



# Hydrogen-selective natural mordenite in a membrane reactor for ethane dehydrogenation



A.M. Avila, Z. Yu, S. Fazli, J.A. Sawada, S.M. Kuznicki\*

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 2V4, Canada

## ARTICLE INFO

### Article history:

Received 31 October 2013  
Received in revised form 10 January 2014  
Accepted 12 February 2014  
Available online 26 February 2014

### Keywords:

Natural zeolite  
Mordenite  
Ethane dehydrogenation  
Membrane reactor  
Ethylene

## ABSTRACT

Lab-scale ethane dehydrogenation experiments with natural mordenite disks in a membrane reactor showed an increase in ethane conversion and ethylene yield compared to their equilibrium values. Experiments performed with larger membrane permeation area confirmed the trend that higher conversions are expected as the ratio of product permeation and product formation rates increases. Using the lab-scale membrane reactor module an ethylene yield enhancement of ~17% was observed at 500 °C. At a higher reaction temperature (550 °C), ethane dehydrogenation experiments resulted in a ~10% ethylene yield enhancement versus ~6% for comparative experiments at 500 °C. At 550 °C the membrane reactor effectiveness improved since the H<sub>2</sub> permeation rate increased proportionally more than its formation rate. This material screening test revealed natural mordenite as a material to be considered in the development of highly-integrated membrane reactor modules for dehydrogenation of alkanes.

© 2014 Elsevier Inc. All rights reserved.

## 1. Introduction

Ethylene is one of the most important petrochemicals in terms of production (156 millions tons in 2012). Ethylene is used as a raw material for producing various polymers such as polyethylene, polyester, polystyrene, polyvinyl chloride and many other intermediate products. Currently, thermal steam cracking is the conventional process technology for ethylene production. Steam-diluted hydrocarbons are decomposed in high temperature cracking furnaces with very short residence time (0.1–0.5 s). The common feedstocks for this process are different grades of naphtha and natural gas components such as ethane and propane. The availability of shale gas nowadays assures that ethane remains the main feedstock for steam cracking in North America.

The dehydrogenation of ethane through thermal steam cracking is an expensive and energy intensive process. Steam cracking process requires high reaction temperatures (800–850 °C) and demands therefore adequate and costly materials and equipment. In addition, because it generates large amounts of coke deposition in the furnace tubes, it requires frequent maintenance. The ethane conversion during steam cracking typically reaches 65–70% and ethylene yield is around 50%. However, further yield improvements are becoming increasingly difficult necessitating the evaluation of new approaches to produce ethylene [1–3].

The membrane reactor concept using inorganic membranes is shown to be a reasonable option for dehydrogenation reactions [4–8]. The dehydrogenation of ethane is endothermic and is limited by the thermodynamic equilibrium. The membrane reactor combines the reaction and separation process in a single step. In this particular reaction, the membrane plays a role as a selective extractor of at least one of the product species. Consequently, the limited-equilibrium reaction is able to shift to the product side.

Despite its potential, there are only few publications dealing with membrane reactor experiments for catalytic ethane dehydrogenation. Champagne et al. [9] reported experiments of a membrane reactor using a tubular ceramic membrane impregnated with 5 wt% Pt and diluted ethane with hydrogen and argon as feed gas. Gobina and Hughes [10,11] used a Pd–Ag membrane supported on a Vycor glass tube to perform membrane reactor experiments using ethane/N<sub>2</sub> 50:50 feed gas mixture and Pt/Al<sub>2</sub>O<sub>3</sub> as catalyst. Another report considered a membrane reactor based on an alumina membrane using Pt–Sn/Al<sub>2</sub>O<sub>3</sub> and a diluted ethane mixture (10% ethane, 5% H<sub>2</sub>, 85% Ar) [12]. All of these previous reports on ethane dehydrogenation using membrane reactors were performed with diluted ethane feeds and as a result, the reported conversions were higher than expected for pure ethane feed at the same reaction temperature. Membranes reactors were also explored for a continuous dosing of O<sub>2</sub> in the oxidative dehydrogenation reaction of ethane. For instance, Lobera et al. [13] used a solid-state oxygen permeable material while Coronas et al. [14] used a porous alumina membrane.

\* Corresponding author. Tel.: +1 780 492 8819; fax: +1 780 492 8958.

E-mail address: [steve.kuznicki@ualberta.ca](mailto:steve.kuznicki@ualberta.ca) (S.M. Kuznicki).

Currently, as process intensification becomes more important there is a need to evaluate new and cost-effective materials capable of taking part in the development of highly compact reactor-separator modules [8]. The application of membrane reactors requires a parallel development of catalyst and membrane materials. The screening tests for membrane materials are required prior to any development step aiming at increasing permeation area. Potential materials to be integrated into membrane reactors require screening and testing experiments in conditions resembling industrial settings. Membrane materials for ethane dehydrogenation should be able to perform at temperatures of 500 °C or higher. Lower reaction temperatures generate low conversion values and thus reduce driving forces across the membrane for product permeation. Material screening methods should consider the parameters affecting the membrane reactor performance. In general, membrane reactor performance has been associated with the Damkohler and membrane Peclet numbers. The Damkohler number is related to the catalyst activity and the Peclet number to the permeation rate characteristics [6,15].

Natural zeolite membranes have shown permselectivity properties in the separation of hydrogen from carbon dioxide and hydrogen from ethane [16,17]. Natural zeolite materials, especially clinoptilolite and mordenite have greater thermal stability and better resistance to harsh chemical conditions than many common commercial synthetic adsorbents [18]. These properties make natural zeolites materials of great interest for testing and integration into a membrane reactor device for ethane dehydrogenation reaction. Natural mordenite is one of the most siliceous natural zeolites. The mordenite framework contains three sets of intersecting channels (A, B, C). The channels A and B are parallel to the *c*-axis and channels C are parallel to the *b*-axis. The channels A are formed by larger, ellipsoidal 12-membered rings (12MRC aperture  $0.70 \times 0.65$  nm) and by strongly compressed 8-membered rings (8MRc aperture  $0.57 \times 0.26$  nm). The C channels are also formed by eight-membered rings (8MRb aperture  $0.38 \times 0.48$  nm) and they link the larger 12MRC channels to the much smaller 8MRc channels. There is no straight connection between the adjacent 12MRC channels. Thus, mordenite behaves as a one-dimensional channel system for diffusion of relatively large molecules. In particular, it has been reported that natural mordenites have adsorption characteristics corresponding to a small-pore mordenite [19–23]. Thus, the transport of small hydrocarbons are hindered within the zeolite pores in comparison to the faster diffusing H<sub>2</sub> molecules.

The objective of the work presented here is to evaluate natural mordenite membrane disks in a membrane reactor used for the dehydrogenation of ethane. A material-screening membrane reactor was generated using Pt/Al<sub>2</sub>O<sub>3</sub> beads as catalyst and membrane disks coupled to the reaction zone. Outlet molar fractions of reaction species were monitored continually as the reactor system changed between a reactor and membrane reactor mode in situ. The integral mass balance of species as a reactor and membrane reactor mode was considered for the quantification of the reaction rate enhancement. The membrane reactor effectiveness of each experiment was evaluated based on dimensionless numbers that were defined accordingly. The effects of increasing permeation area and reaction temperature were studied comparatively.

## 2. Experimental

### 2.1. Catalyst

The catalyst used was 1 wt% Pt, 0.3 wt% Sn supported in Al<sub>2</sub>O<sub>3</sub> beads (Alfa Aesar®). The catalyst bead size ranged between 1 and 2 mm. This catalyst was selected after performing activity tests

on different catalysts: Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, 1 wt% Pt/Al<sub>2</sub>O<sub>3</sub> and 1 wt% Pt – 0.3 wt% Sn/Al<sub>2</sub>O<sub>3</sub>. The selected Pt–Sn/Al<sub>2</sub>O<sub>3</sub> catalyst showed the highest activity for ethane dehydrogenation at 500 °C.

### 2.2. Membrane preparation

Natural mordenite membrane disks were prepared from rock material (Paradise Quarry Limited-New Zealand) by sectioning using a diamond saw. Table 1 shows the chemical composition provided by the supplier. Membrane size was 19 mm in diameter, and 1.5 mm in thickness. The discs were polished with a diamond polishing lap (180 mesh, Fac-Ette Manufacturing Inc.) followed by washing in an ultrasonic bath for 30 min. Membrane disks were activated at 750 °C for 4 h before use.

### 2.3. XRD and SEM characterization

Membrane disks were characterized by X-ray diffraction analysis (XRD) (Rigaku Geigerflex 2173 with a cobalt Co K $\alpha$  radiation source ( $\lambda = 1.79021$  Å) and by scanning electron microscopy (SEM) (Hitachi S2700 equipped with an X-ray EDS detector). XRD patterns for membrane disks treated at different temperatures (25, 550, 650 and 750 °C during 4 h) showed no significant changes which reflect an adequate thermal stability of the material (Fig. 1). SEM images (top and cross-sectional view) of the natural mordenite membrane disks are shown in Fig. 2.

### 2.4. Membrane permeation tests

The membrane disks were tested using a stainless steel cell and sealed with silicone gaskets. The feed and permeate sides each had a stainless steel tube-shell configuration with an inlet gas flowing through the 1/4" inside tube and an outlet gas flowing through the shell between the 1/4" inside tube and 1/2" outside tube [15]. Single gas permeation of hydrogen and ethane were measured at temperatures ranging from 298 to 473 K and feed pressure of 122.0 kPa. Ethylene permeation was measured at 298 K. Argon was used as a sweep gas for the permeate side. The feed side pressure was controlled by a back pressure regulator and the permeate side was kept at ambient pressure. The flow rate of the feed side and the flow rate of the sweep gas (Ar) were kept at 100 mL/min (STP) and 100 mL/min (STP) respectively, throughout the measurements.

**Table 1**  
Chemical composition of natural mordenite (provided by the supplier).

Compound	Weight %
LOI*	15.36
Na <sub>2</sub> O	1.60
MgO	0.568
Al <sub>2</sub> O <sub>3</sub>	9.382
SiO <sub>2</sub>	56.42
P <sub>2</sub> O <sub>5</sub>	0.115
SO <sub>3</sub>	0.0796
K <sub>2</sub> O	0.70
CaO	12.24
TiO <sub>2</sub>	0.269
Cr <sub>2</sub> O <sub>3</sub>	0.0035
MnO	0.0715
Fe <sub>2</sub> O <sub>3</sub>	2.49
NiO	0.0034
CuO	0.0038
ZnO	0.0078
Rb <sub>2</sub> O	0.0015
SrO	0.0401
Y <sub>2</sub> O <sub>3</sub>	0.0052
ZrO <sub>2</sub>	0.011

\* LOI = loss on ignition at 950 °C for 1 h.

Download English Version:

<https://daneshyari.com/en/article/6533325>

Download Persian Version:

<https://daneshyari.com/article/6533325>

[Daneshyari.com](https://daneshyari.com)