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Effect of solvent on the hydrogenation of 4-phenyl-2-butanone over Pt based catalysts

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ABSTRACT

The hydrogenation of 4-phenyl-2-butanone over Pt/TiO₂ and Pt/SiO₂ catalysts has been performed in a range of solvents and it has been observed that the solvent impacted on the selectivity of ketone and aromatic ring hydrogenation as well as the overall TOF of the titania catalyst with no solvent effect on selectivity observed using the silica supported catalyst where ring hydrogenation was favored. For the titania catalyst, alkanes were found to favor ring hydrogenation whereas aromatics and alcohols led to carbonyl hydrogenation. A two-site catalyst model is proposed whereby the aromatic ring hydrogenation occurs over the metal sites while carbonyl hydrogenation is thought to occur predominantly at interfacial sites, with oxygen vacancies in the titania support activating the carbonyl. The effect of the solvent on the hydrogenation reaction over the titania catalyst was related to competition for the active sites between solvent and 4-phenyl-2-butanone.

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1. Introduction

Hydrogenation reactions are commonly used in the pharmaceutical, fine chemicals and agrochemicals industries for the preparation of a wide range of organic molecules [1]. It is recognised that several different factors can affect the rate and selectivity of a hydrogenation reaction, such as the catalyst used (metal and support) [2], the addition of promoters [3], the choice of metal precursor [4] as well as the solvent used. Even with the number of studies investigating the role of solvents in liquid phase hydrogenations, their effect on the rate and importantly the selectivity of a reaction are at present, difficult to predict for varied reagent/catalyst systems.

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The effect of the solvent on the rate and selectivity of molecules containing various functional groups such as amides, aromatic rings and carboxylic acids [5–8], have been reported; however, the most widely investigated compounds are α , β unsaturated carbonyls [2,9–13] with formation of unsaturated alcohols desired for use in the manufacture of drugs and fragrances. The hydrogenation of unsaturated and aromatic ketones are not as widely studied as that of α , β unsaturated aldehydes with studies predominantly on conjugated systems such as cyclohexenone [14], ketoisophorone [15], benzalacetone [16–22], benzalacetophenone [23,24], benzophenone [23,25,26] with the most widely studied being, acetophenone [23,27–32].

For the hydrogenation of acetophenone, there have been studies using a number of different metals including Pt, Pd, Rh and Ni with the focus on the rate of hydrogenation of the carbonyl group relative to ring hydrogenation [33]. In cases where the selectivity was investigated it was found that hydrogenation of the ketone to phenylethanol tended to be more favored than ring hydrogenation, both in the gas phase [34–36] and liquid phase [37]. However, with the use of supports such as TiO₂ [36], and promoters such as Cr [34] the selectivity to phenylethanol could be increased to as high as 95% [35]. It is proposed that the increased hydrogenation of the carbonyl bond over titania catalysts is from reaction occurring at

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the metal support interface where the oxygen in the carbonyl interacts with oxygen vacancies in the support to weaken the C=O bond thereby increasing the rate of reaction [38,39].

Interestingly, a complete switch in selectivity with solvent has been reported for the hydrogenation of acetophenone over Pd carbon nanofibre catalysts for reactions performed in water and cyclohexane [29]. In water, over the Pd catalyst, ring hydrogenation products cyclohexylethanone and cyclohexylethanol were the major products with carbonyl group hydrogenation to phenylethanol and further hydrogenolysis of the alcohol to ethylbenzene being the other products identified. High selectivity to aromatic ring hydrogenation products was also observed over the Rh catalyst for reaction in water (95.4% compared with 65% for Pd). However, when the hydrogenation of acetophenone was carried out in cyclohexane under the same reaction conditions, 100% selectivity to C=O hydrogenation (and hydrogenolysis products) was reported over Pd/CNF. High selectivity to ring hydrogenation in water was attributed to favorable orientation of the aromatic ring on the metal surface brought about by solvation of the polar functional group and orientation of the ring due to the local structure of water in the proximity of the surface [29].

An effect of solvent on selectivity has also been reported for the hydrogenation of ketoisophorone, investigated by von Arx et al., where only the rate of reaction over Pt/Al₂O₃ was found to be influenced by solvent while for Pd/Al₂O₃ the solvent also affected the selectivity [15]. Reactions were carried out in *n*-hexane, tetrahydrofuran, methanol, acetic acid and methanol/acetic acid mixtures. For the Pd/Al₂O₃ catalyst, the polarity of the solvent was found to have a dramatic influence on the reaction rate with reactions in *n*-hexane and tetrahydrofuran giving the lowest rates as well as lower selectivity to the unsaturated alcohol while the highest rates and selectivities (90% to the unsaturated alcohol) were observed in mixtures of methanol and acetic acid. The increased rate of carbonyl hydrogenation was reported to be due to protonation of the carbonyl group by the acid, promoting its hydrogenation over that of the alkene functionality [15]. The Pt/Al₂O₃ catalyst, however, showed little change in selectivity with solvent polarity with C=C and C=O hydrogenation to levodione and 4-hydroxyisophorone respectively occurring in a 1:1 ratio. Ketoisophorone is a cyclic ketone; however, application of the same conditions to linear ketones, such as 5-hexene-2-one, found that only saturated ketones were obtained.

For compounds where the C=O and the aromatic ring are not adjacent to each other, the selectivity could be expected to differ significantly from that of conjugated compounds. Conjugation can influence the strength and mode of adsorption of a reactant, activating functionalities for hydrogenation. Whether the C=O, aliphatic ketone part of the molecule or the aromatic ring is preferentially adsorbed will depend on factors such as the strength of adsorption of both functionalities relative to that of the products and the interaction of these parts of the molecule with the solvent. The choice of catalyst (metal and support) as well as the solvent used for reaction will also have a strong influence on the adsorption strength and geometry making the choice of solvent/catalyst for a particular selective transformation difficult to predict. There are fewer studies reporting the hydrogenation of molecules where the aromatic and carbonyl functionalities are separated/distal within the molecule such as phenylacetone [40,41] and a range of aromatic ketones including 4-phenyl-2-butanone [42].

The role of solvent was probed in the hydrogenation of phenylacetone by Rylander et al. over Rh/C and Rh/Al₂O₃ catalysts [41]. Reactions were carried out in methanol, ethanol, 2-propanol, tert-butanol, dioxane, acetone, ethyl acetate, dimethylformamide, dimethylsulfoxide and cyclohexane and while ring hydrogenation was always the major product, for the alcohols, the extent of ring hydrogenation increased while C=O hydrogenation decreased on

going from methanol to tert-butanol. No clear trend in selectivity with the property of the solvents was observed in this study. Hydrogenation of phenylacetone was also carried out in tert-butanol over Pt, Ru, Ir, Os, Rh and Pd supported on carbon [41]. Low reaction rates were observed over the Pd catalyst with the fastest rates observed over the Rh catalyst with initial high selectivity for cyclohexylacetone with C=O hydrogenation and hydrogenolysis to minor products phenylpropane and cyclohexylpropane also observed. Over Pt, Ru, Os and Ir, hydrogenation of the C=O group resulted in the major product. Some ring hydrogenation was observed over Pt (selectivity of 15% ring hydrogenation to 85% C=O hydrogenation at 15% conversion) and Ru while only phenylisopropanol was observed over Os and Ir with no further hydrogenation found to occur.

In this study, for the first time, the effect of solvent on the liquid phase hydrogenation of aromatic ketone 4-phenyl-2-butanone, (PBN), over Pt/TiO₂ and Pt/SiO₂ catalysts, to 4-phenyl-2-butanol, (PBL), 4-cyclohexyl-2-butanone, (CBN), and 4-cyclohexyl-2-butanol, (CBL), Scheme 1 is investigated. The role of the solvent on the rate of hydrogenation of this molecule containing both a ketone functionality and an aromatic ring is reported. In addition, a switch in the selectivity between hydrogenation of the aromatic ring and the carbonyl with class of solvent has been found for platinum supported on titania catalyst.

2. Experimental

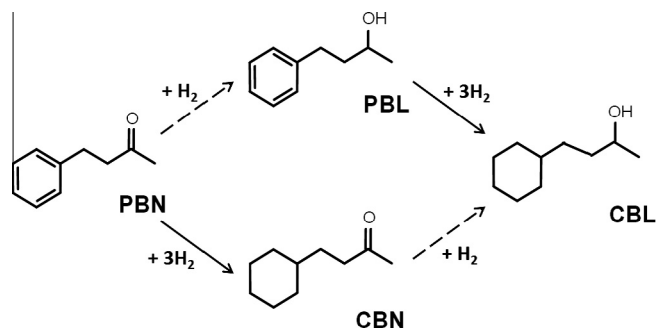
2.1. Materials

Hydrogen was supplied by BOC and was of research grade. 4-Phenyl-2-butanone (98%) and 4-phenyl-2-butanol (97%) were acquired from Sigma–Aldrich. Unless otherwise stated, all the solvents used were obtained from Sigma–Aldrich and were of HPLC grade. The exceptions were: 2-propanol (Fluka \leq 99.9%), trifluoroethanol (Fluorochem 99%), dichloroethane (Riedel De Haën 99%) and *p*-xylene (Fluka \geq 98%). When required, toluene, *n*-hexane and all alcohol solvents were dried over calcium hydride overnight and distilled. The water content of the solvents was measured using Karl-Fischer analysis with a Cou-Lo aqua-max moisture analyser.

The reaction intermediates 4-cyclohexyl-2-butanol and 4-cyclohexyl-2-butanone were prepared in house. 4-Cyclohexyl-2-butanol was synthesized by the hydrogenation of 4-phenyl-2-butanone in a Parr reactor using 4% Pt/TiO₂ (pre-reduced at 60 °C for 1 h, 1 bar H₂) at 5 bar H₂, 70 °C with 1400 rpm stirrer speed in *n*-hexane for 12 h. 4-Cyclohexyl-2-butanone was prepared by oxidation (6 bar air in a Parr reactor) of the 4-cyclohexyl-2-butanol using 4% Pt/TiO₂ at 100 °C for 28 h. In each case, at the end of the reaction, the reaction mixture was filtered and the solvent removed under vacuum giving the desired product at 99% purity determined by ¹H NMR and GC. The intermediates were used without any further purification.

2.2. Catalyst preparation

The 4% Pt/TiO₂ catalyst was supplied by Johnson Matthey and was prepared by incipient wetness from Pt(NO₃)₄ as the precursor with titania as the support (P25, Degussa). The catalyst was dried for 12 h at 120 °C and then calcined at 500 °C for 6 h. The catalyst was ground using a mortar and pestle and sieved to \leq 45 μ m for all reactions with the exception of the mass transfer studies where the catalyst was sieved into various fractions (300–212, 212–150, 150–106 and $<$ 45 μ m). The 5% Pt/SiO₂ catalyst was supplied by Johnson Matthey. This catalyst was also ground using a mortar and pestle and sieved to \leq 45 μ m for all reactions.



Scheme 1. Hydrogenation pathway of 4-phenyl-2-butanone (PBN) to 4-phenyl-2-butanol (PBL), 4-cyclohexyl-2-butanone (CBN) and 4-cyclohexyl-2-butanol (CBL). Solid arrows indicate aromatic ring hydrogenation and dashed arrows indicate C=O group hydrogenation.

2.3. Catalyst characterization

X-ray diffraction measurements were performed using Cu K_{α} radiation (1.5405 Å) on a PANalytical X'PERT PRO MPD diffractometer in reflection geometry using a NaI scintillation counter, a curved graphite crystal monochromator and a nickel filter. The scattered intensities were collected from 5° to 80° (2θ) by scanning at 0.017° (2θ) steps with a counting time of 0.5 s at each step.

The surface area, pore volume and average pore diameter were measured by N_2 adsorption–desorption isotherms at 77 K using Micromeritics ASAP 2010. The pore size was calculated in the adsorption branch of the isotherms using Barrett–Joyner–Helend a (BJH) method and the surface area was calculated using the Brunauer–Emmett–Teller (BET) method.

Scanning Transmission Electron Microscopy (STEM) images were recorded on a 200 kV JEOL JEM-2010F instrument using a high-angle annular dark-field (HAADF) detector and an electron beam probe of 0.5 nm. The particle size distribution was obtained by counting up to 1000 particles and considering a cubooctaedral morphology.

2.4. Typical reaction procedure

All of the reactions were performed in a Hazard Evaluation Laboratory (HEL) autoclave pressure reactor with a gas inducing impeller and baffles. The reactor was heated by an internal heating coil and the temperature was monitored by a thermocouple in the solution. Hydrogen was added by a mass flow controller throughout the reaction, to maintain a constant pressure.

Typically, the reactions were undertaken using the following procedure. The catalyst (0.1 g) and solvent (30 ml) were added to the HEL reactor. The reactor was then sealed and purged with hydrogen before heating to 60 °C while stirring the mixture at 800 rpm. Upon reaching 60 °C the reactor was held at this temperature and the mixture was stirred at 1000 rpm for 1 h to reduce the catalyst. Following the reduction of the catalyst, a solution of 4-phenyl-2-butanone (13.5 mmoles) in fresh solvent (20 ml) was added to the reactor containing the slurry of the pre-reduced catalyst. The HEL reactor was sealed and purged with hydrogen and the reactor was then heated to the reaction temperature, during which the mixture was stirred at 800 rpm. When the required temperature was reached (typically 70 °C) the stirring was stopped and the reactor was pressurised. The reaction started immediately upon reaching the required pressure (typically 5 bar) by starting the stirrer at 1400 rpm. The reactions were typically performed for 2 h, during which time regular reaction samples of about 2 ml were taken for analysis by GC.

The samples for GC were passed through a syringe filter to remove the catalyst before being diluted with solvent in a 1:10

ratio. The samples were analyzed using a Perkin–Elmer Clarus 500 GC equipped with a FID with an Agilent HP-5 column.

The composition of the reaction mixture was determined by comparison of the GC peak areas with those of known concentration and the percent of each component quoted relative to the total molar concentration.

The rates were calculated by fitting a polynomial function to the concentration change with time and taking the differential of the curve at $t = 0$. Unless otherwise stated, the selectivities are associated with the selectivity to 4-cyclohexyl-2-butanone at 15% conversion. In all cases, the selectivities were determined by:

$$\%S = \frac{\text{moles of product A}}{\text{sum of moles of all products}} \times 100$$

3. Results

3.1. Catalyst characterisation

The BET surface area of the 4% Pt/TiO₂ (P25) catalyst was 56 m² g⁻¹ compared with 58 m² g⁻¹ for the support with pore sizes of 2.2 and 2.5 nm, respectively. XRD analysis of the support shows an anatase to rutile ratio of 3:1, which remains constant after catalyst preparation. Pt peaks could not be observed in the XRD pattern obtained (Fig. S1), which suggests that the Pt particles are very small. TEM analysis showed a metal particle size of 2.2 nm and a dispersion of 33% (Fig. S2).

The BET surface area of the Pt/SiO₂ catalyst was 294 m² g⁻¹ and XRD analysis (Fig. S3) of the Pt peaks by the Scherrer equation gave a particle size of 6.9 nm while particle diameter of 3.0 nm obtained from the TEM with a dispersion of 26% (Fig. S4).

3.2. Mass transfer

To ensure that the rates of reaction obtained were comparable, and under kinetic control rather than limited by transport of a reagent, a mass transfer study of 4-phenyl-2-butanone hydrogenation was performed in *n*-hexane, chosen because of its high rate of reaction.

The stirrer speed was varied between 300 and 1400 rpm (Fig. S5) and, although, the initial rate increased up to 800 rpm, thereafter, no further increase was observed showing that at 1400 rpm, the stirrer speed used herein, the rate is not limited by transport of gas into the liquid phase. A linear variation in the initial rate of reaction with mass of catalyst (proportional to the external surface area of the catalyst) over the range 20–140 mg, was observed (Fig. S6) showing that external liquid to solid mass transfer of neither the gas nor liquid phase reagent is a limiting factor. An Arrhenius plot was constructed between 5 °C and 80 °C (Fig. S7) from which was calculated an apparent activation energy of 40.4 kJ mol⁻¹ which although near the boundary of possible diffusional limitation, when considered along with the small particle size used it is concluded that the reaction is not under diffusion control and the observed rate is dominated by kinetic control. All experiments were carried out with a particle size fraction of <45 μm, to maximise the external surface area of the catalyst and minimise the diffusion path of the reagents in the catalyst particle. As the particles break up under stirring, the effect of particle size could not be tested. Analysis of the catalyst particle size after stirring at 1400 rpm, showed a size of <45 μm, irrespective of the initial particle size. Furthermore, no reaction was observed in the absence of H₂ (Fig. S8) and the reaction was found to be apparent first order in hydrogen (Fig. S9) and apparent zero order in 4-phenyl-2-butanone under the concentrations used (Fig. S10).

3.3. Kinetic data

Fig. 1 shows the rate of conversion of 4-phenyl-2-butanone for a selection of the solvents tested with rates of reaction ranging from 0.0026 mol dm⁻³ min⁻¹ for *n*-hexane (and 0.0027 mol dm⁻³ min⁻¹ for 2-propanol) to 0.0007 mol dm⁻³ min⁻¹ in toluene. The similarity of the rates of reaction in *n*-hexane and 2-propanol clearly show that the polarity of the solvent alone does not control the outcome of the reaction. As shown in Fig. 1, the alkane solvent gave a similar rate to that observed in the secondary alcohol studied. In contrast, the reaction in the primary alcohol was found to be slower than that in the secondary alcohol and lower rates still were found on using the aromatic solvent with the exception of tert-butyl toluene with the ether giving the lowest rate of those shown here.

Similarly to the work reported by Bertero et al. [27,28] the rate of reaction was not found to be controlled by combinations of physical properties of the solvents, the Kamlet–Taft parameters (hydrogen bonding donation (α) and accepting ability (β) or polarisability (π^*) or Catalan parameters (SA-H, SA-B, SPP) Figs. S11 and S12 [43–60]. Importantly, H₂ solubility, viscosity and density also did not show any significant correlation with the rates observed, Fig. S13, [61–63] nor did the dielectric constant (ϵ) or polarisability ($E_T(30)$, E_T^N), Fig. S14. As with the initial rates of reaction, the selectivity to 4-cyclohexyl-2-butanone was not found to be dependent on the physical parameters of the solvents.

In all solvents tested, 4-phenyl-2-butanone, 4-cyclohexyl-2-butanone and 4-cyclohexyl-2-butanol were formed in differing amounts. Fig. 2 shows reaction profiles for reactions at 5 bar in *n*-hexane and 2-propanol where comparable rates but different selectivities were observed. In *n*-hexane, 4-cyclohexyl-2-butanone was the main product formed whereas in 2-propanol 4-phenyl-2-butanol was predominantly observed. At higher pressures (12 bar), the reaction proceeded to completion with the fully hydrogenated product 4-cyclohexyl-2-butanol formed in both solvents. This variation in selectivity, as well as rate, with solvent was not observed for reactions over a 4% Pt/SiO₂ catalyst where the major product in all solvents tested (except toluene) was found to be 4-cyclohexyl-2-butanone (Fig. S15 showing initial rate and Fig. S16 showing selectivity for Pt/SiO₂ reactions in a range of solvents). In the case of toluene, a very slow reaction was observed reaching only 3% conversion after 2 h of reaction with 70% selectivity to 4-phenyl-2-butanol.

The kinetic profiles for each of the solvents tested are presented in the supplementary information, Figs. S17–S36 for Pt/TiO₂ (P25), and this information is summarized, hereafter, to provide comparisons of the initial rate and selectivity as a function of the solvent

type depending on their chemical structure, alkanes and chloroalkanes, aromatics, primary and secondary alcohols and ethers.

3.3.1. Alkanes

A range of alkanes of different chain length both linear and cyclic were tested including *n*-hexane, cyclohexane, *n*-decane and 1,2-dichloroethane and the initial rates and selectivities are summarised in Figs. 3 and 4, respectively.

The reactions in all the standard alkanes studied led to similar initial rates of reaction, ranging from 0.0024 mol dm⁻³ min⁻¹ in cyclohexane to 0.0028 mol dm⁻³ min⁻¹ in decane. In comparison, dichloroethane was found to give a much slower reaction, at 0.0018 mol dm⁻³ min⁻¹, than found for the non-halogenated alkanes. 4-Cyclohexyl-2-butanone was the major product formed in all the alkanes studied; however, the exact proportions of each of the products did vary between solvents, with selectivity to this product found to be 67% in *n*-hexane which increased to 81% in *n*-decane. The reaction carried out in dichloroethane resulted in the greatest amount of the fully hydrogenation product 4-cyclohexyl-2-butanol but 4-cyclohexyl-2-butanone was still the major product in this solvent.

In the case of the alkane solvents, the high selectivity to 4-cyclohexyl-2-butanone is thought to be the result of the strong adsorption of the aromatic ring in the molecule on the platinum compared with the weaker adsorption of the alkane solvent. It should be noted that hydrogenation of the aromatic ring was also the preferred reaction pathway over a Pt/SiO₂ catalyst which did not show significant solvent variation in terms of selectivity. Furthermore, a comparison of the hydrogenation of the reaction intermediates 4-phenyl-2-butanol and 4-cyclohexyl-2-butanone in *n*-hexane showed that aromatic ring hydrogenation routes are faster than carbonyl hydrogenation in agreement with the proposal that the aromatic ring adsorption is favored in alkanes (Fig. 5).

3.3.2. Aromatics

In aromatic solvents, the rate of reaction and selectivity to 4-cyclohexyl-2-butanone were found to vary significantly, Figs. 6 and 7 respectively. A high reaction rate was observed in tert-butyl toluene which was comparable to the rate observed in alkanes, 0.0024 mol dm⁻³ min⁻¹ compared with 0.0026 mol dm⁻³ min⁻¹ in *n*-hexane. Again, as found for the alkane solvents the selectivity to 4-cyclohexyl-2-butanone was high in tert-butyl toluene. In contrast, however, the rate of reaction and selectivity to 4-cyclohexyl-2-butanone in toluene and *p*-xylene were both low

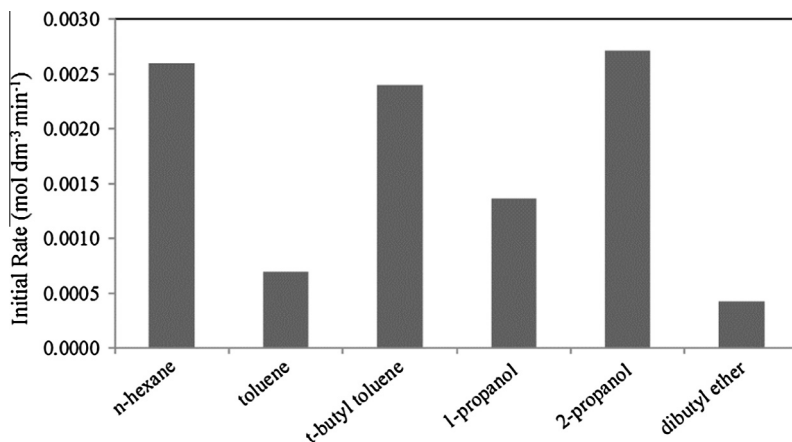


Fig. 1. Initial rate of hydrogenation of 4-phenyl-2-butanone to products over Pt/TiO₂ in *n*-hexane, toluene, tert-butyl toluene, 1-propanol, 2-propanol and dibutyl ether. Using 0.1 g 4% Pt/TiO₂, 13.5 mmol 4-phenyl-2-butanone, 5 bar H₂, 70 °C and 50 ml of the respective solvent.

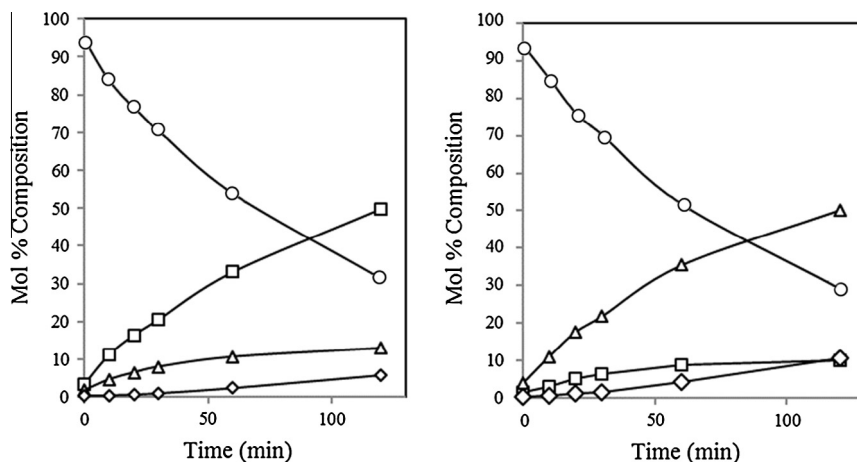


Fig. 2. Mol% composition of the reaction mixture as a function of reaction time for the hydrogenation of 4-phenyl-2-butanone in 2-propanol (left) and *n*-hexane (right): 0.1 g 4% Pt/TiO₂, 13.5 mmoles 4-phenyl-2-butanone, 5 bar H₂, 70 °C and 50 ml of the respective solvent. (○) 4-phenyl-2-butanone; (□) 4-phenyl-2-butanol; (Δ) 4-cyclohexyl-2-butanone and (◇) 4-cyclohexyl-2-butanol.

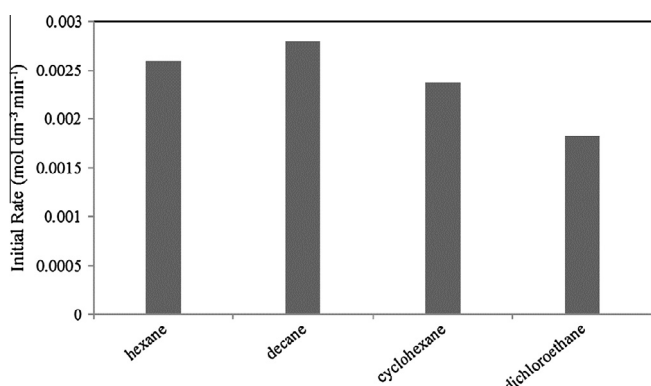


Fig. 3. Initial reaction rates for the hydrogenation of 4-phenyl-2-butanone in alkane solvents. Reactions performed at 70 °C, 5 bar H₂, with stirring at 1400 rpm, 0.1 g 4% Pt/TiO₂ and 13.5 mmoles 4-phenyl-2-butanone in 50 ml of the respective solvent.

at 0.0007 mol dm⁻³ min⁻¹ and 0.0005 mol dm⁻³ min⁻¹ and 28.6% and 29.3%, respectively.

3.3.3. Alcohols

Reactions in a range of primary and secondary alcohol solvents were also compared. Fig. 8 shows that, in general, the rate of reaction was significantly faster in the secondary alcohols, with rates

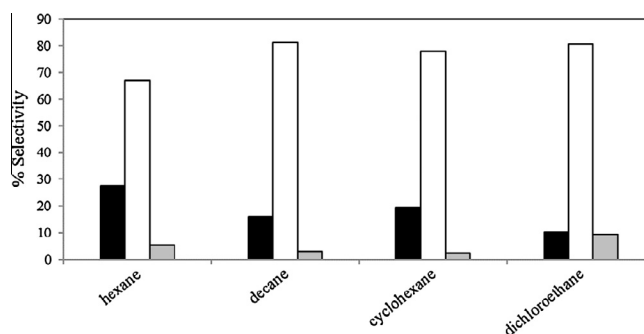


Fig. 4. %Selectivity to 4-phenyl-2-butanol (black), 4-cyclohexyl-2-butanone (white) and 4-cyclohexyl-2-butanol (grey) from the hydrogenation of 4-phenyl-2-butanone in alkane solvents calculated at 15% conversion. Reactions performed at 70 °C, 5 bar H₂, with stirring at 1400 rpm, 0.1 g 4% Pt/TiO₂ and 13.5 mmoles 4-phenyl-2-butanone in 50 ml of the respective solvent.

between 0.0003 mol dm⁻³ min⁻¹ for 2-octanol and 0.0035 mol dm⁻³ min⁻¹ for 2-pentanol, compared with primary alcohols, where the rates were found to be between 0.0002 for 1-octanol and 0.0016 mol dm⁻³ min⁻¹ for 1-pentanol. Similar rates were found for the alkanes and the secondary alcohols. The exceptions to this trend were 1- and 2-octanol where the rates were similar and significantly slower than all other alcohols tested. Reactions were also performed in water but the rates were found

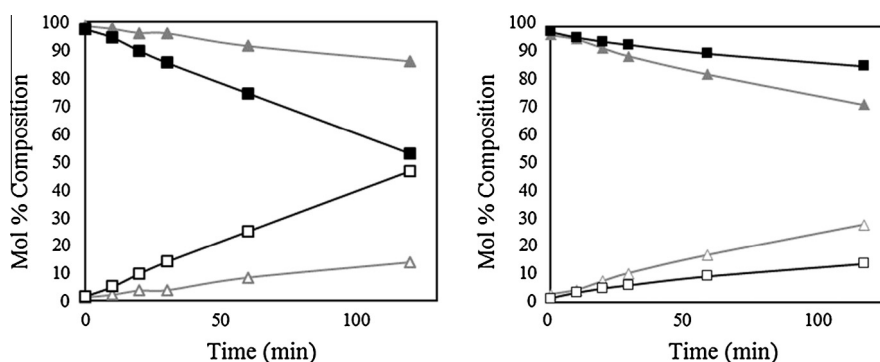


Fig. 5. Mol% composition as a function of reaction time for the hydrogenation of 4-phenyl-2-butanol (filled squares) in *n*-hexane (left) and 2-propanol (right) to 4-cyclohexyl-2-butanol (open squares), ring hydrogenation, and 4-cyclohexyl-2-butanone (filled triangles) to 4-cyclohexyl-2-butanol (open triangles), C=O group hydrogenation: 0.1 g 4% Pt/TiO₂, 70 °C, 5 bar H₂, 13.5 mmoles 4-phenyl-2-butanone.

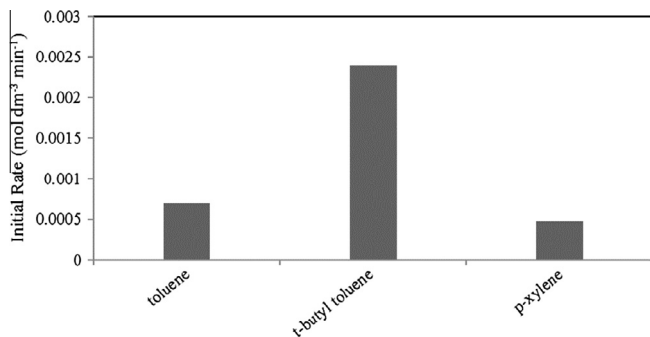


Fig. 6. Initial reaction rates for the hydrogenation of 4-phenyl-2-butanone in aromatic solvents. Reactions performed at 70 °C, 5 bar H₂, with stirring at 1400 rpm, 0.1 g 4% Pt/TiO₂ and 13.5 mmoles 4-phenyl-2-butanone in 50 ml of the respective solvent.

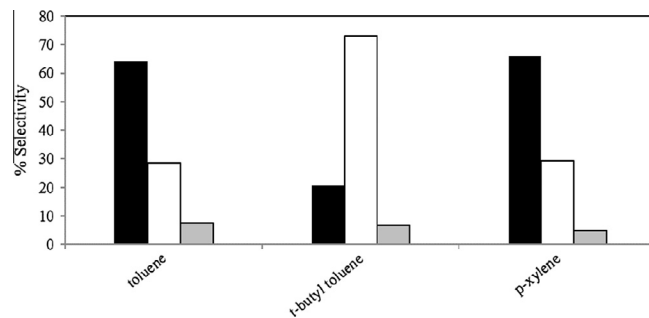


Fig. 7. %Selectivity to 4-phenyl-2-butanol (black), 4-cyclohexyl-2-butanone (white) and 4-cyclohexyl-2-butanol (grey) from the hydrogenation of 4-phenyl-2-butanone in aromatic solvents calculated at 15% conversion. Reactions performed at 70 °C, 5 bar H₂, with stirring at 1400 rpm, 0.1 g 4% Pt/TiO₂ and 13.5 mmoles 4-phenyl-2-butanone in 50 ml of the respective solvent.

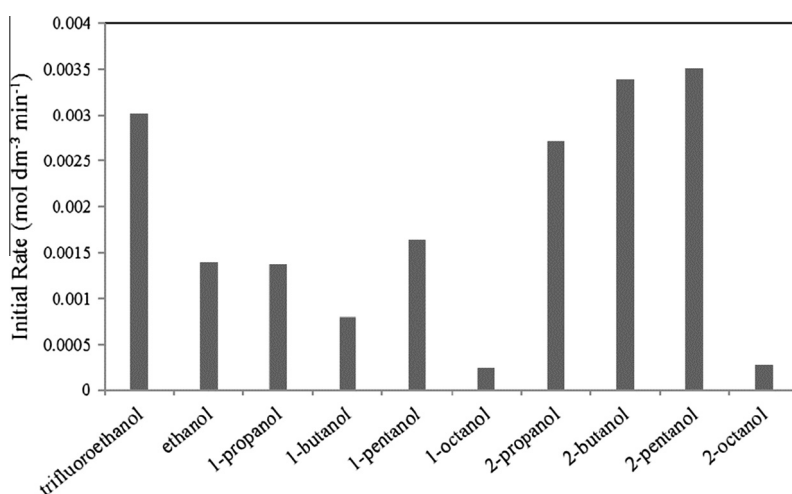


Fig. 8. Initial reaction rates for the hydrogenation of 4-phenyl-2-butanone in various dried alcohols. Reactions performed at 70 °C, 5 bar H₂, with stirring at 1400 rpm, 0.1 g 4% Pt/TiO₂ and 13.5 mmoles 4-phenyl-2-butanone.

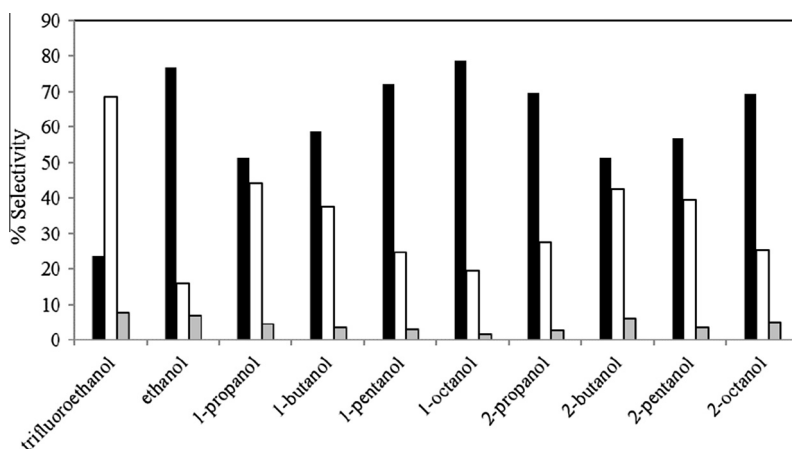


Fig. 9. %Selectivity to 4-phenyl-2-butanol (black), 4-cyclohexyl-2-butanone (white) and 4-cyclohexyl-2-butanol (grey) from the hydrogenation of 4-phenyl-2-butanone in dried alcohol solvents calculated at 15% conversion. Reactions performed at 70 °C, 5 bar H₂, with stirring at 1400 rpm, 0.1 g 4% Pt/TiO₂ and 13.5 mmoles 4-phenyl-2-butanone in 50 ml of the respective solvent.

to be very slow and the mixture was biphasic at all points in the reaction, therefore, no further reactions were performed in water.

In terms of selectivity, unlike the reactions carried out in alkanes, the alcohol solvents all showed a low selectivity to

4-cyclohexyl-2-butanone with 4-phenyl-2-butanol formed as the major product (Fig. 9). In addition, as the chain length of the primary alcohols increased from C3 to C8, an increase in the amount of 4-phenyl-2-butanol compared with 4-cyclohexyl-2-butanone

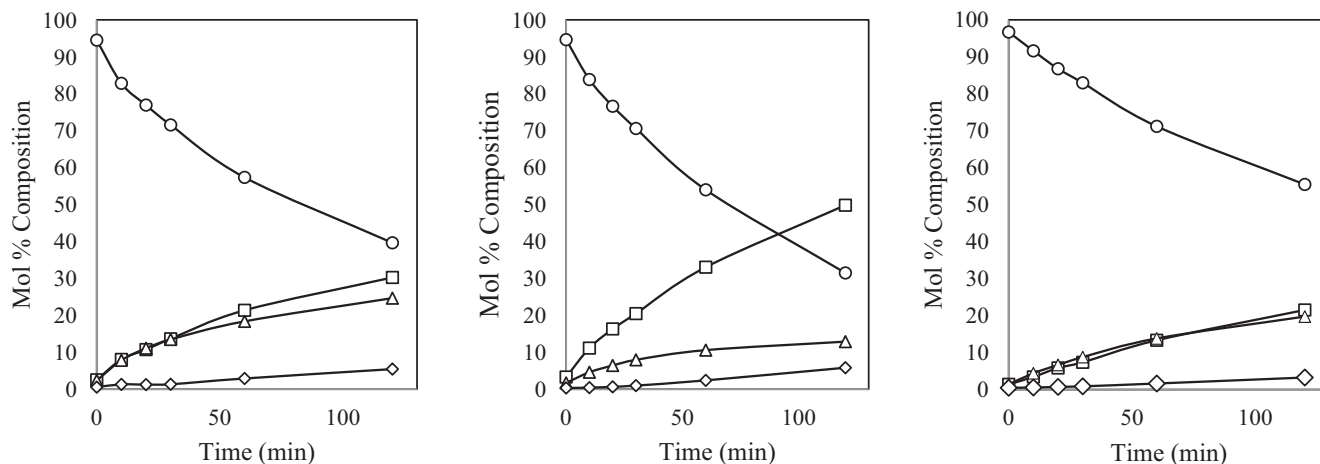


Fig. 10. Mol% composition as a function of reaction time in as received (left), dried (centre) and with water added (right) 2-propanol. Reaction performed at 5 bar using 0.1 g 4% Pt/TiO₂, 13.5 mmoles 4-phenyl-2-butanone and 50 ml 2-propanol. (○) 4-phenyl-2-butanone; (□) 4-phenyl-2-butanol; (Δ) 4-cyclohexyl-2-butanone and (◇) 4-cyclohexyl-2-butanol.

formed was observed. This trend was also observed with the secondary alcohols, with the exception of 2-propanol. The exception to the low selectivity to 4-cyclohexyl-2-butanone was observed when the reaction was carried out in trifluoroethanol, where the rate of reaction of 0.003 mol dm⁻³ min⁻¹ and selectivity to 4-cyclohexyl-2-butanone of 69%, shows similar behaviour to when the reaction was performed in alkanes.

All the results shown in Figs. 8 and 9 were obtained using alcohols, which had been dried over CaH₂ and a significant change in the selectivity was observed on using the solvents as received. Fig. 10 shows that, in the case of 2-propanol, an almost equal amount of ring and carbonyl hydrogenation was observed when the solvent was used as received. In comparison, following drying and distillation of the solvent an increase in the formation of 4-phenyl-2-butanol combined with a suppression of the formation of 4-cyclohexyl-2-butanone was observed. In this case, the selectivity changed to 70% 4-phenyl-2-butanol and 28% 4-cyclohexyl-2-butanone. Karl-Fischer analysis of the as received solvent and after purification showed that the water content had been reduced from 0.023 wt% to 0 wt%. On addition of water (0.07 wt% in the reaction) to a dried alcohol reaction mixture the selectivity of the reaction changed to 38% 4-cyclohexyl-2-butanone and 56% 4-phenyl-2-butanol, which is more similar to that obtained using the as received solvent, Fig. 10. Very low water contents were observed by Karl Fischer analysis in the as received *n*-hexane and toluene solvents and no effect of drying these solvents on the rate and selectivity of the reaction was observed.

3.3.4. Ethers

The rate of reaction and selectivity were also measured in a range of ether based solvents which had either linear alkyl chains (such as diethyl ether and dibutyl ether), were sterically hindered (such as methyl tert-butyl ether) or were cyclic, such as tetrahydrofuran. The reaction proceeded slowly in ether solvents where the alkyl chain was linear with initial rates of 0.0004 mol dm⁻³ min⁻¹ for both linear ethers, Fig. S37. However, no reaction occurred in the sterically hindered or cyclic ethers. It is possible that the ethers adsorb onto the metal surface and in the case of the sterically hindered and cyclic ethers, block the sites from reaction [64]; however, there is sufficient mobility in the linear alkyl chains to allow some reaction to occur. A change in selectivity was also observed between the linear alkyl chain ethers that did facilitate the reaction, Fig. S38. In diethyl ether the major

product was 4-phenyl-2-butanol with a selectivity of 65% compared with 29% 4-cyclohexyl-2-butanone. In comparison, in dibutyl ether selectivities of 47% and 48% to 4-phenyl-2-butanol and 4-cyclohexyl-2-butanone were observed.

4. Discussion

4.1. Effect of solvent on rates of reactions

From comparison of the silica and titania based catalysts, it is clear that the presence of titania results in the variation of the rate and the selectivity of the hydrogenation of 4-phenyl-2-butanone with solvent. Both catalysts had similar metal particle sizes, 2.2 nm and 3.0 nm for titania and silica, respectively, and, therefore, these effects are not likely to be associated with structure sensitivity processes. The changes between the catalysts are thought to be due to one site being available for hydrogenation on the silica based system whereas a dual site model is proposed and described below for the titania based catalyst. The selectivity over the Pt/SiO₂ catalyst indicates that the ring hydrogenation occurs predominantly on the Pt site, whereas there is a second site on the Pt/TiO₂ catalyst which predominantly results in carbonyl hydrogenation.

In order to understand the changes in rate with the solvent on the titania based catalysts, the strength of adsorption and the steric hindrance of the resulting solvent adsorbed layer are thought to be important. While the hydrogenation rates in alkanes and secondary alcohols were similar, primary alcohols exhibited lower reaction rates which likely reflect the structure of the adsorbed alcohol on the surface of the catalyst. Both primary and secondary alcohols will adsorb onto the catalyst through exchange with the support hydroxyl groups; however, the space occupied by a single secondary alcohol is significantly larger than for a primary alcohol resulting in a much lower density adsorbed layer. This increased packing of the primary alcohols is proposed to create a barrier which limits the ability of the reagent to adsorb and hence reduces the rate of reaction compared with the less densely packed secondary alcohol layer. Similar effects have been noted previously for butanone hydrogenation [65]. The dissociative adsorption of alcohols to form an alkoxide and atomic hydrogen on the metal surface has also been reported to account for the high rate of reaction of secondary alcohols in the hydrogenation of acetophenone [27,28]. This additional source of hydrogen at the metal surface

could also contribute to the higher rates observed in this study in the secondary alcohols.

For reactions in aromatic solvents, toluene and *p*-xylene, a significant reduction in rate was observed compared with the alkanes, for example. Similarly, linear ethers also gave a low reaction rate while no reaction was observed in tetrahydrofuran or methyl tert-butyl ether. In all these systems, the solvents are likely to be strongly adsorbed on the Pt sites and the solvent competes with the adsorption of the aromatic ring of 4-phenyl-2-butanone. This limits sites available for ring hydrogenation, thereby decreasing this pathway and lowering the overall rate of reaction. In addition, the strongly adsorbed solvent reduces the number of sites available for H₂ dissociation which will also contribute to the decreased rate.

4.2. Effect of solvent on selectivity

The high selectivity to 4-cyclohexyl-2-butanone over the Pt/SiO₂ catalyst and in the presence of alkanes (solvents with weak interactions with the catalyst), over the Pt/TiO₂ catalyst suggests the preferred mode of adsorption of 4-phenyl-2-butanone on the Pt is through the aromatic ring. This is consistent with the reaction of the partially hydrogenated products in *n*-hexane where hydrogenation of 4-phenyl-2-butanone to 4-cyclohexyl-2-butanone occurred at a significantly faster rate than hydrogenation of 4-cyclohexyl-2-butanone to 4-cyclohexyl-2-butanol showing that aromatic ring adsorption and reaction is the preferred pathway over Pt/TiO₂, Fig. 5. However, this selectivity ratio changes with temperature. Fig. 11 shows the variation of selectivity between 5

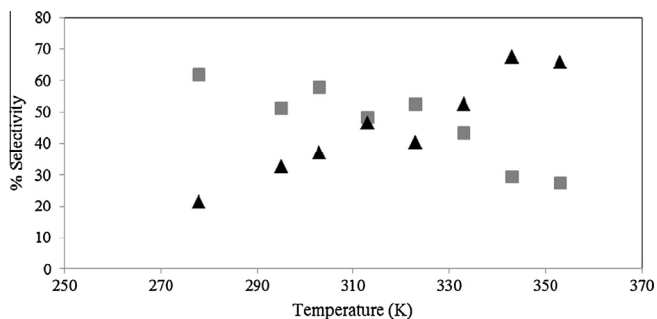


Fig. 11. %Selectivity as a function of reaction temperature for hydrogenation of 4-phenyl-2-butanone (at 15% conversion). Reactions performed with 13.5 mmoles 4-phenyl-2-butanone, 0.1 g 4% Pt/TiO₂, 5 bar H₂ in 50 ml of *n*-hexane. Grey squares: selectivity to 4-phenyl-2-butanol and black triangle: selectivity to 4-cyclohexyl-2-butanone.

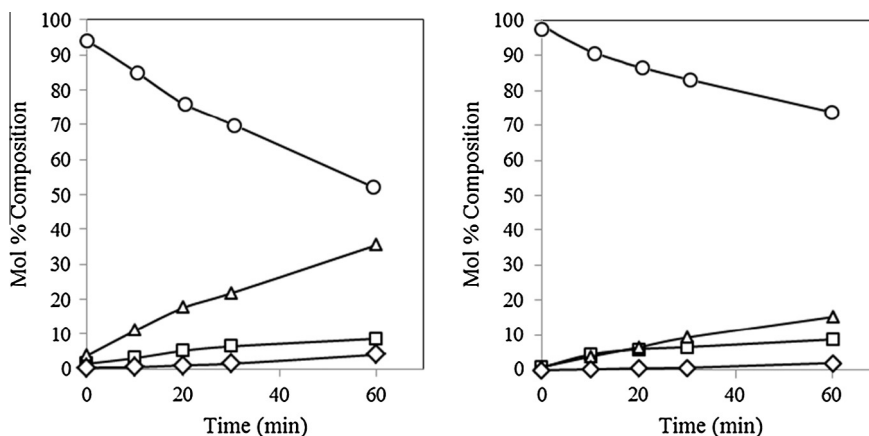


Fig. 12. Mol% composition as a function of reaction time for the reaction in *n*-hexane (left) and *n*-hexane spiked with toluene (right). Reactions performed with 13.5 mmoles 4-phenyl-2-butanone, 0.1 g 4% Pt/TiO₂, 5 bar H₂ in 50 ml of *n*-hexane. (○) 4-phenyl-2-butanone; (□) 4-phenyl-2-butanol; (Δ) 4-cyclohexyl-2-butanone and (◇) 4-cyclohexyl-2-butanol.

and 80 °C in *n*-hexane over the Pt/TiO₂ catalyst. At lower temperatures, the selectivity to 4-phenyl-2-butanol is higher suggesting higher activation energy for aromatic ring hydrogenation. The change in selectivity with temperature suggests there are two activation energies for the reaction which is consistent with the suggestion that there are two different active sites for hydrogenation of 4-phenyl-2-butanone over Pt/TiO₂. Two active sites for the hydrogenation of 4-phenyl-2-butanone over Pt/TiO₂ was determined from a kinetic model by Wilkinson et al. wherein activation energies of 48.4 and 30.4 kJ mol⁻¹ for aromatic ring and carbonyl group hydrogenation respectively were reported [66].

The postulation of two active sites on the catalyst, one for ring and an additional site for C=O hydrogenation is also evident from comparison of the Pt/SiO₂ and Pt/TiO₂ results. In all solvents, except toluene, the major product is 4-cyclohexyl-2-butanone for Pt/SiO₂. In the case of the silica support, the oxide cannot readily participate in the reaction, unlike in the case of a reducible oxide, such as titania, and thus the ring hydrogenation occurs most readily, as this is the functionality which adsorbs most strongly on the platinum. Whilst some C=O hydrogenation does occur on the silica based catalyst, this is strongly promoted in certain solvents, when titania is used as the support. In the case of titania, oxygen vacancies close to the metal nanoparticle form easily under reducing conditions and these have been proposed to promote C=O hydrogenation [5,39]. In this case, the C=O can adsorb via the oxygen, filling the vacancy and weakening the C=O bond thus increasing the hydrogenation rate. Competition for these two sites with the solvents then determines the selectivity observed over titania. This is illustrated by comparing the different solvent effects on the selectivity of the reaction.

The higher selectivity to 4-cyclohexyl-2-butanone observed for the reaction over Pt/TiO₂ in alkane solvents suggests the preferred mode of adsorption of 4-phenyl-2-butanone on the Pt is through the aromatic ring. A switch in the selectivity, to 4-phenyl-2-butanol, was observed upon changing from an alkane solvent to a solvent which would strongly interact with the catalyst, for example aromatic or alcohol solvents. In the aromatic solvents, the solvent adsorption on the catalyst competes with adsorption of the aromatic ring of 4-phenyl-2-butanone suppressing the formation of 4-cyclohexyl-2-butanone resulting in low rates of reaction and increased selectivity to 4-phenyl-2-butanol. The effect of site blocking can even be observed when a small amount of toluene (equal in mass to the 4-phenyl-2-butanone) is added to the reaction mixture using *n*-hexane as the solvent. Fig. 12 shows that, upon addition of toluene, the conversion decreases from 49% to 27% after 1 h of reaction with a decrease

in the selectivity to 4-cyclohexyl-2-butanone from 75% to 49% and a small increase in the amount of 4-phenyl-2-butanone formed from 4% in the *n*-hexane reaction to 8% in the toluene doped *n*-hexane reaction. The decrease in rate is mainly due to suppression of the ring hydrogenation pathway while the C=O hydrogenation pathway is not affected. As a result of the suppression of the ring hydrogenation pathway, the selectivity is altered by reduction in cyclohexyl-product formation rather than enhancement of the formation of 4-phenyl-2-butanone. From these results it is clear that the change in the solvent mainly affects the ring hydrogenation pathway. Although toluene adsorbs onto the surface, the observed rate is not simply due to competitive hydrogenation of the toluene as only 3% of the toluene added into the system was hydrogenated to methylcyclohexane. The rate and selectivity observed in aromatic solvents are explained by the aromatic solvents blocking the sites for ring hydrogenation rather than undergoing competitive hydrogenation with 4-phenyl-2-butanone. This effect was probed further by comparing the rates and selectivities found in the presence of a more sterically hindered tert-butyl group in the form of tert-butyl-toluene in which the reaction proceeds similarly to that observed in the alkane solvents. In this case, the bulkier solvent cannot adsorb strongly onto the catalyst surface and block active sites and, with no site blocking, the ring hydrogenation is the dominant pathway in this solvent.

In the alcohol solvents, high selectivity is observed toward 4-phenyl-2-butanone from C=O hydrogenation. As found with the aromatic solvents, the major effect of alcohol adsorption is to suppress the ring adsorption. However, unlike the case of the aromatic solvents where the rate of C=O hydrogenation was not affected, in the presence of alcohols, most significantly for secondary alcohols, the C=O hydrogenation is enhanced resulting in a fast rate of reaction along with a high selectivity to 4-phenyl-2-butanone. Hydrogenation of intermediates in 2-propanol showed that the rates of the aromatic ring and C=O hydrogenation were closer in value than was the case in *n*-hexane (Fig. 5). When the ring hydrogenation sites are blocked by adsorption of alcohols on the metal, and the hydroxyl sites on support where the C=O group would hydrogen bond are exchanged, the C=O group can still strongly adsorb on TiO₂ in O vacancies/Ti⁴⁺ cation sites as has been observed for acetone adsorption on titania in ethanol [67]. This increased local concentration of 4-phenyl-2-butanone near the interfacial sites increases the rate of hydrogenation to 4-phenyl-2-butanone. For secondary alcohols, increased active H from dissociative alcohol adsorption on the Pt could also be responsible for the enhanced rate [28].

5. Conclusions

The effect of the solvent on the hydrogenation of 4-phenyl-2-butanone over a Pt/SiO₂ catalyst was found to only change the rate of reaction with no change in selectivity. 4-Cyclohexyl-2-butanone, resulting from hydrogenation of the aromatic ring, was the major product over this catalyst. Conversely, over a Pt/TiO₂ catalyst, a switch in selectivity is observed in aromatic and alcohol solvents compared with alkanes, which is due to strong adsorption of the solvents on the catalyst. In aromatic solvents (toluene and *p*-xylene), due to adsorption of these solvents on Pt metal sites, which are proposed to be the sites for hydrogenation of the aromatic ring of 4-phenyl-2-butanone, 4-cyclohexyl-2-butanone formation is suppressed and a low reaction rate with a high 4-phenyl-2-butanone selectivity is observed. In the alcohol mediated reactions, the solvent can adsorb on both the support and on the Pt metal forming a dense overlayer, in the case of primary alcohols, over the catalyst surface due to increased packing efficiency of the hydrocarbon chains relative to secondary

alcohols. While adsorption at ring hydrogenation sites is restricted in alcohols, the C=O group of 4-phenyl-2-butanone can adsorb in oxygen vacancies on the titania support. Adsorption (and activation) of the C=O group in the vacancy at the interface of Pt particles is proposed to be the second active site.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcat.2015.06.008>.

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