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Separation of kinetics and mass-transport effects for a fast reaction: the selective hydrogenation of functionalized alkynes

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Abstract

A kinetic study has been made into the hydrogenation of 3-methyl-1-pentyn-3-ol over palladium on silica catalysts. This reaction already proceeds at very high rates under mild reaction conditions and, therefore, mass-transfer inside the catalyst particle inevitably influences the reaction progress, making the determination of the reaction kinetics difficult. To be able to determine the reaction mechanism and the kinetic parameters, a model has been drawn up in which both mass-transfer and kinetics are modeled simultaneously. This model is able to accurately describe the reaction progress. The model can also be used to explain the effect of commonly used reaction modifiers like quinoline on the reaction. Quinoline can be added to increase the selectivity to the desired alkene intermediate. From the calculations it is shown that the primary function of this type of modifier is to decrease the reaction rate. The lower reaction rate and thereby relatively smaller mass-transfer resistance in the catalyst is most likely a primary cause for the increased selectivity when a reaction modifier is used.

Keywords: Mass-transport; Alkene; Hydrogenation; Palladium; Catalyst; Alkyne

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1. Introduction

Hydrogenation of 3-methyl-1-pentyn-3-ol over palladium on silica catalysts has been investigated as a fast model reaction for the hydrogenation of functionalized alkynes [1]. In this reaction (Fig. 1) the alkene is the desired product and complete hydrogenation to the alkane should be avoided. Hydrogenation was performed over a palladium on silica catalyst.

In selective hydrogenations in fine chemical industry sometimes reaction modifiers are added to the reaction system to increase selectivity [2]. The manner in which such a modifier functions is commonly thought to be by the prevention of adsorption of the intermediate product, while the adsorption of the primary reactant is not effected. The exact mode of operation of this type of modifier is still a matter of discussion in literature, e.g. [3]. The effect of adding such a modifier (quinoline) to this reaction system was also investigated in this paper. By means of kinetic modeling of the reaction with and without modifier present a better insight in the mode of operation of the modifier is obtained.

2. Experimental

The palladium on silica catalysts were prepared using an ion-exchange type method with an palladiumacetate solution in dry toluene, followed by a liquid-phase reduction at room temperature using molecular

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Nomenclature

C_{cat}	catalyst concentration ($\text{m}^3_{\text{catalyst}}/\text{m}^3_{\text{liquid}}$)
C_i	concentration (mol/m^3)
D_i	diffusion coefficient (m^2/s)
$k_{\text{a},i}$	adsorption rate constant (m^3/mol/s)
k_i	reaction rate constant (m^3/mol/s)
K_i	adsorption constant (m^3/mol)
N_{s}	number of adsorption sites (mol/m^3)
r	radial position in catalyst particle (m)
R	catalyst particle diameter (m)
t	time (s)

Greek letter

θ	surface occupancy (–)

Subscripts

A	alkane
bulk	in liquid bulk
E	alkene
H_2	hydrogen
Q	quinoline (modifier)
sat	saturation concentration (for hydrogen in liquid)
Y	alkyne
1	alkyne–alkene reaction
2	alkene–alkene reaction
$*$	vacant sites

hydrogen, washing with pentane and drying in vacuum. The catalyst was stored in a nitrogen atmosphere. The detailed recipe for this preparation can be found in [4].

Hydrogenation experiments were performed in glass slurry-reactor at 298 K and 1 bar pressure with (dry) ethanol as solvent. A gas-inducing stirrer (1500 rpm) was used to keep a hydrogen saturated liquid phase. Liquid samples were taken during the experiment and analyzed by means of gas chromatography to follow reaction progress.

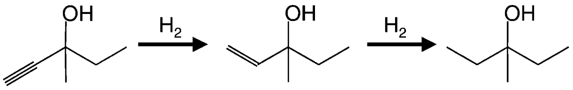

Fig. 1. Hydrogenation of 3-methyl-1-pentyn-3-ol. The first partial hydrogenation step yields the desired product.

3. Results and discussion

3.1. Reaction kinetics

In Fig. 2 a typical graph is shown for a hydrogenation experiment of 3-methyl-1-pentyn-3-ol. It can be seen that the reaction proceeds via a sequential reaction mechanism, with the hydrogenation of the alkene only becoming significant once all the alkyne has been converted. This type of reaction behavior is commonly described by a Langmuir–Hinshelwood (L–H) kinetic expression. In the first part of the reaction progress the relatively strong alkyne adsorption is preventing the complete hydrogenation of the alkene product. Once most alkyne has been converted, the hydrogenation of the alkene starts occurring at a high rate. The corresponding L–H rate expressions are given in Eqs. (1)–(3).

$$r_{\text{Y}} = \frac{\partial C_{\text{Y}}}{\partial t} = -\frac{k_1 C_{\text{cat}} K_{\text{Y}} C_{\text{Y}} C_{\text{H}_2}}{1 + K_{\text{Y}} C_{\text{Y}} + K_{\text{E}} C_{\text{E}} + K_{\text{A}} C_{\text{A}}} \tag{1}$$

$$\begin{aligned} r_{\text{E}} = \frac{\partial C_{\text{E}}}{\partial t} &= \frac{k_1 C_{\text{cat}} K_{\text{Y}} C_{\text{Y}} C_{\text{H}_2}}{1 + K_{\text{Y}} C_{\text{Y}} + K_{\text{E}} C_{\text{E}} + K_{\text{A}} C_{\text{A}}} \\ &\quad - \frac{k_2 C_{\text{cat}} K_{\text{E}} C_{\text{E}} C_{\text{H}_2}}{1 + K_{\text{Y}} C_{\text{Y}} + K_{\text{E}} C_{\text{E}} + K_{\text{A}} C_{\text{A}}} \end{aligned} \tag{2}$$

$$r_{\text{A}} = \frac{\partial C_{\text{A}}}{\partial t} = \frac{k_2 C_{\text{cat}} K_{\text{E}} C_{\text{E}} C_{\text{H}_2}}{1 + K_{\text{Y}} C_{\text{Y}} + K_{\text{E}} C_{\text{E}} + K_{\text{A}} C_{\text{A}}} \tag{3}$$

The initial values at $t = 0$ for solving these differential equations are the starting concentrations in the reactor, i.e. the concentration of alkyne added for C_{Y} and 0 for C_{E} and C_{A}. The hydrogen concentrations used in the modeling were obtained from the IUPAC solubility data series [5].

If only one single experiment is modeled, these equations can be fitted easily to the measurement without any systematic deviations between model and measurement. However, if experiments are performed with different alkyne concentrations at the start of the experiment, one observes that the maximum relative yield of alkene decreases with a lower starting concentration. The kinetic parameters obtained from fitting each experiment individually are different. This type of behavior cannot be explained by just a simple L–H kinetics.

Performing the experiments using different size catalyst particles results in both different rates and

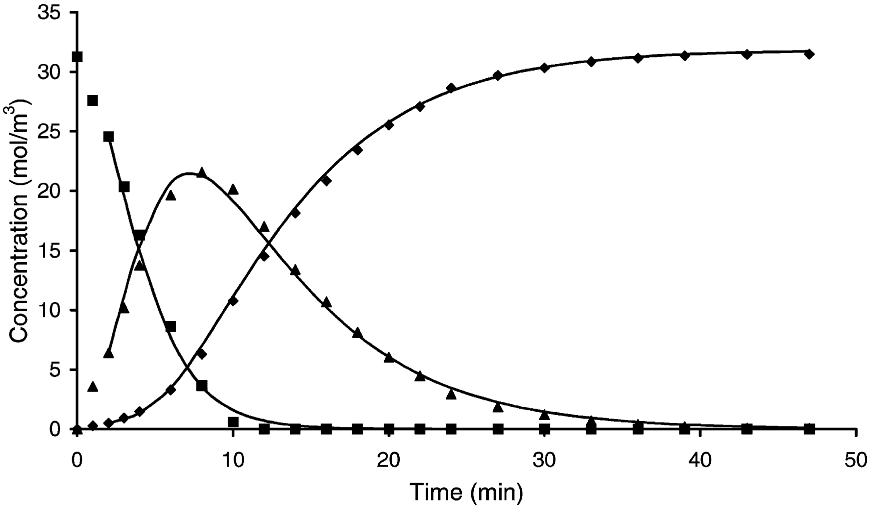

Fig. 2. Kinetics model fitted to experiment. Hydrogenation of 3-methyl-1-pentyn-3-ol over 2 wt.% Pd on Davisil 643 catalyst (0.53 kg/m^3 catalyst, 298 K, initial alkyne concentration 32 mol/m^3). Markers: experiment, (■) alkyne concentration, (▲) alkene concentration, (◆) alkane concentration. Lines, results of kinetic fit. First 2 min of experiment not included in fitting.

selectivities. The results of these experiments are summarized in Table 1. These results indicate that the reaction is not kinetically controlled and that mass-transfer might have to be taken into account.

For similar liquid-phase alkyne hydrogenations at comparable mild conditions, it is reported that mass-transfer effects on the reaction are small. One such example is the hydrogenation of phenylacetylene over palladium [6], for which normal L–H kinetics suffice without having to include mass-transfer into the modeling. For this same reaction Jackson and Shaw [7] do not report any mass-transfer effects either. However, they report an activation energy of only 26 kJ/mol, which is very low and unlikely. If internal mass-transfer limits a reaction, it is commonly known that the observed activation energy is half the true activation energy [8]. Comparing the observed activation energy of 26 kJ/mol by Jackson and Shaw [7] to that of 52 kJ/mol reported by Chaudhari et al. [6] leads to the conclusion that the lower value must have been an internally mass-transfer limited one. In the current work the experiments similarly point to the conclusion that mass-transfer inside the catalyst particles is important. Either the hydrogenation of 3-methyl-1-pentyn-3-ol is intrinsically faster, or the catalyst used in this study is more active.

Experiments performed with different high (>1000 rpm) stirring rates and catalyst concentrations resulted in identical catalyst activities and selectivities. These experiments make it possible to exclude external mass-transfer limitations. Fitting a model including internal mass-transfer to a set of experiments results in an improved fit, which is satisfactory for predicting the observed rates. In Fig. 3 the observed catalyst efficiencies calculated from Table 1 are compared to predicted catalyst efficiencies, calculated by means of a Thiele-moduli [9]. These efficiencies are calculated on the assumption of an intrinsic rate of 9.7 mmol/g$_{Pd}$/s, with a reactant concentration of 300 mol/m^3 and hydrogen being the mass-transfer

Table 1
Activities and selectivities (maximum yield of desired alkene) obtained with different size 2 wt.% Pd on silica catalyst particles and different reactant concentrations[a]

Catalyst particle size (μm)	Activity (mmol/g$_{Pd}$/s)		Maximum alkene yield (%)	
	300 mol/m^3	30 mol/m^3	300 mol/m^3	30 mol/m^3
4–20	9.33	8.33	90.4	81.5
35–74	7.67	5.50	90.2	68.2
149–250	2.50	2.50	79.7	52.2

[a] Hydrogenation of 3-methyl-1-pentyn-3-ol, 298 K, 1 bar H_2, 0.75 kg/m^3 catalyst.

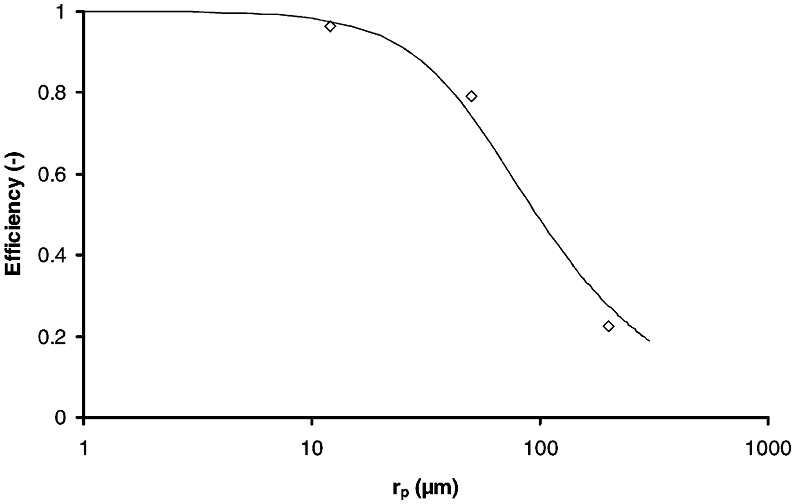

Fig. 3. Comparison between observed catalyst effectiveness factors (symbols) and theoretical effectiveness factors (line) calculated by means of a Thiele modulus as a function of the catalyst particle radius. Efficiencies calculated on the assumption of an intrinsic rate of 9.7 mmol/g_{Pd}/s, with a reactant concentration of 300 mol/m^3 and hydrogen being the mass-transfer limiting component.

limiting component. For the interparticle diffusion coefficients the estimation method by Wilke and Chang [10] was used. It can be seen that the agreement between measured rates and calculated rates is good.

To model the reaction satisfactory for the selectivity as well, it is necessary to add a direct alkyne–alkane hydrogenation step. In practice such a one-step hydrogenation is unlikely, it is more likely that the alkene produced on the catalyst surface is hydrogenated further to the alkane, before it has a chance to desorb, i.e. the catalyst surface composition is not in equilibrium with the surrounding liquid. Using such a model makes the unrealistic direct alkyne–alkane hydrogenation step in the model obsolete. Therefore, a model is used which includes both internal transport in the catalyst particles and a catalyst surface which is not at equilibrium with the liquid. This model should be able to match both the observed activities and selectivities.

The differential equations describing the model described above are:

Concentrations inside the particles:

$$\frac{\partial C_i}{\partial t} = D_i\left(\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r}\frac{\partial C_i}{\partial r}\right) - k_{a,i}N_s C_i \theta_* + \frac{k_{a,i}}{K_i}N_s\theta_i \tag{4}$$

$$\frac{\partial C_{H_2}}{\partial t} = D_{H_2}\left(\frac{\partial^2 C_{H_2}}{\partial r^2} + \frac{2}{r}\frac{\partial C_{H_2}}{\partial r}\right) - k_1 N_s \theta_Y C_{H_2} - k_2 N_s \theta_E C_{H_2} \tag{5}$$

Surface compositions in the catalyst particles:

$$\frac{\partial \theta_Y}{\partial t} = k_{a,Y}C_Y\theta_* - \frac{k_{a,Y}}{K_Y}\theta_Y - k_1\theta_Y C_{H_2} \tag{6}$$

$$\frac{\partial \theta_E}{\partial t} = k_{a,E}C_E\theta_* - \frac{k_{a,E}}{K_E}\theta_E + k_1\theta_Y C_{H_2} - k_2\theta_E C_{H_2} \tag{7}$$

$$\frac{\partial \theta_A}{\partial t} = k_{a,A}C_A\theta_* - \frac{k_{a,A}}{K_A}\theta_Y + k_2\theta_E C_{H_2} \tag{8}$$

$$\theta_* = 1 - \sum_i \theta_i \tag{9}$$

With boundary conditions:

$$r = 0: \quad \frac{\partial C_i}{\partial r} = 0 \tag{10}$$

$$r = R: \quad C_i = C_{i,\text{bulk}} \tag{11}$$

For the bulk:

$$\frac{\partial C_{i,\text{bulk}}}{\partial t} = -D_i\frac{3}{R}C_{\text{cat}}\left.\frac{\partial C_i}{\partial r}\right|_{r=R} \tag{12}$$

$$C_{H_2,\mathrm{bulk}} = C_{H_2,\mathrm{sat}} \tag{13}$$

The initial value of the alkyne concentration in the bulk is equal to the initially added concentration. The alkyne and alkene bulk concentrations are assumed to be 0. All initial concentrations inside the catalyst particles are assumed to be 0. Some calculations were performed starting at a later time than $t = 0$. For these calculations the appropriate starting concentrations from the gc-analyses of the experiments were used for the bulk concentrations.

In this model hydrogen adsorbs at different sites than the organic molecules and that the occupancy is very low. The hydrogen occupancy is assumed to be in equilibrium with the surrounding liquid. Therefore, the hydrogen occupancies are not modeled separately. In Formulas 4 and 6–8, equilibrium constants for adsorption (i.e. the ratio between the rate constant for desorption and the rate constant for adsorption) were used instead of the separate rate constants for desorption since this proved to result in a more stable fitting procedure. For the organic molecules the rate constants for adsorption were first fitted with a different parameter for each of the three components. In the fitting process the values obtained for alkyne, alkene and alkane were very similar (less than 20% difference) and had overlapping confidence intervals. Therefore, it was decided to use one single adsorption rate constant for these components. This is physically reasonable since the adsorption rate constant represents the collision rate of a molecule with an adsorption site. As the three components are similar the diffusion rate and thus collision rate should be similar. This simplification reduces the number of parameters to be fitted and thus the accuracy of the values obtained. For the rate constants for the alkyne–alkene hydrogenation and the alkene–alkane hydrogenation also rate constants with similar values and largely overlapping confidence intervals were obtained. Therefore, it was decided to also use only one parameter for these rate constants. This can be physically justified by the assumptions that both reactions have a similar rate-determining step.

The kinetic model was fitted simultaneously to a collection of eight different experiments, each consisting of 15–20 experimental data points. These experiments had different initial reactant concentrations and catalyst particle sizes. The parameters obtained were able to describe the experiments well. An example of one of the experimental sets, together with the calculated model fit is shown in Fig. 2. The parameters obtained, together with their confidence intervals are given in Table 2. It can be seen that the adsorption of the alkyne is very strong compared to the alkene and alkane adsorption, which adsorb approximately equally strong. This strong alkyne adsorption explains the high intrinsic selectivity possible for this reaction, since in the presence of alkyne the surface coverage on the catalyst of the alkene remains low. The observed selectivity dependence on the particle size (Table 1) is easily explained from the concentration profiles of the reactants in the catalyst particles (Fig. 4). As a result of an insufficiently fast mass-transfer the alkene concentration inside the larger particles is higher (and the alkyne concentration lower), causing more overhydrogenation to occur. These figures also explain the differences in observed activity for the different catalyst particles sizes, as inside the bigger catalyst particles there clearly is a hydrogen shortage.

3.2. Effect of reaction modifier

In selective hydrogenations in fine chemical industry sometimes reaction modifiers are added to the

Table 2
Values of parameters fitted to experiments, together with their 95% confidence intervals

Parameter	Value	Confidence interval		Units
		Minimum	Maximum	
K_Y	0.31	0	0.72	m^3/mol
K_E	0.0071	0.0063	0.0079	m^3/mol
K_A	0.011	0.0075	0.015	m^3/mol
$k_1 = k_2$	478000	443000	512000	m^3/mol/s
$k_{a,i}$	197000	0	587000	m^3/mol/s

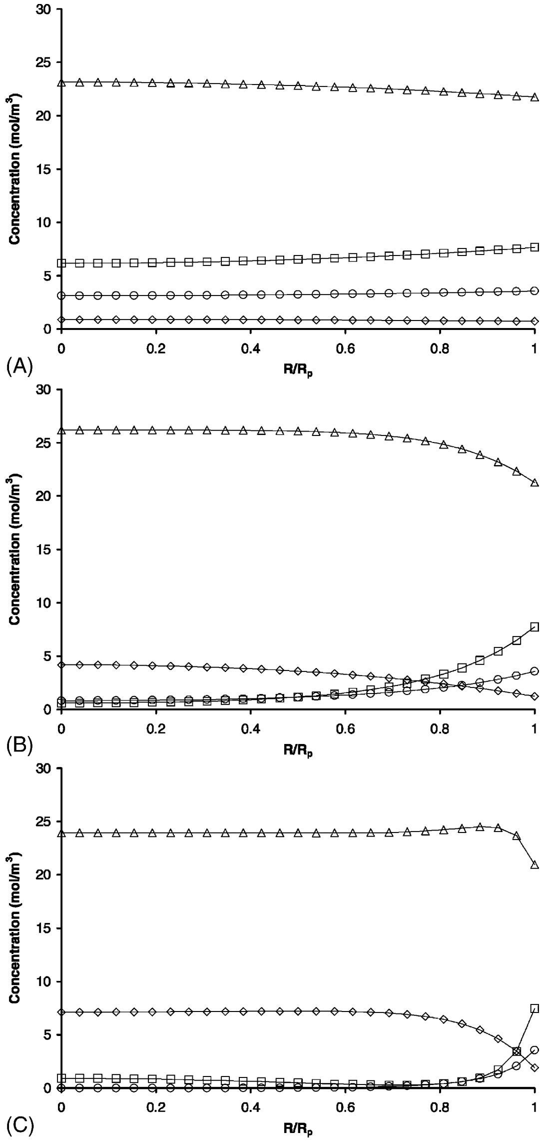

Fig. 4. Concentration profiles inside the three different catalyst particle sizes used for the hydrogenation of 3-methyl-1-pentyn-3-ol over 2 wt.% Pd on silica catalysts (298 K, 0.5 kg/m^3 catalyst, initial alkyne concentration 30 mol/m^3). Calculated using kinetic parameters from Table 2. All figures show the intraparticle concentration profiles at an identical conversion of 75%. Particle diameters: (A) 10 μm, (B) 50 μm and (C) 200 μm. (○) Hydrogen concentration, (□) alkyne concentration, (△) alkene concentration and (◇) alkane concentration.

Table 3
Effect of the addition of different levels of quinoline (reaction modifier) on the activity and selectivity (maximum yield of desired alkene) for the hydrogenation of 3-methyl-1-pentyn-3-ol[a]

Quinoline (mol/m^3)	Activity (mmol/g$_{Pd}$/s)	Maximum alkene yield (%)
0	7.67	90.2
23	6.50	95.8
220	4.17	97.4

[a] 2 wt.% Pd on silica catalyst (35–74 μm), 298 K, 1 bar H_2, 0.75 kg/m^3 catalyst, 300 mol/m^3 reactant.

reaction system to increase selectivity [2]. The effect of adding such a modifier (quinoline) to this reaction system was investigated. The effect of adding different amounts of quinoline to the reaction mixture is given in Table 3.

Commonly, the effect of a quinoline or similar type of modifier is explained from its competitive adsorption, adsorbing less strongly than the component to be hydrogenated and stronger than the desired product, in this way preventing product adsorption and thus over-hydrogenation. In the model, however, simply adding a moderately strong adsorbing non-reactive component in a L–H kinetics does not result in an increased yield of the desired product. If mass-transfer plays a role in the reaction the modifier does show an influence in the calculations. The effect of the modifier, however, is nothing more than simply reducing the overall reaction rate and thus the effect of mass-transfer on the reaction. The slower reaction rate in the catalyst particles allows for the alkene being produced to have more time to diffuse out of the particles before re-adsorbing and being hydrogenated further. In this way the lower catalyst activity results in the higher selectivity.

When adding quinoline adsorption in the reaction model used for the hydrogenation of 3-methyl-1-pentyn-3-ol, the selectivity enhancing effect can be modeled. For quinoline as reaction modifier Eq. (14) for the occupancy is added

$$\frac{\partial \theta_Q}{\partial t} = k_{a,Q} C_Q \theta_* - \frac{k_{a,Q}}{K_Q} \theta_Q \qquad (14)$$

Boundary conditions 10–12 also apply for quinoline. Fitting the model containing these equations to a number of experiments with quinoline present resulted in a value for the equilibrium constant for adsorption of quinoline of 1.63 m^3/mol (1.47–1.79 confidence interval). Quinoline apparently adsorbs even more strongly than the alkyne, which is the explanation of the reduction in the overall reaction rate. Although quinoline incorporated in the model in this manner does result in a higher selectivity in the calculations, this predicts only about 50% of the observed increase in selectivity. The entire selectivity enhancing effect apparently is more complex and requires further investigation. In literature, commonly electronic effects are used to explain selectivity enhancing effects of reaction modifiers [2], i.e. the reaction modifier donates/accepts electrons from the catalyst surface to explain the effect. This would imply that the adsorption constants for the different reactants and products would be different due to the different electronic properties of the catalyst surface. In the current modeling work the adsorption and reaction constants were assumed to be constant. To confirm an electronic effect and determine new adsorption and reaction parameters, however, a larger amount of experiments with reaction modifiers would be required. This is because of the large number of kinetic parameters in the model presented in this paper requiring many experiments to determine the relevant parameters with an acceptable accuracy.

From the above interpretation it follows that a simple manner to increase the yield of the desired product is to reduce the reaction rate by other means. This can be done in several ways, e.g., by reducing the temperature or by reducing the metal loading on the catalyst. In order to check this assumption, experiments have been performed at lower temperatures with the same catalyst. For the 35–74 μm catalyst lowering the reaction temperature to 363 K (which reduced the reaction rate by close to a factor of 10), the selectivity increased but only slightly (maximum yield of 91.5%). In the interpretation of this experiment it should be kept in mind that also the mass-transfer rate is slowed down by lowering the temperature (higher liquid viscosity and lower diffusivity), having a selectivity lowering effect.

4. Conclusions

It has been demonstrated that it is possible to satisfactorily model a complex reaction system, controlled by both kinetics and mass-transfer, and to obtain the relevant kinetic parameters. For the selective hydrogenation of 3-methyl-1-pentyn-3-ol, it was shown that mass-transfer effects strongly influence the maximum yield of the desired product. The selectivity enhancing effect of the addition of a reaction modifier, such as quinoline, is for a large part the result of mass-transfer effects.

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