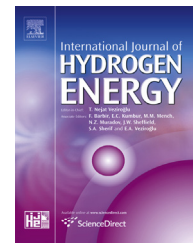Available online at www.sciencedirect.com

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Sulphur trioxide decomposition with supported platinum/palladium on rutile catalysts: 1. Reaction kinetics of catalyst pellets

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ABSTRACT

An investigation was undertaken to evaluate the intrinsic reactivity, stability and associated diffusional parameters of catalyst pellets consisting of platinum and palladium on rutile for the conversion of sulphur trioxide to sulphur dioxide. This catalyst was prepared by the sintering at 1103 K of a catalyst preparation consisting of 0.5 wt% platinum and 0.5 wt% palladium on mainly anatase (TiO_2) and the experimentation was carried out with a micro pellet reactor. A three dimensional heterogeneous model was generated for the reaction in the micro pellet reactor with five cylindrical pellets and solved using a CFD software code. A reversible reaction rate for the reaction was found to be applicable and the catalyst was found to reach a constant activity within an acceptable time period after start-up. Arrhenius parameters (reaction rate) were evaluated for the catalyst pellets and an overall kinetic model for the catalyst pellets suitable for designing fixed bed reactors was validated.

Introduction

Various processes have been identified as viable options for the production of hydrogen which include the Hybrid Sulphur cycle and Sulphur Iodine cycle with both involving a sulphur trioxide decomposition reactor [1]. This endothermic reaction can be carried out with a catalyst in a packed bed with different modes of heating following the homogeneous decomposition of sulphuric acid [2,3]. In order to achieve acceptable conversions this reaction needs to be carried out at high temperatures and with reactors consisting of special materials capable of handling the corrosive gases present.

Under these conditions it is also essential to use a thermally stable catalyst to ensure prolonged operation.

Many of the catalyst evaluated include the platinum group metals (PGM) [4—6] and metal oxides [7—10] based catalysts. The most suitable catalysts in terms of activity were found to be the platinum group metals on supported titania [3]. Pet-kovic et al. [6] reported that a catalyst consisting of 0.05 wt% platinum and 0.05 wt% palladium supported on pure rutile displayed the most favourable stability. The reaction kinetics of suitable catalysts for the decomposition of sulphur dioxide have been published, which consisted mostly of first order rate equations. Activation energies for platinum group metal based catalysts between 70.7 and 73.1 kJ/mol [2,10,11] and for

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ferric oxide catalysts between 138.6 and 301.8 kJ/mol [12–15] have been reported. Advanced models based on the Langmuir–Hinshelwood theory were examined by Petropavlovskii et al. [28] for palladium on alumina catalyst and reported all associated reaction rate parameters. Detailed reaction rate studies with other reaction rate models have not been reported except for proposals to incorporate the reverse reaction [16].

The experimental determination of the reaction kinetics reported by most investigators consists of using powdered catalyst samples in micro differential-packed (integral) reactors and fluidized beds. These studies involved essentially the determination of catalyst stability and relative activity of different catalysts formulations. However, for the advanced modelling and design of pilot and industrial packed bed reactors with pellet catalysts, it is desirable to evaluate the overall reactivity of the catalyst pellets consisting of intrinsic kinetics and intraparticle diffusion. Equipment for this evaluation can include micro differential-, packed bed- and spinning basket type reactors using the pellets [17]. The spinning basket type reactor has many moving parts and seals and could be problematic for reactions with very corrosive chemical components. The use of a laboratory-scale fixed bed (integral) with many pellets would require consideration of the packing effects (pressure drop and porosity). However, a differential bed with a small number of separate pellets (micro pellet reactor) would eliminate packing effects but would require modelling of the flow, heat and mass transfer mechanisms and chemical effects around the pellets. The modelling can be achieved by using computation fluid dynamics (CFD) with chemical reaction for the prediction of the velocity, temperature and concentration (conversion) profiles around the pellets and within the pellets respectively [18–20]. The construction is relatively simple, which could include external heating and with which moderate conversion can be obtained suitable for reaction rate evaluation. In order to contribute to the development of the HyS process with specific attention confined to the design and operation of a fixed bed, an investigation was undertaken to determine the overall reaction kinetics of a supported platinum and palladium catalyst using an electrically heated micro pellet reactor. The catalyst chosen for this investigation consisted of a sintered platinum and palladium on rutile catalyst prepared from a catalyst synthesised on a support consisting mostly of anatase. The objective of this paper is to present (1) the design of the micro pellet reactor used, (2) the modelling of the reactor accounting for momentum, heat and mass transfer in the bulk gas stream and within the pellets, and (3) a kinetic model for the overall kinetics of the catalyst pellets with an intrinsic reaction rate equation with associated parameters.

Experimental

Catalyst preparation and properties

Preparation
Fresh catalyst. The catalyst used was prepared at The University of Cape Town Catalysis Research Centre [21], South Africa. The catalyst was prepared by incipient impregnation of
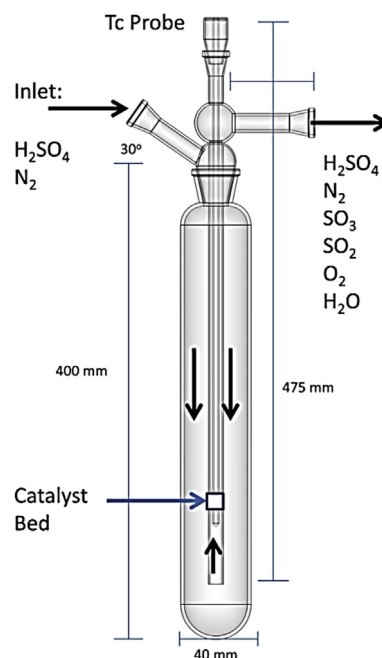

Fig. 1 – Sketch of micro pellet reactor.

the platinum metals on titania extrudates consisting of 75 wt % anatase (TiO_2) and 25 wt% rutile phase (Degussa P25). The titania extrudates were cylindrical pellets with a diameter of 1.7 mm and between 3 and 6 mm long and were dried before impregnation. The extrudates were impregnated with an aqueous solution of $Pd(NH_3)4Cl_2.1H_2O$ and $Pt(NH_3)4Cl_2.1H_2O$ with calculated concentrations to ensure the desired loadings. After impregnation the extrudates were dried, washed and dried again followed by calcined at 673 K for 18 h.

Sintered catalyst. To eliminate the effect of the contraction of the anatase phase to a rutile phase at the relatively high reaction temperatures it was considered necessary to sinter the fresh catalyst before reduction and reaction. The sintering was accomplished in a stainless steel tube at a temperature of 1103 K which was larger than the highest operating temperature adopted for the reaction experimentation programme. A batch of 1 kg was packed in a heated tube in the presence of air for a period of 12 h.

Characterisation
The characterisation of the fresh catalyst and the sintered catalyst consisting of the determination of the metal composition, metal dispersion and particle sizes and total surface area were accomplished [21]. The concentration of the platinum and palladium was assessed with a Varian 110 ICP-OES system with appropriate acids and neutralization. Metal dispersion as well as metal particle sizes were determined by hydrogen chemisorption according to a ASTM standard (D3908) and by Transmission Electron microscopy (TEM). The total area was determined by adsorption of nitrogen with a Micromeritics Tristar 3000 analyser. The assessment of the titania phase was accomplished with Scanning Electron Microscopy (SEM).