COMPARISON OF DIFFERENT METHODS FOR QUANTITATIVE ANALYSIS OF TAP PULSE-RESPONSE DATA

M. P. Lobera[a], **C. Téllez**[a], **J. Herguido**[a], **M. Menéndez**[a], **Y. Schuurman**[b]

[a] Aragon Institute for Engineering Research (*I3A*), *University of Zaragoza, 50009 Zaragoza, Spain.*
[b] Institut de Recherche sur la Catalyse et l'Environnement de Lyon– Université Lyon1 -2 Av. Einstein, 69626 Villeurbanne Cedex FRANCE.

1. Introduction

The temporal-analysis-of-products or TAP reactor [1] has been recognized as an important transient experimental method for heterogeneous catalytic reaction studies. A TAP pulse response experiment involves injecting a very small amount of gas per pulse. As a result, the pressure rise in the micro-reactor is small, and gas molecules move through the reactor by Knudsen diffusion. The time-dependent exit flow rate of each gas is detected by a mass spectrometer and the intensity of the transient response is proportional to the exit flow rate of the corresponding gas. Quantitative information of the phenomena in the reactor can be extracted from the size and the shape of the responses by the use of mathematical models that describe the diffusion process in the reactor [2]. Kinetic evaluation of TAP experiments is typically based on analytical or numerical solution of partial differential equations describing chemical and transport process in the micro-reactor. Different methods have been proposed in the literature, including moment analysis [2, 3], thin-zone model [4, 5] and a numerical solution [6].

In this work different methods to obtain rate constants from pulse experiments are compared and evaluated. The reaction studied is the dehydrogenation of propane over a supported platinum catalyst. Two principal operating variables have been varied: the temperature and the amount of catalyst. Moreover, the effect of the Knudsen diffusion coefficient ($D_{e,cat}$) on the activation energy (E_a) and the propane conversion was studied.

2. Experimental

Vacuum transient experiments of propane dehydrogenation over Pt-Sn-K/γ-Al_2O_3 were carried out in the TAP-2 reactor in single pulse mode. The catalyst used in this study was prepared by incipient wet impregnation; details of the catalyst preparation have been given in a previous work [7]. Experiments were carried out with different amounts of stable Pt-Sn-K/γ-Al_2O_3 catalyst sandwiched between two inert zones. The range of operating conditions was as follows: temperature, 573–873 K; molar fraction of propane, 0.5; molar fraction of argon, 0.5; catalyst mass, 10-100 mg. The catalyst was heated to the desired reaction temperature under vacuum at a rate of 10 K/min.

3. Results

The conversion was obtained from the following mass balance, assuming no propane conversion at 573 K:

$$X = \frac{PI(573K) - PI(T)}{PI(573K)} \qquad (1)$$

The area of PI-normalized flow of gas i is equal to the number of moles of gas i that leaves the reactor per mole of the limiting reactant gas A in the inlet pulse [2]. Figure 1shows the propane conversion that is obtained by the mass balance equation (1), as a function of amount of catalyst for the different reaction temperatures. The propane conversion increases initially increases linearly with the amount of catalyst and then levels off. These curves are very similar to “W/F” curves in flow reactors. However, the conversion in the TAP reactor at a given temperature does not change with pulse intensity so the amount of catalyst has been varied.

To obtain kinetic data from the TAP curves several possibilities exists. First of all a kinetic model needs to be determined. From the propane pulse response shape as a function of the temperature it was deduced that the reaction of propane runs irreversible over the catalyst rather than a chemisorption of propane. The following reaction is assumed:

$$C_3H_8 + x^* \quad C_3H_{8-x}^* + xH^* \tag{2}$$

Furthermore it was assumed that this reaction is first order in propane and that the number of active sites does not change by admitting a series of single propane pulses.

The rate constant, *k*, corresponding to a given conversion can be calculated by a moment analysis or by modeling the full pulse response curve. These two approaches can then be further classified by defining which reactor model needs to be taken into account. Generally all reactor models are based on Knudsen diffusion only, but they differ in the number and nature of the inert and catalyst zones. For example if the catalyst zone can be considered thin compared to the overall reactor length (Thin Zone Model, TZM [4,5]) an easy expression is obtained relating the conversion and the rate constant:

$$X = \frac{k_a^{'}\tau_{cat}^{dif}}{1 + k_a^{'}\tau_{cat}^{dif}} \tag{3}$$

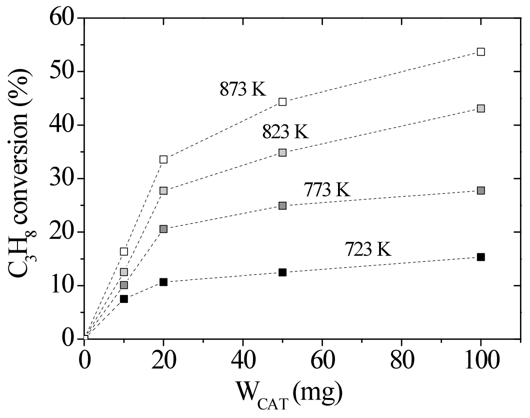

Fig. 1. Propane conversion as a function of mass of catalyst for different temperatures (symbols are experimental data and the lines are a visual help)

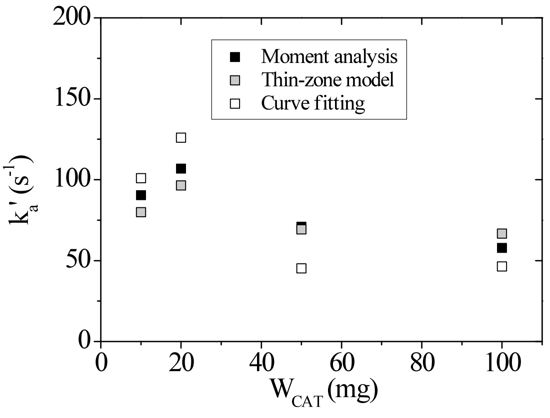

Fig. 2. Calculated rate constants by different methods from the experimental propane conversion as a function of the amount of catalyst. T_B=823 K.

Figure 2 shows the results of using three different methods, zeroth moment, TZM and full curve fitting, to calculate the rate constant. This has been done for the different amounts of catalysts. Rather similar values for the rate constants are obtained by the three different methods. From figure 2 it follows that the first order irreversible rate constant decreases with increasing catalyst amount. This might be due to an experimental error that depends on the catalyst amount or one of the assumptions of the model that appears to be incorrect. If one uses the first moment rather than the zeroth the dependence of the rate constant on the catalyst amount is even stronger. In this case it can be (partly) attributed to the fact that even minor changes in the mean residence time leads to very different values of the rate constant. Surprisingly the TZM gives similar values than the two other methods even at larger amounts of catalysts.

Table 1. *Values of activation energies obtained by different models.*

	E_a (kJ mol^{-1})	
Moment analysis	Value	S.D. 95% C.I.
10 mg	31.69	± 1.4
20 mg	60.37	± 3.2
50 mg	65.80	± 1.5
100 mg	69.06	± 3.7
Curve fitting		
10 mg	50.61	± 2.3
20 mg	69.65	± 3.4
50 mg	70.81	± 4.1
100 mg	75.78	± 4.6
Thin-zone model	60.30	± 1.8

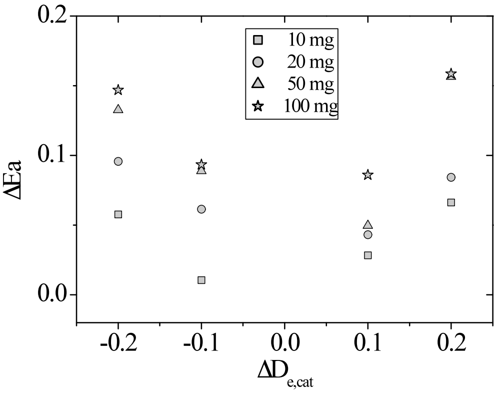

Fig. 3. Effect of the relative change of the propane diffusivity in the catalyst zone on the relative value of the activation energy.

Table 1 shows the activation energy calculated by the three different methods. The values are significantly lower in the case of 10 mg than for the other amounts.

Using the same data set the influence of the value of the propane diffusivity in the catalyst zone on the value of the activation energy has been investigated. The results are plotted in Figure 3. In the case of amount of catalysts higher than 20 mg, the exact value of the diffusivity has a significant effect on the value of the activation energy.

4. Conclusions

Evaluation of different methods of quantitative data analysis of TAP response curves has shown that the three methods yield comparable results. There seem to exist an optimal catalyst loading in the sense that over small amounts of catalysts a significantly smaller value of the activation energy is measured whereas at high amounts the value of the activation energy is sensitive to the exact value of the diffusivity in the catalyst zone.

The use of the zeroth moment gives a more accurate estimation of the values of the rate constants than the first moment.

Acknowledgments

The authors thank DGI (Spain) for financial support in the project CTQ2004-01721/PPQ.

References

[1] J.T. Gleaves, G.S. Yablonskii, P. Phanawadee, Y. Schuurman, Appl. Catal. A 160 (1997) 55.
[2] P. Phanawadee, Doctoral Dissertation. Washington University, 1997.
[3] G.S. Yablonsky, S.O. Shekhtman, S. Chen, and J. Gleaves, Ind. Eng. Chem. Res. 37 (1998) 2193.
[4] S.O. Shekhtman, G.S. Yablonsky, S. Chen, J.T. Gleaves, Chem. Eng. Scie. 54 (1999) 4371.
[5] S.O. Shekhtman, G.S. Yablonsky, J.T. Gleaves, R. Fuchimi, Chem. Eng. Scie. 58 (2003) 4843.
[6] Y. Schuurman, Catalysis Today 121 (2008) 187.
[7] M. P. Lobera, C. Téllez, J. Herguido, M. Menéndez, Appl. Catal. A 349 (2008) 156.
[8] G.D. Svoboda, J.T. Gleaves, P.L. Mills, Ind. Eng. Chem. Res. 31 (1992) 19.
[9] W.L.M. Weerts, M.H.J.M. de Croon, G.B. Marin, Surf. Sci. 367 (1996) 321.