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Determination of reactivity distributions from steady-state isotopic transient data: A model study

M. Rothaemel[1,a,*], K.F. Hanssen[a], E.A. Blekkan[a], D. Schanke[2,b], A. Holmen[a]

[a] *Department of Industrial Chemistry, Norwegian University of Science and Technology (NTNU), N-7034 Trondheim, Norway*
[b] *SINTEF Applied Chemistry, N-7034 Trondheim, Norway*

Abstract

The potential of different mathematical methods for the recovery of reactivity distributions, $f(k)$, from steady-state isotopic transient kinetic analysis (SSITKA) data has been tested and compared using a model catalyst system that consisted of a mechanical mixture of two catalysts with catalytic sites of known and different reactivity. Fitting one or two exponential functions to the measured transients confirmed the presence of two different pools of reaction intermediates, but the use of this method for determination of $f(k)$ is limited to simple catalytic systems. For more complicated systems, the Tikhonov/Fredholm method might be superior to the inverse Laplace transform method. © 1998 Elsevier Science B.V.

Keywords: SSITKA; Transient experiments; Fischer-Tropsch; Co catalysts; Ni catalysts; Mathematical modelling

1. Introduction

Steady-state isotopic transient kinetic analysis (SSITKA), mainly developed by Happel et al. [1,2] and Biloen et al. [3,4], has proved to be a powerful technique for studying heterogeneously catalyzed reactions. From the mathematical analysis of experimental SSITKA data it is possible to derive information about rate constants and surface coverages using different mechanistical models to describe the surface phenomena [5]. While using these methods, only averaged rate constants can be derived; the application of more sophisticated approaches involving complex mathematical models can yield reactivity distributions, usually assigned as $f(k)$, based on the measured transients. Although these advanced methods have been successfully applied in the past [6–9], it remains desirable to further investigate the reliability of $f(k)$ thus determined.

In the present study, a model catalyst system with a defined bimodal reactivity distribution was artificially created by using a mixture of two non-interacting catalysts with different reactivities. Thereafter, different mathematical methods were applied for the evaluation of the measured transients and their potential in the recovery of the reactivity distributions compared. As a model reaction the Fischer–Tropsch synthesis (as represented by CH_4 formation from synthesis gas) was chosen.

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*Corresponding author.

[1] On leave from: Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany. Present Address: Lurgi Öl-Gas-Chemie GmbH. Gwinnerstrasse 27-33, 60388 Frankfurt/Main, Germany.

[2] Present Address: Statoil Research Center, Postuttak, N-7005 Trondheim, Norway.

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2. Experimental

2.1. Apparatus

The experimental set-up consists of a catalytic microreactor especially built for fast switching experiments. The on-line measurement of the transients was carried out using a Balzers QMG 420 quadrupole mass spectrometer while the catalytic activity and the product distribution were determined using an HP 5880 GC equipped with a GS-Alumina column (J&W Scientific) and an FID. For details of the experimental set-up, see Bariås [10] and Larsson et al. [11].

2.2. Catalyst preparation and pretreatment

The catalysts were prepared using standard incipient wetness techniques and aqueous solutions of the metal salts. Co(17.1 wt.%)/Al_2O_3 (S_{BET}=138 m^2/g) was prepared by impregnating $Co(NO_3)_2$ on PURALOX alumina (S_{BET}=167 m^2/g), whereas Ni(10 wt%)/Al_2O_3 (163 m^2/g) was prepared by impregnating $Ni(NO_3)_2 \cdot 6H_2O$ on Vista B alumina (S_{BET}=179 m^2/g). The catalysts were dried overnight, crushed and sieved. The particle fraction between 38 and 75 μm was used for the catalytic experiments. The Co/Al_2O_3 has also been calcined in air at 300°C. Prior to the experiments, the catalysts were reduced in situ at 480°C for 12 h followed by cooling in He to the reaction temperature.

2.3. Experimental procedure

For all the experiments, 100 mg of catalyst were mixed with 200 mg of SiC of the same particle-size distribution. For the run with the catalyst mixture, 50 mg of each pure catalyst were used. All described experiments were carried out at 200°C and a pressure of 1.85 bar with flow rates of 78 ml/min He, 2 ml/min CO, 20 ml/min H_2 and 0.08 ml/min Ar (at STP conditions) resulting in a H_2/CO ratio of 10. Activity data were obtained after 3 h on-stream when a steady-state level was approached. At this point, the SSITKA experiments were carried out by switching from unlabeled CO/H_2 to labeled $^{13}CO/H_2$ feed. Once the concentrations for all components had reached a steady-state level, the opposite step was performed. The transient concentration changes were monitored on-line by the QMG using the following *m/e* ratios for the identification of the different compounds: H_2 (2), He (4), $^{12}CH_4$ (15), $^{13}CH_4$ (17), ^{12}CO (28), ^{13}CO (29), Ar (40). For the data evaluation, the response for AMU 17 ($^{13}CH_4$) during the second switch was used. The reactor was operated differentially with conversion <5% to achieve a pseudo-gradientless behavior in order to use the CSTR approximation which simplifies the mathematical analysis of the data.

The following gases and gas mixtures were used for the experiments: ^{13}CO (>99% ^{13}C, Cambridge Isotope Lab), ^{12}CO/Ar (24 : 1, Norsk Hydro), H_2 (99.995%, Norsk Hydro), and He (99.998%, Norsk Hydro).

3. Mathematical methods

The basic evaluation of the transient data was performed by integration and correction of the calculated residence times for gas phase hold-up and chromatographic effects [10]. In order to obtain information about the reactivity distribution, three different methods were applied to fit the experimentally obtained transient curves:

(i) *Basic analysis by fitting to exponential functions [5]*

It is well known from the SSITKA theory that, for a single pool of surface intermediates giving rise to a non-adsorbing product in an irreversible reaction of the 1st order, the resulting transient can be described as an exponential function:

$$F(t) = \exp(-t/\tau) \quad (1)$$

that depends only on the residence time τ of the surface species. The 1st-order rate constant can be calculated from the reciprocal of the surface residence time ($k=1/\tau$). In the case of multiple non-interacting (parallel) pools of surface intermediates, all of which lead to the same non-adsorbing product via a reaction of the 1st order, the resulting transient can be described as a sum of the contributions of every single pool, e.g. for two pools:

$$F(t) = x_1 \exp(-t/\tau_1) + x_2 \exp(-t/\tau_2) \quad (2)$$

where τ_1 and τ_2 correspond to the pool-specific residence time while x_1 and x_2 correspond to the fraction of surface species in each pool compared to the total number of sites.

(ii) *The inverse Laplace transform (ILT) method [6]*

Instead of using distinct values for the residence times and, hence, for the rate constants of the surface sites, the ILT method was developed to derive a continuous reactivity distribution of the catalyst surface. Assuming irreversible 1st-order reaction on all sites, the transient product formation after a switch is given by:

$$r^*(t) = \Theta_0^* \int_0^\infty kf(k)\exp(-kt)\mathrm{d}k \tag{3}$$

where Θ_0 is the initial surface coverage of intermediates that react to the detected product with a certain distribution $f(k)$ of rate constants corresponding to several different surface sites. The ILT method is based on the fact that $r^*(t)$ represents the Laplace transform of $\Theta_0 kf(k)$, hence an inverse Laplace transformation of the measured $r^*(t)$ or $F(t)$ transients can be applied to extract the $f(k)$ distribution. The numerical procedure requires a fit of the experimental transient to a sum of exponential terms according to:

$$r^*(t) = \sum_{n=1}^{N} a_n \exp(-k_n t) \tag{4}$$

in order to determine the coefficients a_n. The number of exponential terms, N, has to be infinity. For practical purposes, only a limited number (N<20) resulting in a sufficiently large upper limit of the reaction rates has to be used to fit the data. After the values for the coefficients are known, the values for $\Theta_0 f(k_n)$ can be calculated from:

$$a_n = (\pi/\omega_{\max})\Theta_0^* k_n^2 f(k_n) \tag{5}$$

The rate constants in the exponentials, k_n, are given by the series:

$$k_{n+1} = k_1 \exp(n\pi/\omega_{\max}) \tag{6}$$

based on the user-supplied starting values for k_1, the smallest rate constant to be used, and on the parameter $\omega_{\max}$ which determines the spacing of the constants. $\omega_{\max}$ can be calculated from the noise of the experimental data, ε, according to:

$$\varepsilon = \sqrt{\pi/\cosh(\pi\omega_{\max})} \tag{7}$$

As pointed out by de Pontes et al. [6], any attempts to increase the resolution by decreasing the noise value is equivalent to extracting information from below the noise and leads to unreliable results. To obtain a smoother $f(k)$ distribution, the user instead has to repeat the fitting of the experimental transient using several different starting values for k_1. Regarding the determined rate constants, it should be noted, that if the initial surface coverage, Θ_0, is unknown, only the effective, pseudo-1st order rate constants $k_i' = k_I\Theta_0$ can be derived.

(iii) *The Tikhonov/Fredholm (TF) method [8]*

According to this method, the reactivity distribution $f(k)$ can be extracted from the measured $F(t)$ or $r^*(t)$ transients by the so-called Tikhonov regularization of Eq. (3) which can be regarded as a Fredholm integral equation of the first kind. It is beyond the scope of this work to describe the underlying mathematical theory and the application for this specific problem; the interested reader is referred to the original article of Hoost and Goodwin ([8] and the references therein). In the present work, a computer program supplied from the group of Prof. Goodwin was used for the application of the TF method in analyzing the experimental data. With respect to the determination $f(k)$ distribution, the same argument concerning the effective pseudo-1st order rate constants described above for the ILT method also holds here.

3.1. *Data treatment and optimization*

The surface residence times were derived from the integration of the experimental transients and correction for the chromatographic effect [12]. As Zhang and Biloen [13] pointed out, this effect is negligible if the residence time of CO amounts to <20% of $\tau(CH_4)$ which is the case in the present work (see Table 2). Prior to the mathematical evaluation of the transients using the three described methods, the experimental data were smoothed slightly using a fast-Fourier transformation method to reduce the contribution of noise. The correction for gas-phase hold-up was carried out by shifting the time axis by an appropriate offset as determined by the steep decrease of the Ar transient after switching. This simple method of correction (as compared to a mathematical deconvolution) is justified in this case because the residence time of Ar (<2.5 s) is much smaller than the residence times of all other involved compounds.

For the fitting of exponentials as well as for the ILT method, the sum of absolute deviations between simulated and experimental responses was chosen as the goal function because the noise of the signal did not depend on its intensity in the experiments. The optimization itself was performed using a simple random-search algorithm. In the program package from Prof. Goodwin's group for the application of the TF-method, the optimization was performed *via* a golden-section search method.

4. Results and discussion

4.1. Catalytic and SSITKA results

The conversion of CO and the product selectivities are summarized in Table 1. The level of conversion was always below 5% which is necessary to use the CSTR approximation for SSITKA experiments carried out in a plug-flow reactor. Besides methane as the main product (S>70%), C_2 and C_3 hydrocarbons were also detected.

The responses for AMU 17 after the $^{13}CO/H_2 \rightarrow {}^{12}CO/H_2$ switch are shown in Fig. 1. It is obvious that the shape of the measured transients for the Co and Ni catalysts are very different. The transient obtained using the mechanical mixture of both catalysts resembles an intermediate between the other transients. The initial rapid decrease can be attributed mainly to the reactivity of centers on the Co, while the long tailing is most probably due to the Ni sites. On the Co catalyst, the residence time, τ, of the precursor species that result in the formation of methane (as determined by integration of the transient) amounts to 29.5 s which is much smaller compared to a residence time of 137.1 s on the Ni catalyst (see Table 2), hence the overall site activity is ≈4.7 times higher on Co than on Ni. It might be expected that this difference in the reactivity is large enough to ensure a separation of the contributions of Co and Ni when the above-mentioned mathematical methods are applied for the evaluation of the data.

Table 1
Conversion and selectivities obtained for the different catalysts at 200°C, 1.85 bar and $H_2 : CO=10$

Catalyst	X(CO)%	S(CH_4)%	S(C_2)%	S(C_3)%
Co/Al_2O_3	4.7	78.0	12.0	10.0
Ni/Al_2O_3	3.8	76.9	11.8	11.3
$Ni–Co/Al_2O_3$	4.4	70.7	13.8	15.4

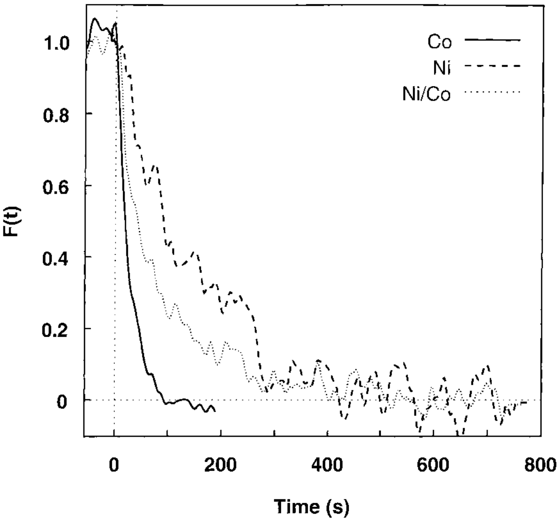

Fig. 1. $^{13}CH_4$ responses after the switch $^{13}CO/H_2 \rightarrow {}^{12}CO/H_2$ over the different alumina-supported catalysts used.

In the following, the results of mathematical analysis of the experimental data applying the three described methods are presented.

4.2. Fit to exponential functions

As described above, the transient for a single surface pool can be mathematically described as an exponential function with the surface residence time as the only parameter. In the case of several pools in parallel the transient is composed by a sum of exponential functions, each representing one pool with a defined surface residence time and fraction of total surface sites. Table 2 contains the results of the application of this simple fitting method to the experimental data. Furthermore, for all experiments the fits using one exponential and the sum of two exponentials were compared. For the Ni/Co catalyst, however, in the latter case the residence times obtained from the fit for both single catalysts were used and compared to the fit that could be achieved without any fixed parameters. The residence times as determined from integration of the transients served as a standard value for comparison.

For the pure catalysts, the addition of a second exponential did not improve the fit (cf. last column

Table 2
Results from integration and fitting of the transients to exponential function

Catalyst	Method	τ (s)	Pool fraction	Error [a]
Co/Al_2O_3	Integration of transient [b]	29.5		
	Fit w/1 exponential	26.2		1.00
	Fit w/2 exponentials	26.1/26.2	0.54/0.46	1.00
Ni/Al_2O_3	Integration of transient [b]	137.1		
	Fit w/1 exponential	138.3		1.00
	Fit w/2 exponentials	137.9/138.5	0.44/0.56	1.00
Ni–Co/Al_2O_3	Integration of transient	(80.1)		
	Fit w/1 exponential	(71.5)		3.20
	Fit w/2 exponentials	26.2 [c]/138.3 [c]	0.49/0.51	1.05
	Best fit by 2 exponentials	19.8/133.2	0.46/0.54	1.00

[a] Compared to the smallest error obtained for the respective fitting of every experiment.
[b] After correction for the chromatographic effect ($\tau(CO)_{Co}$=3.9 s, $\tau(CO)_{Ni}$=9.1 s).
[c] Fixed during the fitting procedure.

of Table 2); the two parameters for the surface residence times are almost identical to the values obtained using only a single exponential. For the Ni/Co mixed catalysts, however, the fit with two exponentials (using the residence times determined for both the pure catalysts) led to a marked improvement compared to the single exponential; the deviation between calculated and measured signal decreased to approximately one third. Also, on comparing the shapes of the simulated and the measured transient for the Ni/Co catalyst (cf. Fig. 2), it becomes obvious that (at least) two exponential terms are required to achieve a satisfying agreement.

When analyzing experimental data, however, the residence times of the different pools that exist on the catalyst surface are usually not known in advance. Hence, the fitting procedure of the Ni/Co transient was repeated without using the fixed residence times. As can be seen from Table 2, the quality of the fit improved further and the determined parameters shift slightly, but the obtained values for the residence times remain reasonably close to the values of each of single catalysts.

However, it can be expected that the successful application of this method is limited to cases where the contributions of the different sites are considerably large and the specific activities of each pool are significantly different (as for the investigated model system).

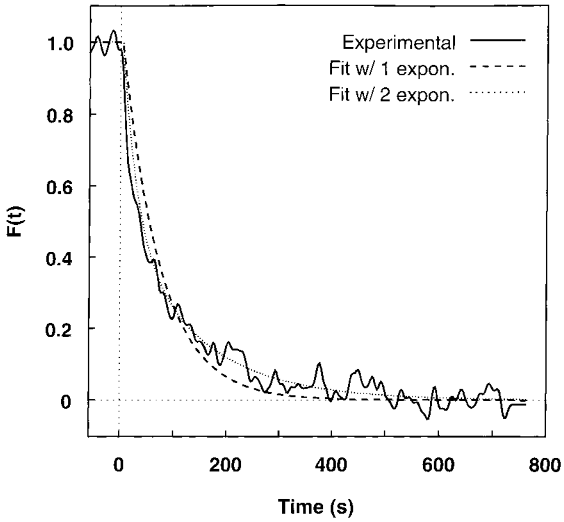

Fig. 2. Comparison of measured and fitted transients over the (Ni/Co)/Al_2O_3 catalyst. The fitting curves were obtained using one and two exponential terms (see inset and text).

4.3. Determination of the reactivity distribution

In the following, the results applying the ILT and the TF methods are compared regarding their ability to recover the reactivity distribution for the pure and the mixed catalyst. To study the influence of noise in the experimental data, a synthetic data set without any noise was also used as input.

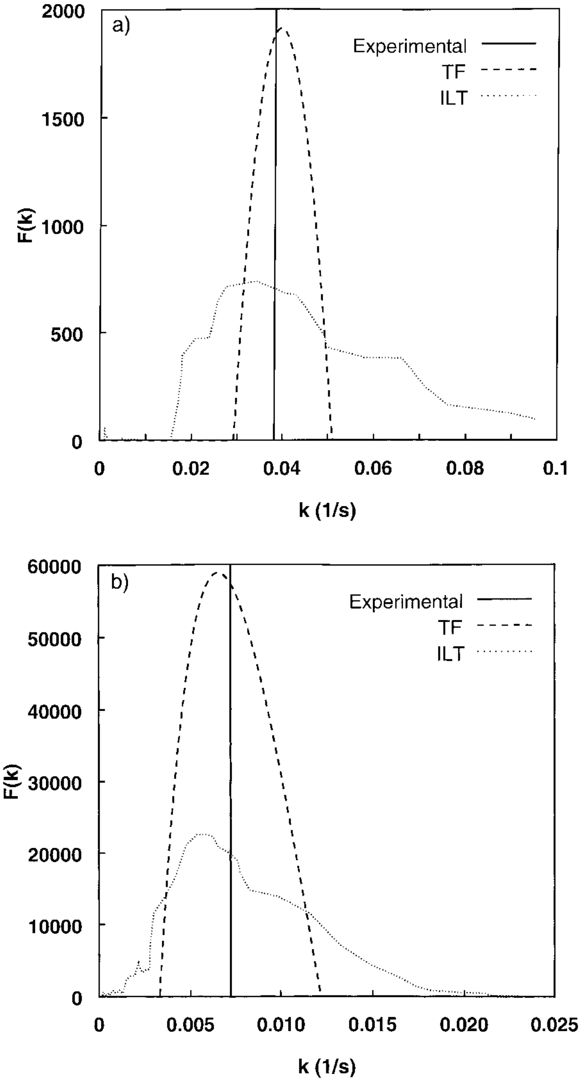

Fig. 3. Recovered reactivity distribution on (a) Co/Al_2O_3 and (b) Ni/Al_2O_3 using the ILT and TF methods (see insets). The lines indicate the values for the rate constants of the two metals as derived for the pure catalysts by fitting to an exponential decay (see Table 2).

4.3.1. *Pure catalysts*

The obtained distributions for the rate constants of different sites on the catalyst surface for the pure materials are shown in Fig. 3(a) and (b) together with the rate constants that were calculated from the surface residence time as obtained by the fit to the exponential function. Obviously, both methods result in a satisfying recovery of the rate constants of the metal centers, but the TF method leads to more precise results, seen as sharp peaks in the *f*(*k*) distribution, compared to the ILT method. It should be noted that, for both catalysts, a unimodal distribution of rate constants is obtained which indicates only a limited heterogeneity of the surface sites with respect to the range of reactivities for the conversion of synthesis gas to methane. This is in agreement with the above-described observation that the transients can be fitted using only one exponential decay term (i.e. assuming just one type of surface site with a distinct reactivity).

4.3.2. *Mixed catalyst*

The recovered reactivity distributions from the transient for the Ni/Co mixed catalyst are shown in Fig. 4(a) and (b) together with the values for the rate constants of both metal sites as obtained from the fitted exponential fit for the pure catalysts (see Table 2).

From Fig. 4(a) it can be easily seen that, by using the ILT method, it is not possible to recover the presence of two pools on the catalyst surface. As can be seen from comparing Fig. 3(a) and (b) to Fig. 4(a), the obtained *f*(*k*) is mainly composed of the contribution of the Ni sites while the intensity in the region of the Co catalyst is just slightly increased. It can be safely assumed that, without any prior knowledge of the types of surface sites, the obtained reactivity distribution would not point at two different catalytic centers on the surface.

The application of the TF method led to significantly better results; the calculated reactivity distribution clearly depicts the two pools (Co and Ni) that are present on the surface catalyst. However, the maxima of the two peaks are slightly shifted toward the values for each pool that were obtained by fitting an exponential decay to the transients. Fig. 5 shows a comparison between the measured and the calculated responses using the reactivity distribution from Fig. 4(b); the agreement is satisfying and comparable to the quality of the fit using two exponentials (cf. Fig. 2).

It is noteworthy that the application of both these methods possibly suffers from the fact that the initial coverage of reactive surface intermediates, Θ_0 in Eq. (3), is not constant throughout the complete *f*(*k*) distribution for both the Co and Ni centers. However, it

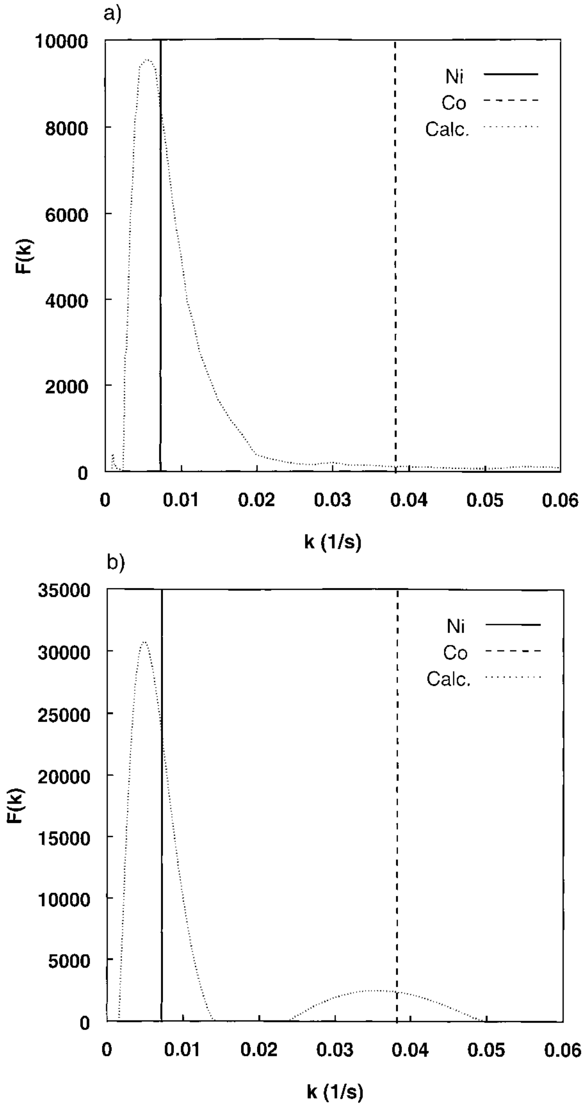

Fig. 4. Recovered reactivity distribution on a mixed (Ni/Co)/Al_2O_3 catalyst using (a) the ILT and (b) the TF methods. The lines indicate the values for the rate constants of the two metals as derived for the pure catalysts by fitting to an exponential decay (see Table 2).

seems reasonable to assume that, due to a large reactivity difference, this fact will only influence the absolute values for $f(k)$ but not the distribution itself. Furthermore, it also seems likely that on any catalyst surface exhibiting a marked heterogeneity, i.e. a number of different pools, different coverages for the species in each pool have to be considered.

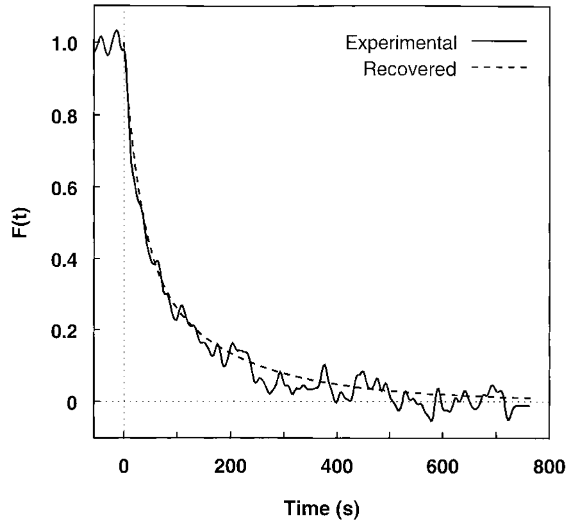

Fig. 5. Comparison of measured and calculated transients (applying the TF method and the reactivity distribution from Fig. 4(b)) for the mixed (Ni/Co)/Al_2O_3 catalyst.

4.3.3. Synthetic data

Due to the non-satisfying recovery of the reactivity distribution from the measured transient – especially applying the ILT method – and in order to test the influence of noise in the experimental data, both mathematical methods were tested using a synthetic (noise-free) data set as input. In order to obtain a direct comparison of the results, the fitting function of the Ni/Co transients based on the sum of two exponentials (see above and Table 2) was used. Fig. 6(a) and (b) show the obtained reactivity distribution applying both methods.

Using the IFT method two peaks for both surface pools are now obtained. The peaks fall close to the values of the rate constants for the Co and Ni sites. It needs to be mentioned that a problem in the application of the ILT method to the analysis of the synthetic data is the determination of $\omega_{\max}$, which depends of the noise in the experimental data and determines the spacing of the parameters based according to Eqs. (6) and (7). Due to the absence of noise in the synthetic data, $\omega_{\max}$ was estimated based on a very small value of ε=0.0001.

The TF method led to very sharp peaks in the $f(k)$ distribution and an even better recovery of the Co and Ni surface pools compared to the analysis of the experimental data (cf. Fig. 4(b)).

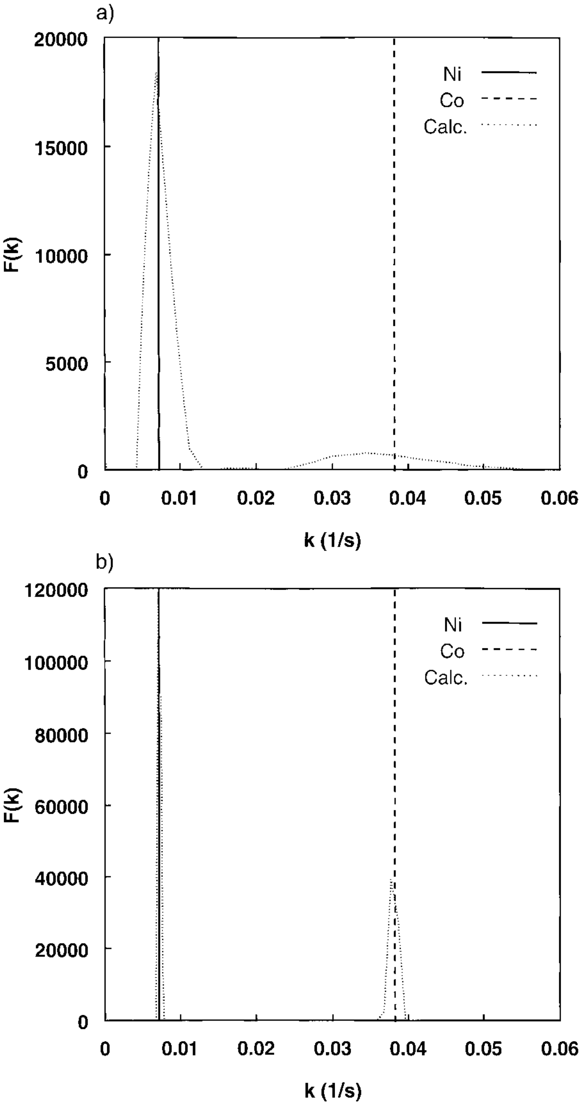

Fig. 6. Recovered reactivity distribution from a synthetic data set that is composed of two pools (k_1=1/(29.5 s) and k_2=1/(137.1 s), see Table 2) using (a) the ILT and (b) the TF methods.

The main difference between the synthetic and the real data set is, obviously, the absence of noise in the former one; hence, the inferior quality of the recovered reactivity distribution in the latter case can be ascribed to the influence of noise. This, in turn, implies that the results of mathematical analysis can be improved by reducing the noise in experimental data.

5. Conclusions

The potential of three mathematical methods for the recovery of reactivity distributions from SSITKA data was tested and compared using a model system that consisted of two catalytic sites of different reactivity. Fitting the experimental transient to both, one and two exponentials confirmed the presence of the two different pools of reaction intermediates. From the two other methods applied for the calculation of continuous $f(k)$ distributions, the Tikhonov/Fredholm (TF) method proved to be superior to the inverse Laplace transform (ILT) method. While the latter led to an ambiguous $f(k)$ distribution, the TF method was able to recover the two surface pools from the transients.

When comparing the three methods, the fitting of exponentials to the transients is (a) the most simple and, in turn, fastest method and (b) least sensitive to noise. It can be applied for standard routine analysis of SSITKA data. If one expects that the reactivity distribution on the actual catalyst exhibits a complicated structure (as compared to distinct site activities as in the present study), the more advanced methods (especially the TF method) might be superior. In this case, the contribution of noise to the experimental data has to be minimized in order to guarantee reliable results.

Regarding the limits of applicability, it can be assumed that the contributions of different sites have to be large enough and the activities of each pool have to be significantly different to obtain satisfactory results.

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