

An on-line FTIR study of the liquid-phase hydrogenation of 2-butanone over Pt/Al₂O₃ in *d*₈-toluene

The importance of anhydrous conditions

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Abstract

Liquid-phase heterogeneous catalytic hydrogenation of 2-butanone over Pt/Al₂O₃ was performed in anhydrous *d*₈-toluene with on-line FTIR measurements and further perturbations of water. The hydrogenation rates of both 2-butanone and solvent *d*₈-toluene were strongly affected by the presence of water and unusual spectral changes were observed after the perturbations of reactant and water. It is suggested that hydrogen bonding is responsible for the unusual spectral changes. The marked decrease in the reaction rates and the unusual spectral changes, taken together, seem to suggest that anhydrous experiments are important both for preparative studies as well as kinetic and mechanistic studies of the un-activated simple ketone hydrogenation over Pt/Al₂O₃ (i.e. 2-butanone) and should be implemented when possible.

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1. Introduction

Group VIII metals such as Pt, Ru, Rh and Ni have been used in catalytic hydrogenation of carbonyl compounds [1]. Due in part to the low reactivity of 2-butanone, catalytic hydrogenation of this un-activated simple ketone has been less studied. The liquid-phase catalytic hydrogenation of this ketone has been reported with a homogeneous ruthenium complex [2] and several heterogeneous catalysts [3–7]. A few bimetallic catalysts such as RhSn/SiO₂ and RuPt/C have shown improved reaction rates; however, these are rather special cases [6,7]. 2-Butanone hydrogenation in toluene over a more traditional Pt/Al₂O₃ catalyst has apparently not been studied in detail.

Recently, a compact experimental apparatus for on-line spectroscopic study of fine-chemistry liquid-phase heteroge-

neous catalysis was designed and characterized with respect to gas–liquid mass transfer, mixing, liquid–solid mass transfer and intra-particle diffusion [8]. The utility of the experimental set up was demonstrated by the heterogeneous catalytic hydrogenation of acetophenone (Aceph) over Pt/Al₂O₃ in *d*₈-toluene/h₈-toluene at 0 °C. A Langmuir–Hinshelwood–Hougen–Watson (LHHW) model was successfully used to fit the kinetic data of acetophenone hydrogenation to 1-phenylethanol with the effects of solvent and water included [9]. The advantages of on-line liquid-phase spectroscopy together with multivariate techniques such as band-target entropy minimization (BTEM) [10–14] and two-band-target entropy minimization (tBTEM) [15] for exploratory studies of heterogeneous catalytic systems have also been demonstrated.

One important observation from this on-line FTIR study was that, over Pt/Al₂O₃ catalyst, water had a strong inhibiting effect on the hydrogenation rates of acetophenone and solvent *d*₈-toluene. Indeed, it is known that anhydrous conditions are often important in catalytic organic syntheses. Water-promoted deactivation during hydrogenation was observed on a supported nickel catalyst [16,17]. In the presence of water, catalytically

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inactive species Ni(OH)₂ was formed on the catalyst surface. A strong chemical inhibition of the catalytic sites was observed on Pd/Al₂O₃ during α -methylstyrene hydrogenation with very low concentrations of water [18]. A three-fold decrease in activity was observed when the relatively anhydrous reagent was substituted by a commercially available reagent. Water-promoted deactivation of Pd/Al₂O₃ catalyst was also observed during isoprene hydrogenation. The poisoning effect was associated with the adsorption of water and the related decrease in active sites for hydrogenation [19].

In the present contribution, the above mentioned experimental set up and methodology are re-applied to the liquid-phase heterogeneous hydrogenation of 2-butanone over Pt/Al₂O₃ in order to understand the differences in reactivity between the activated and the un-activated simple ketones, especially with respect to the effect of water. On-line FTIR spectroscopic measurements of the liquid phase were used throughout this study. In order to determine the influence of water, anhydrous toluene and Schlenk techniques were also employed, and water perturbations were introduced during the catalysis. Furthermore, in order to assess the degree of solvent activation, *d*₈-toluene rather than *h*₈-toluene was used as solvent. Finally, density function theory (DFT) was used to verify and further explain some of the unusual FTIR observations. By undertaking the present type of experimental approach, several new sights into the chemistry and kinetics of liquid-phase hydrogenation of the un-activated simple ketones over Pt/Al₂O₃ were achieved.

2. Experimental

2.1. General issues

2.1.1. Chemicals

Engelhard 4759 (5% Pt/Al₂O₃) was used in this study. It was sieved and the size range 53–75 μ m was selected. The catalysts were pre-reduced in H₂ at 400 °C for 120 min before reaction [20]. *d*₈-Toluene (99.6%, Cambridge Isotope Laboratories) was distilled from sodium–potassium alloy under purified argon for ca. 5 h to remove the trace water and oxygen. 2-Butanone (99%, Aldrich, stated moisture impurity \leq 0.2%) and 2-butanol (98%, Acros Organics) were shaken and stored with anhydrous 4A molecular sieves to remove traces of water and stored under argon. De-ionized water was used without further purifications.

2.1.2. Experimental apparatus and on-line FTIR measurements

The reaction system consisted of a 25 ml stirred tank, a pump, a packed-bed reactor, a FTIR spectrometer with a high-pressure flow-through cell, and an injection block for liquid-phase perturbations. All these components were assembled into a closed recycle configuration [8]. Standard Schlenk techniques [21] were employed in all the experiments. The pressure of hydrogen was kept almost constant during the reaction time by connecting the 25 ml reaction system to a 1 l reservoir. The liquid phase was kept saturated with hydrogen by operating the stirred tank at a stirring speed of 400 rpm. The packed-bed reactor with ca. 0.02 g of catalyst was immersed in a 0 °C water bath (Poly-

science 9505). A SS316 1/16 in. tubing of ca. 60 cm length was positioned prior to the reactor in the water bath to keep the inlet temperature of reactants at 0 °C. The remaining parts of the experimental apparatus were maintained at a room temperature of ca. 22 °C.

A Perkin-Elmer spectrometer 2000 with deuterated triglycine sulfate (DTGS) detector was used to collect the FTIR spectra with a data interval of 0.2 cm⁻¹ for the range 1000–4000 cm⁻¹. Spectral resolution was 4 cm⁻¹. Purified nitrogen (99.99%, Saxol, Singapore) was used to purge the FTIR spectrometer system. The path length of the sturdy high-pressure FTIR cell with 15 mm thick CaF₂ windows was ca. 0.0371 cm. The pressure dependence of the cell's path length, in the interval of 1.0–3.0 bar, can be neglected in this study.

2.1.3. Experimental procedure

All the experiments were performed in a similar manner [8]. First, the catalyst was pre-packed in a 2.1 mm (diameter) \times 50 mm (length) HPLC cartridge. The rest of the cartridge was filled with inert quartz sand. The whole reaction system was evacuated before 15 ml *d*₈-toluene was transferred to the stirred tank under argon. After that the system was briefly evacuated again and the required hydrogen partial pressure was added to the stirred tank. The magnetic stirring (400 rpm) was then started in order to saturate the solvent with hydrogen. The controlling needle valves were subsequently opened and the circulation pump (ca. 5 ml/min) was started. A period of ca. 15 min was used to ensure saturation of hydrogen in the recycle system and thermal equilibration of the apparatus. At a time $t=0$ min, a program was executed to record the spectra every minute. Then at a pre-determined time $t=10$ min, 20 μ l of 2-butanone was injected through one of the HPLC valves. At this point, the hydrogenation runs were initiated. Further perturbations of reagent, product and water were performed at pre-determined times.

2.1.4. Band-target entropy minimization

BTEM was used to obtain pure component spectral estimate of *h*₆-*d*₈ methylcyclohexane from the multi-component spectra. *h*₆-*d*₈ methylcyclohexane was the primary product for the hydrogenation of *d*₈-toluene over Pt/Al₂O₃ [9]. The information entropy concept is the basis for this self-modeling curve resolution. The spectral estimate was obtained without the use of any a priori information or libraries. Details of the mathematics and implementation are provided elsewhere [8–14].

2.1.5. Other software

DFT calculations were performed with Material Studio using a gradient-corrected potential GGA-PBE with DNP atomic orbital basis sets.

2.1.6. Molar absorptivities and experimental reference spectra

The molar absorptivities of 2-butanone and 2-butanol were obtained from dilute solutions with different concentrations using *d*₈-toluene as solvent. Calibrations were performed,

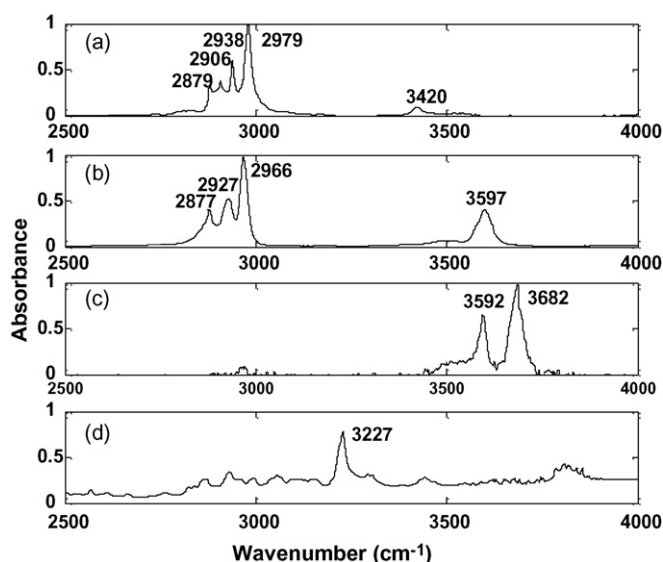


Fig. 1. The experimental reference spectra of the species present in the region 2500–4000 cm^{-1} . (a) 2-Butanone; (b) 2-butanol; (c) water; (d) solvent d_8 -toluene plus cell and background.

and the determined molar absorptivities of 2-butanone (at ca. 2979 cm^{-1}), 2-butanol (at ca. 2966 cm^{-1}) and water (at ca. 3680 cm^{-1}) were ca. 61.9, 158.1 and 73.7 l/(mol cm), respectively. Based on some judicious comparisons to related compounds, an approximate value of 400 l/(mol cm) was chosen for the molar absorptivity of h_6 - d_8 methylcyclohexane at ca. 2903 cm^{-1} . The experimental reference spectra in the range of 2500–4000 cm^{-1} for 2-butanone, 2-butanol, water and d_8 -toluene plus cell and background are shown in Fig. 1.

2.1.7. Mixing time

Non-steady state results are reported throughout this study. The long time-scale transients in these experiments are dominated by the ketone hydrogenation kinetics, and the short time-scale transients are dominated by mixing in the recycle apparatus. In the present experimental system, the characteristic mixing time of ca. 3 min was observed. Details about the characterization of the system can be found elsewhere [8].

2.2. Experimental design

2.2.1. Hydrogenation experiment

Three sets of experiments at different hydrogen partial pressures with multiple perturbations were performed. Three different hydrogen partial pressures, namely, 1.55, 2.07 and 2.50 bar were used in each set of experiments. The detailed experimental designs of one typical experiment with hydrogen partial pressure at 2.07 bar are shown in Table 1. Four 2 μl product perturbations, seven 20 μl 2-butanone perturbations and one water perturbation were included. These multiple perturbations were designed to cover a wide range of experimental conditions in one semibatch run and to facilitate the subsequent deconvolution of pure component spectra and multivariate analysis [8].

Table 1

Experimental designs for hydrogenation of 2-butanone with multiple perturbations conducted at 2.07 bar hydrogen partial pressure over Pt/Al₂O₃ in d_8 -toluene

Time (min)	Spectral number	Reactant (μl)	Product (μl)	Water (μl)
10	10	20		
50	51	20		
90	92	20		
130	133	20		
170	172	20		
210	212		2	
252	254		2	
292	294		2	
330	332		2	
370	373	20		
410	411	20		
450	452			2
537 = end	538			

2.2.2. Control experiment

One set of perturbations of reactant, product and water was carried out, in the presence of 0.02 g catalyst but not in the presence of hydrogen to confirm that: (i) no observable reaction of 2-butanone occurred under the current mild and relatively anhydrous reaction conditions and (ii) the unusual spectral changes occurred even when no catalytic hydrogenation occurred. Inert gas helium (ca. 1.1 bar) was used instead of hydrogen as the buffer gas on the system.

2.2.3. Transfer hydrogenation test

One semibatch experiment was performed to test the possibility that transfer hydrogenation occurred between the product 2-butanol and d_8 -toluene to give 2-butanone and h_6 - d_8 methylcyclohexane. During the first 2 h only solvent d_8 -toluene and dissolved hydrogen were pumped through the catalyst bed in order to get experimental evidence of solvent hydrogenation under the current reaction conditions (0 °C and 1.0–3.0 bar hydrogen partial pressures). Then two perturbations of 2 μl 2-butanol were injected into the reaction system at times $t = 120$ and 160 min. The loading of the catalyst was ca. 0.02 g and the hydrogen partial pressure was kept almost constant at ca. 1.54 bar. No observable C=O vibrations were detected during this experiment. Therefore, no transfer hydrogenation appears to occur.

3. Results

3.1. 2-Butanone hydrogenation

Hydrogenation of 2-butanone to 2-butanol over Pt/Al₂O₃ catalyst occurred under the current mild and relatively anhydrous reaction conditions. As an illustration, some experimental spectra measured under 2.07 bar hydrogen partial pressure were further processed. Accordingly, the 10th experimental spectrum (right before the first reactant perturbation) was subtracted from the 25th, 35th and 45th experimental spectra. The resulting difference spectra are shown in Fig. 2a. Although water signals are present in this figure, the prominent signal increase at 3596 cm^{-1}

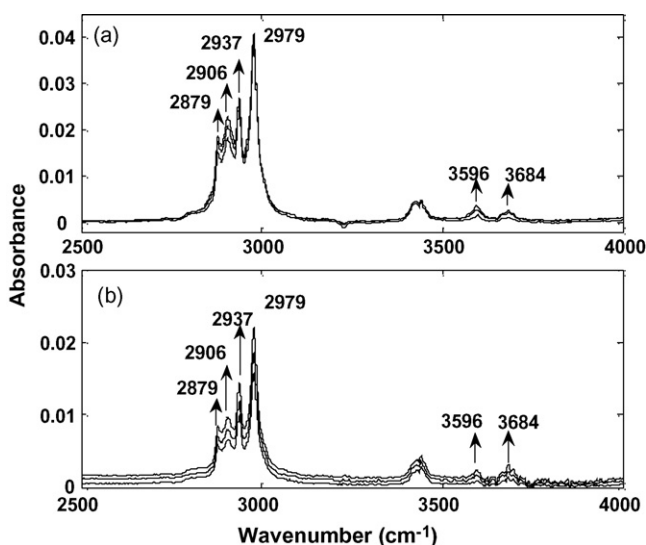


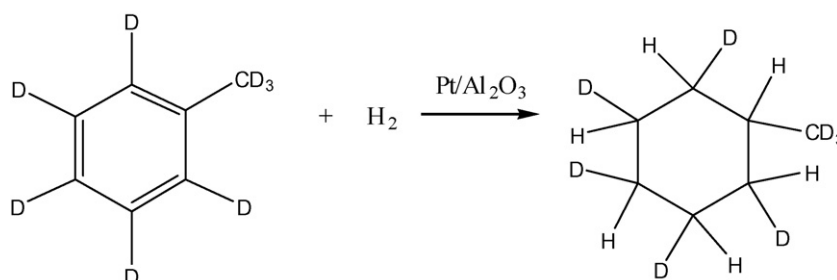
Fig. 2. Difference spectra resulting from some experimental spectra subtracted by the solvent spectrum after the first reactant perturbation. (a) Hydrogenation experiment at ca. 2.07 bar hydrogen partial pressure; (b) control experiment at ca. 1.1 bar helium partial pressure.

in Fig. 2a is clearly due to product 2-butanol formation (compare with references in Fig. 1b and c). This signal increase does not arise from diol formation between 2-butanone and water molecules because no marked signal increase at 3596 cm^{-1} (Fig. 2b) was observed after the first reactant perturbation in the control experiment which was performed with similar water concentrations but in the absence of hydrogen.

3.2. Competitive hydrogenation of solvent

Hydrogenation of the solvent in the presence of just catalyst (no reactant) at 0°C and 1.54 bar hydrogen partial pressure was observed (Scheme 1). The 10th spectrum was subtracted from the 40th, 80th and 120th experimental spectra in this 2 h test. The resulting difference spectra are plotted in Fig. 3a. The new spectral signals with spectral maximum at 2903 cm^{-1} were observed. These new signals are from C–H vibrations of $\text{h}_6\text{-d}_8$ methylcyclohexane, which was identified previously by a mass spectrometer (MS) with a significant fragment at 106 m/z in a related study [9].

Competitive hydrogenation of the solvent d_8 -toluene was observed in the experiments conducted with catalyst, hydrogen and 2-butanone. The 20th, 25th, 30th, 35th and 40th measured



Scheme 1. The reaction scheme of d_8 -toluene hydrogenation to $\text{h}_6\text{-d}_8$ methylcyclohexane over $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst.

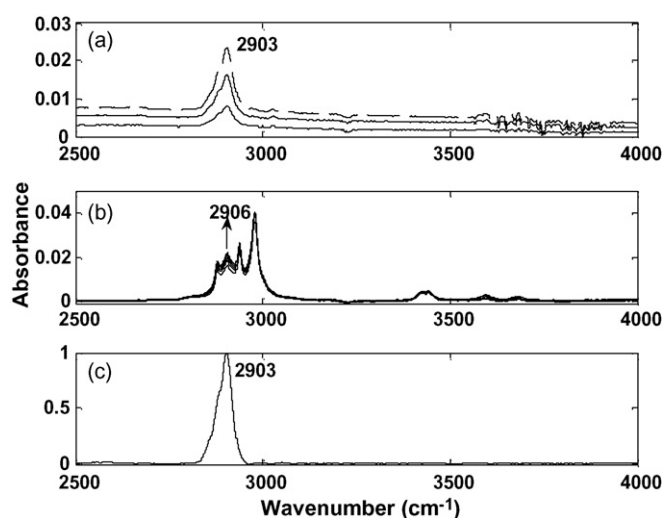


Fig. 3. Competitive hydrogenation of solvent d_8 -toluene. (a) Difference spectra resulting from the 40th, 80th and 120th experimental spectra subtracted by the 10th experimental spectrum during solvent hydrogenation experiment; maximum for $\text{h}_6\text{-d}_8$ methylcyclohexane at 2903 cm^{-1} ; (b) raw experimental spectra during 2-butanone hydrogenation experiment. Arrow indicates a spectral maximum for product 2-butanol at 2906 cm^{-1} ; (c) resulting BTEM estimate of $\text{h}_6\text{-d}_8$ methylcyclohexane deconvoluted from the spectral data in (b).

spectra at 0°C and 2.07 bar hydrogen partial pressure are shown in Fig. 3b. The signal intensity in the C–H vibrational region changed as a function of reaction time. A spectral maxima at 2906 cm^{-1} is due to the product 2-butanol. Deconvolution of the reaction spectra using BTEM provided an excellent pure component spectrum of $\text{h}_6\text{-d}_8$ methylcyclohexane (Fig. 3c) which was embedded in the reaction spectra. Further analysis shows that the contribution of the $\text{h}_6\text{-d}_8$ methylcyclohexane signal is quite small compared to the spectral changes due to reactant and product.

In a previous study, competitive hydrogenation of solvent d_8 -toluene was also observed in acetophenone hydrogenation at 0°C over the same $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst [9]. Under otherwise similar reaction conditions, the rate of d_8 -toluene hydrogenation to $\text{h}_6\text{-d}_8$ methylcyclohexane was higher in the presence of the un-activated 2-butanone than in the presence of the activated acetophenone. Specifically, with $20\ \mu\text{l}$ reactant in 15 ml solution with only trace water, and at 0°C and ca. 1.5 bar hydrogen partial pressure, d_8 -toluene hydrogenation rates were ca. 6×10^{-6} and $4 \times 10^{-6}\text{ mol}/(\text{min g-cat})$ in the presence of 2-butanone and acetophenone, respectively. This difference is almost certainly due

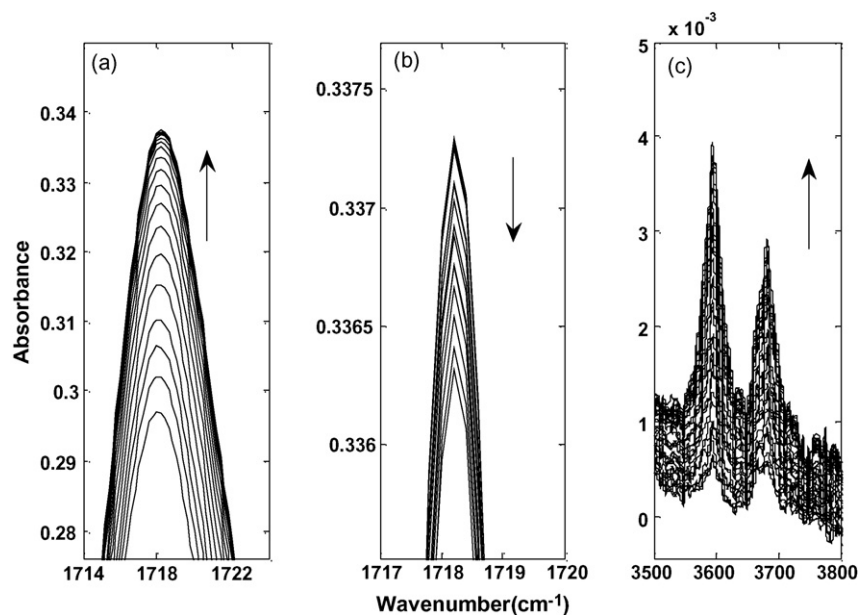


Fig. 4. Various spectra after the first reactant perturbation in the hydrogenation experiment performed at 2.07 bar hydrogen pressure. (a) Experimental spectra 14–35 in the C=O vibrational region; (b) experimental spectra 36–50 in the C=O vibrational region; (c) difference spectra resulting from the spectra 14–50 subtracted by the 10th spectrum in the O–H vibrational region.

to the strong competitive adsorption of acetophenone resulting in the displacement of toluene from the catalyst surface.

3.3. Unusual spectral changes caused by reactant and water perturbations

3.3.1. Reactant perturbations

In some catalytic experiments, reactant perturbations were performed. After each reactant perturbation the spectral absorbance of the carbonyl moiety in 2-butanone underwent an expected stepwise increase (due to the sudden concentration increase), but then continued to increase slowly for an additional period, before decreasing due to the consumption during the catalytic hydrogenation.

As an illustration, the experimental spectra of the carbonyl moiety in 2-butanone after the first reactant perturbation at 2.07 bar hydrogen partial pressure are mentioned. At the 10th spectrum, 20 μl 2-butanone was injected into the system. There was an almost immediate step increase in the intensity of the associated carbonyl band. Fig. 4a shows the subsequent slow increase in the intensity of the carbonyl band (spectra 14–35). After this period, a decrease in the intensity of the carbonyl band occurred, as seen in Fig. 4b (spectra 36–50). Fig. 4c shows the O–H vibration region 3500–3800 cm^{-1} (after subtraction by the 10th experimental spectrum) and the continuous increase in the 2-butanone and water bands during the same interval (spectra 14–50). The increase in 2-butanone arises from reaction and the increase in water arises from: (i) introduction during perturbations and subsequent slow dissolution into the anhydrous liquid phase and (ii) from contact of the liquid phase with the wetted parts of the piston-cylinder chamber of the metering pump.

The same phenomena were observed in the control experiment which was performed in the absence of catalytic

hydrogenation (catalyst present, but no hydrogen), but in the presence of perturbations. The absorbance of 2-butanone underwent an expected stepwise increase after each reactant perturbation, and this was then followed by a gradual increase for a period of time. No decrease in the intensity was thereafter observed, since no catalytic hydrogenation occurred. As noted in Section 2.1, the characteristic time for mixing was of the order of 3 min, and therefore, mixing is not the cause of the unusual spectral changes.

3.3.2. Water perturbations

After each water perturbation the spectral absorbance of the carbonyl moiety in 2-butanone increased continuously for some time, even though 2-butanone was being consumed in the catalytic reaction. As an illustration, a 2 μl water perturbation was performed at the 450th experimental spectrum at 2.07 bar hydrogen partial pressure. The spectra 454–484 in this hydrogenation experiment were analyzed. Two regions, namely, 1700–1750 and 3500–3800 cm^{-1} were taken from the original spectral data, and the difference spectra (with respect to the 453rd experimental spectrum) are shown in Fig. 5. The same phenomena were observed in the control experiment. The absorbance of the carbonyl moiety in 2-butanone increased continuously for some time after the water perturbation.

3.4. Effect of water on reaction rates

Since the absorptivities of the C=O moiety in 2-butanone were affected by the presence of other components in solution, this band was not used for further quantitative analysis. Instead, the C–H and O–H vibrational region 2500–4000 cm^{-1} was analyzed in order to quantify the reaction rates of the two catalytic hydrogenations present in this system. Experimental references

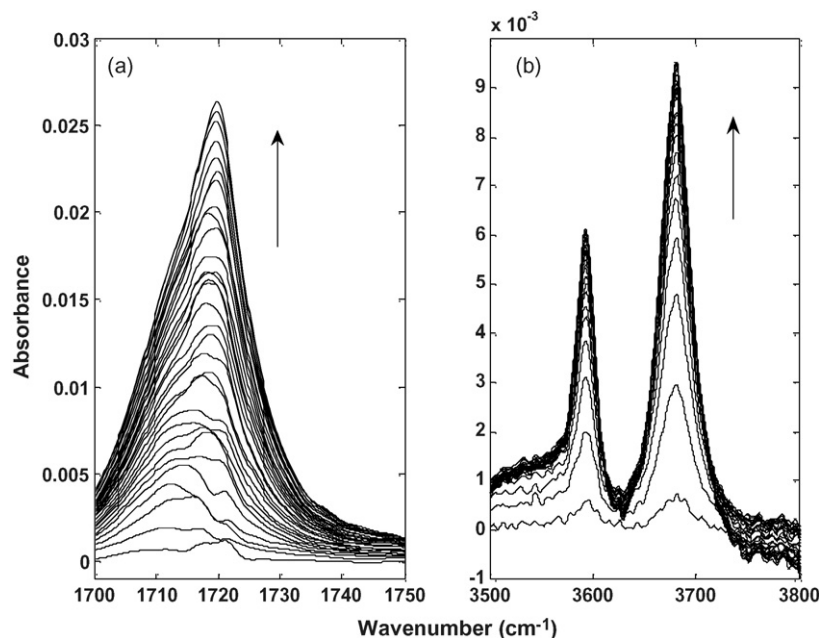


Fig. 5. Difference spectra resulting from the spectra 454 to 484 subtracted by the 453rd experimental spectrum in two regions. (a) 1700–1750 cm^{-1} ; (b) 3500–3800 cm^{-1} .

were used in the multivariate analysis. Rates were evaluated in the absence of added water and after subsequent perturbations of water. Intervals involving 25 spectra were used for each rate determination.

The catalytic hydrogenation was performed at ca. 2.5 bar hydrogen partial pressure. Two perturbations of 2 μl water were performed at the 375th and 415th experimental spectra. The corresponding rates of 2-butanone hydrogenation and d_8 -toluene hydrogenation as a function of water concentration, evaluated over the spectra 345–369, 385–409 and 465–489, are shown in Fig. 6.

Fig. 6 shows that both reaction rates are very sensitive to the presence of water. In fact, both the catalytic hydrogenations of solvent and 2-butanone were virtually stopped by the presence of ca. 8×10^{-3} M (ca. 860 ppm, mol/mol) dissolved water. The concentrations of 2-butanone and 2-butanol at the 340th

spectrum were approximately 7.9×10^{-2} and 1.25×10^{-2} M 2-butanone, respectively, and at the 490th spectrum were approximately 7.88×10^{-2} and 1.3×10^{-2} M, respectively. Therefore, only ca. 4% conversion occurred during the spectra 340–490 and this level of conversion should have little effect on the reaction kinetics.

4. Discussion

4.1. Overview

Under relatively anhydrous reaction conditions, 2-butanone was selectively hydrogenated to 2-butanol over $\text{Pt}/\text{Al}_2\text{O}_3$ in toluene. Furthermore, under similar anhydrous reaction conditions, the reaction rate for the hydrogenation of the un-activated ketone (2-butanone) is roughly one order of magnitude slower than the rate of hydrogenation of the activated ketone (acetophenone) [9]. This observation is consistent with: (i) the intrinsically higher reactivity of the activated ketone and (ii) the anticipated higher adsorption equilibrium constant for acetophenone compared to 2-butanone and hence the higher surface coverage on platinum.

Hydrogenation of 2-butanone on $\text{Pt}/\text{Al}_2\text{O}_3$ under mild reaction conditions demonstrated two new interesting features: (i) water had a very strong inhibiting effect on the catalytic hydrogenation rates and (ii) quantitative on-line spectroscopic measurements of the catalytic system were complicated by hydrogen bonding with the un-activated carbonyl moiety in 2-butanone.

4.2. Effect of water on reaction rates

As shown in Section 3.4, the injection of water into the reaction system resulted in an obvious and very significant

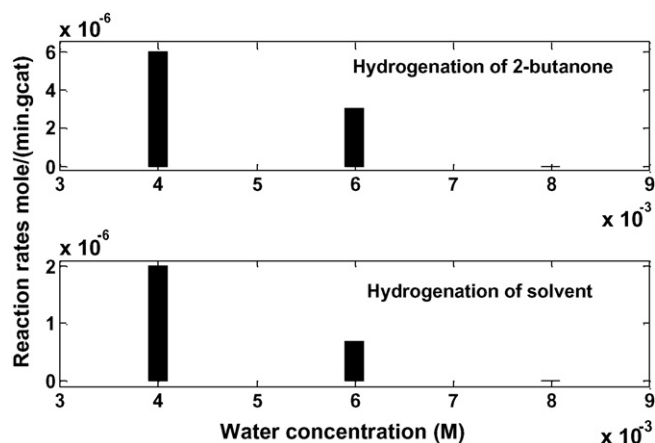


Fig. 6. The effect of water on the hydrogenation rates of 2-butanone and d_8 -toluene.

decrease in the catalytic hydrogenation rates of 2-butanone and solvent. The formation rates of 2-butanol and h_6-d_8 methylcyclohexane dropped from ca. 6×10^{-6} mol/(min g-cat) and ca. 2×10^{-6} mol/(min g-cat) at ca. 430 ppm water (before water perturbation) to ca. 2×10^{-7} mol/(min g-cat) and ca. 8×10^{-10} mol/(min g-cat) at ca. 860 ppm water (after the second 2 μ l water perturbation). These results demonstrate that the catalytic hydrogenation of un-activated simple ketone over Pt/Al₂O₃ catalyst was very sensitive to trace amount of water.

The decrease in reaction rates is probably due in part to the magnitude of the adsorption equilibrium constant for water. Although the data in the present study did not provide a good regression for a Langmuir–Hinshelwood–Hougen–Watson (LHHW) model, the previous acetophenone system showed a clear ordering of the adsorption equilibrium constants $K_{\text{water}} \gg K_{\text{ketone}} \approx K_{\text{alcohol}} > K_{\text{toluene}}$ [9]. Therefore, even a very small concentration of water can successfully compete for the coordination sites. Some irreversible deactivation may be occurring as well. Such catalyst deactivation resulting from water poisoning might arise from the decrease in active sites for hydrogenation due to more-or-less irreversible changes on the Pt crystallites.

It should be noted that the commercial 2-butanone product usually has a water impurity of ca. 0.2% (ca. 8000 ppm, mol/mol) which is much higher than the amount needed to inhibit the hydrogenation of this un-activated simple ketone on Pt/Al₂O₃. If such a commercial reagent with high moisture content was used directly, the lack of hydrogenation activity for 2-butanone over Pt/Al₂O₃ catalyst under mild reaction conditions would not be surprising.

4.3. Spectral changes and hydrogen bonding

The spectral changes observed in the carbonyl moiety of 2-butanone in Section 3.3 are most convincingly explained in terms of hydrogen bonding with water. Indeed, perturbations of water increased the absorptivities of the C=O fundamental stretch in both the control experiment as well as the catalytic experiments.

DFT simulations of optimized geometries for free 2-butanone, 2-butanone with one equivalent coordinated water and 2-butanone with two equivalents coordinated water were performed. These computations were performed since it is known that the coordination of water to 2-butanone is ca. 3:1 and this can only be achieved in aqueous solution [22]. The present experimental situation represents a relatively anhydrous environment so less hydrogen bonding is expected.

The corresponding infrared spectra were also estimated. Fig. 7 shows these spectral estimates. This figure clearly shows that: (i) there is a shift to lower wavenumbers as a function of increased hydrogen bonding and that (ii) more importantly, there is an increase in the absorptivities. The latter prediction in particular, is quite consistent with the experimental observations. The absorptivities of the C=O moiety in 2-butanone were always greater after hydrogen bonding with water. For completeness however, it can also be noted that the C=O vibrational spectra

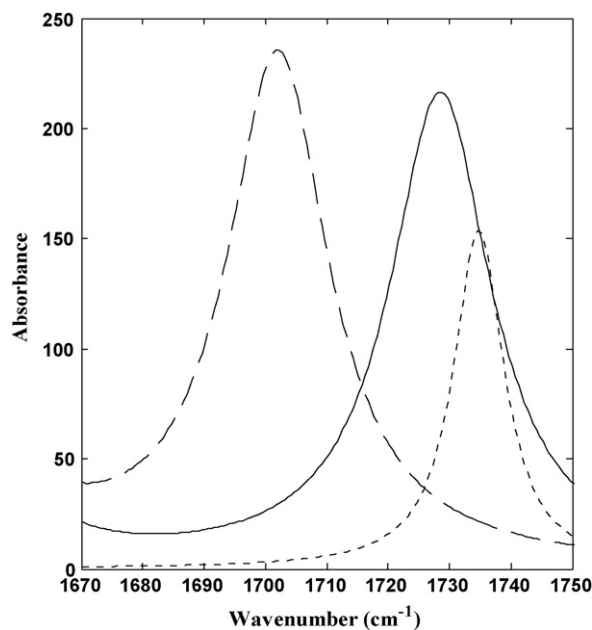


Fig. 7. DFT-predicted infrared spectra of C=O moiety in 2-butanone in the region of 1670–1750 cm⁻¹. Dotted line, no coordinated water; solid line, perturbation with one water molecule; dashed line, perturbation with two water molecules.

in Fig. 5 are quite asymmetric, indicating more than one type of species/coordination exist.

It is important to note that similar changes in the absorptivities of the C=O moiety in acetophenone were not observed in our previous study [9]. The relatively anhydrous spectra in C=O vibrational region were similar to those involving the deliberate addition of water and the C=O vibrational spectra were symmetric. This difference in acetophenone might be related to the conjugation between the phenyl group and the carbonyl moiety.

4.4. Other possible reactions and hydrogen bonding

In principle, two possible side reactions might also occur under the current reaction conditions. One is gem-diol formation between 2-butanone and water molecules [23,24]. The other one is hemiacetal/acetal formation between 2-butanone and 2-butanol molecules [25]. However, somewhat acidic or basic environments are frequently required in order to accelerate these formations. No additional BTEM estimates were recovered in this study, other than 2-butanone, 2-butanol, water and h_6-d_8 methylcyclohexane, and no further experimental evidence for the existence of these two reactions was observed. Therefore, these two side reactions were not further considered in the calculations of reaction rates and kinetics.

With regard to the possible additional modes of hydrogen bonding, alcohol–ketone and alcohol–water perturbations were considered; however, these perturbations are widely regarded to be weaker than water–ketone perturbation due to the presence of relatively large alkyl group in 2-butanol [26,27]. Finally, the spectra obtained in this study from the O–H stretching region of the alcohol showed no indications of unusual or inexplicable

absorptivity changes upon the perturbations with reactant or water.

5. Conclusion

Liquid-phase heterogeneous hydrogenation of 2-butanone was performed in anhydrous d_8 -toluene with multiple perturbations and monitored with on-line FTIR measurements. Due to the special solvent used, the C–H vibration region 2500–4000 cm^{-1} allowed the quantitative analysis of the reactant, product, h_6 - d_8 methylcyclohexane and dissolved water as well as the evaluation of the associated time dependent rates. With the deliberate perturbation of water, the strong inhibiting effect of water on the reaction rates was quantified and hydrogen bonding with the reactant was spectroscopically observed. Under anhydrous conditions, simple ketones (i.e. 2-butanone) can be hydrogenated over Pt/ Al_2O_3 at rates approaching those observed for the activated ketones. Therefore, the present results seem to suggest that special care should be taken for the catalytic hydrogenations of un-activated simple ketones over Pt/ Al_2O_3 (i.e. 2-butanone), both for preparative studies as well as kinetic and mechanistic studies.

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