KINETIC MEASUREMENTS OF GAS-SOLID
HETEROGENEOUS CATALYZED REACTIONS
INVOLVING COMMERCIAL-SCALE PARTICLES
USING A NOVEL JET-LOOP REACTOR

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Abstract

Development of new catalytic materials for the selective conversion of next-generation feedstocks to clean fuels and chemicals, or improvement of catalyst compositions for existing processes involving current generation feedstocks, requires reliable kinetic models for design of new reactor configurations or for analysis of transport-kinetic interactions in existing reactor systems (Berty, 1999; Davis and Davis, 2012; Doraiswamy and Uner, 2013; Fogler, 2010; Froment and Bischoff, 1990; Roberts, 2008; Salmi et al., 201). Procurement of accurate kinetic data for kinetic model discrimination by combining statistical sequential experimental designs with kinetic parameter estimation techniques (Schwaab et al., 2006; 2008) requires a reactor system that can generate the required kinetic equation response variables, such as reaction rates, specie concentrations, and temperatures, for a given sequence of user-defined input variables. A novel jet loop reactor is described that allows direct measurement of reaction rates for gas-solid catalyzed reactions. The oxidation of SO₂ to SO₃ over V₂O₅-based catalysts is used as a test reaction since increasing emphasis is being placed on development of new catalysts having higher activity at lower temperatures with resulting lower SO₂ emissions for more environmentally-friendly processes.

Keywords

Jet-loop, SO₂ oxidation, Heterogeneous catalysis, Gas-solid reaction.

Introduction

Experimental reactors for measurement of solid-catalyzed reaction kinetics can be broadly classified according to the catalyst form (powder, granule, or pellet) and the number of phases present (gas, gas-liquid, gas-liquid-liquid). It is generally agreed that for the purpose of generating kinetic data, laboratory-scale reactors that operate isothermally that allow direct evaluation of reactant conversions, product yields, and reaction rates from experimental measurements of flow rates and specie concentrations, such as that provided by devices where the fluid flow patterns approach perfect back-mixing, are preferred for various practical reasons over those where the flow patterns approach perfect plug-flow (Berty, 1984; Berty 1999). Among various designs with nearly perfect fluid back-mixing, recycle reactors are preferred as important tools for catalyst testing and kinetic studies. Recycle

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reactors are also useful for the study of most commercially important reactions, although some exceptions occur, especially for cases where the catalyst activity changes rapidly when compared to typical fluid residence times. Some examples of various recycle reactor designs that have appeared in the open literature are shown in Figure 1. The primary objective of this work is to describe the development, application and modeling of a new experimental reactor for studying the kinetics of gas-solid catalyzed reactions for commercial-size particles based upon the propulsive jet concept.

Figure 1. Various types of recycle reactors and photograph of a new jet-loop reactor.

Materials and Methods

A photograph of the new reactor design is shown in Figure 1. The one shown here is constructed of Type 316 stainless steel, although versions have been constructed from Hastelloy C276 and other advanced metal alloys. The catalyst chamber is sealed on both ends by Swagelok™ VCR fittings with metal gaskets for ease of installation. The one shown here can accommodate several commercial size catalysts whose largest dimension is ca. 16 mm.

The test reaction used is the oxidation of SO₂ to SO₃ over V₂O₅-based catalysts, which is the basis for all H₂SO₄ processes. The reaction gases are mixed upstream and introduced at a steady flow rate from a gas manifold and removed through the outlet whose back-pressure is maintained constant by a back-pressure regulator. Analysis of SO₂, O₂ and N₂ in the feed and product gases is performed with an on-line GC. A pitot tube located on the return leg is used to measure the internal gas recirculation rate. A large number of experiments were conducted in which the total gas flow rate, gas temperature, reactor total pressure, catalyst particle size, nozzle size, and nozzle location were systematically varied to assess the effect of these variables on the gas recycle rate.

Results and Discussion

An example of typical kinetic data is provided in Figure 2. These data are based upon temperatures between 400 to 475°C using a gas feed consisting of ca. 1% SO₂, 7.5% O₂ and 82.5% (bal) N₂ at flow rates between 100 sccm to 900 sccm. The resulting rate data are fitted to a rate model that accounts for reversible reaction behavior, although more complex rate equations can be evaluated for goodness-of-fit using robust parameter estimation methods.

The agreement between the reaction rates vs %SO₂ conversion data is shown below in Figure 2. A parity plot (Figure 2) shows a comparison between the experimental and model-predicted %SO₂ conversions at a selected temperature (425°C). Other detailed results will be presented that demonstrate the utility of the proposed jet loop reactor as a relatively simple but effective reactor type for studying the kinetics of gas-solid catalyzed reactions having either fundamental importance or commercial application.

![parity plot for SO₂ conversion](image)

Macroscopic and microscopic models that describe momentum transport effects under different process conditions and hardware configurations are also given.

Conclusions

Development of novel catalysts for SO₂ oxidation to SO₃ having higher activity at lower temperatures is driven by the need for reduced SO₂ emissions for more environmentally-friendly processes. The proposed jet loop reactor is well-suited for this corrosive application since contains no moving parts, it can be fabricated using various materials of construction that are inert to the reaction environment (e.g., quartz, type 316 SS, Hastelloy C276), and it is relatively inexpensive vs other existing commercially-available designs.

References