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LTA zeolite composite membrane preparation, characterization and application in a zeolitic membrane reactor

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Abstract

An LTA membrane has been crystallized inside a porous ceramic tube and applied to synthesis of methanol from carbon dioxide and hydrogen in a zeolite membrane reactor (ZMR). The results obtained with the ZMR were compared with those gained from one traditional reactor (TR) used under the same operating conditions. CO_2 conversion obtained with the ZMR at 210 °C reached 17% under conditions where the equilibrium value without zeolite membrane (TR) is equal to about 6%.

Keywords: Zeolite membranes; Methanol synthesis; Zeolite membrane reactor

1. Introduction

Zeolite membranes have a promising future for applications in zeolite membrane reactors (ZMRs) due to their selectivity, permeability and stability with respect to higher temperatures and chemical aggressive media. They can be especially used to improve the yield and the selectivity of the reactions that are limited by the equilibrium. These reactors by increasing process productivity can become an excellent alternative for traditional reactors (TRs). Many chemical transformations that not are limited kinetically, such as hydrogenation and dehydrogenation reactions, catalytic reforming, etc., can be studied utilising a ZMR [1].

Zeolitic membranes in one unity can include the double function of separator and catalyst.

The applications of ZMRs have been almost exclusively limited to the hydrogen removal in dehydrogenation of hydrocarbons and sometimes in processes such as hydrogen-producing decomposition or synthesis gas production.

Ciavarella [2] has studied isobutane dehydrogenation and has found that the continuous subtraction of hydrogen from the reaction environment increases isobutane production.

Pantazidis [3] has used a zeolitic membrane with catalyst V–Mg–O for propane (ODPH) dehydrogenation. This membrane acts as a barrier for the gas and it increases propane quantity for low propane–oxygen ratio. The zeolitic film has a high influence on the membrane performances.

Bredesen [4] suggests that soon the zeolitic membranes can be used for the production of hydrogen with CMSR (catalytic membrane steam reforming).

Julbe [5] prepared supported V-MFI membranes by direct incorporation of vanadium species. This type of catalytic membrane seems particularly interesting for oxidative dehydrogenation reactions of alkanes in catalytic membrane reactor applications. The modification of the membrane reactivity by vanadium was demonstrated by the specific ability of the V-MFI membrane to decompose alkanes at 450 °C. All these applications were based on zeolite membrane capacity to remove hydrogen.

Zeolite membrane peculiarities can be exploited by removing molecular species that condense inside small

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pores, nevertheless there are few examples in the literature [6]. We studied the preparation of catalytic zeolite transition metal-containing thin films and membranes [7].

CO_2 hydrogenation is a promising process to produce methanol and in addition to contemporaneously reduce the amount of CO_2 in the atmosphere. Synthesis of methanol from syngas (CO/H_2 or $CO_2/CO/H_2$) is a very important and well-known industrial process. Nevertheless, the synthesis yield of methanol is thermodynamically limited by equilibrium. In order to increase the reaction yield, the condensable products (CH_3OH and H_2O) of the reaction can be removed by using a ZMR.

The reactions that occur during the hydrogenation of CO_2 are the following:

$$CO + 2H_2 \rightleftarrows CH_3OH \quad \Delta H_{298\,K} = -90.90\ \text{kJ/mol} \tag{1}$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O \quad \Delta H_{298\,K} = +41.19\ \text{kJ/mol} \tag{2}$$

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \quad \Delta H_{298\,K} = -49.41\ \text{kJ/mol} \tag{3}$$

Reactions (1) and (2) are both reversible and exothermic; both reactions show positive Gibbs free-energy changes due to reaction at temperatures higher than 150 °C for (1) and 180 °C for (3); both reactions proceed under volume contraction. The highest methanol conversions are obtained at low temperature and high pressures. Reaction (2), the reverse water gas-shift reaction, takes place simultaneously with methanol synthesis: it is an endothermic reaction that proceeds without volume change. The removal of water and methanol would increase the reagent conversion.

In this work the preparation and characterization of a tubular LTA composite membrane by the synthesis method called Multi In Situ Crystallization (MISC) [8] is described. Then experimental results concerning its application to hydrogenation reaction in CMR are analysed. This paper reveals that higher CO_2 conversion was obtained with respect to a traditional reactor.

2. Experimental

The LTA membrane has been prepared by three reaction cycles. Every cycle consists of mixture reaction preparation, gel ageing, hydrothermal reaction, washing then drying and it can be subdivided into two stages. In the first one, a gel containing silica and aluminate is prepared dissolving finely divided silica in an alkaline hydroxide solution. In the second stage, this mixture is used for hydrothermal treatment in the presence of the porous support. Schumacher Gmbh (Germany) supplied the ceramic tubular support. The as-made membrane, after every reaction cycle, was submitted to a gaseous permeation test using pure nitrogen in order to evaluate the zeolitic film formation compactness and the absence of synthesis macrodefects.

The single-channel, asymmetric support was 200 mm long, the internal and external diameters were 7 mm and 10 mm, respectively. The reaction mixture has been: 0.5 Al_2O_3:SiO_2:Na_2O:120 H_2O and the hydrothermal synthesis has been performed at 100 °C for 5 h in static conditions by using Morey-type PTFE-lined autoclaves. In order to decrease the synthesised zeolitic crystal size, the reaction mixture was aged at 60 °C. The synthesis of this membrane is analyzed in the work of Tavolaro [9]. The zeolite membrane area is about $4.40 \times 10^{-3}\ m^2$.

The synthesized zeolitic structure was identified by a Philips PW 1730/10 X-ray diffractometer using Cu Kα radiation, while the morphology and crystal sized were observed by a scanning electronic microscope (SEM). A zeolite continuous film of zeolite has been prepared on the inner tubular surface of the support. Furthermore, zeolite crystals have been grown inside the porous support, while no crystals have been formed on the outer of the substrate.

The ends of the alumina support were subject to enameling, while four graphite o-rings (99.53% C and 0.47% S) furnished by Gee Graphite Ltd. (England), 2.8 g each, ensure, in the reactor and in the cell for permeation tests, that permeate and lumen streams do not mix with each other in the membrane module.

The zeolite membrane reactor was made of a stainless steel shell containing the tubular composite membrane 20 cm long that was packed with 8 g of catalyst. The catalyst used was a bimetallic Cu/ZnO on Al_2O_3 (type MK-101) supplied by Haldor-Topsoe. It was heated at 250 °C for one day in the presence of one gas nitrogen and hydrogen mixture containing 93.4% vol. nitrogen and 6.4% vol. hydrogen, then it was cooled and used in the CO_2 conversion reaction. The lumen volume of the zeolite membrane was $7 \times 10^{-6}\ m^3$.

An additional experiment was performed with a traditional reactor (of equal volume and weight of catalyst).

Fig. 1a shows the system used for conversion by the traditional reactor. Fig. 1b represents the scheme of the membrane reactor module and the flow diagram used of the experimental reaction system to study the methanol production. Steady-state conditions were used to study the reaction.

3. Results and discussion

Fig. 2 shows an X-ray diffraction pattern obtained by the scratched crystalline powder analysis relative to the zeolitic layer grown on the tubular support inner surface.

This diffraction analysis, especially the study of the ranging interval between 7 and 18 2θ, reveals that there is a pure LTA structure.

Fig. 3a shows the SEM microphotograph of the composite tubular membrane inner surface and it reveals that the synthesized crystalline film has a same homogeneous morphology. Fig. 3b shows an enlarged microphotograph of the same surface and it underlines that this zeolitic layer is probably constituted of many small cube-like interconnected zeolitic crystals formed by a homogeneous nucleation.