Production of ultrapure hydrogen in a Pd–Ag membrane reactor using noble metals supported on La–Si oxides. Heterogeneous modeling for the water gas shift reaction

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ABSTRACT

Two different catalysts, Rh(0.6% wt/wt)/La$_2$O$_3$(27% wt/wt)·SiO$_2$ and Pt(0.6% wt/wt)/La$_2$O$_3$(27%)·SiO$_2$, were tested in the WGS reaction. Their performances were first studied in a conventional fixed-bed reactor. Their activities were similar and they were both very stable. However, as Pt(0.6)/La$_2$O$_3$(27)·SiO$_2$ showed a much higher selectivity to the desired reaction, the performance of a membrane reactor employing this catalyst was studied. The effects of the H_2O/CO ratio, space velocity, sweep gas flow rate and size of the catalyst particle on CO conversion and H_2 recovery were studied at laboratory scale under isothermal conditions. A 1-D heterogeneous model was developed in order to properly reproduce the experimental results obtaining good agreement between the simulation results and laboratory data. The experimental and theoretical results confirm the existence of significant external mass-transfer limitations in the fluid-particle interface for these very active formulations.

1. Introduction

Hydrogen production has been extensively studied in the last two decades as a key element of the energy matrix. Hydrogen is industrially obtained from the steam reforming of natural gas or heavier hydrocarbons. In the case of fuel cell applications, this hydrogen stream needs to be purified by means of the water gas shift reaction (WGSR) usually conducted in one or two steps, and CO Preferential Oxidation (CO-PrOx) to avoid poisoning of the PEM fuel-cell anode catalyst. Since the WGS reaction rate is slower than the other reactions involved in the steam reforming process, and is limited at high temperatures by the thermodynamic equilibrium, the WGS reactor is the largest and heaviest process component [1]. A similar situation occurs in the case of fuel processors used to produce pure H_2 in situ to feed a PEM fuel cell [2]. An attractive alternative is to conduct the WGSR in a membrane reactor (MR), using only one vessel to

obtain ultrapure hydrogen. In this work, a commercial dense Pd membrane is used to obtain pure H_2 (<10 ppm CO) reaching conversion values above equilibrium. In order to increase the permeation through the membrane, a sweep gas (SG) stream (i.e. Argon) is employed. In a practical application, the sweep gas should be overheated steam to facilitate separation.

Ma and Lund [3] suggested that the reaction rate is the rate-limiting step in a membrane reactor operating adiabatically where the WGS reaction is carried out at high temperatures using catalysts based on Fe/Cr. For this reason, in recent years numerous papers have been published concerning the development of more active catalysts. A key factor is the stability of the well-performing supported noble metal formulations shown in the current literature. Several studies have been published concerning the use of Pt catalysts in the WGSR but only a few of them include stability data [4]. Panagiotopolou and Kondarides have reported that Pt/TiO_2, Pt/CeO_2 and Pt/CeO_2–TiO_2 catalysts display a strong metal support interaction, showing the best performance. As a matter of fact, few papers provide data about deactivation of WGS catalysts. Concerning this point, a recent review [5] highlights the need to report relevant deactivation data of promising catalysts to evaluate their practical use. Bi et al. [6] performed the WGS reaction catalyzed by $Pt/Ce_{0.6}Zr_{0.4}O_2$ in a membrane reactor employing a supported palladium membrane with a thickness of 1.4 µm. The authors emphasized the development of catalysts with faster kinetics than the commercial formulations. Although their catalyst complied with this condition at temperatures above 623 K, no data were provided about its stability-deactivation behavior. Note that the minimum temperatures at which the Pd membrane can efficiently operate are 623–673 K. At lower temperatures, the strongly adsorbed CO reduces the H_2 flow through the membrane, while higher temperatures affect its durability.

Most theoretical studies focused on membrane reactors for the WGS have proposed isothermal mathematical models [7–9]. However, when higher reactor scales are under consideration, the thermal effects should be taken into account [10–12]. All these isothermal and non-isothermal models assume negligible mass-transfer resistances on the gas–solid interface. Certainly, the use of pseudohomogeneous mathematical models is appropriate to reproduce experimental results when the controlling step is the catalytic reaction. However, for other operating conditions (e.g., in the presence of high catalyst activities and/or for the typical low process flow rates used at laboratory scale) the influence of the mass transfer limitations should be taken into account by means of heterogeneous models.

The aim of the present study was to develop a heterogeneous approach to model the behavior of a lab membrane reactor using a very active noble metal supported formulation. Newly developed Rh [13] and Pt catalysts – active, selective, stable and non-carbon forming – were used in the membrane reactor. The influence of the main operating and design variables (space velocity, sweep gas flow rate, catalyst particle diameter) on the CO conversion and H_2 recovery in the membrane reactor was analyzed.

2. Experimental

2.1. Catalyst preparation

The $La_2O_3 \cdot SiO_2$ support was prepared by incipient wetness impregnation of SiO_2 with lanthanum nitrate (Anedra). The SiO_2 (Aerosil 300) employed in the solid preparation was previously calcined at 1173 K. The solids were calcined at 873 K. After calcination the load of lanthanum given as La_2O_3 was 27 wt%. The Pt and Rh supported catalysts were prepared by incipient wetness impregnation using $Pt(NH_3)_4 \cdot Cl_2 \cdot H_2O$ (Strem Chemicals, Inc., 99.95%-Pt) and $RhCl_3 \cdot 6H_2O$ (Alfa Aesar, 99.99%) as precursors. The samples were kept at room temperature for 4 h and then dried at 343 K overnight. The apparent densities of both catalysts were the same: 0.5 g/cm³.

Prior to use, both catalysts were ground to a particle size lower than 20 µm (verified by SEM). In the Pt containing formulation, in order to obtain larger catalyst particles (230 µm), the solid was pressed and sieved to the required size.

2.2. Catalyst characterization

The fresh-reduced and used (after exposure to WGSR conditions) catalysts were analyzed by X-Ray Diffraction (XRD) using an XD-D1 Shimadzu instrument and Cu Kα radiation at 30 kV and 40 mA. The scanning rate was 1.0°/min for values between $2\theta = 10°$ and 60°. BET surface areas (S_g) were measured by N_2 physisorption at its boiling point in a Micromeritics Accusorb 2100 E sorptometer.

The Raman spectra of fresh and used solids were recorded using a LabRam spectrometer (Horiba-Jobin-Yvon) coupled to an Olympus confocal microscope (a 100× objective lens was used for simultaneous illumination and collection), equipped with a CCD detector cooled to about 200 K using the Peltier effect. The excitation wavelength was in all cases 532 nm (Spectra Physics diode pump solid state laser). The laser power was set at 30 mW.

2.3. Catalytic measurements

2.3.1. Conventional fixed-bed reactor

Catalytic measurements were conducted in a conventional flow system isothermally operated at atmospheric pressure. The tubular quartz reactor had an inner diameter of 9.5 mm, the same as the membrane reactor. The feed stream gas mixture was made up of CO (Linde, 2.3), H_2O (distilled) and Ar (Indura S.A., 5.0). CO and Ar were controlled using MKS mass flow controllers, while the steam was generated in a preheater fed with water from a syringe pump (Apema S.R.L.) at the desired flow rate. The reaction temperature was controlled through a thermocouple placed inside the catalyst bed. The catalysts were heated in Ar at 673 K at a rate of 1.5 K min^{-1}, afterward they were reduced in flowing H_2 (Indura S.A., 5.0) at the same temperature for 2 h. The reaction was carried out at 673 K and the feed stream gas mixture was made up of CO and H_2O ($H_2O/CO = 2$–3). The reactor was operated in both differential and integral modes. The gases leaving the reactor flowed through an ice-cooled trap and a tube packed with silica gel to remove water before the gas chromatographic