Catalysis Today 79–80 (2003) 383–389

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Application of transient methods in three-phase catalysis: hydrogenation of a dione in a catalytic plate column

Esa Toukoniitty, Johan Wärnå, Tapio Salmi,
Päivi Mäki-Arvela, Dmitry Yu. Murzin*

Laboratory of Industrial Chemistry, Process Chemistry Group, Åbo Akademi University,
Biskopsgatan 8, FIN-20500 Turku/Åbo, Finland

Abstract

The continuous enantioselective hydrogenation of 1-phenyl-1,2-propanedione was investigated in fixed-bed reactor at 25 °C and 5 bar H_2 over a knitted Pt silica fibre catalyst modified with (−)-cinchonidine. Transient data were quantitatively modelled based on the reaction mechanism which assumes two parallel and tilted adsorption modes for the modifier and two distinct adsorption modes for 1- and 2-carbonyls, each of them requiring different number of surface sites. A dynamic axial dispersion model described the tube reactor with the Peclet number estimated from the separate impulse experiments carried out with an inert tracer. The modelling revealed that inclusion of sorption dynamics of components is of critical importance for the adequate description of transient data.

Keywords: Transient kinetic; Gas chromatograph; Peclet number

1. Introduction

Transient kinetic experiments are an established and valuable tool in investigation of heterogeneously catalysed processes in gas phase. The primary interest for transient kinetics in catalysis originates from the need to study deeply the adsorption, surface reaction and desorption mechanisms occurring on the catalyst surface. At a transient state, the surface steps proceed at different velocities for a single overall reaction, which provides additional information compared to traditional steady-state experiments. Furthermore, transient experiments provide unequivocal information about the catalyst durability. More recently, the interest on transient catalytic kinetics has grown due to the fact that transient phenomena are continuously present in some catalytic systems, such as reverse-flow (Matros) reactors, and in automotive exhaust catalysis. The state of art of the transient approach is reviewed by Bennett [1].

For liquid-phase systems, transient studies are much more scarce than for gas-phase systems. Liquid-phase systems have a slow dynamics and the intrinsic kinetic phenomena can be obscured by mass transfer effects and catalyst deactivation. We have, however, recently demonstrated that transient kinetic experiments can provide information about a sophisticated liquid-phase system [2,3]. Enantioselective hydrogenation of ketones over chirally modified noble metal catalysts [4] represents the high technology of contemporary catalysis: heterogeneous catalysts

---

* Corresponding author. Tel.: +358-2-215-4985;
fax: +358-2-215-4479.
E-mail address: dmurzin@abo.fi (D.Yu. Murzin).

doi:10.1016/S0920-5861(03)00067-1

Nomenclature

A	cross-section area
c	concentration
D	dispersion coefficient
k	rate constant
l	reactor length coordinate
L	reactor length$(c_0^* S)^{-1}$
m	mass
M	modifier
$\dot{n}$	molar flow rate
Pe	Peclet number
Q	sum of squares
r	reaction rate
S	specific surface area
t	time
$\dot{V}$	volumetric flow rate
V_R	reactor volume
w	flow velocity
z	dimensionless reactor length coordinate

Subscripts and superscripts

ads	adsorbed
B	bulk property
cat	catalyst property
des	desorbed
e	enantioselective step
i	component index
j	reaction index
L	liquid phase
r	racemic step

Greek letters

ρ	catalyst bulk density
τ	residence time
ε	liquid holdup

enable a clean and selective production route to optically pure compounds, which are needed in pharmaceutical industry. In the present work we have investigated continuous enantioselective hydrogenation of a diketone, 1-phenyl-1,2-propanedione over a knitted Pt-fibre catalyst modified with cinchonidine. Some qualitative results of the work has been published earlier [2,3]; the aim of the present work is to apply quantitative modelling on the transient data and to demonstrate the power of the transient approach in revealing liquid-phase sorption and reaction processes taking place in complex organic systems.

2. Experimental section

Hydrogenation of 1-phenyl-1,2-propanedione (A) was carried out in a fixed-bed reactor (10 cm length and 1.2 cm internal diameter) at 25 °C and 5 bar hydrogen. The detailed qualitative results are reported in a separate article [2]. The hydrogen and liquid flows were 60 and 2.3 $\text{cm}^3\,\text{min}^{-1}$, respectively. Ten layers of the 5 wt.% Pt/SiO_2 fibre catalyst (0.4 g) were used resulting in the catalyst bed thickness of 1.5 cm. Glass beads were used as an inert packing material. The reactor set-up and the catalyst support material are illustrated in Fig. 1.

The 5 wt.% Pt/SiO_2 catalysts were prepared by impregnation of fibrous SiO_2 support with an aqueous solution of hexachloroplatinic acid [3]. Prior to the reaction, the catalyst was reduced in situ under flowing hydrogen at 400 °C for 2 h. The liquid phase containing the modifier (cinchonidine), the solvent (ethyl acetate), and the reactant (A), were deoxygenated with H_2 for 10 min prior the reaction. The concentrations of reactant and modifier were varied between 0.0075–0.05 and $0\text{–}34 \times 10^{-5}\,\text{mol}\,\text{dm}^{-3}$, respectively. Samples were taken at the reactor outlet and analysed with a gas chromatograph.

The flow pattern of the reactor was characterised by separate impulse experiments with an inert tracer component (10 wt.% NaCl in H_2O). The tracer experiments were carried out by injecting 50 μl of the tracer at the reactor inlet and measuring the conductivity response at the outlet of the reactor with a conductivity cell operated at atmospheric pressure. In order to get proper conductivity response water was employed as liquid phase. The liquid and hydrogen flow rates were the same as in the hydrogenation experiments. The liquid hold up was evaluated by weighing the reactor.

3. Reaction stoichiometry and kinetic model

The reaction stoichiometry is displayed in Fig. 2. As shown in the figure, the complete reaction scheme comprised nine components. Components A, B, C, F and H in the scheme were distinguishable

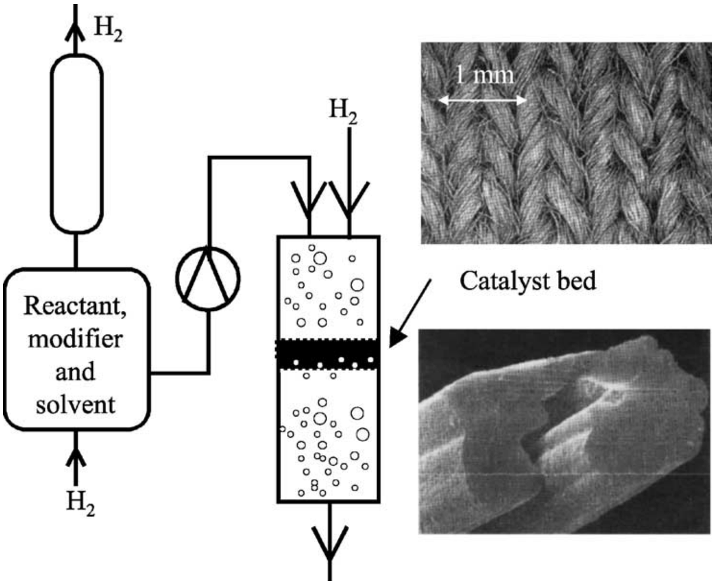

Fig. 1. Reactor set-up and a SEM image of the knitted silica fiber catalyst and a single silica fiber.

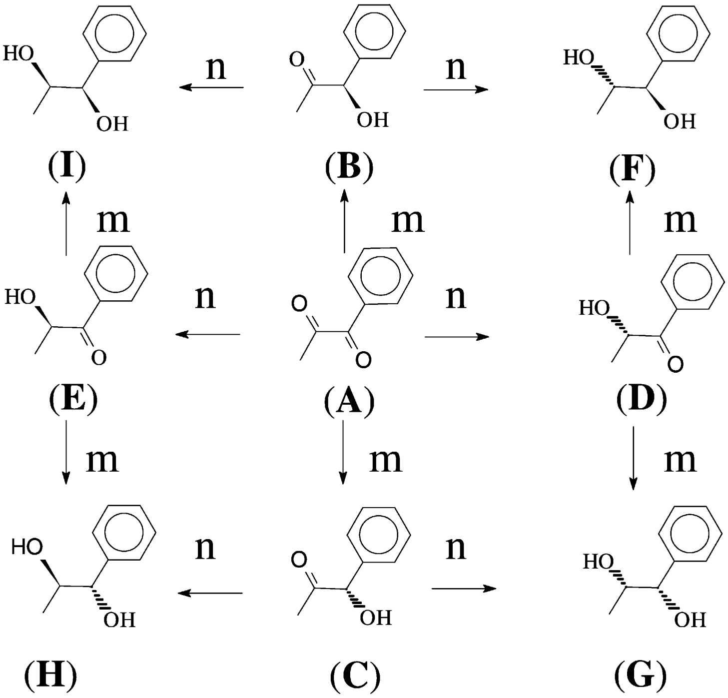

Fig. 2. Reaction scheme.

by chromatographic analysis, whereas the sums D + E and I + G were obtained for (*R*)- and (*S*)-2-hydroxy-1-phenylpropanone and (1*S*,2*S*)- and (1*R*,2*R*)-1-phenyl-1,2-propanediols, respectively. The kinetic modelling was based on Fig. 2. Kinetic studies demonstrated that the system can show a high enantioselectivity, the main product being B. In current experiments the enantioselectivity $\mathrm{es} = c_\mathrm{B}/c_\mathrm{C}$ was typically three to four and the regioselectivity $\mathrm{rs} = (c_\mathrm{B} + c_\mathrm{C})/(c_\mathrm{D} + c_\mathrm{E})$ was typically five to six.

Previous investigations of our group have indicated that the modifier (M) strongly affects the enantioselectivity and regioselectivity. The modifier can adsorb on the surface in a parallel adsorption mode contributing to enantioselective hydrogenation as well as in a tilted mode, which is assumed to act just a spectator on the catalyst surface. Due to the lack of rate acceleration in the presence of modifier, the racemic hydrogenation route cannot be discarded and therefore, a proper kinetic model includes both racemic and enantioselective hydrogenation steps.

Kinetic studies showed that the hydrogenation rate and product distribution are practically independent of the hydrogen concentration. This can be expressed with a non-competitive model for hydrogen adsorption and by assuming that the sites accessible for hydrogen adsorption are saturated with respect to hydrogen. The overall effect becomes a zero-order dependence on hydrogen pressure. Consequently, the role of adsorbed hydrogen is disregarded in the subsequent treatment. Previous kinetic experiments in a batch reactor [5] showed that the overall reaction order with respect to the reactant is about 0.7, which suggests the adsorption of the organics on the surface. However, the batch experiments do not reveal the adsorption dynamics on the surface. A kinetic model based on rapid adsorption and slow hydrogenation steps was able to explain our batch reactor data [5]. The challenge is now to investigate how much the kinetic behaviour is altered under the transient period and how it can be explained by adsorption dynamics.

Based on the discussion above, the kinetic model can be developed as follows. The reactant adsorption is described by

$$\mathrm{A} + m^* \Xi \mathrm{A}_1 m^* \qquad \mathrm{A} + n^* \Xi \mathrm{A}_2 n^*$$

where A_1m^* and A_2n^* denote the adsorption modes of 1- and 2-carbonyls, and *m* and *n* the number of sites needed for adsorption, $m > n$. The adsorption of the modifier in two forms is described by

$$\mathrm{M} + p^* \Xi \mathrm{M}p^* \qquad \mathrm{M} + q^* \Xi \mathrm{M}q^*$$

where *p* and *q* refer to the parallel and tilted adsorption modes, respectively. The racemic hydrogenation steps can all be described with the same concept. Here just the hydrogenation of the reactant (A) is shown as an example:

$$\mathrm{A}_1m^* + \mathrm{H}_2(\mathrm{ads}) \rightarrow 0.5\mathrm{B} + 0.5\mathrm{C} + m^*$$
$$\mathrm{A}_2n^* + \mathrm{H}_2\,(\mathrm{ads}) \rightarrow 0.5\mathrm{D} + 0.5\mathrm{E} + n^*$$

The enantioselective hydrogenation of the reactant to the *R*-enantiomers is described by

$$\mathrm{A}_1m^* + \mathrm{M}p^* + \mathrm{H}_2\,(\mathrm{ads}) \rightarrow \mathrm{B} + m^* + \mathrm{M}p^*$$
$$\mathrm{A}_2n^* + \mathrm{M}p^* + \mathrm{H}_2\,(\mathrm{ads}) \rightarrow \mathrm{D} + n + \mathrm{M}p^*$$

The further formation of the diols progresses through hydrogenation of the primary products (B, C, D, E); for instance, for B, the adsorption and hydrogenation steps are written as

$$\mathrm{B} + n^* \Xi \mathrm{B}n^*$$
$$\mathrm{B}n^* + \mathrm{M}p^* + \mathrm{H}_2\,(\mathrm{ads}) \rightarrow \mathrm{I} + n^* + \mathrm{M}p^*$$

For the other products, the reactions follow an analogous path. The numbers of necessary adsorption sites are listed in Fig. 2.

The rate equations follow directly from the mechanisms. The rate of a racemic hydrogenation step is given by

$$R_\mathrm{r} = k_\mathrm{r} c_{s^*} \tag{1}$$

with $s = m$ or $s = n$ whereas the rate of an enantioselective hydrogenation step is described by

$$R_\mathrm{e} = k_\mathrm{e} c_{s^*} c_{\mathrm{M}p^*} \tag{2}$$

The hydrogen concentration is not explicitly visible in Eqs. (1) and (2), since the hydrogen adsorption was assumed to be non-competitive and the hydrogen concentration is de facto incorporated in the rate constants.

Analogously, the rates of adsorption and desorption steps are based on the reaction mechanism; for example, the adsorption rate of a component is given by

$$r_\mathrm{ads} = k_\mathrm{ads} c_{s^*} - k_\mathrm{des} c_{s^*} \tag{3}$$

4. Reactor model

The tube reactor containing the catalyst layers was described with a dynamic axial dispersion model. Since the hydrogenation kinetics turned out to be independent of hydrogen partial pressure, i.e. the concentration of dissolved hydrogen, the mass balance of hydrogen in gas phase was discarded. The reaction temperatures were low, which implies that also the volatilities of the organic compounds are negligible. Thus, just the mass balances for the liquid phase remain. According to the concept of dynamic axial dispersion model, the mass balance equation for an organic compound in an infinitesimal volume element (ΔV) can be written as

$$\dot{n}_{\mathrm{Li,in}} + \left(-D\frac{\mathrm{d}c_{\mathrm{Li}}}{\mathrm{d}l}A\right)_{\mathrm{in}} + r_i\Delta m_{\mathrm{cat}} = \dot{n}_{\mathrm{Li,out}} + \left(-D\frac{\mathrm{d}c_{\mathrm{Li}}}{\mathrm{d}l}A\right)_{\mathrm{out}} \quad (4)$$

After introducing the notations

$$\dot{n}_{\mathrm{Li}} = c_{\mathrm{Li}}\dot{V}_{\mathrm{L}}, \qquad w_{\mathrm{L}} = \frac{\dot{V}_{\mathrm{L}}}{A}, \qquad \tau_{\mathrm{L}} = \frac{L}{w_{\mathrm{L}}},$$

$$\Delta V_{\mathrm{L}} = \varepsilon_{\mathrm{L}}\Delta V_{\mathrm{R}}, \qquad \Delta V_{\mathrm{R}} = A\Delta l, \qquad V_{\mathrm{R}} = AL,$$

$$z = \frac{l}{L}, \qquad Pe_{\mathrm{L}} = \frac{wL}{D}, \qquad m_{\mathrm{cat}} = \rho_{\mathrm{B}}\Delta V_{\mathrm{L}}$$

carrying out the differentiations and letting the volume element shrink, the mass balance becomes

$$\frac{\mathrm{d}c_{\mathrm{Li}}}{\mathrm{d}t} = r_i\rho_{\mathrm{B}} + (Pe_{\mathrm{L}}\varepsilon_{\mathrm{L}}\tau_{\mathrm{L}})^{-1}\frac{\mathrm{d}^2c_{\mathrm{Li}}}{\mathrm{d}z^2} - (\varepsilon_{\mathrm{L}}\tau_{\mathrm{L}})^{-1}\frac{\mathrm{d}c_{\mathrm{Li}}}{\mathrm{d}z} \quad (5)$$

For the adsorbed compounds, the mass balance equations are simply given by

$$\frac{\mathrm{d}c_j^*}{\mathrm{d}t} = S^{-1}r_j \quad (6)$$

where c_j^* is the concentration of the surface species and S is the specific surface area of the catalyst. By introducing the fractional coverages ($\theta_j = c_j^*/c_0^*$), the balance becomes

$$\frac{\mathrm{d}\theta_j}{\mathrm{d}t} = Lr_j, \quad L = (c_0^*S)^{-1} \quad (7)$$

As revealed by Eq. (5), the balance contains just two adjustable hydrodynamic parameters, $\tau_{\mathrm{L}} \times \varepsilon_{\mathrm{L}}$ and Pe_{L}. The Peclet number was estimated from the separate impulse experiments carried out with the inert tracer (NaCl), while the quantity $\tau_{\mathrm{L}} \times \varepsilon_{\mathrm{L}}$

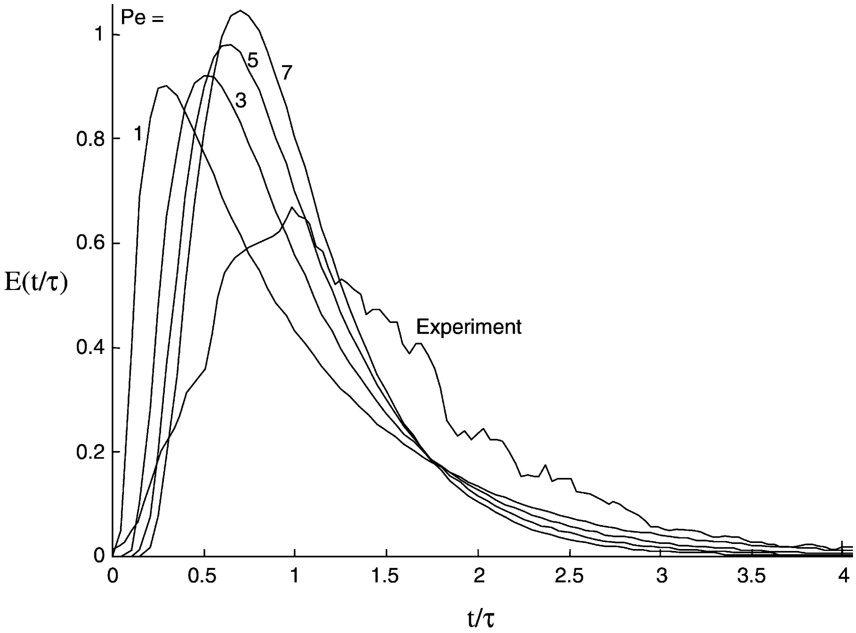

Fig. 3. Experimentally determined and theoretically calculated $E(t/\tau)$ functions using different Peclet (Pe) numbers.

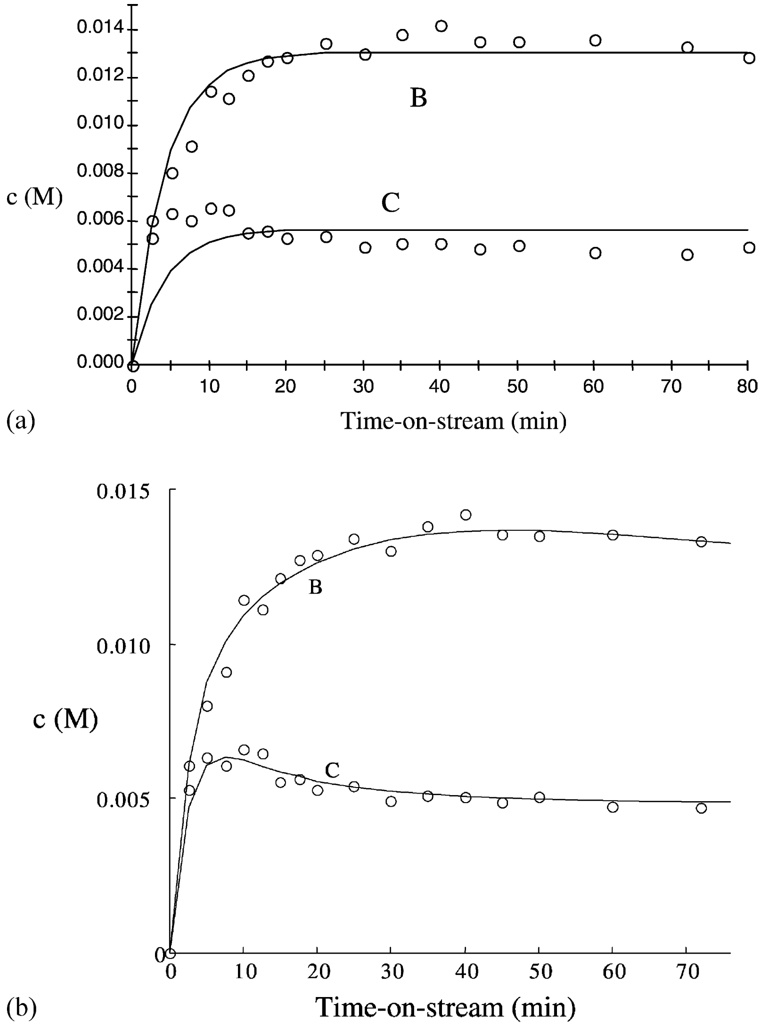

Fig. 4. The model prediction (solid lines) using (a) steady-state kinetic model and (b) transient kinetic model.

was estimated from the kinetic experiments, in order to ensure a correct description of the reactor dynamics.

Some results from the tracer experiments are displayed in Fig. 3. As the figure reveals, the flow pattern deviates from plug flow. The residence time distribution function $E(t)$ was calculated from the experimentally recorded responses, after which the $F(t)$ function was obtained from integration of $E(t)$. The experimental functions were compared to the theoretical ones, the expressions of $E(t)$ and $F(t)$ obtained from the analytical solution of the dynamic, non-reactive axial dispersion model with closed Danckwerts' boundary conditions were used in comparison. A comparison is shown in Fig. 3, which suggests that a reasonable value for the Peclet number is $Pe = 3$.

5. Modelling results

The model equations (6) and (7) were solved numerically by a stiff ODE solver during the estimation of kinetic parameters, which were obtained from the minimisation of the objective function:

$$Q = \sum (y_{i,\mathrm{exp}} - y_i)^2 \tag{8}$$

where y_i denotes the following variables c_A, c_B, c_C, $c_D + c_E$, c_F, c_H and $c_I + c_G$ according to the primary observations. The objective function minimization was carried out with a hybrid simplex–Levenberg–Marquardt method. The minimization was commenced with simplex method, but was switched to the more rapid Levenberg–Marquardt method, as the minimum of the objective function was approached [6].

The fit of the model is illustrated in Fig. 4. For the sake of comparison, the steady-state kinetic model involving adsorption quasi-equilibria and slow hydrogenation steps was fitted to the data. This model fits very well to the batch reactor data, as demonstrated previously [5]. The model is, however, not sufficient to describe the transient behaviour of the system, which is shown in Fig. 4a, the assumption of adsorption quasi-equilibrium predicts too rapid responses, indicating that the sorption dynamics of the compounds is of crucial importance. When the kinetics of adsorption is included in the model, the fit of the model is significantly improved (Fig. 4b). Further modelling work is in progress with an aim to incorporate deactivation phenomena and more precisely take into account secondary reactions.

6. Conclusions

Transient kinetic experiments provide valuable additional information about the behaviour of complex organic reaction systems, which was illustrated here with continuous enantioselective hydrogenation of 1-phenyl-1,2-propanedione over a fibre catalyst. The catalyst stability, the origin of deactivation as well as the details of the adsorption behaviour of the reaction participants were revealed by transient experiments. Quantitative modelling of the data was based on kinetic experiments and characterisation of the reactor flow pattern by an inert tracer. The example showed that the modelling should be based on a true dynamic approach and a steady-state model for the liquid-phase kinetics cannot directly be applied on transient data.

Acknowledgements

This work is part of the activities at the Åbo Akademi Process Chemistry Group within the Finnish Centre of Excellence Programme (2000–2005) by the Academy of Finland. Financial support from Finnish Graduate School in Chemical Engineering (GSCE) is gratefully acknowledged.

References

[1] C.O. Bennett, Adv. Catal. 44 (1999) 329.
[2] E. Toukoniitty, P. Mäki-Arvela, A. Kalantar Neyestanaki, T. Salmi, D.Yu. Murzin, Appl. Catal. A 235 (2002) 125.
[3] E. Toukoniitty, P. Mäki-Arvela, A. Kalantar Neyestanaki, T. Salmi, R. Sjöholm, R. Leino, E. Laine, P.J. Kooyman, T. Ollonqvist, J. Väyrynen, Appl. Catal. A 216 (2001) 73.
[4] M. von Arx, T. Mallat, A. Baiker, Top. Catal. 19 (2002) 75.
[5] E. Toukoniitty, B. Ševčíková, P. Mäki-Arvela, J. Wärnå, T. Salmi, D.Yu. Murzin, J. Catal. 213 (2003) 7.
[6] H. Haario, Modest 6.0—A User's Guide, ProfMath, Helsinki, 2001.