Catalytic Hydroprocessing of Chlorobenzene and 1,2-Dichlorobenzene

The hydrodechlorination reactions of chlorobenzene and 1,2-dichlorobenzene on a NiMo/γAl_2O_3 catalyst were examined in a differential microflow reactor. The NiMo catalyst had high activity and selectivity for dechlorination; no hydrogenation of the aromatic ring was detected. The dechlorination reactions were examined at temperatures ranging from 275 to 375°C. In this temperature range the rates of adsorption and surface reaction are comparable and neither controls the overall reaction rate. A kinetic model, incorporating adsorption, desorption and surface reaction rates, has been used to model the data.

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Introduction

Hydroprocessing has been used for decades in the petroleum refining industry to remove oxygen, nitrogen, and sulfur functionalities from heavy fuels. The chemistry and the kinetics of denitrogenation, desulfurization, and deoxygenation have been studied extensively and several comprehensive reviews of the literature are available (Rollman, 1977; Gates et al., 1979; Shah and Krishnamurthy, 1981). Recently, new applications for catalytic hydroprocessing have emerged in the waste treatment industry (Kalnes and James, 1988). Hydroprocessing can be used as a stand-alone treatment process for waste streams containing polychlorinated biphenyls (PCBs), chlorinated solvents, and fluorinated solvents. Hydroprocessing can also be used as a unit operation in waste oil recycling and other recycling operations. Much of the available literature on hydroprocessing reactions is applicable to these new problems, however, the focus of many of these new processes is dehalogenation and there is little information available in the literature on hydrodehalogenation reactions of typical hydroprocessing catalysts (Arnold and Lazier, 1935; LaPierre et al., 1978a,b). There are several published studies on hydrodechlorination reactions over noble metal catalysts (Coq et at., 1986; La Pierre et al., 1978c; Dini et al., 1975), but, noble metal catalysts are not well suited to waste processing since they can easily be poisoned (Del Angel et al., 1983). The goal of this study is to begin the examination of dehalogenation reactions over robust hydroprocessing catalysts. The catalyst used in this work was selected after a variety of catalysts were screened for activity (Hagh and Allen, 1990). This paper examines the dechlorination reactions of chlorobenzene and 1,2-dichlorobenzene on the chosen catalyst. Chlorinated benzenes were chosen as model compounds since they are representative of the halogenated species found in many organic wastes.

Experimental Method

The kinetic studies of chlorinated benzene dehalogenation were performed in a microflow differential reactor system. The reactor system consisted of:

A 1 L stirred autoclave (rated for 13.8 MPa at 230°C)

A SSI 100 LC pump controlled by a SSI 210 Guardian (rated for 0.05–9.99 cm^3/min at 41.3 MPa)

A tubular fixed-bed reactor (1/4 in dia. Hastelloy-C tubing)

A Lindberg 55122 Moldatherm hinged tube furnace (rated for 1,100°C) controlled by an Omega CN9111 temperature controller

A 250 μL sampling valve (Hastelloy-C)

Two 500 mL pressure vessels (rated for 13.8 MPa at 230°C)

The stirred autoclave was used to saturate the feed to the reactor with hydrogen. The feed to the reactor typically contained 0.01–0.05 wt frac. of reactant (e.g., chlorobenzene) in *n*-hexadecane saturated with dry, oxygen-free hydrogen at a controlled temperature and pressure. Typical temperature and pressure in the saturator were 170°C and 8.27 MPa. The saturated mixture was then pumped at a controlled rate over a heated reactor bed. The bed consisted of a catalyst section, preceded and followed by inert alundum sections. The tempera-

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ture of the catalytic section of the reactor was controlled within ±1°C as measured by an Inconel-sheathed thermocouple inserted directly in the catalyst bed. The product stream was sampled using a high-pressure sampling valve. Depending on the degree of corrosivity, the product stream was stored in either a 500 mL stainless steel vessel or a 500 mL Hastelloy-C vessel. These vessels were used to maintain back pressure in the system and were periodically drained to maintain a constant reactor pressure. Reaction pressures depended on hydrogen concentration but were typically in excess of 11 MPa. Three-way valves at the entrance and exit of the reactor allowed for *in-situ* sulfiding of the catalyst.

A commercial NiMo/γAl_2O_3 catalyst was used for the differential reactor studies. The manufacturer's specifications are listed in Table 1. The NiMo/γAl_2O_3 catalyst was crushed to less than 250 μm grain size and was sulfided for 3 h *in situ* with 2.0–3.0 cm^3/min of 10% H_2S in H_2 at 400°C.

Product analysis was carried out on a Perkin Elmer Sigma 2000 gas chromatograph with a Perkin Elmer LDI 100 integrator. The GC was equipped with a 30 m long, 0.25 mm ID fused silica capillary column (Supelco SPB5; bonded phase) and a flame ionization detector. The initial column temperature was 80°C, and the temperature was ramped at 25°C to a final temperature of 200°C. The carrier gas used was helium (99.9%). Naphthalene (98%) was used as an internal standard. The products were identified using an HP-MSD gas chromatograph/mass spectrometer. All the chemicals used in this study, except *n*-hexadecane (Fisher certified; 99%), were supplied by the Aldrich Chemical Co. The material balance closure was always greater than 95%.

Adsorption and desorption experiments were performed by replacing the hydrogen in the reaction system with helium (99.999%). The fixed-bed reactor was packed with 2.73 g of presulfided NiMo/γAl_2O_3 catalyst (vs. 0.04 g for differential kinetic experiments) and was plugged by glass wool at both ends. Hexadecane saturated with helium was fed over the catalyst bed. At the start of the adsorption experiments, the feed was switched to a 2 wt. % chlorobenzene in *n*-hexadecane mixture, saturated with helium. Chlorobenzene concentration in the effluent was monitored as a function of time. When chlorobenzene concentration in the effluent reached steady state, the feed to the reactor was switched back to *n*-hexadecane saturated with helium. Again, chlorobenzene concentration was monitored in the effluent.

Results and Discussion

Reactor characterization studies

Before initiating detailed kinetic studies in the differential, microflow reactor, several reactor characterization studies were done. These studies focused on the catalytic activity of the reactor walls, the reactions of the carrier solvent, the extent of mass transfer limitations, and the need for continuous sulfiding of the catalyst.

The catalytic effect of the reactor walls was a concern because both the reactor walls and the reaction zone thermocouple contained traces of Ni. To determine whether these materials were catalyzing dechlorination, a 0.0216 wt. frac. chlorobenzene solution in *n*-hexadecane was pumped through a reactor filled with only the alundum packing material. At a flow rate of 1.6 cm^3/min and a reactor temperature of 350°C, less than 0.1% of the chlorobenzene was dechlorinated. At the same conditions, a reactor containing 0.04 g of catalyst dechlorinated 30% of the chlorobenzene fed. Thus, the reactor and packing materials did not play a significant role in the dechlorination reactions. A second experimental concern was the integrity of the solvent *n*-hexadecane. At the most severe reaction conditions used in this work, less than 2% of the *n*-hexadecane underwent cracking reactions and none of the products interfered with the analysis of the dechlorination reaction products.

Mass transfer limitations in the reactor were examined both theoretically and experimentally. Based on the correlation of Wilke and Chang (1955), the bulk diffusivity of chlorobenzene in *n*-hexadecane was calculated to be approximately 10^{-4} cm^2/s at 350°C. Using this diffusivity, the calculation procedure of Satterfield (1970) indicated that there were no bulk mass transfer limitations. Transport of reactants within the catalyst pores was examined experimentally by varying the size of catalyst pellets. The results shown in Table 2 indicate that there were no strong intraparticle mass transfer effects for the catalyst particle sizes used in this work (<250 μm).

Hydrogen concentrations in the saturator were estimated by equating liquid and vapor phase fugacities. Liquid phase fugacities were calculated using the Chao-Seader correlation and gas phase fugacities were calculated using the Soave-Redlich-Kwong (SRK) equation of state (Henley and Seader, 1981). Binary interaction parameters for the SRK equation were reduced from hydrogen solubility data in *n*-hexadecane at elevated temperatures and pressures (Lin et al., 1980). Molar concentrations of reactants at reactor conditions were calculated using the Lee-Kesler correlation with Plocker mixing rules, details of which are given elsewhere (Broderick, 1980).

Finally, several experiments were performed to determine if continuous sulfiding of the catalyst was necessary. Catalyst activity was constant for at least 12 h, both with and without continuous sulfiding with H_2S. The presence of H_2S did not significantly affect catalyst stability but did lower reaction rates somewhat. Because catalyst activity was stable without continuous sulfiding, all subsequent experiments were done on presulfided catalyst without continuous sulfiding.

Table 1. NiMo/$\gamma A1_2O_3$ Catalyst Used for Differential Reactor Studies

Sample no.	SN-6658
American Cyanamid code	HDN-60
Composition	23.0% MoO_3, 3.0% NiO, 3.2% P alumina support
N_2 surface area, m^2/g	150
Pore volume, cm^3/g	0.35
Compacted bulk density, g/cm^3	0.90

Table 2. Intraparticle Mass Transfer Effects

Catalyst Particle Size μm	Rate of Chlorobenzene Dechlorination mol CB/g cat · min × 10^4	
	300°C	350°C
<250	4 ± 1.4	20 ± 3.0
250–355	4 ± 1.0	17 ± 4.0
355–470	3 ± 2.5	15 ± 4.1

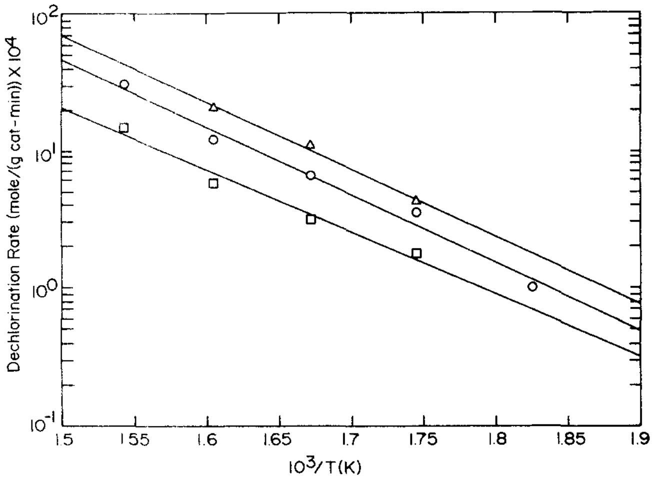

Figure 1. Reaction rates for dechlorination of chlorobenzene as a function of temperature.
$C_{H_2} = 0.22–0.32M$ ○ $C_{CB} = 0.15–0.18M$
△ $C_{CB} = 0.09–0.10M$ □ $C_{CB} = 0.04–0.05M$

Dechlorination kinetics

The rate data for chlorobenzene hydrodechlorination obtained in this work are reported in Figures 1–3. Each reaction rate was obtained by measuring conversions at three or more flow rates in the range 1.6–2.2 cm^3/min. Conversion under differential conditions should be a linear function of flow rate. Deviation from linearity could be due to experimental uncertainty or deviation from differential reactor behavior. Ninety-five percent confidence limits for the reaction rates were calculated based on the deviation of the experimental data from the theoretically required straight line through the origin. Thus, the confidence limits reported as error bars in Figures 2 and 3 combine experimental uncertainty and deviation from differential reactor behavior.

Figure 1 shows the temperature dependence of the reaction rates, measured over the range 275–375°C. These experiments were performed at three different chlorobenzene concentrations with hydrogen concentration held constant. The data indicate that a constant activation energy process is controlling the reaction, but the chlorobenzene concentration dependence is complex. Note that the maximum rate at all temperatures is reached at the intermediate chlorobenzene concentration. This feature is shown more clearly in Figure 2, which plots reaction rate vs. chlorobenzene concentration. The dependence of reaction rate on hydrogen concentration is also complex, as shown in Figure 3.

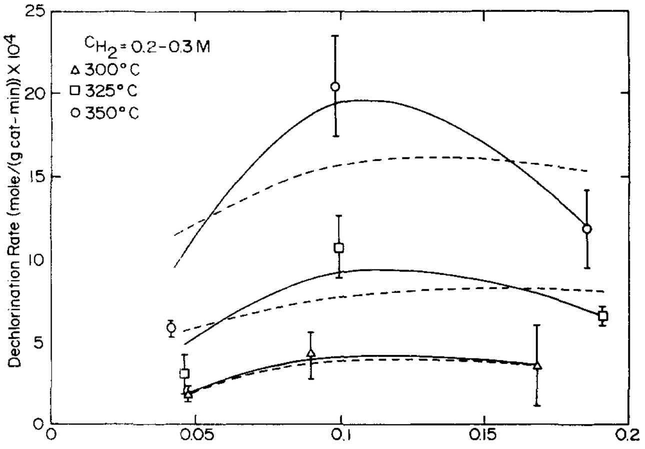

Figure 2. Experimental data and model predictions for rate of chlorobenzene dechlorination as a function of chlorobenzene concentration.
----Langmuir-Hinshelwood rate expression
——Eq. 7

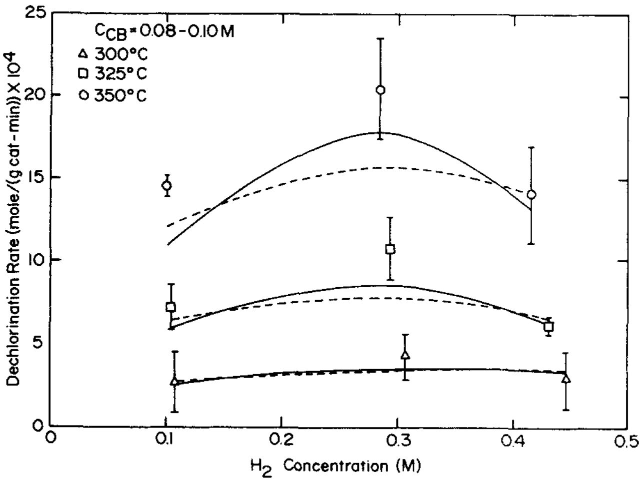

Figure 3. Experimental data and model predictions for rate of chlorobenzene dechlorination as a function of hydrogen concentration.
----Langmuir-Hinshelwood rate expression
——Eq. 7

Several experiments were done to assess the rates of adsorption and desorption processes. Direct measurements of adsorption and desorption rates are difficult to perform using industrial catalysts, but the method described in the experimental section provides an order of magnitude assessment of the rates of adsorption and desorption. Consider the estimation of desorption rate. The reactor is initially saturated with chlorobenzene (CB) and so all of the chlorobenzene in the feed leaves in the effluent. Suddenly, the concentration of chlorobenzene in the feed is switched to zero. The amount of chlorobenzene desorbed per unit mass of catalyst divided by the time required for that material to desorb provides an order magnitude estimate of desorption rate. A similar procedure can be used to obtain an order of magnitude estimate of the rate of adsorption. These experiments were done at reaction temperatures and at flow rates large enough to insure that bulk transport was not rate limiting. For both adsorption and desorption, the estimated rates were of order 10^{-4} mol CB/g cat · min.

Adsorption and desorption rates were also measured indirectly by examining the hydrodechlorination of 1,2-dichlorobenzene (DCB). If a molecule of DCB is partially dechlorinated to CB, the CB can either desorb or it can remain on the surface, eventually forming benzene, which desorbs. If the rate of dechlorination of CB is faster than its rate of desorption, then benzene (BZ) will be the dominant product from hydrodechlorination of DCB. On the other hand, if CB is observed to be the dominant product of DCB dechlorination, then the rate of desorption is faster than the rate of surface reaction for CB, and

Table 3. 1,2-Dichlorobenzene Hydrodechlorination Reaction Rates

Temp °C	Concentration, mol/L		DCB Conversion %	Reaction Rates** mol/g cat · min × 10^4			
	DCB*	H_2		$-R_{DCB}$	$+R_{CB}$	$+R_{BZ}$	R_{BZ}/R_{CB}
300	0.05	0.05	6.5	1.8 ± 1.0	0.8 ± 0.5	0.9 ± 0.6	1.1
325	0.05	0.05	22	6.4 ± 0.4	2.1 ± 0.9	4.6 ± 1.1	2.2
350	0.05	0.05	32	9.4 ± 1.0	3.1 ± 1.4	6.4 ± 1.0	2.1

*DCB: dichlorobenzene

** $-R_{DCB}$: rate of disappearance of dichlorobenzene

$+R_{CB}$: rate of appearance of chlorobenzene

$+R_{BZ}$: rate of appearance of benzene

the reaction is operating in a surface reaction controlled regime. Thus, the rate limiting step for dechlorination of CB can be deduced in part from the selectivity of DCB dechlorination reactions.

The rates and product selectivities for DCB dechlorination observed in this study are shown in Table 3. At all temperatures the rates of benzene production are comparable to the rates of chlorobenzene production. So, the surface reaction and desorption rates are of the same order of magnitude and neither appears to be the rate limiting step for CB dechlorination at 300–350°C.

Our goal now is to use these data to develop a kinetic model of the dechlorination of chlorobenzene. At steady state, the rate of adsorption of CB on the surface should be equal to its combined rate of desorption from the surface and disappearance due to an irreversible reaction

$$k_{a,CB}C_{CB}\,C_v = k_{d,CB}C_{CB\cdot s} + k_s C_{CB\cdot s}C^2_{H\cdot s} \tag{1}$$

where

k_s is the intrinsic surface reaction kinetic constant
$k_{a,CB}$ is the CB adsorption constant
$k_{d,CB}$ is the desorption constant
C_{CB_s} is the CB surface concentration
C_{H_s} is the hydrogen atom surface concentration
C_{CB} is the CB bulk concentration
C_v is the vacant site concentration

The reaction was assumed to be irreversible due to the exothermic heat of reaction (−16 kcal/mol at 325°C). Further evidence of the irreversibility of the reaction is given by the data of Table 4, which indicate that benzene concentration does not have a significant effect on the dechlorination rate. Equation 1 assumes that CB requires one vacant site to adsorb and two adsorbed atomic hydrogens take part in the reaction. A number of alternative surface chemistries were examined (Hagh, 1989); none fit the data as well as the rate expression resulting from this assumed surface chemistry.

Table 4. Effect of Benzene Concentration on Chlorobenzene Hydrodechlorination Rates

Temp. °C	Concn. at Reaction Conditions mol/L			CB Dechlorination Rate mole/gcat · min × 10^4
	CB	BZ	H_2	
300	0.05	0	0.26	1.8 ± 0.08
300	0.03	0.17	0.26	1.3 ± 1.1
350	0.05	0	0.25	3.1 ± 1.2
350	0.05	0.25	0.25	3.6 ± 0.2

CB: chlorobenzene; BZ: benzene

Hydrogen surface concentration is assumed to be in equilibrium with its bulk concentration.

$$C^2_{H\cdot s} = K_{H_2}C_{H_2}C_v^2 \tag{2}$$

which in combination with Eq. 1 results in an expression for CB surface concentration:

$$C_{CB\cdot s} = \frac{K_{CB}C_{CB}C_v}{1 + \dfrac{k_s}{k_{d,CB}}K_{H_2}C_{H_2}C_v^2} \tag{3}$$

where K_{H_2} is the hydrogen adsorption/desorption equilibrium constant, and K_{CB} is the CB adsorption/desorption equilibrium constant. If $k_{d,CB}$ is much larger than k_s, Eq. 3 reduces to

$$C_{CB\cdot s} = K_{CB}C_{CB}C_v \tag{4}$$

which amounts to an establishment of CB adsorption/desorption equilibrium. Adsorption and desorption experiments and the DCB hydrodechlorination selectivity data of Table 3 indicate that the rates of CB desorption and surface reaction have the same order of magnitude; thus, CB adsorption/desorption equilibrium cannot be assumed. Assuming that CB and hydrogen adsorb on the same type of site, a balance of surface sites requires that:

$$C_t = C_v + C_{CB\cdot s} + C_{H\cdot s} \tag{5}$$

where C_t is total concentration of active sites, and benzene and HCl surface concentrations are assumed to be nearly zero at differential conditions. The assumption of negligible benzene surface concentration is supported by the data of Table 4, which show that relatively large benzene concentrations have a negligible effect on dechlorination rate. Similar data are not yet available for HCl, so it is not clear whether HCl inhibits dechlorination. Because of the low conversions used in this work, it is unlikely that HCl inhibition significantly affects the observed rates, however this is clearly an area that merits further study.

Table 5. Kinetic Model Parameters

Temp. °C	Langmuir-Hinshelwood Model, Surface Reaction as a Rate Limiting Step Eq. 8			Model with Adsorption, Desorption, and Surface Reaction Proceedings at Comparable Rates Eqs. 6,7			
	k*	K_{H_2}**	K_{CB}**	k*	K_{H_2}**	K_{CB}**	θ
300	18,400	35.9	11.5	45,100	8.68	62.9	37.9
325	113,000	76.5	17.8	125,000	6.17	79.4	74.2
350	115,000	50.4	17.5	159,000	2.62	72.9	134.2

*L^2/mol · gcat · min
**L/mol

Returning to the kinetic model, substitution of Eqs. 2 and 3 in Eq. 5 yields:

$$C_t = C_v + \frac{K_{CB}C_{CB}C_v}{1 + \frac{k_s}{k_{d,CB}} K_{H_2}C_{H_2}C_v^2} + (K_{H_2}C_{H_2})^{1/2}C_v \qquad (6)$$

The rate of disappearance of CB is,

$$r_s = k_s C_{CB\cdot s} C_{H\cdot s}^2 = \frac{kC_{CB}C_{H_2}(C_v/C_t)^3}{1 + \theta K_{H_2}C_{H_2}(C_v/C_t)^2} \qquad (7)$$

where $k = k_s C_t^3 K_{CB} K_{H_2}$, and $\theta = k_s C_t^2 / k_{d,CB}$. Evaluation of the parameter θ will be one of the goals of the kinetic modeling. The value of this dimensionless parameter will be a strong indicator of whether adsorption, desorption, or surface reaction controls the overall rate. As θ approaches zero, CB adsorption/desorption goes to equilibrium and the rate expression assumes the familiar surface reaction controlled Langmuir-Hinshelwood form:

$$r_s = \frac{kC_{CB}C_{H_2}}{[1 + K_{CB}\,C_{CB} + (K_{H_2}C_{H_2})^{1/2}]^3} \qquad (8)$$

As θ approaches infinity, desorption controls the overall rate and the reaction is zero order in reactant concentrations. Figures 2 and 3 show that the proposed model, Eqs. 6 and 7, provides a better fit to the CB hydrodechlorination data than the Langmuir-Hinshelwood model, Eq. 8. The model parameters are reported in Table 5 and were reduced from CB dechlorination data with a derivative-free nonlinear regression routine (Ralston, 1988).

The apparent activation energy for CB hydrodechlorination using the above model is 59 kJ/mol and the heat of adsorption of hydrogen is 29 kJ/mol. Broderick (1980) and Sapre (1980) have reported apparent activation energies of 120 and 140 kJ/mol for dibenzothiophene hydrodesulfurization and biphenyl hydrogenation on sulfided CoMo/γAl_2O_3 catalyst in experimental systems similar to those used in this study. They also calculated hydrogen heat of adsorption to be about 29 and 21 kJ/mol, respectively, so the results of this study are in reasonable agreement with previous work.

The most significant parameter defined in this study is θ, a ratio of intrinsic surface reaction rate constant to the CB desorption constant. A very small value of θ would point toward a surface reaction controlled mechanism, whereas a large value of θ would indicate that adsorption or desorption is the rate limiting step. In this study θ had an activation energy of 33kJ/mol, increasing from 38 at 300°C to 134 at 350°C.

This result has important implications for waste processing. If complete dechlorination is the desired goal, as it is in PCB remediation, then a high value of θ and a reaction temperature above 350°C would be desired. On the other hand, if partial dechlorination is the desired goal, as in some recycling operations, then a low value of θ and a reaction temperature below 300°C would be desired.

Acknowledgment

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Notation

C_{CB} = CB bulk concentration, mol/L
$C_{CB\cdot s}$ = CB surface concentration
C_{H_2} = hydrogen bulk concentration, mol/L
$C_{H\cdot s}$ = atomic hydrogen surface concentration
C_t = total concentration of active sites
C_v = concentration of vacant sites
$k_{a,CB}$ = CB adsorption rate constant
$k_{d,CB}$ = CB desorption rate constant
K_{CB} = CB adsorption/desorption equilibrium constant, L/mol
K_{H_2} = H_2 adsorption/desorption equilibrium constant, L/mol
k_s = surface reaction rate constant, mol/g cat · min
$k = k_s C_t^3 K_{CB} K_{H_2}$
r_s = net rate of surface reaction, mol/g cat · min
$\theta = k_s C_t^2 / k_{d,CB}$

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Errata

In the paper titled "Analysis of Autocatalytic Reactions in Isothermal Catalyst Particles" (March 1990, p. 342), the following corrections are made:

Definition of parameter α in Eq. 8 on p. 343:

$$\alpha = k_u/k_1 a_0^a \text{ should be } \alpha = k_u/k_1 a_0^n$$

Equation 13 on p. 343: $w_1(1, t_2, t_2)$ should be $w_1(1, t_1, t_2)$
Equation B1 on p. 351: *gi* should be G_i and w_{18} should be w_1
Line above Eq. B6 on p. 352: $q_i^3 \rightarrow q_{i3}$