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Kinetics of alkylation of benzene with ethanol on $AlCl_3$-impregnated 13X zeolites

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Abstract

The commercially available 13X (NaX) zeolite in the form of extrudates were impregnated with 15% $AlCl_3$ and characterized by qualitative methods. Experimental runs for the kinetic study were carried at three different temperatures (400, 425, and 450°C) with a constant benzene to ethanol molar ratio of 3:1 and varying the space velocity under isothermal conditions in the reactor. Experiments were carried out to choose the zone in which the mass transfer resistances were negligible. Different models based on Langmuir–Hinshelwood–Hougen–Watson reaction mechanisms were proposed and a mathematical fit for the best model was found. The activation energy and frequency factor were evaluated by using Arrhenius relationship. The model parameters were estimated by non-linear regression analysis. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Kinetics; Alkylation; $AlCl_3$-impregnation; 13X zeolite; Benzene ethylation

1. Introduction

The process of alkylation of benzene with ethylene on Friedel–Crafts catalysts is a traditional one and accounts for more than 90% of ethyl benzene production. The use of these catalysts, however, gives rise to many problems such as handling, safety, waste disposal, and corrosion. Recently, many efforts have been put on developing alternative environment-friendly catalyst systems. Zeolite-based catalyst systems are gaining importance in this respect and have been replacing the conventional catalysts. The vapor phase alkylation of benzene with ethanol in the presence of ZSM-5 zeolites is the famous Mobil–Badger process, which is now in commercial practice for production of ethyl benzene. The direct use of ethanol, instead of ethylene, as an alkylating agent with benzene for this reaction has some advantages. A long stable catalyst life is observed when alcohol, rather than olefin, is used as an alkylating agent. In addition to the academic interest, the direct use of ethanol in the manufacture of ethyl benzene is also of economical significance to those countries where biomass derived alcohol is an additional raw material for the manufacture of chemicals.

Enormous work has been reported on alkylation reactions on ZSM-type zeolites compared to alkylation on X-type zeolites [1–8]. Only a few researchers have performed alkylation reactions of aromatics on the basic forms of X-type of zeolite [9–13]. The alkylation of benzene with 1-decene and also the transalkylation of dialkylbenzene with benzene have been carried out with $AlCl_3$ as catalyst [14]. The alkylation reaction has been reported to be second order of magnitude faster than the transalkylation reaction. In the alkylation of benzene with propylene, addition of cumene–$AlCl_3$ complex to alumino-silicate catalyst has been reported to increase its activity [15].

From the above discussions, it is evident that there is no work reported in the literature on alkylation with $AlCl_3$-impregnated zeolite catalyst. But there are some information on $AlCl_3$-catalyzed alkylation reactions. It was, therefore, thought desirable to study the alkylation of benzene with ethanol with $AlCl_3$-impregnated zeolite catalyst in detail. The specific objectives of this study were to determine the kinetics of benzene alkylation with ethanol, to develop a kinetic model, and to estimate the unknown parameters of the kinetic model so as to obtain an intrinsic rate expression.

2. Experimental

2.1. Catalyst preparation

The catalyst was prepared from 13X (NaX) zeolites obtained from SD Fine Chemicals, India. It was calcined at

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Nomenclature

B	benzene
E	ethanol
E_a	activation energy (kJ/mol)
EB	ethyl benzene
F	total feed rate (kg mol total/h)
F_{BO}	feed rate of B (kg mol/h)
k	kinetic constant (kg mol/(kg.h))
k_0	frequency factor (kg mol/(kg. h))
K	equilibrium constant (dimensionless)
K_B	adsorption constant for benzene (atm^{-1})
K_E	adsorption constant for ethanol (atm^{-1})
K_{EB}	adsorption constant for ethyl benzene (atm^{-1})
K_H	adsorption constant for hydrogen (atm^{-1})
K_W	adsorption constant for water (atm^{-1})
p	partial pressure (atm)
P	total pressure (atm)
r	rate of reaction (kg mol/(kg cat. h))
r_B	rate of reaction of benzene (kg mol/(kg cat. h))
r_{cal}	predicted rate of reaction of B (kg mol/(kg cat. h))
r_{obs}	experimentally observed rate of reaction of B (kg mol/(kg cat. h))
t	time (h)
X_B	fractional benzene conversion (dimensionless)
W	mass of the catalyst (kg)

Subscripts

B	benzene
E	ethanol
EB	ethyl benzene
H	hydrogen
W	water

350°C for 1 h to expel moisture and cooled. The calcined zeolite (100 g) was refluxed with 250 ml of 6% (w/v) $AlCl_3$ solution in ethyl alcohol for 4 h. Then the alcohol was totally evaporated. The catalyst particles thus obtained got impregnated with $AlCl_3$ and were dried in an air oven at 100 ± 5°C and further calcined at 350°C for 6 h. The characteristics of the catalyst thus prepared are: SiO_2/Al_2O_3 ratio, 2.286; $AlCl_3$ content, 15% (w/w); surface area (BET), 478 m^2/g. X-ray diffractogram of the doped catalyst exactly matched with the parent unmodified zeolite indicating no structural change with the doping.

2.2. Experimental set-up and product analysis

The catalytic experiments were carried out in a fixed-bed, continuous down-flow, cylindrical stainless steel (SS316) reactor (0.025 m ID and 0.33 m in length) preceded by a preheater and followed by a condenser. The same reactor tube was used in all the experiments. In a typical run, about 0.03 kg of catalyst (which occupied 0.1 m height of the reactor) was charged into the reactor and the reaction was carried out at 22.13 atm total pressure. The catalyst was activated for 3 h in an atmosphere of hydrogen before the experimental runs were started. The benzene–ethanol mixture was introduced with the help of a metering pump and vaporized in the preheater before contacting the catalyst. The reactant vapors along with hydrogen entered the reactor, which was electrically heated. The desired pressure in the reactor was adjusted with the help of a needle valve at the bottom of the reactor and read from the pressure gauge fitted at the top of the reactor. The product vapors, along with unreacted reactants, were condensed in the condenser and the liquid samples collected were analyzed in a gas chromatograph with a 4.2 m × 3.2 mm SS column containing 5% Benton 34 and 7% Dionyl phthalate stationary phase on Celite-545 solid support using a flame ionization detector (FID). The material balance was checked and it was up to 99.6%.

It is experimentally observed that ethyl benzene is the only product and the side reactions of ethanol forming products other than ethyl benzene are also not observed. On the basis of this observation, the conversion of benzene is defined as follows: if Y_E, Y_B and Y_{EB} are the mole fractions of ethanol, benzene and ethyl benzene, respectively, in the product stream, then 1 mol of the product will contain Y_B moles of benzene, Y_E moles of ethanol and Y_{EB} moles of ethyl benzene. Hence the amount of benzene converted by alkylation is Y_{EB} moles. Therefore, total benzene fed into the reactor = benzene in liquid product + benzene converted by alkylation = $(Y_B + Y_{EB})$ moles.

Hence, fractional conversion of benzene by alkylation is defined as:

$$X_B = \frac{\text{moles of benzene converted}}{\text{moles of benzene fed}} = \left[\frac{Y_{EB}}{Y_B + Y_{EB}}\right]$$

3. Results and discussion

Experiments carried out earlier with catalysts containing different amounts of $AlCl_3$, namely, 2.5, 3.0, 10.0, 15.0, 20.0% (w/w) gave maximum conversion of benzene with catalyst containing 15.0% $AlCl_3$. All results reported here were, therefore, obtained by carrying out reactions with this catalyst only. Moreover, after an initial maximum activity, the catalyst activity was found to be stabilized at around 80% of the conversion obtained in first hour and no further decrease in conversion was observed with time on stream, indicating no deactivation of $AlCl_3$ by hydrolysis with water generated by the reaction. The stabilized (or steady state) conversions were considered for the kinetic study. Almost same activity was also observed even after five repeated regenerations and no corrosion of the reactor tube was noticed during the experimentation.

In any kinetic study, the resistances due to film (external) and pore (internal) diffusion must be minimized in order to propose an intrinsic rate. For the estimation of external diffusion effects, two series of runs were taken with different amounts of catalyst. In one series the amount of

Table 1
Effect of external diffusional resistance on conversion of benzene[a]

W/F (kg h/(kg mol))	Conversion of benzene (X_B)	
	b	c
3.20	0.110	0.115
4.35	0.120	0.122
8.92	0.152	0.155
15.87	0.170	0.171

[a] Conditions: feed ratio (benzene/ethanol) = 3 : 1; temperature = 450°C; pressure = 22.14 atm; hydrogen to feed ratio (H/F) = 3.34; *b*: with 0.03 kg catalyst; *c*: with 0.05 kg catalyst.

catalyst taken in the reactor was 0.03 and 0.05 kg in the other series. Keeping *W*/*F* ratio constant, runs were taken for each series with a constant benzene-to-ethanol molar ratio of 3:1 at a fixed temperature and pressure of 450°C and 22.13 atm, respectively, and a fixed hydrogen-to-feed (H/*F*) molar ratio of 3.34. The results are shown in Table 1. It is observed from this table that the conversions for both the series at constant *W*/*F* are independent of feed rates. The external mass transfer resistance is, therefore, negligible. Since the mass transfer is a function of rate of flow of feed, it can be concluded that above a minimum value of feed flow rate the external mass transfer effect is negligible. The minimum flow rate of feed employed was $1.5 \times 10^{-4}\,\text{m}^3/\text{h}$ corresponding to *W*/*F* ratio of 15.87 kg cat. h/(kg mol of liquid feed) and for all other investigations a flow rate of feed above this minimum was used.

To test the pore diffusion limitations, experiments were carried out with two catalyst sizes of 1.58 and 3.16 mm, respectively. The experimental runs were taken at a fixed pressure, *W*/*F* and H/*F* of 22.14 atm, 15.87 kg cat. h/(kg mol of feed liquid) and 3.34, respectively at each of the three temperatures 400, 425 and 450°C. The experimental data obtained are presented in Table 2. The results showed that there was no change in benzene conversion with catalyst size indicating negligible intraparticle mass transfer resistance in the particle size range studied.

In the case of reactions catalyzed by zeolites, two distinct diffusional processes are involved: (i) macropore diffusion in between the catalysts and (ii) micropore diffusion inside the zeolite crystal. The above observation on effects of particle size indicates the absence of only the macropore diffusional resistance. The resistance due to the micropores could not be evaluated, as it requires modification of the conditions of synthesis of the zeolite affecting the micropore size of the crystals, which would subsequently affect the diffusional characteristics. As the channel dimensions of 13X zeolites are comparable with the kinetic diameters of the hydrocarbon molecules like benzene and ethyl benzene, micropore diffusion cannot be ruled out. Hence, the kinetic parameters described here include these micropore diffusional effects, if any.

Table 2
Effect of pore diffusion on conversion of benzene[a]

Particle size, d_p (mm)	Fractional conversion of benzene (X_B)		
	400°C	425°C	450°C
1.58	0.14	0.16	0.17
3.17	0.14	0.15	0.17

[a] Conditions: feed ratio (benzene/ethanol) = 3 : 1; total pressure = 22.14 atm; catalyst to feed ratio (W/F) = 15.87 (kg h/(kg mol)); hydrogen to feed ratio (H/F) = 3.34.

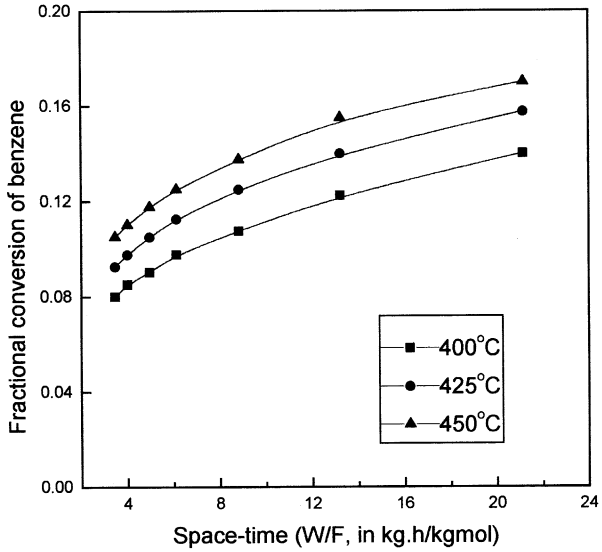

Fig. 1. Effect of space–time on benzene conversion.

In the absence of gas-film or pore diffusional resistance, a mechanism involving chemisorption and surface reaction will control the rate of catalytic reaction. In the present study, the cases involving chemisorption as rate controlling step were not considered. Hence, only those cases where surface reaction is rate controlling were taken for investigation.

Kinetic runs were carried out at three different temperatures, viz., 400, 425 and 450°C. At each temperature, *W*/*F* was varied by changing the liquid feed rate. Hydrogen was used as a carrier gas in all experiments. In all these runs, the molar ratio of benzene-to-ethanol was kept at 3:1, whereas the molar ratio of liquid hydrocarbon feed to hydrogen was maintained at 0.30. The effect of space–time (*W*/*F*) on benzene conversion at three different temperatures is presented in Fig. 1. It is observed that benzene conversion increases with an increase in space–time at all temperatures.

Different models based on Langmuir–Hinshelwood mechanisms were formulated using the approach suggested by Hougen and Watson. In this the various mechanisms which might control the reaction are based on single site and dual site. Alkylation of benzene with ethanol to form ethyl benzene and water can be represented by the following reaction mechanism:

$$C_6H_6 + CH_3CH_2OH = C_6H_5CH_2CH_3 + H_2O$$

The possible isothermal rate equations for the above reaction based on single and dual site mechanisms for the case where surface reaction is the rate controlling are presented below.

1. Single-site mechanism:
   - Model 1: E in gas phase

$$r=\frac{kK_{\mathrm{B}}[p_{\mathrm{E}}p_{\mathrm{B}}-(p_{\mathrm{EB}}p_{\mathrm{W}}/K)]}{1+K_{\mathrm{B}}p_{\mathrm{B}}+K_{\mathrm{EB}}p_{\mathrm{EB}}+K_{\mathrm{W}}p_{\mathrm{W}}+K_{\mathrm{H}}p_{\mathrm{H}}} \qquad (1)$$

   - Model 2: B in gas phase

$$r=\frac{kK_{\mathrm{E}}[p_{\mathrm{E}}p_{\mathrm{B}}-(p_{\mathrm{EB}}p_{\mathrm{W}}/K)]}{1+K_{\mathrm{E}}p_{\mathrm{E}}+K_{\mathrm{EB}}p_{\mathrm{EB}}+K_{\mathrm{W}}p_{\mathrm{W}}+K_{\mathrm{H}}p_{\mathrm{H}}} \qquad (2)$$

2. Dual-site mechanism:
   - Model 3: both B and E adsorbed

$$r=\frac{kK_{\mathrm{B}}K_{\mathrm{E}}[p_{\mathrm{E}}p_{\mathrm{B}}-(p_{\mathrm{EB}}p_{\mathrm{W}}/K)]}{(1+K_{\mathrm{B}}p_{\mathrm{B}}+K_{\mathrm{E}}p_{\mathrm{E}}+K_{\mathrm{EB}}p_{\mathrm{EB}}+K_{\mathrm{W}}p_{\mathrm{W}}+K_{\mathrm{H}}p_{\mathrm{H}})^2} \qquad (3)$$

Models 1 and 2 were rejected on the basis of negative adsorption constants or improper trends of these constants with temperature. A mathematical fit for Model 3 was performed as follows.

For each temperature, the space–time-conversion data have been analyzed and the rates of reaction were obtained by differential analysis of the plug flow reactor equation:

$$r_{\mathrm{obs}}=\frac{\mathrm{d}X_{\mathrm{B}}}{\mathrm{d}(W/F_{\mathrm{BO}})} \qquad (4)$$

Since the conversion of benzene is small (17%), the reverse reaction is neglected. Further, if we assume that the adsorption of water and hydrogen does not compete with the adsorption of hydrocarbons, the influence of water and hydrogen adsorption could be neglected. With these assumptions, the rate equation for Model 3 becomes

$$\text{Rate of disappearance of benzene, } r_{\mathrm{B}}=\frac{kK_{\mathrm{B}}K_{\mathrm{E}}p_{\mathrm{B}}p_{\mathrm{E}}}{(1+K_{\mathrm{B}}p_{\mathrm{B}}+K_{\mathrm{E}}p_{\mathrm{E}}+K_{\mathrm{EB}}p_{\mathrm{EB}})^2} \qquad (5)$$

The partial pressures in the above equation are related to the conversions and total pressure P by the following relationship:

$$p_{\mathrm{E}}=\frac{(0.33-X_{\mathrm{B}})P}{5.78-X_{\mathrm{B}}} \qquad (6)$$

$$p_{\mathrm{B}}=\frac{(1-X_{\mathrm{B}})P}{5.78-X_{\mathrm{B}}} \qquad (7)$$

$$p_{\mathrm{EB}}=\frac{X_{\mathrm{B}}P}{5.78-X_{\mathrm{B}}} \qquad (8)$$

Therefore,

$$r_{\mathrm{B}}=\frac{kK_{\mathrm{B}}K_{\mathrm{E}}(1-X_{\mathrm{B}})(0.33-X_{\mathrm{B}})P^2/(5.78-X_{\mathrm{B}})^2}{[1+\{K_{\mathrm{B}}(1-X_{\mathrm{B}})+K_{\mathrm{E}}(0.33-X_{\mathrm{B}})+K_{\mathrm{EB}}X_{\mathrm{B}}\}\{P/(5.78-X_{\mathrm{B}})\}]^2} \qquad (9)$$

Table 3
Estimated kinetic and adsorption constants

Constant	Temperature (°C)		
	400	425	450
k (kg mol/(kg atm h))	1.87	2.76	3.91
K_{B} (atm^{-1})	0.60	0.54	0.50
K_{E} (atm^{-1})	0.14	0.13	0.12
K_{EB} (atm^{-1})	43.06	42.11	41.80

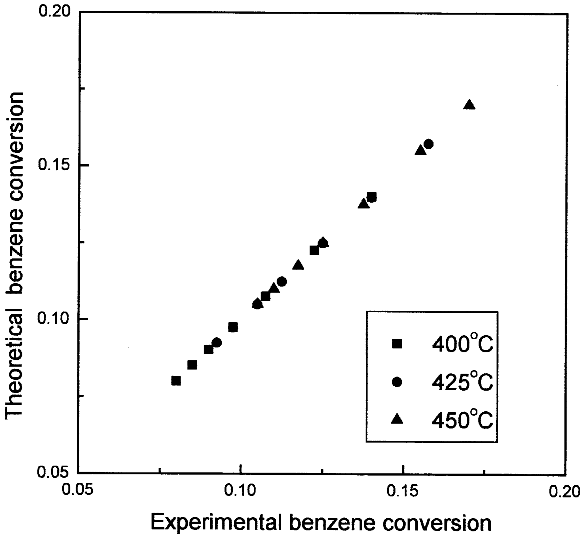

Fig. 2. Comparison of theoretical benzene conversion with experimental data.

The above rate equation contains four unknown parameters, viz., k, K_{E}, K_{B} and K_{EB}. These parameters were estimated by treating each temperature data separately. As the rate equation is non-linear with respect to unknown parameters, a non-linear regression program based on Marquardt's algorithm was used to obtain a mathematical fit for the above rate equation by minimizing the objective function for the residual sum of squares (Φ) [16]:

$$\Phi=\sum_{i=1}^{n}(y_i-y_i') \qquad (10)$$

where n is the number of responses, y_i the experimental conversion, and y_i' the predicted conversion.

The initial rate estimates of the various constants of the rate expression were made from the product distribution pattern (p_{B}, p_{E} and p_{EB}). The kinetic and adsorption constants estimated by non-linear regression are tabulated in Table 3. It is evident from this table that with an increase in temperature the kinetic constants increase, which is the right trend for these parameters and the adsorption constant shows a decreasing trend with increase in temperature as expected.

The kinetic constants evaluated and tabulated at various temperatures were used to determine the activation energy and frequency factor using Arrhenius relationship, $k = k_0 \exp(-E_a/RT)$. A plot of $\ln k$ versus $1/T$ gave a straight line. From the slope and intercept of this straight line, the activation energy was calculated to be 60.03 kJ/mol and the frequency factor k_0 as $8.45 \times 10^4\,\mathrm{kg\,mol/(kg\,.\,h)}$. Similar values of activation energy and frequency factor have been reported by Bhat et al. [5].

The experimentally observed rate of reaction and the theoretically predicted rate values at the three temperatures are plotted in Fig. 2. A fairly good correlation is observed between the observed and predicted rates. Hence, the proposed kinetic model fits well into our experimental observations.

4. Conclusions

An attempt was made on systematic kinetic study of the alkylation of benzene with ethanol on $AlCl_3$ impregnated 13X zeolites for the first time. The catalyst was found to be stable and non-corrosive. From the product distribution pattern, a reaction mechanism was derived on the basis of L–H–H–W model with dual site mechanism. The differential reactor technique was employed and observed rates were computed from the conversions and a non-linear regression computer program was used to estimate the unknown parameters in the rate equation. The activation energy and the frequency factor were computed from the Arrhenius equation.

The proposed reaction model was found to be in conformity with the trend shown by the kinetic and adsorption constants in the temperature range 400–450°C. The kinetic model based on the proposed reaction mechanism predicts the rate values comparable with the experimental rates.

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References

[1] J.R. Anderson, T. Mole, V. Christov, Mechanism of some conversions over ZSM-5 catalysts, J. Catal. 61 (1980) 477–484.

[2] K.H. Chandavar, S.B. Kulkarni, P. Ratnaswamy, Alkylation of benzene with ethanol over ZSM-5 zeolites, Appl. Catal. 4 (1982) 287–295.

[3] K.H. Chandavar, S.B. Kulkarni, P. Ratnaswamy, Alkylation of benzene to propyl and isopropylbenzene over ZSM-5 zeolites, J. Chem. Technol. 34 (1984) 165–173.

[4] B. Lee, I. Wang, Kinetic analysis of ethylation of toluene on HZSM-5, Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 201–208.

[5] Y.S. Bhat, A.B. Halgeri, T.S.R. Prasada Rao, Kinetics of toluene alkylation with methanol on HZSM-8 zeolite catalyst, Ind. Eng. Chem. Res. 28 (1989) 894–899.

[6] D. Fraenkel, M. Levy, Comparative study of shape-selective toluene alkylation over HZSM-5, J. Catal. 118 (1989) 10–21.

[7] J.L. Sotelo, M.A. Uguina, J.L. Valverde, D.P. Serrano, Kinetics of toluene alkylation with methanol over Mg-modified ZSM-5, Ind. Eng. Chem. Res. 32 (1993) 2548–2554.

[8] P.A. Parikh, N. Subbrahmanyam, Y.S. Bhat, A.B. Halgeri, Kinetics of zeolite catalyzed toluene isopropylation, Chem. Eng. J. 54 (1994) 79–85.

[9] T. Yashima, K. Sato, T. Hayasaka, N. Hara, Alkylation on synthetic zeolites. III. Alkylation of toluene with methanol and formaldehyde on alkali cation exchanged zeolites, J. Catal. 26 (1972) 303–312.

[10] J.M. Garces, G.E. Vrieland, S.I. Bates, F.M. Scheidt, Basic molecular sieve catalysts — side chain alkylation of toluene by methanol, Stud. Surf. Sci. Catal. 20 (1985) 67–74.

[11] J. Engelhardt, J. Szanyi, J. Valyon, Alkylation of toluene with methanol on commercial X zeolite in different alkali cation forms, J. Catal. 107 (1987) 296–306.

[12] P.E. Hathaway, M.E. Davis, Base catalysis by alkali metal zeolites. III. Alkylation with methanol, J. Catal. 119 (1989) 497–507.

[13] C. Yang, Z. Meng, Side-chain alkylation of *p*-xylene with methanol on alkali cation zeolites, Appl. Catal. 71 (1991) 45–54.

[14] B.R. Serebreyakov, V.N. Pilin, Kinetics of benzene alkylation with 1-decene in the presence of soluble quantities of catalyst complex, Chem. Abstr. 103 (1985) 5721r.

[15] I.M. Kolesnikov, T.V. Zaitseva, Characteristics of the alkylation of benzene by propylene in the presence of aluminosilicate modified with a complex of aluminium chloride with aromatic hydrocarbons and promotion of catalysts, Chem. Abstr. 103 (1985) 141529m.

[16] D.W. Marquardt, An algorithm for least-squares estimation of nonlinear parameters, J. Soc. Ind. Appl. Math. 11 (2) (1963) 471–481.