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Kinetics of cinnamaldehyde hydrogenation–concentration dependent selectivity

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Abstract

For the isothermal hydrogenation of cinnamaldehyde over Pt/C/monolithic catalysts three kinetic models have been evaluated, each model based on different sets of assumptions. A single-site and a two-site model with the surface reactions as rate-controlling steps were unable to describe the experimental data satisfactorily, while a single-site model with adsorption, surface reactions, and desorption all rate controlling could describe the experimental data adequately. This model includes apparent direct reaction steps from reactant to various end-products, due to the competition between desorption and subsequent conversion of intermediates at the catalyst surface. The selectivity to the unsaturated alcohol increases with increasing reactant concentration, which is ascribed to a change in adsorption mode, possibly due to some assembling phenomena of the reactant at the catalyst surface. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cinnamaldehyde; Selective hydrogenation; Kinetics; Pt/C catalysts

1. Introduction

The production of fine chemicals is an area in which multi-phase reactors are commonly used. Due to a combination of a low temperature stability of the organic components and the low solubility of the gaseous reactant, a multi-phase reactor is most suitable. Multifunctional molecules need to be converted selectively into the desired product. The numerous compounds that can be formed during these reactions make it difficult to develop a satisfactory kinetic model. The selective hydrogenation of cinnamaldehyde into cinnamyl alcohol is an example of such a complex reaction (Fig. 1). The aim of this study is to develop a suitable kinetic model to describe the hydrogenation of cinnamaldehyde.

Cinnamaldehyde is an example of an α,β-unsaturated aldehyde. In literature, only a few kinetic descriptions exist regarding the kinetics of the hydrogenation of α,β-unsaturated aldehydes in the liquid-phase [1–4]. These descriptions start often from the assumption of a two-site model, one-site for C=O hydrogenation and one-site for C=C hydrogenation, without justifying the increased number of parameters, compared to a single-site model. This study is used to develop several kinetic models based on either a single-site or a two-site model, and using either the surface reactions as rate controlling steps with adsorption and desorption in quasi-equilibrium or with competition between adsorption/desorption and the surface reactions. The reaction network shown in Fig. 1, which has been elucidated by applying each component of this scheme as a reactant, forms the starting point for the model development.

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Nomenclature

A	rate constant matrix
C	concentration (mol l^{-1})
k	rate constant (dimensions depend on system considered)
K	adsorption constant (l mol^{-1})
N	number of sites (mol kg^{-1})
r	rate (mol s^{-1} kg^{-1})
t	time (s)

Greek symbol

θ	fractional occupation (–)

Subscripts

ads	adsorption or if adsorbed on the surface
calc	calculated
CAL	cinnamaldehyde
CHP	cyclohexylpropanol
COL	cinnamyl alcohol
des	desorption
exp	experimental value
H	hydrogen
HCAL	hydrocinnamaldehyde
HCOL	3-phenyl-1-propanol
i	component i
j	step j
MST	β-methylstyrene
PHP	phenylpropane
T	Total of $*$ sites
$*$	$*$ site
#	# site
$-$	reverse

2. Kinetic models

Three different kinetic models have been developed.

Model I. The first model is a Langmuir–Hinshelwood–Hougen–Watson (LHHW) model using the following assumptions:

1. One type of sites: all reactions occur on the same catalytic site ($*$ sites).
2. Hydrogen does not show competitive adsorption on the metal surface. The effect of the hydrogen concentration is included in the reaction rate constants.
3. The surface reactions are rate determining, adsorption and desorption are in quasi-equilibrium.
4. Reactions are irreversible, dehydrogenation cannot occur.
5. β-Methylstyrene is immediately converted to phenylpropane, without desorption.
6. Cyclohexylpropanol and phenylpropane do not readsorb on the surface.

Model II. The second model is an LHHW model using the assumptions presented for model I, except for assumption 3, which is modified as follows:

> The surface reactions are in competition with adsorption and desorption. Neither of them is in quasi-equilibrium.

Model III. The third model is an LHHW model using the assumptions presented for model I, except for a modification of assumption 1, and an extension of assumption 3:

1. Two different types of sites exist. Over one type of site reactions involving C=C bonds take place ($*$ sites), over the second type of site reactions involving C=O bonds occur (# sites).
2. The surface reactions are rate determining, adsorption and desorption are implicitly considered in quasi-equilibrium. Also the change from $*$ to # sites is in quasi-equilibrium.

These models are generally developed as follows. A detailed description of each of the models is presented by Vergunst [5].

The adsorption, desorption, and elementary irreversible surface reaction of a component i on site $*$ read

$$r_{\mathrm{ads},i} = k_j N_T C_i \theta_* \qquad (1)$$

$$r_{\mathrm{des},i} = k_{-j} N_T \theta_{i*} \qquad (2)$$

$$r_j = k_j N_T \theta_{i*} \qquad (3)$$

It should be noted that the hydrogen dependency is included in the rate constants. The occupation of sites does not change in the steady state

$$\frac{\mathrm{d}\theta_{i*}}{\mathrm{d}t} = 0 \qquad (4)$$

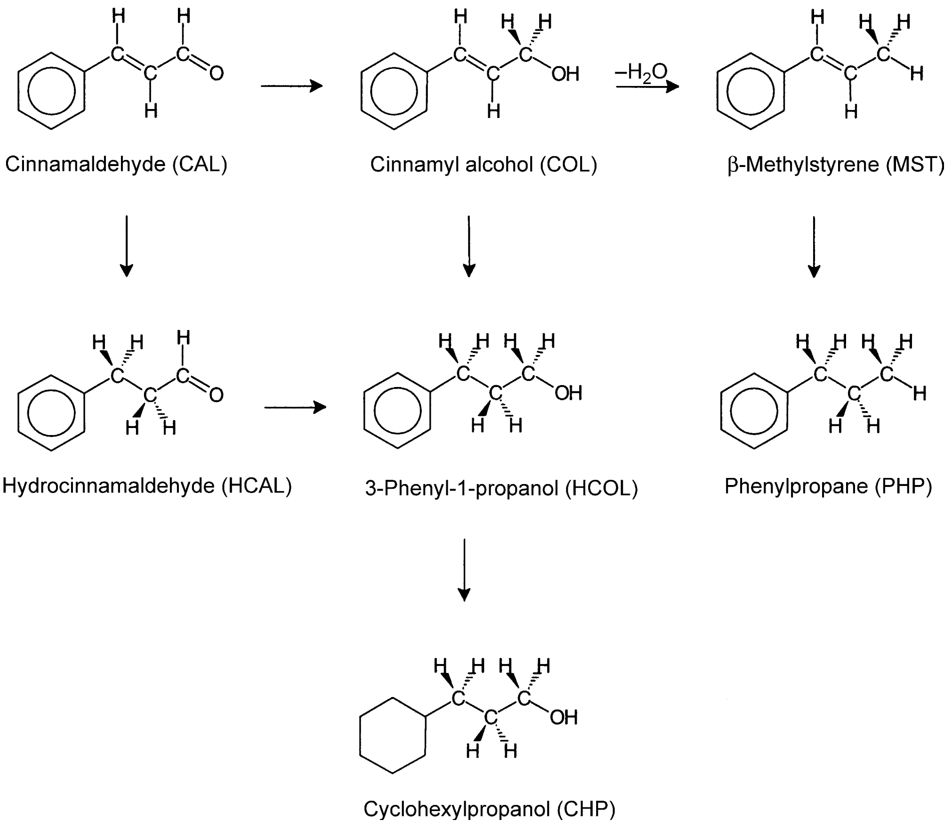

Fig. 1. Reaction network for cinnamaldehyde hydrogenation [5].

The site balance reads

$$\sum_i \theta_{i*} + \theta_* = 1 \tag{5}$$

The following reaction rate expressions evolve under the assumptions described above:

$$\frac{\mathrm{d}}{\mathrm{d}t}[C] = \frac{A_{ij}[C]}{\mathrm{LHHW}_*} \tag{6}$$

with

$$[C] = [C_{\mathrm{CAL}} C_{\mathrm{COL}} C_{\mathrm{HCAL}} C_{\mathrm{HCOL}} C_{\mathrm{MST}} C_{\mathrm{PHP}} C_{\mathrm{CHP}}]^{\mathrm{T}} \tag{7}$$

$$\mathrm{LHHW}_* = 1 + K_{\mathrm{CAL},T} C_{\mathrm{CAL}} + K_{\mathrm{COL},T} C_{\mathrm{COL}} + K_{\mathrm{HCAL},T} C_{\mathrm{HCAL}} + K_{\mathrm{HCOL},T} C_{\mathrm{HCOL}} \tag{8}$$

From Fig. 2 the appropriate matrix A_{ij}, which contains the reaction rate constants k, can be deduced. The effects of the liquid volume in the reactor and the catalyst mass are included in the reaction rate constants of matrix A_{ij}.

Models. The resulting models can be described as follows. Model I is a single site model. Only single

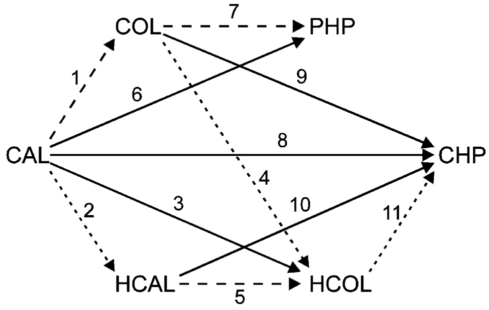

Fig. 2. Reaction scheme for models I (all dashed arrows), II (all arrows), and III (dashed arrows, short dashed arrows occur on * sites, long dashed arrows occur on # sites).

step hydrogenations can occur. In model II multi-step hydrogenations can occur, like the direct conversion of cinnamaldehyde into 3-phenyl-1-propanol. Molecules that are adsorbed on the surface face the competition between desorption and consecutive hydrogenation. If these multi-step hydrogenations are not required, the accompanying reaction rate constants will become zero, and model II simplifies to model I. Model III looks similar as model I, only some of the reactions take place on different sites with different adsorption coefficients [5].

3. Experimental methods

The catalyst used for the cinnamaldehyde hydrogenation experiments is a Pt/C/monolithic catalyst, prepared according to Vergunst et al. [5,6]. The 400 cpsi per 62 cells cm^{-2} cordierite monolithic support of 43 mm diameter and 50 mm length was loaded with 17.7 wt.% carbon and 1.23 wt.% Pt, with an average metal particle size of 4.1 nm, as observed with TEM. The total catalyst mass was 39.4 g. The hydrogenation experiments were carried out in a 300 ml stirred batch autoclave, equipped with an insert to mount the monolithic catalyst [7]. The reactor was filled with 150 ml reaction mixture, $\sim$0.7 M cinnamaldehyde in toluene. The reaction was carried out at 303 K and 5.0 MPa total pressure. The reaction mixture composition was analyzed several times during an experiment using gas chromatography. The models were fitted to the experimental data using MICROMATH® SCIENTIST® for WINDOWS™, Version 2.0. In addition, experiments at an higher initial cinnamaldehyde concentration (3.3 M cinnamaldehyde in toluene) have been carried out.

4. Results and discussion

Fig. 3 shows the experimental results for a cinnamaldehyde hydrogenation experiment carried out at low and high initial cinnamaldehyde concentration. Comparing hydrogenation results obtained with a low initial cinnamaldehyde concentration with hydrogenation results obtained at high initial cinnamaldehyde concentration shows that the amount of cinnamaldehyde converted is almost equal, but that the product distribution is shifted from cinnamyl alcohol towards 3-phenyl-1-propanol. The experiment performed at low initial cinnamaldehyde concentration has been used for kinetic model discrimination.

Fig. 4 shows the experimental data, fits, and residuals for a cinnamaldehyde hydrogenation experiment. Models I and III (left and right column) do not satisfactorily describe the experimental data, especially for the components present in low concentration (center row). Both the maxima of the cinnamyl alcohol concentration and the hydrocinnamaldehyde concentration, calculated with models I and III do not coincide with the experimental data. In addition, the shape of the cyclohexylpropanol formation curve does not correspond with the experimental values. The residuals for models I and III show systematic deviations. The

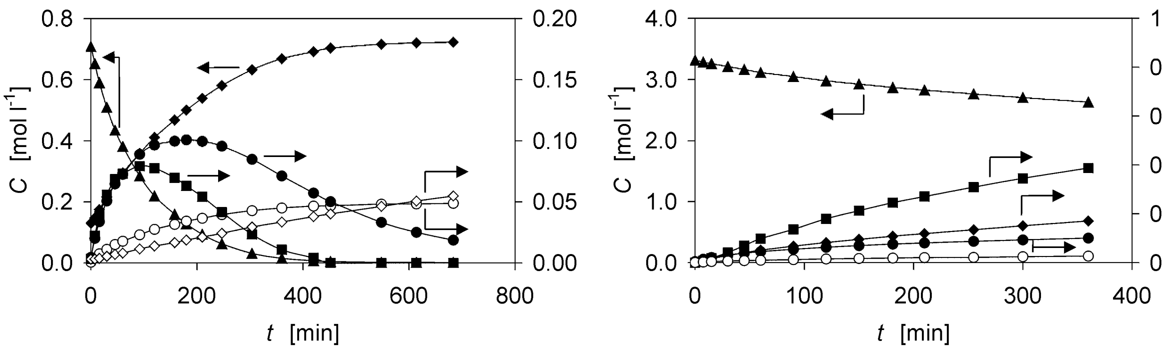

Fig. 3. Cinnamaldehyde hydrogenation experiments at low initial (left) and high initial concentration (right) ($T = 303$ K, $P = 5.0$ MPa, solvent toluene). (▲) Cinnamaldehyde; (■) cinnamyl alcohol; (●) hydrocinnamaldehyde; (◆) 3-phenyl-1-propanol; (○) phenylpropane; (◇) cyclohexylpropanol.

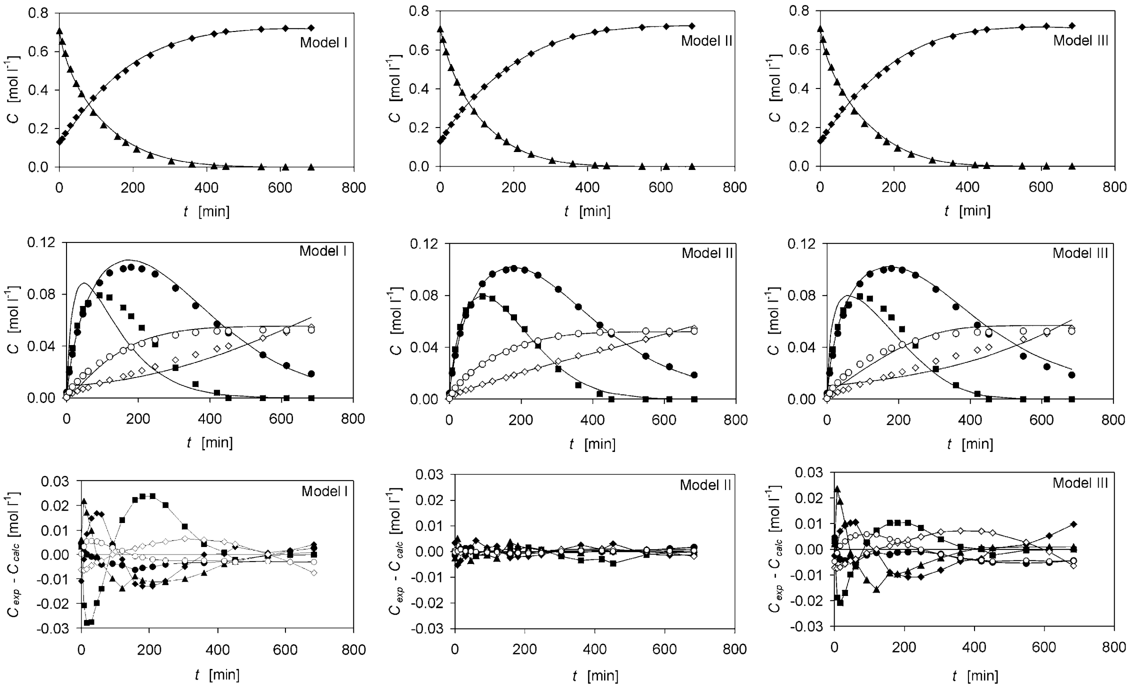

Fig. 4. Experimental data (symbols) and fitted models (lines) (top row: components present in high concentration, center row: components present in low concentration, and residuals (bottom row)) as a function of time for a cinnamaldehyde hydrogenation experiment (0.7 M in toluene) over a Pt/C/monolithic catalyst at $T = 303\,\mathrm{K}$, $P = 5.0\,\mathrm{MPa}$. (▲) Cinnamaldehyde; (■) cinnamyl alcohol; (●) hydrocinnamaldehyde; (◆) 3-phenyl-1-propanol; (○) phenylpropane; (◇) cyclohexylpropanol.

fitting results of model II (center column) show good agreement between experimental and calculated data.

Models I and III are very similar. Only single hydrogenation steps can occur, because adsorption and desorption are in quasi-equilibrium. The difference between models I and III is that in model III some of the reactions occur on different sites with different adsorption parameters. Model II is rather different. Because adsorption, desorption and surface reactions are all rate controlling, a molecule to which two hydrogen atoms are added has the choice to either desorb or react further on the surface. Therefore, multi-step hydrogenations can occur in this model, like the conversion of cinnamaldehyde into 3-phenyl-1-propanol. The results presented in Fig. 3 show that the prediction of model II agrees best with the experimental data. The residuals of model II are smallest, while also systematic deviations, as observed for models I and III are not observed. Both models I and III imply that 3-phenyl-1-propanol is formed out of cinnamyl alcohol and hydrocinnamaldehyde, because adsorption and desorption are in quasi-equilibrium, while the concentration versus time curves do not show the characteristic S-shape, as expected for secondary products [8]. Multi-step hydrogenations are therefore required, so that model II is the best. Kinetic models including multi-steps transformations are not very common, although they have been used successfully before for hydrodenitrogenation [9].

In literature several models exist, that describe the hydrogenation of α,β-unsaturated aldehydes in the liquid-phase [1–4]. All these models start from the assumptions of a two-site model and the surface reactions rate controlling. Comparing our model with these models, it can be noted that the model developed in this study requires more parameters, but that it provides a better description of the experimental data as well. The assumption that the surface reaction is rate determining, as assumed by Hotta and Kubomatsu [1,2], Tronconi et al. [3], and Neri et al. [4]

cannot be made, as proven by the worse description of the experimental data by model I. The direct hydrogenation of cinnamaldehyde into 3-phenyl-1-propanol is a step that is required to obtain a good description of the experimental data. The use of a two-site model [1–4] resulted in a worse agreement between experimental data and the used model, than using a single-site model with adsorption, desorption, and surface reaction as rate limiting steps.

Model II with the kinetic parameters obtained from the hydrogenation experiments performed at low initial cinnamaldehyde concentration, has been used to predict the performance at high initial cinnamaldehyde concentration as well (comparable activity but much higher cinnamyl alcohol selectivity). Both activity and selectivity of this experiment could not be predicted satisfactorily. From several potential explanations, like the effect of cinnamaldehyde, solvent, or reactant concentration, it was deduced that the effect of cinnamaldehyde concentration was most likely. At low cinnamaldehyde concentration, cinnamaldehyde will preferably adsorb flat on the surface. With increasing concentration, less space is available and cinnamaldehyde will adsorb with the C=O group only, which requires less space on the surface (Fig. 5). Depending on the mode of adsorption of cinnamaldehyde, either the C=C group or C=O group is converted resulting in a shift in selectivity [5]. This adsorption orientation has been described by Gallezot and Richard [10], and the effect of concentration dependent adsorption modes by Jin et al. [11]. It is suggested that a kind of self-assembling of the aromatic rings takes place, resulting in an end-on adsorption and increased selectivity towards the unsaturated alcohol.

The effect of hydrogen pressure can be important as well in multi-phase hydrogenation reactions. Extending model II with a hydrogen dependency is not straightforward. The effect of hydrogen is included in the reaction rate constant k_j of the elementary surface reaction (3). Because adsorption, desorption, and surface reactions are all rate controlling, the resulting reaction rate constants, depicted in Fig. 2, and the ‘adsorption coefficients’ of Eq. (6) are compound functions of the elementary reaction rate constants k_j and

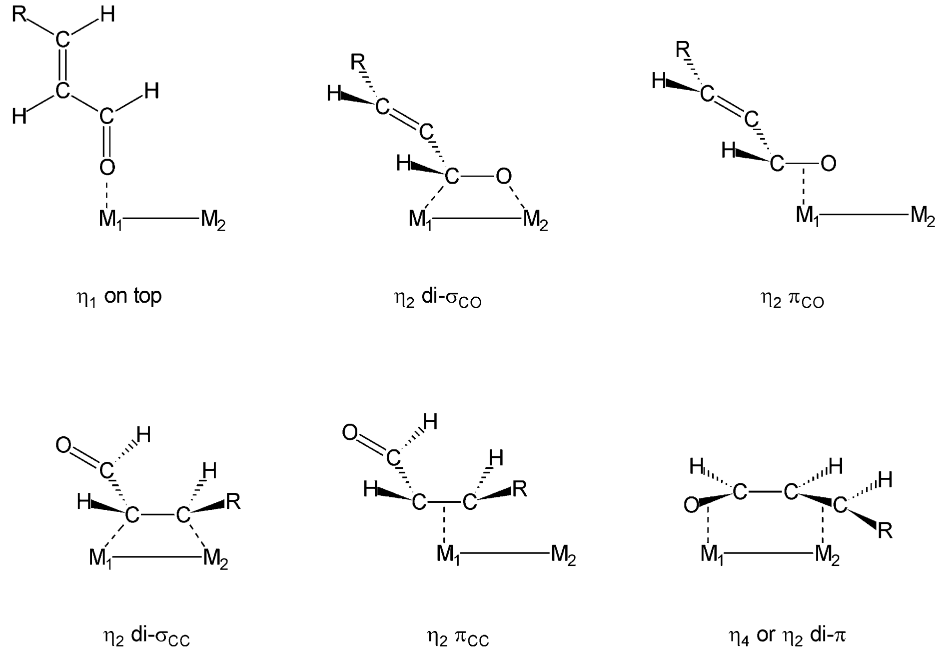

Fig. 5. Various adsorption modes of cinnamaldehyde [12,13]. The η_1 on top requires less adsorption space than, for example, the η_2 di-σ_{cc} adsorption mode. The three left adsorption modes result in the hydrogenation of the C=O bond, while the other adsorption modes result in the C=C hydrogenation [5].

k_{-j}, so that these parameters all include a complex hydrogen dependency, which cannot easily be written explicitly. Model II can be used to describe cinnamaldehyde hydrogenation experiments performed at various hydrogen pressures, but all the reaction rate constants change with each different hydrogen pressure used.

Inclusion of the concentration dependent cinnamaldehyde adsorption orientation and of the effect of hydrogen in model II is required for a more general application of this model, but it also makes this model too complicated to arrive at an explicit rate expression. On the basis of the current experimental data this degree of sophistication is not justified.

5. Conclusions

The liquid-phase hydrogenation of cinnamaldehyde over Pt/C/monolithic catalysts is kinetically described best using a single-site model with both adsorption, surface reaction, and desorption as rate controlling steps. This competition led to apparent direct reaction steps from reactant to end-products. A single- or two-site model with the surface reactions as rate controlling steps, did not provide a satisfactory description of the experimental data. The effect of cinnamaldehyde concentration on the selectivity of the reaction was explained by adsorption orientation of cinnamaldehyde on a catalytic site. Including the effect of concentration dependent adsorption orientation and the effect of hydrogen pressure within the kinetic model is required for a more general applicability of the model.

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