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Transport in catalytically active porous membrane application in seawater deoxygenation for pressure maintenance.

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TRANSPORT IN CATALYTICALLY ACTIVE POROUS MEMBRANE APPLICATION IN SEAWATER DEOXYGENATION FOR PRESSURE MAINTENANCE

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ABSTRACT

In this study, inorganic tubular ceramic membranes with highly-dispersed catalytic metal: palladium and platinum were produced on both meso and macro-porous membranes. The membranes were characterised by energy dispersive x-rays (EDAX), scanning electron microscopy (SEM), BET liquid nitrogen adsorption and hydrogen gas transport behaviour. They were tested for sea water deoxygenation by feeding seawater saturated with hydrogen under various operating conditions and monitoring the downstream oxygen removal rate. The results far exceeded those of a traditional fixed bed catalytic reactor.

KEYWORDS: Hydrogen, Seawater, Catalyst, Deoxygenation, Membrane

1 INTRODUCTION

Oxygen dissolved in or other fluid may be the cause of corrosion in various installations. On the other hand, in the beverage production industries such as beer production, it leads directly to the oxidation of dissolved organic matter, decreasing the quality of the product and this phenomenon is the subject of several studies [1-9]. Therefore, its content must be substantially reduced. Water, which could be sourced from sea, lake or river is required for enhanced petroleum recovery and for several other process applications such as in microelectronics, food industry, atomic and thermal power plants [1]. This need stems from its use either during production or manufacturing of components/products. The quality of this water is highly paramount for an efficient production to occur. In the oil and gas industry for example, it is the norm for the reservoir pressure of an oil well to be maintained by seawater injection during water-flooding operations (the process of sweeping the oil to the producers) [2]. This process is called improved and enhanced oil recovery [3, 4]. The advantages of the use of sea compared to other surface water sources is therefore enormous, but majorly, it is readily available, abundant in nature and creates little or no environmental impact by its use. Sea water properties vary from one location to another, but the downside of using untreated seawater is that it contains contaminants: dissolved oxygen (DO), suspended solids, dissolved solids, planktons and bacteria which are undesirable depending on the application, hence the need for its treatment prior to use [5, 6]. For the purpose of this study, the contaminant of interest is DO because without its removal it can lead to corrosion of wellheads and subsea structures.

EXPERIMENTAL PROCEDURE

A photograph of the experimental system used in this study is presented in Figure 1 and consists of the feed delivery system, the reactor and analytical system respectively.

Material and Methods

Materials used for this work include a 15nm pore size commercially available tubular ceramic membranes consisting of 77% alumina + 23% TiO₂, purchased from Ceramiques Techniques et industrielles (CTI SA) France. The support has a 7 mm inner diameter and 10 mm outer diameter, with a total length of 368 mm of which 318 mm is the permeable length. Figure 2 shows the pictorial diagram of the fresh support, the Pt and Pd metal dispersed systems respectively. The six gases used for the characterisation of gas permeation

including nitrogen (N₂), argon (Ar), helium (He), carbon dioxide (CO₂), oxygen (O₂) and hydrogen (H₂). The gases were supplied by BOC, UK. A fixed-bed catalyst reactor was constructed inhouse and also used for performance comparison.

Feed delivery Section

In the feed delivery section, a digital pressure gauge was connected to the control valve in which it was used to regulate the amount of hydrogen gas leaving the cylinder. This section comprises mainly of the water and hydrogen supply which fed into the reactor from different sides and this was because less resistance is experienced with the fixed-bed reactor arrangement. The plastic tubing was used to connect the water from the tap to the reactor, while stainless steel tubes were used for the hydrogen gas connections. All fittings in the hydrogen connection were tested for leaks.

Fixed-bed catalytic reactor section

In this section, the mesh containing the catalyst pellet was suspended inside the reactor and forced up towards the neck closer to the entry points for both the water and hydrogen gas. The reactor was then clamped onto the rig.

Analytical Section

In the analytical section, a 500 mL was used to collect the water sample exiting the fixed-bed reactor or membrane reactor and measurement of the dissolved oxygen (DO) after the experiment was done by submerging the DO probe inside the collected water in the beaker and reading it off directly.

Membrane Characterisation

The membranes were characterised by conventional and advanced methods for the examination of both chemical and physical characteristics, morphology and pore size and transport characteristics. These included scanning electron microscopy with energy dispersive x-rays (SEM/EDXA), Fourier-Transform Infrared Spectroscopy (FTIR), Bunauer-Emmett-Teller (BET) using liquid nitrogen adsorption and gas transport permeation respectively.

Kinetic Experimental runs

The test rig was initially tested with an inert gas (helium) before carrying out the analysis with hydrogen gas. This was done to ensure that no leak was present. The hydrogen detector was clamped above the rig for safety reasons. Hydrogen gas was introduced from the top of the reactor while the tap water was introduced from the side. The volumetric water flowrates were calculated manually using a 500 mL beaker, number of turns of the tap and a stopwatch. As the tap was turned on, the timer was also started immediately, the water and hydrogen were allowed to flow through the suspended catalyst bed or membrane into a collecting beaker under the reactor until 500 mL of water was collected. After this, both the hydrogen supply, timer and tap are turned off.

RESULTS AND DISCUSSION

Figure 3 shows a plot of DO concentration against deoxygenating on-stream reaction time at ambient temperature and pressure. The lowest DO concentration was recorded as the on-stream reaction time approached 30 min. This trend in deoxygenating on-stream reaction time was also similar to the results reported by other researchers. The results obtained also confirms that the on-stream reaction time plays an important role in water deoxygenation. As a result of the observations from this graph, each change in flow rate was given at least 30 min on-stream time before measuring the final DO concentration. This length in time could be explained as the time required for all the active sites on the catalytic surface to be saturated with the adsorbed species. Only when this is achieved will there be efficient chemical reaction between the desorbed species for an effective reduction or removal in the level of DO present. This is a typical procedure in process applications where variables are allowed to run for a certain amount of time before stability in results are obtainable.



Figure 1: Photograph of the experimental system used in this study.

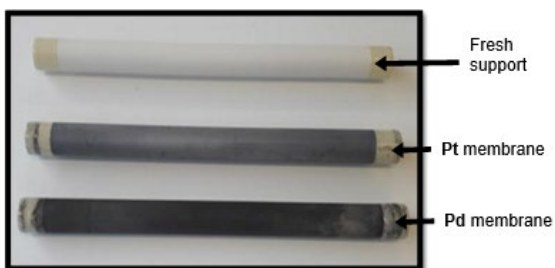


Figure 2: Fresh and metal-dispersed systems membrane

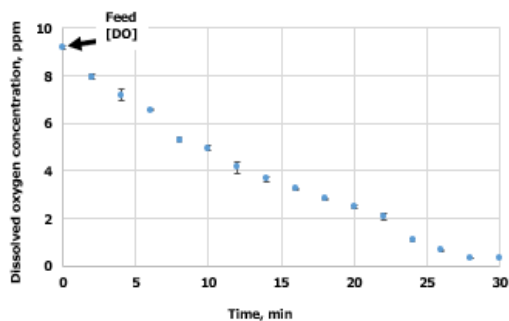


Figure 3: Exit dissolved oxygen concentration against time (mins)

CONCLUSIONS

The method of catalyst impregnation was also carried out to favour high dispersion of the catalyst. The platinum impregnated membranes gave high affinity for DO and therefore requires no regeneration. The ceramic support has highly dispersed metals incorporated into their pores, which promotes the efficient distribution of hydrogen thereby enhancing the catalytic recombination of hydrogen and DO in water resulting in almost complete DO removal.

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