Liquid-Phase Hydrogenation of Cinnamaldehyde Over Ir Catalysts: A Kinetic Modeling Study

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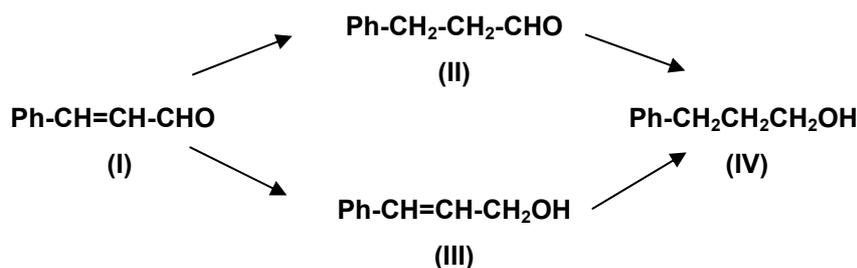Chemistry Department, Yarmouk University, Irbid, Jordan

Abstract

The liquid phase hydrogenation of cinnamaldehyde in toluene over alumina supported Ir catalysts was investigated under mild conditions (cinnamaldehyde concentration = 0.015 M – 0.060 M, hydrogen pressure = 3- 7 bar and T = 55- 95ºC). The Ir-particle size was determined by XRD to be ~6 nm with a dispersion of 28-35% and in good agreement with that determined by means of hydrogen chemisorption measurements. Under above reaction conditions, the order of reaction was experimentally found to be -0.5 with respect to cinnamaldehyde and 1 with respect to hydrogen. The apparent activation energy was practically zero. The kinetic data could be modeled based on the assumption that the Langmuir-Hinshelwood surface reaction between competitively adsorbed cinnamaldehyde and hydrogen is the rate determining step. The adsorption equilibrium constant of cinnamaldehyde, K_A, and the modified surface rate constant, $k_s K_H$, were calculated to be 87 M^{-1} and 5×10^{-4} M min^{-1} bar^{-1} g_{cat}^{-1}, respectively.

Keywords: Selective hydrogenation; Cinnamaldehyde; Iridium; Kinetics.

Introduction

The selective hydrogenation of cinnamaldehyde (I) has been the subject of extensive research due to the fact that one of its semi-hydrogenated products, namely cinnamyl alcohol (III) is highly important in the perfumery and pharmaceuticals industries [1,2]. There are, however, major difficulties associated with the process arising from both thermodynamic and kinetic considerations. From a thermodynamic point of view, it is always more favorable to produce the saturated aldehyde or the saturated alcohol than to produce the corresponding unsaturated alcohol [3]. The reactivity of the unsubstituted isolated C=C group in hydrogenation reactions catalyzed by unpromoted metals is also known to be always higher than the reactivity of the corresponding isolated carbonyl group [4]. Several approaches have been adopted to enhance the selectivity towards the unsaturated alcohol. These include studying the effect of metal type [5] and size [6] and its promotion with other metals or salts [7-9], the effect of reaction conditions [10] and the application of biphasic catalyst systems [11].

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$$\text{Ph-CH}_2\text{-CH}_2\text{-CHO}$$
(II)

$$\text{Ph-CH=CH-CHO}$$
(I)

$$\text{Ph-CH}_2\text{CH}_2\text{CH}_2\text{OH}$$
(IV)

$$\text{Ph-CH=CH-CH}_2\text{OH}$$
(III)

Despite the great interest in the selective hydrogenation of cinnamaldehyde in the liquid phase, up to now, only few kinetic studies have been reported in literature. This lack of information is caused mainly by the complexity of this reaction, where numerous compounds can be formed. Often a first-order rate law has been used to model the cinnamaldehyde hydrogenation experiments. However, this simple rate equation did not describe the cinnamaldehyde kinetics satisfactorily. Tronconi *et al*. [12], Neri *et al*. [13] and Vergunst *et al*. [14] provided more extensive kinetic models for this complex reaction. Troconi *et al*. and Neri *et al*. studied the effect of temperature on the selective hydrogenation of cinnamaldehyde over a Pt-Sn/Nylon catalyst and a Ru/Al$_2$O$_3$ catalyst, respectively. Their models are based on Langmuir-Hinshelwood kinetics with the adsorption of reactants and products being reversible and competitive while hydrogen is activated on a different site and does not compete with the organic compounds [12,13]. A two-site model is also assumed, one type of site for the adsorption of the carbonyl bond (C=O) and another type of site for olefinic bond (C=C) adsorption. They found that other models using one type of sites only or using competitive hydrogen adsorption gave less satisfactory results. On the other hand, Vergunst *et al*. [14] concluded in their study over Pt/C/monolithic catalysts that a single-site model in which adsorption, surface reaction and desorption are all rate determining gives the best results. However, the effect of hydrogen pressure and initial cinnamaldehyde concentration on the activity and selectivity could not be included in the model successfully.

Given that Iridium is highly selective in the hydrogenation of cinnamaldehyde to cinnamyl alcohol, remarkably little attention has been devoted to the kinetics of this reaction over Ir. Such, a detailed kinetic study has been recently initiated and included an investigation of the kinetics of the hydrogenation reaction of phenylpropanal (II) to phenylpropanol (IV) over Ir/Al$_2$O$_3$ [15] and that of the hydrogenation of cinnamyl alcohol (III) to phenylpropanol (IV) [16]. This work is a continuation to the previous studies aiming at modeling the kinetics of cinnamaldehyde hydrogenation under mild conditions and determining its various kinetic parameters.

Experimental

5% Ir/Al$_2$O$_3$ catalyst was prepared by adsorbing the appropriate amounts of IrCl$_4$ (Ferax Laboratories) from aqueous solution over γ-Al$_2$O$_3$ (Merck). The excess water was then removed slowly by evaporation in a rotary evaporator and the catalyst

precursor was dried overnight at 120ºC, followed by calcination under oxygen (Arab Gas Co.) for one hour at 300ºC followed by reduction with hydrogen (Arab Gas Co.) for 2.5 hours at same temperature. The prepared catalyst was characterized by x-ray diffraction (XRD) using a Phillips-PW 1729 generator with a Co-K$_\alpha$ tube (λ = 1.789 Å) in the range of 2θ = 30-105º. The scanning rate was 0.5º/min. Volumetric hydrogen chemisorption measurements were conducted in a home-built glass apparatus [17].

The hydrogenation of cinnamaldehyde was performed in a stainless steel hydrogenator (Parr-4842) with Waltow-945 control unit at its maximum stirring speed (1200 rpm). Before reaction, the catalyst was activated in the reaction vessel with hydrogen at 120ºC, aiming thereby at removing all surface impurities and adsorbed water. The reaction solution was thereafter introduced through the sampling port and temperature is then allowed to stabilize. Timing of reaction is started as soon as the hydrogen gas is admitted. The composition of the reaction mixture was then analyzed periodically by means of gas Chromatography (HP 5890 with thermal conductivity detector and 10 m long × 530 µm HP-5 column).

Results and Discussion

Catalyst Characterization

Figure 1 shows the Co-K$_\alpha$ x-ray diffraction pattern corresponding to alumina and alumina-supported Ir catalyst. The diffraction pattern of alumina indicates very poor crystallinity; the diffraction lines are weak and very broad. Moreover, the background intensity (>200 counts) is rather high. Such diffuse backgrounds are characteristic of amorphicity or poor crystallinity. The alumina support may be considered to be amorphous. The BET surface area of Al_2O_3 was measured in a previous work and was determined to be ~130 m²/g [18]. In comparison, the Ir-containing sample shows rather sharp diffraction lines, the most prominent are at 53.8º and at 44.1º, indicating that the Ir particles are crystalline. The Ir crystallite size was estimated applying Scherrer's equation to the 53.8º diffraction line and was found to be ~6 nm corresponding to a dispersion ranging between 28-35% (details of particle size determination can be found in [17]).

The dispersion of Ir particles was also determined by means of hydrogen chemisoprtion measurements at room temperature. The ratio of strongly adsorbed hydrogen atoms to the total number of Ir atoms in the catalyst (H/Ir) was thereby determined to be 0.78±0.02. In hydrogen chemisorption measurements, it is usually assumed that each hydrogen atom adsorbs on a single metal atom. If this were true, the above H/Ir ratio would correspond to an unrealistic large dispersion of 80%. On the other hand, hydrogen-to-metal ratio exceeding 1 for Pt and Rh and exceeding 2 for Ir were, reported for highly dispersed Pt, Rh and Ir supported on alumina and silica catalysts [19]. This, however, makes dispersion determination by means of hydrogen chemisorption impossible since the H/Metal ratio cannot be assumed. For this purpose, Kip et al. calibrated their H-chemisorption measurements versus EXAFS

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(extended x-ray absorption fine structure) measurements [19]. Following the calibration curve of Kips et al., our catalysts would have a dispersion of ~33% which is in good agreement with the value extracted from XRD.
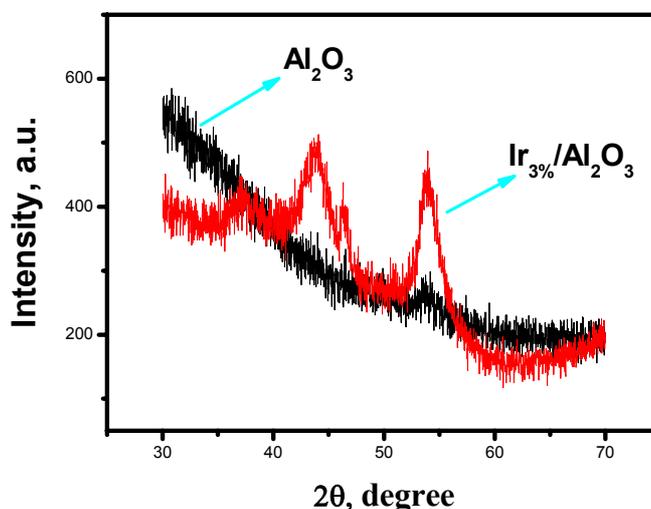
**Figure 1:** Co-K_α XRD- pattern of Al_2O_3 and Al_2O_3-supported Ir catalyst.

Kinetic Results

All hydrogenation reactions in this study have been carried out over 0.4g of 5% Ir/Al_2O_3 catalyst in toluene. No reaction products other than phenylpropanal (HCALD), cinnamyl alcohol (CAL) and phenylpropanol (PP) could be detected in significant amounts. The effect of reaction parameters such as temperature, hydrogen pressure, concentration of cinnamaldehyde (CALD) were studied by monitoring conversion as a function of time. Figure 2 represents an example of the concentration-time curves collected in such an experiment. From such a curve, the reaction rate in the initial range (initial rate of reaction, $rate_o$) where the concentration of the reacting substance drops linearly, can be graphically determined as shown in the figure.

$$rate_o = [CALD]_o \frac{\Delta x}{\Delta t}$$

$[CALD]_o$ is the initial concentration of cinnamaldehyde and x stands for the conversion at time t. In some cases, it has been observed that the drop in the concentration of CALD (due to the reaction) does not take place immediately as the hydrogen gas is admitted and the timing for reaction starts. This behavior can be attributed to the fact that just before admitting hydrogen gas, the Ir surface is completely covered by CALD molecules. There are therefore no available adsorption sites for H_2 molecules to adsorb on and the reaction rate is practically zero. Hydrogen molecules start then slowly to displace some CALD molecules from the surface and the reaction rate increases slowly. Some time is needed until equilibrium is established between H_2 and CALD molecules at the surface and H_2 and CALD molecules in solution. In such

cases, the initial rate is determined by considering only the linear decrease in CALD concentration that usually starts 10-20 min after the admission of hydrogen gas.
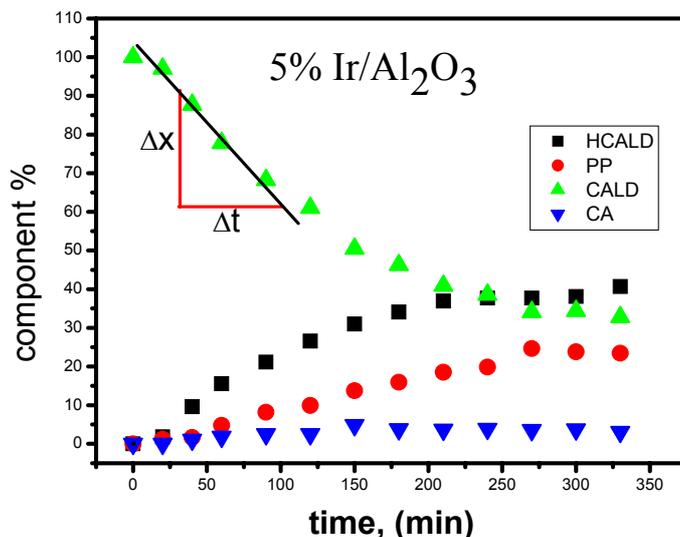
Figure 2: Product distribution in the catalytic hydrogenation of cinnamaldehyde in toluene over 0.40 g of 5% Ir/Al_2O_3 catalyst ($[CALD]_o$= 0.038 M, 65°C, 4 bar H_2).

Effect of CALD concentration

Figure 3 is a double-logarithmic plot of the initial rate of reaction versus the initial concentration of cinnamaldehyde. The hydrogen pressure and the reaction temperature were, thereby, kept constant. From the slope of the fitted line in figure 3 the order of reaction with respect to cinnamaldehyde concentration was determined to be -0.5. The only plausible mechanism that can explain the negative order of reaction with respect to CALD is the Langmuir-Hinshelwood mechanism with competitive adsorption. This means that CALD and hydrogen compete for the same adsorption sites; and as the concentration of CALD increases more and more hydrogen is displaced from the metal surface leading eventually to decreased reaction rates. Based on the above value for the order of reaction with respect to CALD concentration, diffusion limitations (i.e., the transport of CALD or hydrogen from solution to the catalyst surface being the rate determining step) can be excluded since under diffusion limitation first order kinetics would be expected. The above result affirms thus that the system is indeed in the kinetic regime which is a prerequisite in any kinetic study. The issue of diffusion limitations in the selective hydrogenation of CALD was previously investigated in detail over Pd/SiO_2 catalysts under the same reaction conditions as applied in this work [8]. The experimental findings in the above study (where the reaction was found to proceed much faster than in this work) confirm the absence of any diffusion limitations and support thus the above conclusion of absence of diffusion limitations in this work.
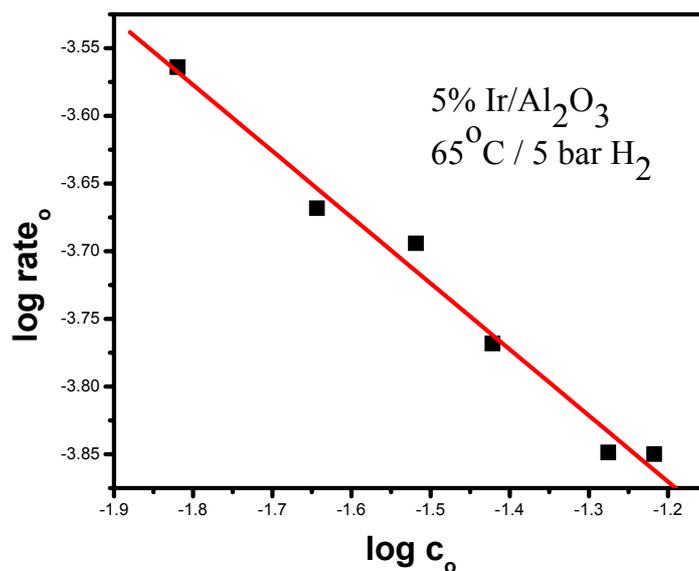
Figure 3: Double-logarithmic plot of the initial rate of hydrogenation vs. the initial concentration of cinnamaldehyde.

Effect of hydrogen pressure

To investigate the effect of hydrogen pressure on the reaction rate, a series of cinnamaldehyde hydrogenation experiments was performed with a constant initial CALD concentration (0.038 M) at 65°C. The magnitude of hydrogen pressure (constant throughout the experiment) was, thereby, varied between 3 and 7 bar. The results are summarized in figure 4. The order of reaction with respect to hydrogen is determined graphically and was found to be equal to 1. In the absence of diffusion limitations, this value is, however, rather unexpected since hydrogen is chemisorbed dissociatively on noble metals [20]. Nevertheless, it has been reported for H chemisorption on Ir(110)-(1×2) [21], H on Ni(100) and Ni(111) [22], H on Pt(110-(1×2) [23] and H on Ru(0001) [24]. It
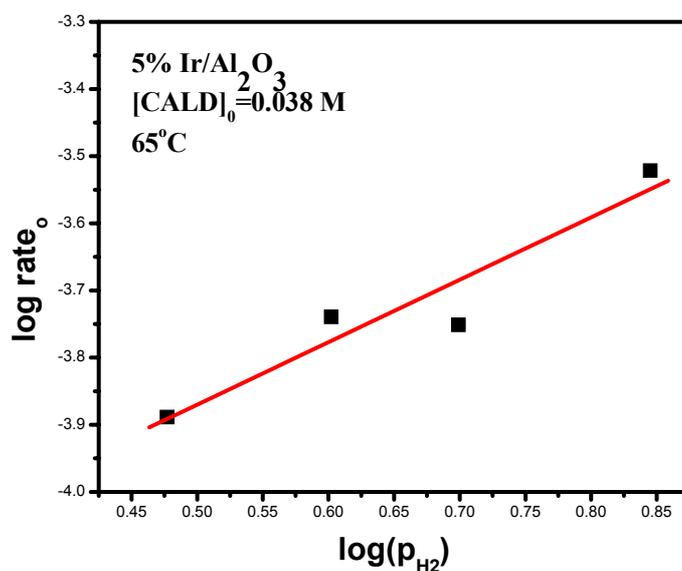

Figure 4: Effect of hydrogen pressure on the initial hydrogenation rate.

is also in agreement with the experimentally determined order of reaction with respect to hydrogen pressure in the hydrogenation of phenylpropanal [15] and that of cinnamyl alcohol over Ir [16]. These studies do not, however, suggest molecular adsorption of hydrogen. A possible explanation of an adsorption order of one (n=1) for dissociative adsorption is that trapping the molecule in the precurcer state (according to the Kisliuk model [25]) is the rate determining step and not the dissociation step. Another possible explanation for the value n=1 is that adsorption proceeds via an island growth mechanism so that the uncovered surface area would be proportional to $(1-\theta)$ [24].
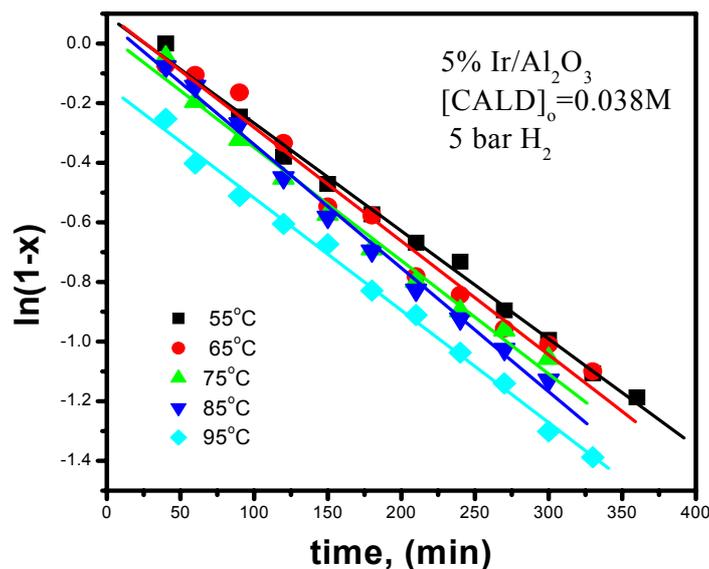
Figure5: Logarithmic plot of the concentration of CALD vs. time for different Temperatures, x stands for conversion.
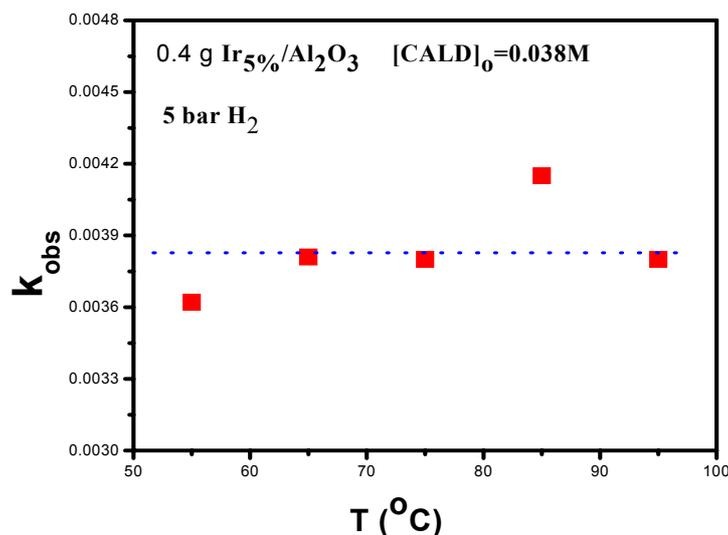
Figure 6: Temperature dependence of the observed rate constant, k_{obs}.

Effect of temperature

The influence of temperature on the kinetics of cinnamaldehyde hydrogenation in toluene was studied at 55, 65, 75, 85 and 95ºC with a constant initial concentration

of CALD (0.038 M) and a constant hydrogen pressure (5 bar). Pseudo first-order behavior was observed in a relatively wide range extending up to more than 70% conversion x in figure 5. The slopes of the linear plots of ln(1-x) vs. time represent thereby the values of the apparent pseudo first-order rate constant k that varies obviously only slightly with changing the reaction temperature (Figure 6). From the slope of the corresponding Arrhenius plot, the apparent activation energy was estimated to be ~1.7 kJ/mol which is practically zero.

Kinetic Modeling

Assuming that the surface reaction is the surface determining step and assuming that it proceeds via the Langmuir-Hinshelwood mechanism, the rate can be expressed as

$$rate = k_s \cdot \theta_A \cdot \theta_H \qquad\qquad \textbf{eqn.1}$$

k_s: *rate constant of the surface reaction between adsorbed hydrogen and adsorbed cinnamaldehyde.*
θ_A: *surface coverage of adsorbed cinnamaldehyde.*
θ_H: *surface coverage of adsorbed hydrogen.*

Since Langmuir-Hinshelwood mechanism assumes established adsorption equilibria of involved species, the surface coverages can be given for competitive adsorption by:

$$\theta_A = \frac{K_A^{1/q} c_A^{1/q}}{1 + K_H^{1/r} p_{H_2}^{1/r} + K_A^{1/q} c_A^{1/q}} \qquad\qquad \theta_H = \frac{K_H^{1/r} p_{H_2}^{1/r}}{1 + K_H^{1/r} p_{H_2}^{1/r} + K_A^{1/q} c_A^{1/q}}$$

K_A: *Adsorption constant of cinnamaldehyde (A).*   **K_H**: *Adsorption constant of hydrogen.*
c_A: *Liquid phase concentration of cinnamaldehyde (A).*   **p_{H_2}**: *Applied hydrogen pressure.*
1/r and 1/q: *Orders with respect to hydrogen and cinnamaldehyde adsorption.*

Notice that in these expressions the adsorption of the reaction product has been neglected. Practically, this corresponds to the initial stage where the concentration of product is zero. Hereby, the initial concentration of CALD must be substituted and the rate of reaction is rate$_o$. The expression for the initial reaction rate for the competitive adsorption model is then:

$$rate_o = k_s \frac{K_H^{1/r} p_{H_2}^{1/r} K_A^{1/q} c_{A,0}^{1/q}}{(1 + K_H^{1/r} p_{H_2}^{1/r} + K_A^{1/q} c_{A,0}^{1/q})^2} \qquad\qquad \textbf{eqn.2}$$

Usually, the adsorption of CALD is assumed to take place monomoleculary, i.e., CALD needs just a single adsorption site to adsorb on. In this case, q equals 1. If q=2, then two adsorption sites are required as was recently reported for the adsorption of cinnamyl alcohol [16]. In the following, the two possibilities are considered.

a) *For q=1*, equation 2 becomes

$$rate_o = k_s \frac{K_H^{1/r} p_{H_2}^{1/r} K_A c_{A,o}}{(1 + K_H^{1/r} p_{H_2}^{1/r} + K_A c_{A,o})^2} \qquad\qquad \textbf{eqn.3}$$

Manipulation gives

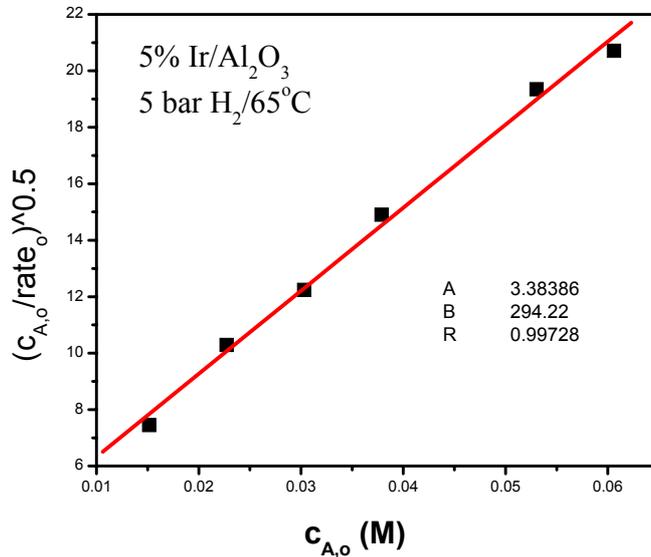$$\sqrt{\frac{c_{A,o}}{rate_o}} = \frac{1+K_H^{1/r}p_{H_2}^{1/r}}{(k_s K_H^{1/r}p_{H_2}^{1/r}K_A)^{1/2}} + \frac{K_A}{(k_s K_H^{1/r}p_{H_2}^{1/r}K_A)^{1/2}}c_{A,o} \qquad \textbf{\textit{eqn.4}}$$

Equation 4 suggests a linear relationship between $(c_{A,o}/rate_o)^{1/2}$ and $c_{A,o}$. Such a linear relationship is indeed obtained (Figure 7). By dividing the slope by the intercept of the line in figure 7, we get

$$\frac{K_A}{1+K_H^{1/r}p_{H_2}^{1/r}} \cong 87$$

Assuming that $1+K_H^{1/r}p_{H_2}^{1/r} \approx 1$ (see below) yields $K_A \approx 87\,M^{-1}$ and

$$k_s K_H = 2.0\times10^{-4}\ M\,\min^{-1} bar^{-1}(0.40\,g_{cat})^{-1}.$$

Figure 7: Competitive adsorption Modeling based on mono-adsorption site assumption.

b) *For q=2, equation 2 becomes*

$$rate_o = k_s \frac{K_H^{1/r}p_{H_2}^{1/r}K_A^{1/2}c_{A,o}^{1/2}}{(1+K_H^{1/r}p_{H_2}^{1/r}+K_A^{1/2}c_{A,o}^{1/2})^2} \qquad \textbf{\textit{eqn.5}}$$

Manipulation gives

$$\sqrt{\frac{c_{A,o}^{1/2}}{rate_o}} = \frac{1+K_H^{1/r}p_{H_2}^{1/r}}{(k_s K_H^{1/r}p_{H_2}^{1/r}K_A^{1/2})^{1/2}} + \frac{K_A^{1/2}}{(k_s K_H^{1/r}p_{H_2}^{1/r}K_A^{1/2})^{1/2}}c_{A,o}^{1/2} \qquad \textbf{\textit{eqn.6}}$$

Equation 6 suggests a linear relationship between $(c_{A,o}^{1/2}/rate_o)^{1/2}$ and $(c_{A,o})^{1/2}$. Such a linear relationship is indeed obtained (Figure 8). By dividing the slope by the intercept of the line in figure 8, we get

$$\frac{K_A^{1/2}}{1 + K_H^{1/r} p_{H_2}^{1/r}} \cong 419$$

Assuming that $1 + K_H^{1/r} p_{H_2}^{1/r} \approx 1$ (see below) yields $K_A \approx 175561\ M^{-1}$ and

$k_s K_H = 2.9 \times 10^{-3}\ M\ \min^{-1} bar^{-1} (0.40\ g_{cat})^{-1}$.
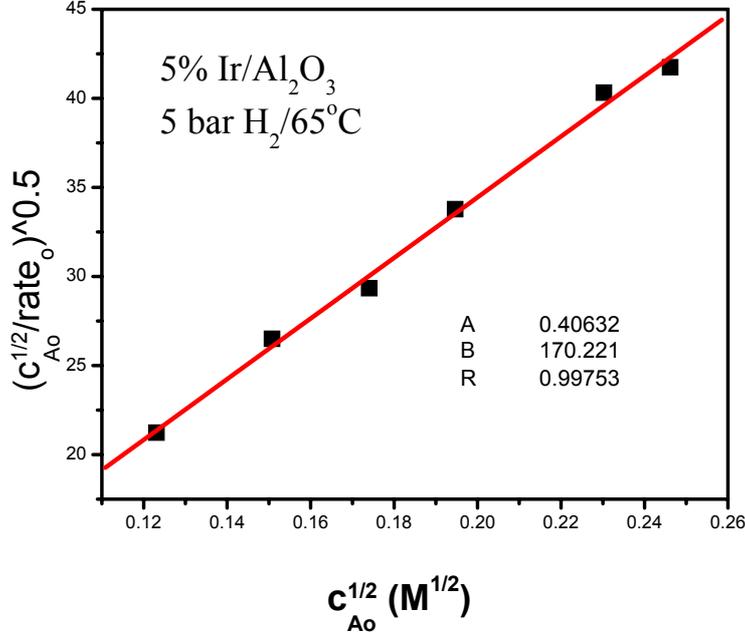
Figure 8: Competitive adsorption Modeling based on di-adsorption site assumption.

As observed, both models (for q=1 and for q=2) fit well the concentration series data. Experimental evidence for the correctness of the q=1 model is however provided from the pressure series. In the following, it is first shown that a reaction order of 1 with respect to hydrogen pressure can be deduced straightforward from equation 3 under the assumption that $1 + K_H^{1/r} p_{H_2}^{1/r} \approx 1$. Eqn.3 reads now

$$rate_o = k_s \frac{K_H^{1/r} K_A c_{A,o}}{(1 + K_A c_{A,o})^2} \cdot p_{H_2}^{1/r} \qquad \textbf{eqn.7}$$

When plotting $\log(rate_o)$ versus $\log p_{H_2}$, we get the value of 1/r from the slope. This has been shown in figure 4 to be equal to 1. Hence (1/r)=1, and r=1. Furthermore, from the intercept I of the line in figure 4, $k_s K_H$ can be determined.

$$\log I = \log \frac{k_s K_H K_A c_{A,o}}{(1 + K_A c_{A,o})^2} = -4.34 \qquad \textbf{eqn.8}$$

Substituting $c_{A,o}$=0.038 M and K_A=87 M^{-1} in equation 8 gives for $k_s K_H$ = 2.6×10^{-4} $M\ \min^{-1} bar^{-1} (0.40\ g_{cat})^{-1}$ which is in good agreement with the value of 2.0×10^{-4} $M\ \min^{-1} bar^{-1} (0.40\ g_{cat})^{-1}$ obtained from the concentration series for q=1. This

result supports the correctness of the q=1 model. On the other hand, the pressure series with q=2 does not reproduce the k_sK_H value extracted from the concentration series according to the q=2 model.

The apparent activation energy of the hydrogenation of cinnamaldehyde in the initial range can be deduced from equation 7 to be a complex function of the true activation energy of the surface reaction between adsorbed cinnamaldehyde and adsorbed hydrogen combined with the heat of adsorption of hydrogen and cinnamaldehyde. The negative heat of adsorption of hydrogen [15] reduces consequently the magnitude of the apparent activation energy, explaining thus its very small value observed in this work.

Based on our results that q=1 (a single adsorption site is needed to adsorb), the η_4 or di-π adsorption mode, where both functional groups (C=C and C=O) are adsorbed at the same time at different spots of the surface, can be excluded. This adsorption mode is nonselective with respect to the formation of cinnamyl alcohol and was reported to be the most favorable mode to adsorb on Pd(111) surface [26].

Kinetic modeling studies of the liquid phase hydrogenation of cinnamaldehyde were also performed by other research groups for Rh/Al$_2$O$_3$ [13], Pt/C [14], Pt/CNF [27], and Pt/C and Ir/C [28]. Modeling was thereby based on the concentration-time data of a single experiment. Successful modeling could, however, be achieved only under the assumption that hydrogen adsorbs on different sites other than those on which the organic compounds (reactants and products) adsorb. This is in contradiction with our results that hydrogen adsorbs competitively with cinnamaldehyde on the Ir surface. The adsorption of hydrogen was also confirmed to proceed competitively in the liquid phase hydrogenation of phenylpropanal [15] and cinnamyl alcohol [16], which are reaction products in the hydrogenation of cinnamaldehyde. This discrepancy may be attributed to the different reaction conditions as well as the different catalyst systems applied. It is also worth mentioning that in the above mentioned studies, the adsorption of the reaction products is assumed to proceed on a single adsorption site. This is not necessarily true. In an earlier investigation of cinnamyl alcohol hydrogenation [16], it was shown that the best kinetic model is obtained under the assumption that cinnamyl alcohol requires two adsorption sites to adsorb on.

Conclusions

The liquid phase hydrogenation of cinnamaldehyde over alumina supported Ir catalysts was investigated in toluene under mild conditions. The results are summarized below:

I)   Under experimental conditions in this work ([CALD]=0.015 M-0.060 M, p_{H_2}=3-7 bar and T=55-95ºC), the order of reaction was experimentally found to be -0.5 with respect to cinnamaldehyde and 1 with respect to hydrogen. The apparent activation energy (E_{app}) was practically zero.

II)   The reaction was found to proceed via Langmuir-Hinshelwood mechanism with competitive adsorption assuming the surface reaction between adsorbed atomic hydrogen and adsorbed cinnamaldehyde molecule to be the rate determining step.

III)   A single site model was found to satisfactorily describe the kinetics of cinnamaldehyde hydrogenation. The adsorption equilibrium constant of cinnamaldehyde, K_A, and the modified surface rate constant, $k_s K_H$, were calculated and found to be 87 M^{-1} and 5.0×10^{-4} M min^{-1} bar^{-1} g_{cat}^{-1}, respectively.

Acknowledgements

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