported Ni, Co and Cu catalysts in the presence of numerous solvents of different nature (protic, aprotic polar, and apolar solvents). They found that the highest catalytic activities were achieved when C2-C3 alcohols were used due to the solvent interactions with metal surface and the appropriate polarization/activation of C═O bond of acetophenone. Similar results were observed by Cheng et al. [20] regarding hydrogenation of acetophenone in the presence of phosphine modified Ru/γ-Al_2O_3 catalyst. The highest conversion was detected in 2-propanol.

In order to establish the most efficient solvent system enabling to achieve high activity and selectivity to desired phenyl alcohols we tested several solvents of different chemical nature. Thus, methanol (MeOH) and 2-propanol (IPA) belong to polar group of solvents, toluene, cyclohexane, and isooctane (IO) are apolar, while tetrahydrofuran (THF) is considered polar but its properties are close to the polar/apolar borderline. We observed a series of non-trivial effects, which are reported in the present study. The phenomena are discussed by considering the solvent polarity, its protic/aprotic character, H_2 solubility, the solvent-catalyst and the reactants-catalyst interactions, as well as the role of water.

Moreover, in this paper we report the results of hydrogenation of structurally diverse array of ketones related to acetophenone, differing by the position of methyl substituent on the aromatic ring, the electron-donating/withdrawing character of substituents, and the length of alkyl chain connected to carbonyl group, carried out in the presence of 2 wt.%Ru/FCN catalyst under very mild conditions (1 bar H_2, 40 °C).

2. Experimental

2.1. Materials and methods

This catalyst was synthesized according to the method described by Duraczynska et al. [10,11]. Briefly, the appropriate amount of functionalized gel-type resin FCN [21] was allow to swell for 30 min in THF. Then the aqueous solution of $RuCl_3 \cdot x\ H_2O$ ($x < 1$) (Aldrich) corresponding to 2 wt% Ru was added to the resin suspension. The whole was gently shaken until the complete discoloration of initially black solution. The resulting black polymer beads were separated by filtration, washed with acetone and dried in air. Subsequently the solid was reduced with excess of methanol solution of $NaBH_4$, washed with water until the wash liquid gave no reaction with $AgNO_3$ solution, and dried in air at ambient conditions.

The infrared spectra were registered in the middle infrared (MIR) 4000–400 cm^{-1} region with the use of Nicolet 380 FTIR spectrometer. The sample (1 mg) was mixed with 200 mg of spectroscopically pure KBr and pressed into disks before the spectra were recorded. Spectra were obtained by co-addition of 64 scans at a resolution of 4 cm^{-1} and processed using the Thermo Scientific OMNIC™ software package.

X-ray photoelectron spectroscopy (XPS) spectra were obtained with a hemispherical analyzer (SES R4000, Gammadata Scienta, pass energy 100 eV). The Al Kα X-ray source (1486.6 eV) was applied to generate core excitation. The system was calibrated according to ISO 15,472:2010. The analysis area of the sample (powder pressed into indium foil) was about 3 mm^2. The electron binding energy scale (BE) was calibrated for maximum of C 1s core excitation at 285.0 eV. The spectra were fitted with the Casa XPS2.3.12 software, using Gaussian/Lorentzian functional (70:30) and Shirley-type background.

Transmission electron microscopic (TEM) studies were performed with FEI Tecnai G^2 transmission electron microscope at 200 kV equipped with EDX and HAADF/STEM detectors.

2.2. Catalytic tests

Hydrogenation experiments were carried out in an agitated batch glass reactor (PARR 5100) at constant pressure of hydrogen (1 bar) and temperature 40 °C. 25 mL of the appropriate solvent or water (in the case of biphasic condition) and 0.2 g of the catalyst were placed in the reactor. Then 25 mL of the reaction mixture containing 300×10^{-5} mole of ketone dissolved in the solvent was added. The whole was vigorously stirred (800 rpm) and the reaction time was set for 6 h. A gas chromatograph (Clarus 500, Perkin Elmer) equipped with Elite-5MS column was used for analyzing the composition of reaction mixture. After catalytic test the samples from both phases (aqueous and organic) were taken and the contents of the individual components were determined by comparison with calibration curves. From the data of GC analysis ketone conversions and selectivities to the desired products were calculated. Catalytic results in the monophasic systems were not affected by an increase of the agitation speed, which pointed to the absence of external mass transport limitations. In biphasic systems, the selected rpm ensured both complete and uniform dispersion of one liquid in the other.

In biphasic solvent system the distribution of all the reagents in both solvent phases was determined by GC method. The known amounts of individual reagents were added into 20 mL biphasic solvent system (1:1 by volume). The whole lot was vigorously mixed with a mechanical stirrer for 45 min. The samples of liquids from both phases were withdrawn immediately after the completion of shaking, and after 5, 15, 30, and 60 min. The concentrations of individual components in both organic and aqueous phases were determined based on calibration curves. The measurement aimed at determination of time required for the biphasic system to reach equilibrium. This served to minimize the error related to quantification of substrate/product concentrations. The experiments have shown that the equilibrium concentrations were established just after stopping the mixing. It has been checked that distribution coefficients measured at the end of each activity test were equal to the values estimated through equilibria determination.

3. Results and discussion

3.1. Characterization of the catalyst

Ru/FCN catalysts of the type used in this study have been thoroughly characterized in our earlier reports [10,11]. For this reason in this work we present only selected data with focus on the nature of Ru/polymer interaction and verification of the nanosize character of Ru species. Fourier transform IR spectra of FCN carrier and 2 wt.%Ru/FCN are presented in Fig. 1. The comparison of both spectra reveals that the most noticeable changes occur within the range characteristic of functional groups of the support, e.g. 1717 cm^{-1}, 1644 cm^{-1}, 1384 cm^{-1}, 670 cm^{-1} and 530 cm^{-1} ascribed to C–O (C=O group), N–H, N–C [10], and O–Ru, and N–Ru [22] vibrations, respectively. Those spectral differences suggest bonding of Ru to polymer matrix via coordination to N– or/and O–containing functional groups.

Table 1
Binding energies (BE) and contributions (%) of individual Ru, N and C peak components.

N 1s		Ru 3p$_{3/2}$		C 1s	
BE (eV)	Share (%)	BE (eV)	Share (%)	BE (eV)	Share (%)
397.5	38.6	458.1	10.4	283.0	26.8
399.8	61.4	461.6	68.3	285.1	51.4
		464.1	21.3	286.9	12.8
				288.3	9.0

High resolution XP spectroscopy was used to characterize surface oxidation states of the catalyst. The XPS spectrum of 2 wt.%Ru/FCN showed three ruthenium states characterized by 3 p$_{3/2}$ energy of 458.1, 461.6 and 464.1 eV, respectively (Table 1). The one with the lowest Ru 3p$_{3/2}$ energy of 458.1 eV may be attributed to carbon or oxygen bound metallic ruthenium. The binding energy of the second, the most abundant, ruthenium state with Ru 3p$_{3/2}$ energy of 461.6 eV corresponds to metallic ruthenium [23–25]. The highest energy state with Ru 3p$_{3/2}$ energy of 464.1 eV suggests the presence of oxidized Ru species such as Ru^{4+} and/or Ru^{3+} [23,24]. The formation of C–Ru and/or C–O–Ru bonds is supported by the presence of carbon state with C 1s energy of 283.0 eV. The other energy states of C 1s component correspond to the presence of C–C and C=O bonds as well as carbon bound to oxygen- or oxygen and nitrogen-containing organic groups. In the N 1s XPS spectrum two nitrogen states appear. The one with binding energy of 397.5 eV is attributed to the formation of N–C–Ru and/or N–Ru bonds. The second nitrogen state (399.8 eV) corresponds to the presence of N–C bonds (in an amine). The results obtained by the XPS technique are consistent with the FT-IR spectra indicating the participation of functional groups of polymer matrix in the bonding of Ru.

High resolution transmission electron micrograph of 2 wt.% Ru/FCN reveals particles of morphology close to spherical, uniformly distributed on the polymer support (Fig. 2). The size of ruthenium particles is within wide range; their diameters do not exceed few nm.

3.2. Solvent effect

The type of solvent may strongly affect both the activity and the

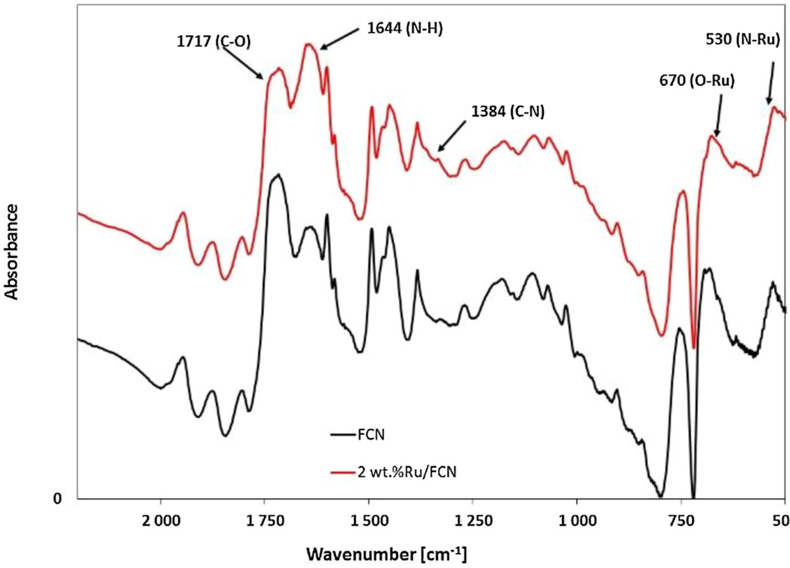


Fig. 1. FT-IR spectra of FCN carrier and 2 wt.% Ru/FCN.

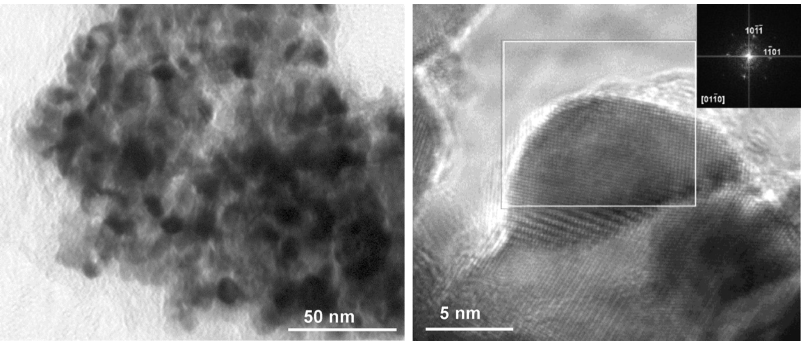


Fig. 2. TEM (left) and HRTEM (right) images of 2 wt.% Ru/FCN and fast Fourier transform (FFT) from the marked area (insert).

Table 2
Solvent effect.

Solvent	ε	ACT Conversion [%]	TOF [h^{-1}]	PhEtol Selectivity [%]	H_2 solubility x_i *10^4	Solubility in H_2O	ACT % org. phase	ACT % aq. phase	PhEtol % org. phase	PhEtol % aq. phase
MeOH	32.7	17	7	69	1.61	Miscible	n.a	n.a	n.a	n.a
MeOH (10%)		24	12	75						
IPA	19.92	13	4	41	2.66	Miscible	n.a	n.a	n.a	n.a
IPA (10%)		23	11	67						
THF	6.15	0	˜ 0	0	2.74	Miscible	n.a	n.a	n.a	n.a
THF (10%)		1	˜ 0	100						
Toluene	2.38	0	˜ 0	0	3.82	0.52 g/L (20 °C)	99	1	89	11
Toluene/H_2O (1:1)	2.38/80.1	29	20	77						
Cyclohexane	2.02	1	˜ 0	100	3.80	Immiscible	96	4	66	34
Cyclohexane/H_2O (1:1)	2.02/80.1	58	32	79						
IO	1.94	2	˜ 0	60	7.96	Immiscible	92	8	48	52
IO/H_2O (4:1)	1.94/80.1	23	11	86						
IO/H_2O (1:1)		61	35	77						

Catalytic conditions: temperature: 40 °C, H_2 pressure:1 bar, reaction time: 6 h. Conversions determined by GC analysis of crude reaction mixtures. TOF calculated from initial hydrogenation rate (below 10% conversion) as moles of converted substrate per mole of Ru per hour.

selectivity of the catalyst as well as determine the mechanism path itself [26,27]. Therefore the search for the proper solvent is of critical importance. The results of our studies devoted to the determination of solvent effect are presented in Table 2. The hydrogenation of unsubstituted acetophenone (ACT) has served as a test reaction. In this case two alternative pathways are observed (Scheme 1). One involves hydrogenation of C═O group to give 1-phenylethanol (PhEtol), the other hydrogenation of aromatic ring of ACT to form cyclohexyl methyl ketone. 1-phenylethanol, the most desired product, found an application as a fragrance or an intermediate in synthesis of various pharmaceuticals. Both products, 1-phenylethanol and cyclohexyl methyl ketone, may be hydrogenated even further to 1-cyclohexylethanol. Hydrogenolysis of 1-phenylethanol and 1-cyclohexylethanol leads to ethylbenzene and ethylcyclohexane, respectively. Due to the possibility of side reactions, achieving high selectivity to 1-phenylethanol is difficult. In our case we observed the formation of all mentioned products in various amounts.

We found that, in general, the 2 wt.%Ru/FCN catalyst exhibits better activity in polar solvents (MeOH and IPA) as compared to apolar solvents (toluene, cyclohexane, isooctane), although a clear relationship regarding the impact of solvent polarity, indicated by the value of its dielectric constant (ε) [28], on the observed conversions, cannot be established. The following order of catalysts activity is observed: toluene ($\varepsilon = 2.38$) = THF ($\varepsilon = 6.15$) ≈ Cyclohexane ($\varepsilon = 2.02$) ≈ IO ($\varepsilon = 1.94$) < IPA ($\varepsilon = 19.92$) < MeOH ($\varepsilon = 32.70$). Surprisingly, no catalytic activity is observed when the hydrogenation reaction is performed in tetrahydrofuran (THF), whose polarity is distinctly higher than that of hydrocarbon solvents. This suggests that, beside polarity, yet another factor, determining the solvent properties, is of importance. It appears, that this factor may be the ability of the solvent molecules to act as hydrogen bond donors. Of the investigated solvents, only MeOH and IPA are protic due to the presence of labile proton bound to oxygen. Toluene, cyclohexane, and isooctane are apolar and aprotic and hence cannot act as H-bond donors. THF, being a polar aprotic solvent, cannot participate in H-bond formation. Comparison of both protic solvents, MeOH and IPA, shows that ACT conversion grows with the solvent polarity and is higher on MeOH. The effect is opposite to that reported for Ni/SiO_2 catalyst by Bertero et al. [18]. The authors argued that the more polar MeOH solvates ACT molecules more efficiently than IPA, thereby hindering the reactant adsorption on the metallic surface. Obviously, in the case of Ru/FCN catalysts it is not the ACT solvation that plays the decisive role. This aspect is addressed in more detail further.

Solvent effect is sometimes related to the variations in hydrogen solubility, as better solubility is expected to afford higher concentration of hydrogen on the catalyst surface [18]. From this point of view, solvents with lower dielectric constant, characterized by higher hydrogen solubility should be preferred. Analysis of the data in Table 2 shows that there is no correlation between the ACT conversion and H_2 solubility in the employed solvents [29]. In particular, the best performance is observed in MeOH, with the lowest H_2 solubility, while only very low activity is displayed in IO, possessing the highest capacity for dissolving hydrogen.

It should be noted, that even in polar solvents the obtained ACT conversions are relatively low, 17% in methanol, and 13% in 2-propanol. The results change dramatically when water is introduced to the reaction mixture. In all instances but THF, much higher conversions are observed. Noteworthy, the addition of water to MeOH, IPA and THF (all miscible with H_2O) is limited by the low solubility of acetophenone in water. The addition of larger amount of water leads to an incomplete dissolution of acetophenone in the reaction medium (visible as tiny, individual drops of the second liquid phase dispersed in the solvent). The largest impact of water is observed with apolar, water-immiscible solvents, such as toluene, cyclohexane and isooctane. The conversions jump from 0% to 29% for toluene, from 1% to 58% for cyclohexane and from 2% to 61% for isooctane upon the addition of water to the appropriate solvent (1:1).

In an attempt to rationalize the experimental data for polar solvents, we propose to consider the impact of solvent not only on ACT substrate [18], but also on the reaction product, 1-phenylethanol. The efficiency of solvation is critically dependent on the protic/aprotic character of the solvent [30]. Thus, polar protic solvents, i.e. MeOH and IPA, are capable of solvating reagents both by dipole-dipole interactions, and by formation of hydrogen bonds. The distinctly higher polarity of MeOH results in stronger solvation ability. If the adsorption of ACT on the catalyst surface were the rate determining step, the solvation effects, hindering ACT interaction with the Ru surface, would be detrimental for the catalyst activity, and a solvent with the lower polarity, i.e. IPA, would be preferred. This is clearly not the case. In contrast, if the reaction rate depended on 1-phenylethanol desorption from the catalyst, the solvation effects should facilitate the removal of the reaction product and enhance the ACT conversion by preventing blockage of the active sites. In that case, the more polar protic solvent would secure a higher catalytic activity. Given the observed dependencies, it is reasonable to assume that the better performance in MeOH, as compared to the less polar IPA, is due to the more efficient solvation and facilitated removal of the reaction product, which makes room for adsorption of ACT molecules. Solvating ability of THF towards the reagents is much lower, because the solvent is not only less polar, but also, as aprotic, not capable of H-bond donation. In view of this, we attribute the lack of activity in THF to the fact that this solvent fails to clean the catalytically active Ru phase from accumulated reaction product. The investigated apolar solvents, toluene, cyclohexane and isooctane, also lack the ability to interact strongly with 1-phenylethanol, hence no meaningful activity is observed when these solvents are used as a reaction medium.

Similar arguments may be employed for explanation of the effect of water addition to the investigated solvents. In MeOH/H_2O and IPA/H_2O systems, addition of a more polar component capable of strong H-bonding renders the solvent even more efficient in solvating the reaction product and accelerating its desorption, which results in an improved activity. The effect is negligible in the case of THF, which shows that 10% of water, forming single phase with the main solvent, is not enough to provide sufficient supply of polar and protic molecules to the catalyst surface and promote desorption of the product in a meaningful way. A different situation occurs with “biphasic” solvent systems (toluene/H_2O, cyclohexane/H_2O and IO/H_2O). It should be noted that in contrast to single solvent case (Fig. 3a) the catalyst remains at the interface between two phases (Fig. 3b) in the static conditions, both before and after the catalytic test. This is understandable, since the hydrophobic part of the polymer support (styrene chain) has affinity to the organic phase and the hydrophilic part (functional groups, to which Ru is bonded) tends towards the aqueous phase.

Thus, it is reasonable to assume that also during the catalytic test the Ru-bearing hydrophilic part would tend to remain in contact with water. In the paragraph describing the phenomena in the polar solvents, it has been pointed out that accumulation of 1-phenylethanol at the catalyst surface has a detrimental effect on catalysis, due to blocking of the active Ru sites, but water acts as an excellent scavenger of adsorbed reaction product and ensures increase of the catalytic activity. Thus, in the case of biphasic systems one should consider solvent-reactant interactions such as the susceptibility of acetophenone and the desired product, 1-phenylethanol, to reside in organic and/or aqueous phases. Of particular importance is the solubility of 1-phenylethanol in aqueous phase, facilitating recovery of active Ru surface. For this reason we have determined the appropriate distribution coefficients and the data are given in Table 2. For IO/H_2O solvent system, where the highest conversion (61%) is observed, 92% of ACT stays in organic phase and 8% in water. But most (52%) of 1-phenylethanol remains in aqueous phase. Regarding cyclohexane/H_2O solvent system (second best conversion of 58%) 96% of ACT resides in cyclohexane and 4% in water. Smaller amount of 1-phenylethanol (34%) stays in water as compared to organic phase (66%). For the system with lowest conversion (29%), i.e. toluene/H_2O, almost all ACT (99%) occupies organic phase, and only 11% of 1-phenylethanol “prefers” water. In view of this, one can notice a clear trend: the higher the affinity of the product to the water phase, the higher the activity. The effect confirms the conclusion on the importance of removal of the reaction product from the Ru catalyst surface. However, when analyzing the data in Table 2, one can notice that, when passing from cyclohexane to isooctane, only a very modest enhancement of activity is observed, despite a considerable increase of organic reagents solubility in water. This suggests that yet another factor may play a role in determining the catalytic performance in the systems involving two immiscible solvents. An important parameter governing the behavior of biphasic liquid systems is the interfacial tension, which influences the degree of dispersion of one phase in the other [31]. The lower is the surface tension between water and the organic liquid, the better the mutual dispersion of both components and the higher the interfacial area. The water/cyclohexane interfacial tension is ca. 49 mN/m [32], while that of water/isooctane system equals 59 mN/m [33]. Therefore, it is expected that, for the same mixing speed, the interface area generated in the case of isooctane will be lower than for cyclohexane. As indicated above, the catalyst resides at the interface, so the development of the contact area between both phases is essential for the efficient catalysis. In view of this, we propose that suppression of the interface area for water/isooctane system, as compared to the cyclohexane/water counterpart, is the reason for the very limited enhancement of the catalytic performance in the former mixture, despite increase of the reagents solubility in water. Noteworthy, the biphasic isooctane/water system for acetophenone hydrogenation (50 °C, 1 bar H_2) has also been employed by Tundo et al. [9]. Using a Pt/C catalyst modified with cynchonidine, the authors reported conversions in the range 25–78%, depending on the amount of modifier.

The above reasoning accounts for the effect of water addition on catalytic activity, but there are other features that make water a particularly advantageous solvent, due to the possible impact on Ru catalyst selectivity. As pointed out in the review by Michel and Gallezot [34] one should consider different mechanisms occurring at water/

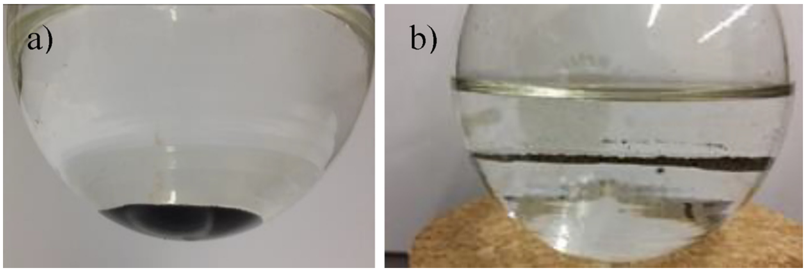


Fig. 3. The location of 2 wt.% Ru/FCN in a) IO b) IO/H_2O solvent system.

ruthenium interface. First, DFT calculations demonstrated that formation of hydrogen bonds between the C═O groups adsorbed on the Ru surface and adjacent co-adsorbed water molecules lowers the activation energy of the first hydrogenation step, leading in consequence to enhanced hydrogenation rate [35]. Second, the dissociation of water increases the surface concentration of H atoms, which contributes to the hydrogenation of carbonyl group [36]. In addition, Li. et al. [37] showed that oxidized ruthenium species, whose presence at the surface of the catalyst used in this work has been revealed by XPS, facilitate the process of water splitting. Moreover, the existing long-range electron polarization of water film [38] on the catalyst surface most likely influences the orientation of the substrate leading to the preferential reduction of C═O group. The addition of water improves the selectivity to the desired product, 1-phenylethanol, as well (Table 2). It may be speculated that it affects the adsorption mode of ACT on the catalyst surface in the way which facilitates the hydrogenation of C═O group, while limiting to some extent the access to aromatic ring.

3.3. Substituent effect

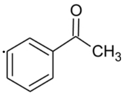
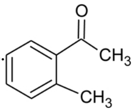
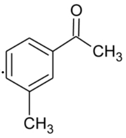
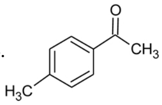
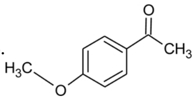
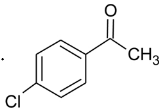
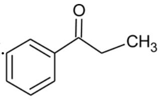
The influence of the functional groups on the catalytic activity of the studied catalyst was investigated for seven ACT derivatives (Table 3).

When comparing acetophenone derivatives with substituents at para position the impact of substituent type, i.e. electron donating vs. electron withdrawing character, can easily be observed. The electron donating groups ($-CH_3$ and $-OCH_3$) (entries 4 and 5, respectively) tend to increase the reaction rate and after 6 h of catalytic test 81% and 99% conversions were observed for 4′-methylacetophenone and 4′-methoxyacetophenone, respectively. The result agrees with the observation of Zaccheria et al. [4], who observed acceleration of hydrogenation upon insertion of electron donating substituents. On the other hand an electron withdrawing group, like –Cl– (entry 6), slows down the process and after the same period of time only 29% conversion is observed. It should also be mentioned that for 4′-chloroacetophenone no products indicating hydrodechlorination process could be detected [2]. The observed trends may be assigned to changes in the polarization of C═O group, which increases upon action of an electron donating substituent, or decreases in the presence of an electron withdrawing group.

When comparing the results for methylacetophenones possessing the $-CH_3$ substituent (electron donating group) in ortho, meta or para position (entries 2, 3, and 4), one can notice that the highest conversion (81%), pointing to a promoting effect, is achieved only in the case of 4′-methylacetophenone, for which the methyl group is located in the para position. For both the 2′-methylacetophenone (ortho) and the 3′-methylacetophenone (meta), the obtained conversions are similar to that of the unsubstituted ACT, i.e. 66% and 62%, respectively, despite the presence of the same electron donating group. When looking for an explanation of this phenomenon, one should consider that a methyl group localized closer to the carbonyl bond constitutes an obvious steric hindrance which adversely affects the reaction rate. Apparently, the resulting inhibiting effect obliterates the promoting influence of electron donation, leaving the activity essentially at the same level.

No steric hindrance is noticed in the case of ethyl phenyl ketone (entry 7) with no functional group on phenyl ring and an extra CH_2 group in the aliphatic chain. In this case the obtained conversion (68%) is similar to that of parent acetophenone (61%).

Table 3
Hydrogenation of acetophenone and its derivatives.

Ketone	Conversion [%]	TOF [h^{-1}]	Selectivity to desired product [%]
1. 	61	35	77
2. 	66	38	87
3. 	62	36	87
4. 	81	75	76
5. 	99	150	72
6. 	29	20	85
7. 	68	40	64

Catalytic conditions: temperature: 40 °C, H2 pressure: 1 bar, reaction time: 6 h, solvent system: IO/H2O (1:1). Conversions determined by GC analysis of crude reaction mixtures. TOF calculated from initial hydrogenation rate (below 10% conversion) as moles of converted substrate per mole of Ru per hour.

4. Conclusions

The product–solvent interactions are of key importance for understanding the performance of Ru/FCN catalyst in hydrogenation of acetophenone. It is proposed that the solvent-induced removal of the reaction product (1-phenylethanol) from the Ru catalyst surface, to make room for the adsorption of substrate molecules, is determining the rate of the catalytic reaction. Solvating efficiency towards 1-phenylethanol increases with the solvent's ability to form dipole-dipole interactions and hydrogen bonds, therefore the solvents of choice should display possibly high polarity combined with protic character. For this reason catalytic activity is observed only in MeOH and IPA, which are both polar and protic, while the use of polar but aprotic (THF) and apolar aprotic solvents (toluene, isooctane and cyclohexane) renders the system inactive. The effect of 10% admixture of water (highly polar component capable of strong H-bonding) is interpreted in similar terms. Thus, addition of H_2O enhances solvating ability of MeOH and IPA, which results in an improved activity, while its effect on poorly solvating THF is insufficient to promote desorption of the product, so that no meaningful activity is observed. The profound impact of water addition to apolar solvents (toluene, isooctane and cyclohexane), which form biphasic systems with H_2O, is related to the hydrophilic/hydrophobic character of Ru/FCN catalyst. Its hydrophilic part (functional groups, to which Ru is bonded) tends towards the aqueous phase and away from the apolar solvent, therefore the surface of Ru may easily come in contact with water. The latter acts as an excellent scavenger of adsorbed reaction product and ensures increase of the catalytic activity.

The effect of substituents depends on their electron-donating/withdrawing character, and/or on their position on the aromatic ring. Electron donating groups tend to increase the reaction rate, while the electron withdrawing group slows down the process. Steric effect for hydrogenation of methylacetophenone isomers, manifested by the highest conversion obtained for the CH_3 group attached at ortho position, is observed.

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