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Pulsed Micro-reactor: An alternative to estimating kinetic parameters of non-catalytic gas–solid reactions

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ABSTRACT

A Pulsed Micro-reactor (PMR) technique is demonstrated as a simple and viable alternative to generate kinetic data for non-catalytic gas–solid reactions. An experimental test rig was designed and fabricated for this purpose. Oxidation of Cu using air and reduction of CuO using methane, encountered in a novel form of combustion known as Unmixed Combustion (UMC), were chosen as representative reactions in this study. Plug flow conditions in the reactor, essential for accurate estimation of kinetic parameters, was confirmed using a Residence Time Distribution (RTD) approach. A simple generic methodology, based on a uniform reaction model is presented which allowed for easy interpretation of data from this reactor system. While the methodology has been validated for both reactions which were prima facie found to be surface reaction controlled, it can easily be extended to pore diffusion limited reactions. The estimated values of reaction orders and activation energies for both reactions and the pre-exponential factor for oxidation were found to be in excellent agreement with those obtained using Thermo Gravimetric Analysis (TGA). A lower value of pre-exponential factor for reduction however was obtained in the present investigation. While the PMR, can provide an initial insight into the reaction mechanism, it can also be used to obtain reaction engineering data related to process development.

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1. Introduction

Gas–solid non-catalytic reactions like coal gasification or pyrolysis, reduction of ores, oxidation and reduction of metal/metal oxides, coking and regeneration of deactivated catalyst are common in process industries. Mathematical modeling of such systems has been of strong interest to researchers for several years and has resulted in a variety of approaches being adopted to understand the transport and kinetic limitations involved (Gokam and Doraiswamy, 1971; Bhatia and Perlmutter, 1980; Bhatia and Perlmutter, 1981). These include the homogeneous, unreacted shrinking core, grain, random pore and modified volumetric models. In addition a variety of customized models have been developed for specific cases (Chang and Kuo, 1999; Gómez-Barea et al., 2008; Haseli et al., 2008; Homma et al., 2005; Kasaoka et al., 1985; Molina and Mondragon, 1998; Silcox et al., 1989).

For such reactions, developing a kinetic rate law to be used in reactor design is challenging as the reaction mechanism involves external and internal pore diffusion along with the surface reaction step. An effective reaction rate constant k''_e can be used to account for these three resistances and the rate equation for such reactions can be expressed using a power law model having form

$$-r''_g = k''_e c_g^n c_s^m \quad (1)$$

where m and n are reaction orders with respect to solid and gaseous reactant respectively.

Generating accurate and reliable data to estimate k''_e is equally important. Traditionally, k''_e can be estimated using a Thermo Gravimetric Analysis (TGA) method (García-Labiano et al., 2004; Dirion et al., 2008; Prigiobbe et al., 2009; Al-Salem and Lettieri, 2010; Abad et al., 2011; Słopiecka et al., 2012) which incorporates a differential reactor for

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Nomenclature

Symbols

a	Stoichiometric coefficient of solid reactant
A_o	Number of moles present in one pulse of reactive gas (mol)
b	Stoichiometric coefficient of gaseous reactant
c_g	Gas concentration in the bulk phase (mol m^{-3})
c_{gi}	Concentration of gaseous reactant at the end of i th pulse (mol m^{-3})
c_{go}	Initial concentration of gaseous reactant (based on N pulses) (mol m^{-3})
c_{gs}	Concentration of gaseous reactant on the surface of the catalyst (mol m^{-3})
c_s	Concentration of solid reactant (mol m^{-3})
c_{si}	Concentration of solid reactant at the end of i th pulse (mol m^{-3})
c_{so}	Initial concentration of the solid reactant (mol m^{-3})
C_{WP}	Weisz–Prater parameter
D_{AB}	Gas phase molecular diffusivity ($\text{m}^2 \text{s}^{-1}$)
D_e	Effective diffusivity ($\text{m}^2 \text{s}^{-1}$)
d_p	Average particle diameter (m)
Di	Dispersion number
E	Activation energy (J mol^{-1})
i	Pulse number
k_o''	Pre-exponential factor ($\text{mol}^{1-m-n} \text{m}^{3m+3n-2} \text{s}^{-1}$)
k_c	External mass transfer coefficient (m s^{-1})
k_e''	Effective reaction rate constant ($\text{mol}^{1-m-n} \text{m}^{3m+3n-2} \text{s}^{-1}$)
k_1''	Reaction rate constant ($\text{mol}^{1-m-n} \text{m}^{3m+3n-2} \text{s}^{-1}$)
m	Reaction order with respect to solid reactant
n	Reaction order with respect to gaseous reactant
N	Total number of pulses required to completely saturate available solid reactant
q	Carrier gas flow rate ($\text{m}^3 \text{s}^{-1}$)
R	Average radius of the particle (m)
Re	Reynolds number, $Re = U d_p \rho_g / \mu$
$-r_g''$	Rate of reaction (mol of gas ($\text{m}^2 \text{solid})^{-1} \text{s}^{-1}$)
$-r_g''(\text{exp})$	Experimental rate of reaction (mol of gas ($\text{m}^2 \text{solid})^{-1} \text{s}^{-1}$)
$-r_s''$	Rate of reaction (mol of solid ($\text{m}^2 \text{solid})^{-1} \text{s}^{-1}$)
S_a	Specific surface area ($\text{m}^2 (\text{kg of catalyst})^{-1}$)
S_o	Chromatogram area for reference gas peak (m^2)
S_i	Chromatogram area for unreacted gas peak for i th pulse (m^2)
Sc	Schmidt number, $Sc = \mu / \rho_g D_{AB}$
Sh	Sherwood number, $Sh = k_c d_p / D_{AB}$
t	Time (s)
T	Thermodynamic temperature (K)
U	Superficial velocity of carrier gas (m s^{-1})
V_b	Active bed reactor volume (m^{-3})

Greek letters

ε	Bed voidage
ε_p	Particle porosity
η	Internal effectiveness factor
μ	Viscosity (Pa s)
ρ_g	Density of gaseous reactant (kg m^{-3})
ρ_b	Solid bed density (kg m^{-3})
ϕ_n^2	Thiele's modulus

determining kinetic parameters of heterogeneous gas–solid reactions based on suitable changes in solid weight. Pulse methods for kinetic investigations have also found interest for this purpose. These are based on the principle wherein a reactant pulse of defined concentration is allowed to pass over a bed of solids until no change in the shape of the pulse response is observed. A special pulse based technique known as Temporal Analysis of Products (TAP) proposed by [Gleaves et al. \(1988\)](#) has also been used for studying kinetic mechanisms. While this technique is extremely exciting and promising in understanding kinetic phenomena at a microscopic level, its application to a certain extent is restricted by affordability and mathematical treatment is reasonably complex. Till date the emphasis of the use of TAP has been on characterizing the reaction kinetics of chemical conversion over heterogeneous catalysts attempting to bridge the gap between surface science experiments and applied catalysis ([Yablonsky et al., 2003](#); [Gleaves et al., 2010](#)).

As an alternative, a Pulsed Micro-reactor (PMR) method proposed by [Attar \(1979\)](#) offers potential for studying kinetics of gas–solid reactions. In this method, a fixed amount of solid placed inside a tubular reactor is swept by an inert stream of carrier gas which flows into a GC. Several pulses of reactant gas are subsequently injected into the carrier gas stream and allowed to react with the solid until it is completely saturated. Near plug flow conditions are assumed to prevail at all times inside the reactor. The product stream from each injected pulse along with unreacted feed gas after saturation can be analyzed using the GC. This reactor system integrated with a GC offers a relatively easy method to determine k_e'' and offers several advantages including determination of isothermal rates of reaction and activation energies of highly exothermic or endothermic reactions. This discontinuous character of operation, allowing for direct integration between the reactor and GC as well as absence of manual handling of samples leads to accurate measurement and ease of operation.

This reactor system has been used over the years to estimate kinetic parameters, with major emphasis on catalytic gas–solid reactions like thermal cracking of mixture of hydrocarbons, xylene isomerization, cyclohexane dehydrogenation and hydrogenation of benzene ([Nand and Sarkar, 1979](#); [Li et al., 1992](#); [Zamostny et al., 2007](#); [Sica et al., 1978](#)). It has also been used to determine conversion, selectivity and yield for a gamut of such reactions, with emphasis on understanding reaction mechanisms involved, catalyst activity and stability ([Choudhary and Rane, 1992](#); [Ruckenstein and Wang, 1999](#); [Ma et al., 2002](#); [Intriago et al., 2006](#); [Ciuparu et al., 2001](#); [Renjun et al., 1986](#)). Its application however has been mostly limited to cases where the kinetics is linear. [Sica et al. \(1978\)](#) have presented the application of this reactor to investigate non-linear kinetics associated with the catalytic hydrogenation of benzene.

[Attar \(1979\)](#) and [Attar and Dupuis \(1979\)](#) have demonstrated the use of this reactor for studying kinetics related to non-catalytic gas–solid reactions wherein they estimated the rate of reaction of hydrogen sulfide gas with alkaline minerals which are present in coal, calcite, dolomite, and sidrite. It must however be noted that the investigations of Attar were also restricted to 1st order reactions with respect to the gaseous reactant. Till date, this reactor system has gained little attention with regard to estimating kinetic parameters of non-catalytic gas–solid reactions due to a possible challenge in interpretation of experimental data, more so when non-linear kinetics is involved. The present investigation aims to demonstrate the use of a PMR to study

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