Composite ionic liquid–polymer–catalyst membranes for reactive separation of hydrogen from carbon monoxide

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ABSTRACT

Novel composite ionic liquid and polyimide membranes with dissolved RuCl$_3$ catalyst for H$_2$/CO reactive separation were fabricated to combine gas diffusive separation and water-gas shift reaction. The CO concentration in the membranes is reduced *via* its reaction with H$_2$O to form CO$_2$ and H$_2$, catalysed by the Ru carbonyl complex which forms in the reaction between dissolved RuCl$_3$ and CO. In order to optimize the membrane configurations and operating conditions, water-gas shift reaction turnover frequencies (TOFs) of the membranes with various concentrations of ionic liquid and RuCl$_3$ were determined at different pressures, temperatures and times-on-stream on a purpose-built test rig. The results show that the ionic liquid, [C$_4$mim][OTf], improves TOFs by increasing the solubilities of H$_2$O and the gases solubilities within the membrane. TOFs were found to increase initially, but reduce as time-on-stream increased, due to the formation and subsequent evaporation of a Ru carbonyl complex. Lower temperature and lower concentration of [C$_4$mim][OTf] were found to minimize the loss of the catalyst. It is suggested that the 2 wt% RuCl$_3 \cdot x$H$_2$O+20 wt% [C$_4$mim][OTf]+PI membrane operated at 140 °C and 2 bar has the best combination of reactivity and durability.

1. Introduction

Fuel cells such as proton-exchange membrane fuel cells (PEMFCs), which use hydrogen and air to produce electricity, are considered to be a promising alternative to traditional carbon-emitting and fossil-fuel burning internal combustion engines [1]. Due to the difficulties involved in storing hydrogen, on-board hydrogen production appears to be the most viable approach [2]. However typical on-board hydrogen production methods, such as liquid-fuel reforming, do not produce pure hydrogen. The most prominent by-product is carbon monoxide, which poisons the platinum electrode of PEMFCs [1]. In order to remove CO from the H$_2$-rich stream, several technologies have been developed, such as cryogenic separation, pressure swing adsorption, preferential CO oxidation (PROX), selective CO methanation, water gas shift (WGS) reaction and selective diffusion of H$_2$ through metal or polymer membranes [3]. For the applications of small-scale fuel cells, the catalytic transformation of CO into other gases and the selective separation membrane are considered to be promising. The water-gas shift reaction [4], which

involves the reaction between carbon monoxide and water to produce hydrogen and carbon dioxide, is an important approach to CO removal in fuel cells.

Two major commercial heterogeneous water-gas shift catalysts are currently in use. The first, a promoted iron oxide catalyst [4] which is used to promote the reaction at high temperature in the region of 350–450 °C, is also known as the high temperature shift (HTS) catalyst. The second is a copper–zinc oxide catalyst which is used at relatively low temperatures of 190–250 °C. This is also known as the low temperature shift (LTS) catalyst. HTS and LTS catalysts have been combined to reduce the CO level to less than 1 wt% [5]. New heterogeneous water-gas shift catalysts have been developed during the last decade, mainly based on nanoparticular precious metal clusters and mixed metal/rare earth materials. However, the commercial LTS copper–zinc oxide catalyst has been shown to exhibit the best performance in terms of activity and stability [6].

Homogeneous catalysts have also been developed for water-gas shift reaction, including early work on base-catalysed systems, transition metal carbonyls in aqueous solution of organic bases and immobilized ruthenium catalysts [7]. Homogeneous catalysts have the advantages of higher activity, uniformity of the catalytic centre and the possibility to use them at lower temperatures compared with heterogeneous water-gas shift catalysts. However,

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heterogeneous catalysts have traditionally been favoured due to their ease of recycle and long-term stability.

Significant attention has been given to ionic liquids in gas separations in recent years. Ionic liquids have several unique properties, such as negligible vapour pressures and selectively high solubilities towards certain gases, which make them ideal for absorption [8] or as additives for membrane gas separations [9]. Ionic liquids can also potentially be designed for purpose, since their physical and chemical properties can be varied by changing the cation–anion combination or by incrementally changing the cationic structure. As a result, it is estimated that there are around 10^6 possible ionic liquids [10], each with different properties, although only a few thousand have actually been synthesized. These favourable properties have been exploited in the development of supported ionic liquid membranes (SILMs) [11,12], consisting of a porous membrane support coated in a layer of ionic liquid, which is chosen specifically to improve the permeability and selectivity of the membrane. Since the ionic liquid is non-volatile, the SILM remains intact for extended operation at ambient conditions and this configuration has been used to separate several binary gas mixtures, including H_2/CO. However, at elevated temperatures and pressures, the SILM approach is not suitable, due to loss of ionic liquid from the membrane surface. More recently, composite ionic liquid polymer membranes (CILPMs) for gas separations, including H_2/CO, have been developed [13,14]. Since the ionic liquid is trapped within the non-porous polymeric membrane material, CILPMs have the advantage of greater mechanical stability over a wide range of temperatures and pressures compared to SILMs. Gas transport in polymer membranes is typically described by the solution-diffusion model [15], whereby the gases must first dissolve in the membrane and then diffuse through the membrane. Therefore, the presence of an ionic liquid within the polymer can enhance gas selectivity by influencing the relative diffusivities and solubilities of the gases within the membrane. By choosing an appropriate ionic liquid which is known to have a higher diffusivity and/or solubility for one gas relative to the other, the selectivity of the polymeric membrane can be enhanced.

The unique properties of ionic liquids have also been exploited in the field of catalysis [16]. In particular, the ability to dissolve gases, organic substrates and inorganic homogeneous catalysts in the ionic liquid phase provides significant opportunities for improvements over traditional heterogeneous or homogeneous catalysis. The recent development of supported ionic liquid phase (SILP) catalysts [17] is applicable to many gas and liquid phase catalytic processes, such as Friedel–Crafts acylations [18], hydroformylations [19] and hydrogenations [20]. SILPs are composed of a solid support, with high surface area, coated with a thin layer of ionic liquid within which a homogeneous catalyst is dissolved [17]. This approach combines the high activities and selectivities of homogeneous catalysts with the stability and ease of separation of heterogeneous catalysts, while the choice of ionic liquid can also significantly influence the mass transfer and, thereby, enhance selectivity. SILP technology has recently been applied to the water-gas shift reaction [21], where homogeneous catalysts supported on silica with ionic liquid were shown to enable the reaction to proceed at very low temperature (120–160 °C).

Process intensification is a recent trend in the chemical industry, whereby novel processing technologies are developed with reduced equipment volumes, increased yield and reduced waste production [22]. Reactive separation, where reactors and separators are combined into one process unit, is one of the most significant approaches towards process intensification, with several configuration being used commercially, such as catalytic distillation and reactive absorption. Membrane reactor technology, integrating the catalyst with the separation membrane, has had significant attention in recent years

in literature [23], with a particular focus the production of hydrogen [24]; however the majority of work has focussed on high temperature applications. Babita et al. [25] recently published a detailed review of membrane reactor technology for the preparation of fuel cell quality hydrogen from water gas shift reaction. While many advances have been made using a range of membranes, there remains significant scope for improvement.

In this work, we aim to combine the enhanced catalytic performance of SILPs with the gas separation properties of CILPMs to design, fabricate and optimize a novel composite ionic liquid–polymer–catalyst membrane for the reactive separation of hydrogen from carbon monoxide, operating at low temperatures and close to ambient pressures.

2. Design of the composite ionic liquid–polymer–catalyst membrane

The composite reactive membrane is composed of three parts: the polymer, which provides the mechanical strength, permeability and selectivity for gas separation; the ionic liquid, which further enhances the permeability and separation selectivity of the membrane; and the catalyst, which enables the reaction to occur at a reasonable rate. Due to the wide range of possibilities which exist in selecting materials for each of these components, it is important to apply rational design principles in choosing the appropriate combination of materials. The following sub-sections explain the material selection for the composite catalytic membranes.

2.1. Rationale for ionic liquid selection

The key properties for selecting the appropriate ionic liquid for use in composite polymer–ionic liquid–catalyst membranes include: low melting point; high thermal and chemical stability; low viscosity; high solubility towards reactants, catalyst and polymer substrate; and low solubility towards reaction products. Non-symmetrical N,N-dialkylimidazolium cations generally give ionic liquids with low melting point [26]. In this class of cations, 1-butyl-3-methylimidazolium cations and 1-ethyl-3-methylimidazolium ($[C_4mim]^+$ and $[C_2mim]^+$) are the most investigated structures, because they both show good thermal stabilities [27] and low viscosities [28] with the anion, bis(trifluoromethane)sulfonimide ($[NTf_2]^-$). Ionic liquids with the anions $[NTf_2]^-$ and trifluoromethanesulfonate ($[OTf]^-$) demonstrate good thermal and hydrolytic stabilities, low melting points and low viscosities [27], which are desirable for their application in composite catalytic membranes.

In the composite catalytic membrane, the catalyst should be dissolved in the ionic liquid homogeneously, which is normally not a problem for transition metal complexes having enough polarity to be soluble in most ionic liquids for catalysis applications [16]. On the other hand, the solubilities of the reactants and the products in the ionic liquids are the main concern for SILP reactions. Usually, the rate and the conversion of a catalytic reaction depend on the concentration of the reactants in a positive order and the concentration of the products in a negative order. For the water gas shift reaction, the solubilities of CO, H_2O, H_2 and CO_2 in the ionic liquid are important. An ionic liquid with high solubilities towards CO and H_2O and low solubilities of H_2 and CO_2 would give high reactivity and conversion.

The solubility of carbon monoxide in some ionic liquids has been studied [29–33]. Ohlin et al. investigated the solubility of CO in many ionic liquids and found that imidazolium-based ionic liquids have the highest CO solubility and increasing chain length of the alkyl substituent leads to higher CO solubility [30]. The anions of ionic liquids also affect CO solubility with the order $[BF_4]^- < [PF_6]^- < [SbF_6]^- < [CF_3CO_2]^- < [NTf_2]^-$. The results of other studies show similar