



# Hydrogen production from energy carriers by silica-based catalytic membrane reactors



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## ABSTRACT

Catalytic membrane reactors equipped with a microporous inorganic membrane have attracted a considerable amount of research interest as an alternative to the current industrial processes for hydrogen production. The present article focuses on the state of the art in the development of silica-based catalytic membrane reactors for hydrogen production from energy carriers. Highly promising energy carriers for the storage and transportation of hydrogen are illustrated. Recent advances in high-performance silica-based microporous membranes for use in hydrogen separation are highlighted. Experimental and theoretical investigations into the application of silica-based catalytic membrane reactors for the dehydrogenation of energy carriers including ammonia, cyclohexane and methylcyclohexane are discussed.

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## 1. Introduction

Hydrogen produced from either the steam reforming of natural gas or the electrolysis of water, is considered an environmentally attractive fuel, and it is expected to play a significant role in sustainable development by helping reduce the emission of greenhouse gases [1,2]. Due to the extremely low volumetric density of gaseous hydrogen, however, scientific and technological obstacles in hydrogen storage and transportation are yet to have been completely overcome; these requires cryogenic temperatures or high pressures [3]. Liquid hydrogen storage materials that store hydrogen via chemical bonding are highly promising as energy carriers because of their liquid-phase nature and relatively high hydrogen content [4,5]. Before the storage and/or transportation of hydrogen, organic or inorganic chemical compounds are hydrogenated to form liquid hydrides, which can then be decomposed to dehydrogenated compounds and hydrogen for utilization. The dehydrogenated compounds can then be recycled via re-hydrogenation. However, the dehydrogenation reactions of hydrogen carriers are limited by thermodynamic equilibrium at low temperatures. Thus, a strong shift in equilibrium that could increase the reaction conversion under mild conditions would help make hydrogen production processes more commercially practical.

Membrane reactors combine heterogeneous catalysts and membranes to allow reaction, separation, and product concentration processes to take place in a single-unit operation [6]. To date, the advantages of membrane reactors over packed bed reactors (PBRs) have been demonstrated via experimental and theoretical/modeling studies [7–10]. Compared with conventional processing, membrane reactors continuously remove the product during the reaction; and, thus, the conversion is increased beyond the equilibrium until the limitations imposed by reaction kinetics become dominant. When used in hydrogen production processes, membrane reactors that are commonly operated at high temperatures use membrane materials that are mainly metal, carbon or ceramic, including palladium and its alloys [9,10], perovskite-type oxides [11,12], porous carbon [13,14], zeolite [15,16], and microporous ceramic oxides (silica, alumina, zirconia, etc.) [17,18]. Palladium-based membranes exhibit extremely high selectivity for hydrogen separation, but have several major drawbacks that significantly limit their practicality: hydrogen embrittlement, surface poisoning, and high membrane cost [7,14,18]. A number of studies have suggested that the silica-based microporous materials with tunable pores could act as a highly selective and permeable membrane with great H<sub>2</sub> separation efficiency and low manufacturing cost [18–20].

This article focuses mainly on the state of the art in silica-based catalytic membrane reactors (CMRs) and on their applications in hydrogen production from energy carriers. First, highly promising energy carriers for the storage and transportation of hydrogen are illustrated. Recent developments in silica-based microporous

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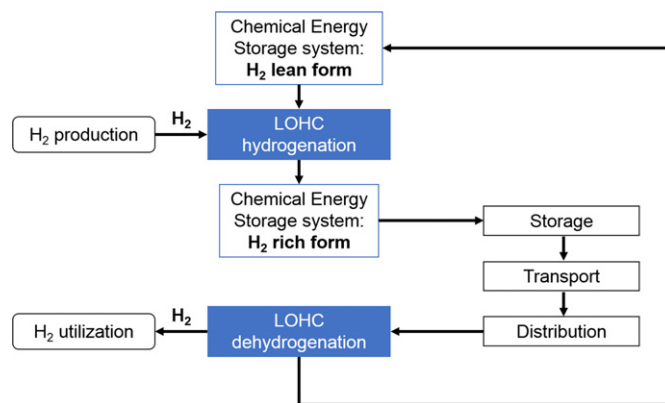
membranes with H<sub>2</sub> permeability and selectivity follow. Subsequently, advances in the application of silica-based catalytic membrane reactors to release hydrogen from energy carriers are highlighted. Finally, mathematical models are proposed for the simulation of hydrogen production processes in catalytic membrane reactors.

## 2. Energy carriers

In principle, hydrogen can be stored either in its elemental form (H<sub>2</sub>) as a gas or a liquid, or in its chemical form. Many substances have been proposed in the literature as potential energy carriers for hydrogen storage and transportation, such as metal hydrides, metal-organic frameworks (MOFs), ammonia (NH<sub>3</sub>), ammonia borane complexes, liquid organic hydrogen carriers (LOHC), etc. The solid-state materials possess high hydrogen storage capacities, but drawbacks such as the high temperature required to desorb hydrogen and the slow hydrogen release kinetics have limited a more widespread utilization [21]. Recently, liquid-state energy carriers have received considerable attention as promising chemical hydrogen storage materials due to their attractive features, which include a high degree of energy density and easy hydrogen storage under ambient conditions. Liquid-phase storage materials have significant engineering advantages that allow distribution, delivery and storage by applying the existing gasoline infrastructure with only minimal modifications [4].

Among these types of energy carriers, NH<sub>3</sub> offers clear superiority in terms of CO<sub>2</sub>-free hydrogen production and energy capacity (17.8 wt% hydrogen). Moreover, NH<sub>3</sub> can be stored as a liquid under a relatively low pressure of 0.86 MPa at 20 °C in stainless steel containers [22]. NH<sub>3</sub> can be synthesized from its constituent elements, H<sub>2</sub> can be produced from fossil fuels or from water electrolysis or gasification of biomass, and N<sub>2</sub> can be separated from air via the Haber–Bosch process. It is worth mentioning that thermochemical water-splitting cycles that use heat from solar or nuclear power have been identified as promising approaches for hydrogen production because of high efficiency, fully recycled chemicals, and the lack of greenhouse gas emissions [23]. The decomposition of NH<sub>3</sub> is a mildly endothermic process that yields H<sub>2</sub> and N<sub>2</sub>, and the equilibrium conversion of NH<sub>3</sub> is dependent on temperature, because the H<sub>2</sub> concentration at equilibrium decreases with decreasing temperature. However, the reaction rate of NH<sub>3</sub> decomposition is inhibited by the presence of hydrogen at low temperatures and high hydrogen partial pressures, as described by the Temkin–Pyzhev mechanism [24], which leads to a low degree of NH<sub>3</sub> conversion.

Liquid organic hydrogen carriers (LOHCs) are formed by pairs of organic compounds. The hydrogen-lean form being is typically an aromatic or heteroaromatic compound, and the hydrogen-rich form is typically an alicyclic or heterocyclic compound [25]. A number of LOHC [4,5,25] have been proposed as energy carriers for hydrogen storage including cyclohexane (CH), methylcyclohexane (MCH) and various derivatives of thiophene, quinaldine and carbazole. Aromatic compounds have H<sub>2</sub> storage capacities up to 7.0 wt% and can be hydrogenated under relatively mild conditions. The methylcyclohexane-hydrogen-toluene cycle [26] is a promising route for hydrogen storage because it is extremely reversible, highly selective, and free of carcinogenic products. The hydrogenation reaction for toluene (TOL) to generate MCH is typically carried out at 100–200 °C with pressures ranging from 2 to 4 MPa using supported noble metal catalysts [27]. To liberate H<sub>2</sub>, MCH dehydrogenation usually proceeds in the presence of supported Pt catalysts at temperatures around 300 °C under pressures slightly above ambient conditions [28]. In 2013, the Chiyoda Corporation established a hydrogen storage and transportation system with a capacity of hydrogen storage and production of 50 Nm<sup>3</sup>/h, in



**Fig. 1.** Schematic view of the storage and transport of regenerative energy equivalents using Liquid Organic Hydrogen Carrier systems.

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a demonstration plant using a liquid organic hydrogen carrier technology that was based on the MCH–H<sub>2</sub>–TOL cycle [29]. Fig. 1 illustrates a schematic view of the storage and transport of regenerative energy equivalents using LOHC systems. After releasing H<sub>2</sub>, the dehydrogenated compounds such as TOL are recycled for hydrogenation.

Table 1 lists the physical properties and reaction kinetics of several energy carriers for hydrogen storage. The decomposition of NH<sub>3</sub> requires the smallest energy input to produce H<sub>2</sub>, which, however, is normally conducted at temperatures above 450 °C due to a low reaction rate limited by the temperatures and hydrogen partial pressures. To maximize the commercial benefit of hydrogen production and utilization, one attractive approach has been to increase the reaction conversion at lower temperatures. The selective removal of hydrogen through a membrane is expected to enhance the reaction conversion by shifting the thermodynamic equilibrium toward complete conversion and provides a flow of high-purity hydrogen.

## 3. Silica-based microporous membranes

Microporous silica (SiO<sub>2</sub>) membranes have been extensively investigated as promising candidates for hydrogen separation because of the amorphous silica structures, which allow the permeation of helium and hydrogen but not the permeation of gas molecules with large molecular sizes.

Generally, silica layers can be deposited on porous substrates via either chemical vapor deposition (CVD) or sol–gel method. In a CVD process, thin silica films are formed by the reaction of one or several gas phase precursors at a given temperature (normally, higher than 400 °C) [30]. Generally, silica membranes prepared by CVD technique have pores with average diameters less than 1 nm, and these membranes show high H<sub>2</sub> selectivity but low permeability [31]. In addition, the CVD method requires relatively high investment costs and precisely controlled conditions for deposition [32]. Recently, plasma-enhanced chemical vapor deposition (PECVD) was introduced to prepare silica membranes with the advantage of depositing silica layers at temperatures as low as room temperature [33,34]. On the other hand, sol–gel-derived silica membranes have typically been prepared by coating a porous support with silica suspensions derived from alkoxide precursors, followed by drying and firing at high temperatures. The resulting membranes showed higher gas permeation rates than CVD-derived silica membranes, and a possible reasons could be the difference in the thickness of silica layers, which were 30–60 nm [35,36] and

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