1

Model Discrimination in Chemical Kinetics

Burcu Özdemir and Selahattin Gültekin*

Doğuş University, Acıbadem, Kadıköy 34722, Istanbul, Turkey

Abstract: In studies on chemical kinetics, generally after the rate data have been taken, a mechanism and an associated rate law model are proposed based on the data taken. Frequently, more than one mechanism and rate law may be consistent with data. In order to find the correct rate law, regression techniques (model discrimination) are applied to indentify which model equation best fits the data by choosing the one with the smaller sum of squares. With this non-linear regression technique, rate parameters with 95% confidence limits are calculated along with residues. Of course, model parameters must be realistic. For example, reaction rate constants, activation energies or adsorption equilibrium constants must be positive by comparing the calculated value of parameters with 95% confidence limits, one can judge about the validity of the model.

In this paper, model discrimination will be applied to certain data from the literature along with the suggested heterogeneous catalytic models such as Langmuir-Hinshelwood Kinetic Model or Rideal-Eley Model.

A reaction of $A + B \rightarrow C + D$ type have been selected (like methanation) with the rate laws given below:

$$-r_{A} = kP_{A}P_{B} / (1 + K_{A}P_{A} + K_{B}P_{B} + K_{C}P_{C} + K_{D}P_{D})^{c}$$
dual-site Langmuir-Hinshelwood Model

$$-r_{A} = kP_{A}P_{B} / (1 + K_{A}P_{A} + K_{B}P_{B} + K_{C}P_{C} + K_{D}P_{D})$$
single-site Langmuir-Hinshelwood Model

$$-r_{A} = kP_{A}P_{B} / (1 + K_{A}P_{A} + K_{B}P_{B})^{2}$$
only reactants are adsorbed

$$-r_{A} = kP_{A}P_{B} / (1 + K_{A}P_{A} + K_{B}P_{B})^{2}$$
dual-site Rideal-Eley Model

$$-r_{A} = kP_{A}^{a} \cdot P_{B}^{b}$$
power-law

In this study,

$CO + 3H_2 \rightarrow CH_4 + H_2O$

reaction rate data were tested for five different models to find the most suitable rate expression by model discrimination method taking the advantage of powerful POLYMATH package program.

INTRODUCTION

Regression Techniques

In empirical studies, in order to determine the parameters for the postulated model, very powerful regression techniques (methods) are used.

Regression methods basically are as follows [1]

- a) *Linear regression* (like y = ax + b), where a and b are to be determined.
- b) Multiple regression (like $y = a_1x_1 + a_2x_2 + \dots + a_nx_n$), where a_i 's are parameters to be determined.
- c) Polynomial regression (like $y = a_n x^n + a_{n-1} x^{n-1} + ... + a_1 x + a_0$), a_i 's are parameter to be determined from regression.

d) Non-linear regression [2].

This is very common and can be used almost under any condition. General form is $y = f(x_1, x_2, ..., x_n, a_1, a_2, ..., a_n)$, where n = # of experiments, m = # of parameters to be determined providing n > m+1.

The common features of the above regression techniques are that it is to make the variance minimum, and to make the correction factor as close to unity as possible. After determination of parameters, the next step is to check to see whether they are physically meaningful or not. For example, if adsorption equilibrium constant is one of the parameters, then it must decrease with increasing temperature as adsorption is an exothermic process (Le Chatelier Principle)

In kinetic studies, generally one faces very complicated rate expressions on heterogeneous catalysts. Those rate expressions may obey Langmuir-Hinshelwood or Rideal-Eley model [3, 4].

In general, if we have a reaction of $A + B \rightarrow C$ we may have possible rate expressions as

^{*}Address correspondence to this author at the Doğuş University, Acıbadem, Kadıköy 34722, Istanbul, Turkey; E-mail: sgultekin@dogus.edu.tr

$$-r_{A} = \frac{kP_{A}P_{B}}{\left(1 + K_{A}P_{A} + K_{B}P_{B} + K_{C}P_{C}\right)^{2}}$$
(Dual-site model)
$$-r_{A} = \frac{kP_{A}P_{B}}{\left(1 + K_{A}P_{A} + K_{B}P_{B} + K_{C}P_{C}\right)}$$
(Single-site model)
$$kP P$$

$$-r_A = \frac{K A_A P_B}{(1 + K_A P_A)^2}$$
 (Dual-site, Rideal-Eley)

$$-r_A = kP_A^a P_B^b$$
 (Apparent power-law expression)

In kinetic studies, for example, one may have three different mechanisms and three different rate-determining steps. Therefore, one will have nine different rate expressions. In order to determine the correct rate expression, *model discrimination method* is being used. The essence of this method is not only to minimize the variance, but also to keep the correction factor as close to one (unity) as possible. In addition to the above two criteria, one also has to check the physical validity of the determined parameters.

RESULTS

Now we will chose the reaction of methanation [4] on Ni catalyst where initial rates are taken at constant temperature at variety partial pressures of reactants and products.

Consider the reaction

 $CO + 3H_2 \rightarrow CH_4 + H_2O$ (methanation)

Assuming the following runs were carried out under the given conditions (see Table 1).

Table 1.	Initial Rates	Obtained at	Various	Partial Pressures
----------	---------------	-------------	---------	-------------------

Run #	Run # r _A *		P _{H2} **	P _{H20} **	P _{CH4} **
1	0.1219	1	1	0	0
2	0.0944	1	1	1	1
3	0.0943	1	1	1	2
4	0.0753	1	1	2	1
5	0.0753	1	1	2	2
6	0.0512	1	1	4	1
7	0.0280	1	1	8	1
8	0.1274	1	2	1	1
9	0.1056	1	2	2	2
10	0.1203	1	4	4 2	
11	0.1189	1	8	1	1
12	0.0782	2	1	1	1
13	0.1204	2	2	1	1
14	0.1057	2	2	2	0
15	0.1056	2	2	2	1
16	0.1056	2	2	2	2
17	0.1552	2	4	1	1
18	0.0533	4	1	1	1
19	0.0911	4	2	1	1
20	0.0317	8	1	1	1
21	0.1476	8	8	1	1

* r_A [mole/kg.cat.s], ** P_i [atm].

We will consider the following plausible rate expressions and by *model discrimination* we will reach hopefully to the true rate expression.

a) All reactants and products are adsorbed with dual-site mechanism:

$$-r_{A} = \frac{kP_{CO}.P_{H_{2}}}{(1 + K_{CO}.P_{CO} + K_{H_{2}}.P_{H_{2}} + K_{H_{2}O}.P_{H_{2}O} + K_{CH_{4}}P_{CH_{4}})^{2}}$$

(Dual-site)

b) All reactants and products are adsorbed with singlesite mechanism:

$$-r_{A} = \frac{kP_{CO}.P_{H_{2}}}{(1 + K_{CO}.P_{CO} + K_{H_{2}}.P_{H_{2}} + K_{H_{2}O}.P_{H_{2}O} + K_{CH_{4}}P_{CH_{4}})}$$

(Single-site)

c) Only reactants are adsorbed with dual-site mechanism:

$$-r_{A} = \frac{kP_{CO}.P_{H_{2}}}{(1 + K_{CO}.P_{CO} + K_{H_{2}}P_{H_{2}})^{2}}$$
 (Only reactants are

adsorbed, dual-site)

d) Only CO is adsorbed; H₂ comes directly from gas phase and reacts with adsorbed CO (Rideal-Eley Mechanism)

$$-r_{A} = \frac{kP_{CO}.P_{H_{2}}}{(1 + K_{CO}.P_{CO})^{2}}$$
(Rideal-Eley, dual-site)

e) A power-law expression:

 $-r_A = k.P_{CO}^a.P_{H_{\gamma}}^b$ (Power-Law)

In the following pages, these five different models were tried on Polymath[®] program. The results are self explanatory, and are given in Figs. (1-5).

Model a:

$$-r_{A} = \frac{kP_{CO}.P_{H_{2}}}{(1 + K_{CO}.P_{CO} + K_{H_{2}}.P_{H_{2}} + K_{H_{2}O}.P_{H_{2}O} + K_{CH_{4}}P_{CH_{4}})^{2}}$$

Output of Model a:

$$r_{A} = kP_{CO}P_{H} / \left(1 + K_{CO}P_{CO} + K_{H}P_{H} + K_{H_{2}O}P_{H_{2}O} + K_{CH_{4}}P_{CH_{4}}\right)^{2}$$

POLYMATH Results

Nonlinear Regression (L-M)

Variable	Ini. Guess	Value	95% Confidence
k	4	7.9628870	0.0367133
ксо	2	5.0877643	0.0124837
КН	4	1.9950241	0.0047754
KH ₂ O	5	1.0969188	0.0030085
KCH ₄	1	0.0046140	0.0015179

Nonlinear regression settings.

Max # iterations = 64

00	1 : C001 ra	×	/ 0.1219							\$	Regres <u>s</u> io	n A <u>n</u> alysis (<u>G</u> raph
	ra	PCO	PH	PH2O	PCH4	C06	C07	C08	C09	C1 📥	\$ B	3 -	Graph 🔲 Residuals
01	0.1219	1	1	0	0								
)2	0.0944	1	1	1	1						Iv <u>H</u> eport		
3	0.0943	1	1	1	2						Linear & Po	ynomial Multiple	linear Nonlinear
4	0.0753	1	1	2	1						f.	≫	LM
5	0.0753	1	1	2	2								2.01
5	0.0512	1	1	4	1						+KCO*PCC	*PH7() +KH*PH+KH2O*	PH20+KCH4*PCH4)^2
	0.0280	1	1	8	1								
0	0.1274	1	2	1	1								e.g. y = 2*x*4
9	0.1056	1	2	2	2						Model Para	meters Initial Gues	SS:
1	0.1203	1	4	2	2						Model parr	n Initial guess	
2	0.0782	2	1	1	1						KCO	0	
3	0.1204	2	2	1	1						KUU	0	
	0.1057	2	2	2	0						KH2O	1	
5	0.1056	2	2	2	1						КСНА	0.01	
5	0.1056	2	2	2	2						Roll+	0.01	
7	0.1552	2	4	1	1								
8	0.0533	4	1	1	1						_		
9	0.0911	4	2	1	1						Deserte		
0	0.0317	8	1	1	1						Dependen	(Variable jia	
1	0.1476	8	8	1	1						Independe	nt Variable/s (FU	
2											Model Vari	able/s K, r	NUU, NH, NH2U, NUH4
3											Available \	ra, ra,	PCO, PH, PH2O, PCH4
4													
5													
ſ													
-		- T3L								<u> </u>			

Fig. (1). Input of the data in POLYMATH Screen for Model a.

🍓 PC	LYMATH 6.10	Educational Rele	ease - [Data Ta	able]	time. In	-							
🛄 F	ile Program	Edit Row C	Column Forr	nat Analysis	Examples	Window	Help						_ 8 ×
	ş 🥵 🔳 🛛 🖇	b 🖻 🛍 🖉	M & 🗵) 📧 💷	i 🖉 🧖	🛛 🗱 🢡							
R001	: C001 ra	× ×	0.1219							4	Regressio	n Analysis Graph	
	ra	PCO	PH	PH2O	PCH4	C06	C07	C08	C09	C1_			- Desiduala
01	0.1219	1	1	0	0			JJ		·			i j nesiuu <u>a</u> is
02	0.0944	1	1	1	1						✓ <u>R</u> eport	Store Model	
03	0.0943	1	1	1	2						Linear & Po	ynomial Multiple linear	Nonlinear
04	0.0753	1	1	2	1						f	*	
05	0.0753	1	1	2	2						Model:		
06	0.0512	1	1	4	1						ra = k*PCC	PH/(1	ксци×рсци)
07	0.0280	1	1	8	1								KCH4TCH4j
08	0.1274	1	2	1	1								e.g. y = 2*x^A+B
09	0.1056	1	2	2	2						Model Para	meters Initial Guess:	
10	0.1203	1	4	2	2						Model parr	n Initial guess	
11	0.1189	1	8	1	1						k	14	
12	0.0782	2	1	1	1						KCO	8	
13	0.1204	2	2	1	1						КН	1	
14	0.1057	2	2	2	0						KH20	1	
15	0.1056	2	2	2	1						KCH4	0.01	
16	0.1056	2	2	2	2								
17	0.1552	2	4	1	1								
18	0.0533	4	1	1	1								
19	0.0911	4	2	1	1						Dependen	t Variable 🛛 ra	
20	0.0317	8	1	1	1						Independe	nt Variable/s PCO, PH,	PH20, PCH4
21	0.1476	8	8	1	1						Model Vari	able/s k, KCO, K	H, KH2O, KCH4
22											Available \	ariables I PCO P	
23											111000010	lia, rco, r	n, Fn20, FCn4
24													
25										•			
↓													
Poly_	cyp_data_single.	pol No Title											
7:26 F	M 7/10/2008	CAPS NUM											1

Fig. (2). Input of the data in POLYMATH Screen for Model b.

Precision

R^2	= 0.9999995
R^2adj	= 0.9999993
Rmsd	= 5.321E-06
Variance	= 7.804E-10

Model b:

$$-r_{A} = \frac{kP_{CO}.P_{H_{2}}}{(1 + K_{CO}.P_{CO} + K_{H_{2}}.P_{H_{2}} + K_{H_{2}O}.P_{H_{2}O} + K_{CH_{4}}P_{CH_{4}})}$$

Output of Model b:

$$r_{A} = kP_{CO}P_{H} / \left(1 + K_{CO}P_{CO} + K_{H}P_{H} + K_{H_{2}O}P_{H_{2}O} + K_{CH_{4}}P_{CH_{4}}\right)^{2}$$

Variable	Ini guess	Value	95% Confidence
k	14.0	2.747922	0.0023620
КСО	8.0	51.41168	0.0593556
КН	1.0	12.89503	0.0368865
KH ₂ O	1.0	2.123223	0.0692380
KCH4	0.01	-1.989895	0.0982922

Nonlinear regression settings

Max # iterations = 64

Precision

R^2	= -1.586834
R^2adj	= -2.233542
Rmsd	= 0.011789
Variance	= 0.0038306
Model c: $-r_A =$	$\frac{kP_{CO}.P_{H_2}}{(1+K_{CO}.P_{CO}+K_{H_2}P_{H_2})^2}$

Output of Model c: $r_A = k P_{CO} P_H / (1 + K_{CO} P_{CO} + K_H P_H)^2$

Variable	Ini guess	Value	95% Confidence
k	14.0	0.7700806	0.6088063
КСО	8.0	1.540737	0.7859312
КН	1.0	0.5896616	0.3142481

Precision

R^2	= 0.7311287
R^2adj	= 0.7012541
Rmsd	= 0.0038007
Variance	= 0.0003539

Model d:
$$-r_A = \frac{kP_{CO}.P_{H_2}}{(1 + K_{CO}.P_{CO})^2}$$

🥹 PC	DLYMATH 6.10	Educational R	elease - [Dat	a Table]	di riser 1	100 100							
	File Program	Edit Row	Column F	Format Analy	sis Example	s Window	Help						_ & ×
	D 🚅 🕼 🔲 🕺 🛍 🛍 🖉 🛤 🐍 🛛 🖾 🖾 📾 💭 ! 🚟 💡												
R001	R001:C001 ra X V 0.1219 Analysis Graph												
	ra	PCO	PH	PH20	PCH4	C06	C07	C08	C09	C1_	\$ ⊠	Gran	h 🔲 Besiduals
01	0.1219	1	1	0	0								
02	0.0944	1	1	1	1						<u> <u> </u> </u>	Store Model	
03	0.0943	1	1	1	2						Linear & Polyr	nomial Multiple linear	Nonlinear
04	0.0753	1	1	2	1						f(x)	1	
05	0.0753	1	1	2	2						Model: 🗡		L-M
06	0.0512	1	1	4	1						ra = k*PCO*F	PH/(1+KCO*PCO+KH*	PH)^2
07	0.0280	1	1	8	1								
08	0.1274	1	2	1	1								e.g. y = 2*x^A+B
09	0.1056	1	2	2	2						Model Param	eters Initial Guess:	
10	0.1203	1	4	2	2						Model parm	Initial guess	
11	0.1189	1	8	1	1						k	14	
12	0.0782	2	1	1	1						KCO	8	
13	0.1204	2	2	1	1						КН	1	
14	0.1057	2	2	2	0								
15	0.1056	2	2	2	1								
16	0.1056	2	2	2	2								
17	0.1552	2	4	1	1								
18	0.0533	4	1	1	1								
19	0.0911	4	2	1	1						Dependent	/ariable Ira	
20	0.0317	8	1	1	1						Independent	Variable /a PC0_PH	
21	0.1476	8	8	1	1						Madel Veriet		Ц
22											Model variat		
23											Available Va	riables ra, PCO, F	PH, PH20, PCH4
24													

Linear & Polynomial	Multiple linear	Nonlinear	🗖 🗖 🖸 🗖
Enter Model <i>i.e.</i> y: ra = k*PCO*PH/(1+KC0	= 2*x^A+ <i>B*in(x)/(C+x)</i> D*PCO)^2	Solve with L-M 💌	☐ Residu <u>a</u> ls ☑ <u>R</u> eport _ Store Model in
Dependent Variable <i>ra</i> Independent Variable/s <i>P</i> CO, <i>PH</i> Model Variable/s <i>k, KC</i> O	Enter initial gue Model parm k KCO	ess for model parameters Initial guess 14 8	column
Data <u>T</u> able Regres <u>s</u> ion A	nalysis Prepare <u>G</u> raph		

Fig. (4). Input of the data in POLYMATH Screen for **Model d**.

Output of Model d: $r_A = kP_{CO}P_H / (1 + K_{CO}P_{CO})^2$

Variable	Ini Guess	Value	95% Confidence		
k	14.0	0.062234	5.47E-06		
КСО	8.0	0.453103	3.977E-05		

Nonlinear regression settings.

Max # iterations = 64

Precision

-1.282797
-1.402944
= 0.0110745
= 0.0028467

Model e: $-r_A = k.P_{CO}^a.P_{H_2}^b$

Output of Model e: ra = k*PCO^a*PH^b

🥶 PO	LYMATH 6.10	Educational Re	elease - [Data]	Table]	a tast 1	ult inte						
🛄 F	ile Program	Edit Row	Column Fo	rmat Analy	sis Examples	Window	Help					_ & ×
	ጅ 💕 🔳 👌	6 🖻 🛍 🖉	M 26	2 🖪 🖪 🗉	1 🖬 🌂	! 🚟 💡)					
R001	: C001 ra	×v	0.1219							÷	Regression Analysis Graph	
	ra	PCO	PH	PH2O	PCH4	C06	C07	C08	C09	C1_	Ø 🔳 ➡ – Grade	- Residuale
01	0.1219	1	1	0	0							I nesiuu <u>a</u> is
02	0.0944	1	1	1	1						Report Store Model	
03	0.0943	1	1	1	2						Linear & Polynomial Multiple linear	Nonlinear
04	0.0753	1	1	2	1						fee	
05	0.0753	1	1	2	2						Model:	L-M
06	0.0512	1	1	4	1						ra = k*PCO^a*PH^b	
07	0.0280	1	1	8	1						<u></u>	
08	0.1274	1	2	1	1							e.g. y = 2*x^A+B
09	0.1056	1	2	2	2						Model Parameters Initial Guess:	
10	0.1203	1	-4	2	2						Model parm Initial guess	
11	0.1189	1	8	1	1						k 14	
12	0.0782	2	1	1	1						a 1	
13	0.1204	2	2	1	1						b 1	
14	0.1057	2	2	2	0							
15	0.1056	2	2	2	1							
16	0.1056	2	2	2	2							
17	0.1552	2	4	1	1							
18	0.0533	4	1	1	1							
19	0.0911	4	2	1	1						Dependent Variable	
20	0.0317	8	1	1	1						Independent Variable Ind	
21	0.1476	8	8	1	1							
22												
23											Available variables ra, PCO, Pl	H, PH2O, PCH4
24												
25												
										•		
Poly_c	.yp_data_Power	r.pol No Title										
7:47 PI	M 7/10/2008	CAPS NUM										

Fig. (5). Input of the data in POLYMATH Screen for Model e.

Variable	Ini Guess	Value	95% Confidence
k	14.0	0.0806184	3.076E-06
a	1.0	-0.0554411	4.271E-05
b	1.0	0.3205555	3.242E-05

Nonlinear regression settings.

Max # iterations = 64

Precision

R^2	= 0.4902824
R^2adj	= 0.4336471
Rmsd	= 0.0052331
Variance	= 6.709E-04

When variance, correction factor (coefficient) and the physical meaningfulness of the parameters are considered, one can clearly see that the **model a** fits the data in a perfect manner. In the remaining other models (i.e. **b**, **c**, **d** and **e**) either because of variance or correction factor or 95% confidence interval or combination thereof, the models seem to be inadequate and as a result they are eliminated.

Received: December 26, 2008

Revised: December 31, 2008

Accepted: December 31, 2008

© Özdemir and Gültekin; Licensee Bentham Open.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (http://creativecommons.org/licenses/by-nc/3.0/) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.

CONCLUSIONS

No matter how the chemical kinetic expressions are complicated, either linear, multiple linear, non-linear or polynomial, one can find a satisfactory rate expression by means of model discrimination method. This discrimination processes are eased especially after the advent of powerful ready package programs such as POLYMATH, MATLAB, MATHCAD [5], and others. One, still, has to be very cautious in that finding the satisfactory rate expression does not mean the true (absolute) rate expression and mechanism are found [6].

ACKNOWLEDGEMENTS

Authors would like to express their thanks to Doğuş University for its financial support.

REFERENCES

- [1] Polymath 6.1 User Guide, **2006**.
- [2] MATLAB R2006b Mathworks' Users Manual, 2006.
- [3] Fogler, H.S. Elements of Chemical Reaction Engineering, 4/E, Prentice-Hall, 2006.
- [4] Satterfield, C.N. Industrial Heterogeneous Catalytic Processes, 2/E, McGraw-Hill, 1990.
- [5] Gültekin, S. Kimya Mühendisliğinde MATHCAD Kullanımı (Usage of MATHCAD in Chemical Engineering), Lecture Notes, Yıldız Technical University, 1997.
- [6] Cutlip, M.B.; Shacham, M. Problem Solving in Chemical and Biochemical Engineering with POLYMATH, Excel and MAT-LAB, 2/E, Prentice-Hall, 2008.