PERGAMON

Chemical Engineering Science 54 (1999) 1997–2017

Chemical Engineering Science

High-temperature membrane reactors: potential and problems

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Abstract

The most recent literature in the field of membrane reactors is reviewed, four years after an analogous effort of ours (Saracco et al., 1994), describing shortly the potentials of these reactors, which now seem to be well established, and focusing mostly on problems towards practical exploitation. Since 1994, progress has been achieved in several areas (sol–gel deposition of defect free sol–gel derived membranes, reduction in thickness of Pd membranes, synthesis of zeolite membranes) whereas stagnation was noticed in some others (high-temperature sealing of membranes into modules, scaling-up of membrane reactor, etc.). As a result, despite the still increasing research efforts, industrial application does not seem to be round the corner, yet. However, several non-permselective membrane reactor opportunities with currently available membranes might pave the way for more sophisticated applications.

Keywords: Inorganic membrane reactor; Catalysis

1. Introduction

There has been a flourishing reviewing activity in the field of inorganic membrane reactors in recent years (e.g. Tsotsis et al., 1993; Saracco and Specchia, 1994, 1998b; Saracco et al., 1994; Armor, 1995; Dalmon, 1997). Almost an entire book was even dedicated to this topic (Hsieh, 1996), a clear sign of the massive interest of the scientific community in this topic. Most reviews were primarily aimed at showing the remarkable potential of membrane reactors, stressing possibilities and application opportunities and critically assessing the open literature. Today, the potential of membrane reactors is rather well assessed and as clear as the technological gap that still has to be filled in order to achieve industrial practice. This survey is therefore mainly focused on hurdles still standing on the way to large-scale application. However, new opportunities, much closer to viability, will also be considered.

Table 1 lists the major challenges for the success of inorganic membranes pointed out in 1994, together with a qualitative assessment of the progress achieved in the meanwhile. The present communication will try to elucidate and quantify such progress and to identify the major issues still needing further research efforts. Three major areas of applications will be addressed, namely:

(1) *Yield-enhancement of equilibrium-limited reactions*: a reaction product is selectively permeating through the membrane, thereby enhancing the per-pass conversion compared to conventional fixed-bed reactors (e.g. for dehydrogenations, Fig. 1a); coupling of reactions at opposite membrane sides has also been envisaged in this context (Fig. 1b);
(2) *Selectivity enhancement*: accomplished by selective permeation (Fig. 1c) or controlled addition (Fig. 1d) of a reactant through the membrane;
(3) *New emerging application opportunities*: a number of potential applications (membrane reactor with separate feed of reactants, catalytic filters and traps, slurry membrane reactor, etc.) were recently investigated, which do not require membrane perm-selectivity to gases and therefore appear to be closer to industrial success.

Polymeric membranes, often applied in bioreactor or liquid-phase applications (e.g. Gao et al., 1995), will not be considered hereafter. However, it is worth mentioning

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0009-2509/99/$ – see front matter
PII: S0009-2509(99)00009-3

Table 1
Major challenges in the development of inorganic membrane reactors

Field/challenges	Progress from 1994	References
Materials science		
Synthesising defect-free and homogeneous membranes having pores of molecular dimensions (<10 Å).	+	Kapteijn et al. (1995), Coronas et al. (1998) and deVos and Verweij (1998)
Reducing the membrane thickness ($\ll 10$ μm) so as to keep gas permeation acceptable.	+	deVos and Verweij, 1998
Reproducing the above results on large scale membranes.	−	Verweij (1998)
Addressing problems of brittleness for both ceramic and Pd-alloy membranes.	+	Shu et al. (1995) and Jeema et al. (1996)
Developing relatively cheap high-temperature sealing systems.	−	no particular progress since Velterop (1991)
Finding new materials with better properties than Pd, γ-Al_2O_3, Vycor glass, …	±	Balachandran et al. (1995) and ten Elshof et al. (1995)
Catalysts science		
Developing new membrane catalysts less sensitive to poisoning or coking.	±	Edlund and Pledger (1994)
Getting a better control of the catalytic activation of ceramic porous membranes.	+	Yeung et al. (1994), Vitulli et al. (1997) and Szegner et al. (1997)
Chemical engineering		
Understanding and modelling highly-selective transport mechanisms.	+	Krishna and van den Brooke (1995), Shelekin et al. (1995) and van den Graaf (1998)
Increasing the membrane area per unit volume.	+	Smid et al. (1996)
Developing complex modelling for large scale membrane reactor modules.	−	Perhaps it is too early to expect this, yet.
Developing technologies for heat supply and temperature control in large scale modules.	−	See above
Developing criteria for the choice of the optimal size of membrane reactors, of the flow patterns and of the number of stages/recycles/intermediate feeds.	−	See above

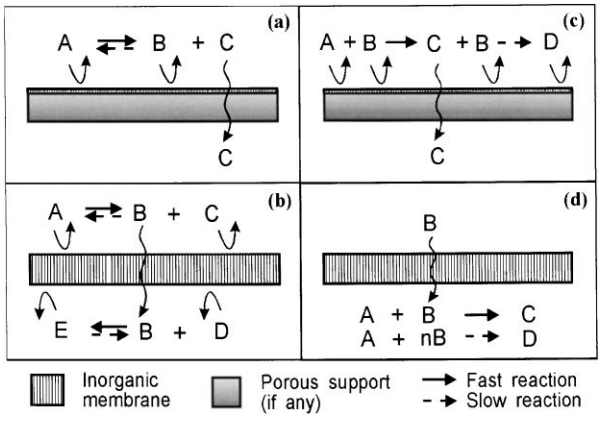

Fig. 1. Prevalent application opportunities of inorganic membrane reactors. Conversion enhancement with catalytic membrane reactors: (a) selective permeation of a reaction product of an equilibrium limited reaction; (b) coupling of reactions. Selectivity enhancement with catalytic membrane reactors: (c) selective permeation of an intermediate, desired product; (d) dosing a reactant through the membrane.

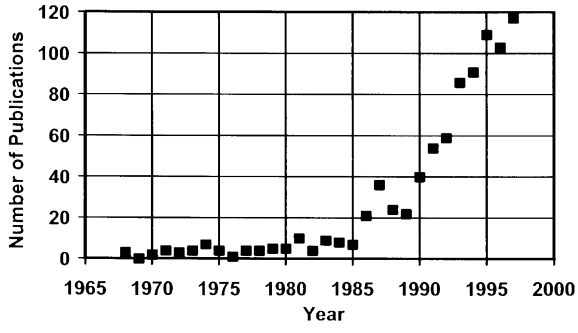

Fig. 2. Variation of the number of publications per year on catalytic membrane reactors since 1965 included in the Chemical Abstracts database.

that polymeric membranes (mostly based on polyimides) are currently being considered for application in reactors with gas-phase reactions at temperatures up to 300°C (Tröger et al., 1997).

Our paper is based on a database search, whose results are worthwhile commenting. For all years from 1965 to 1997, the Chemical Abstracts library was checked with the following keywords: CATALYTIC and MEMBRANE and REACTOR. The obtained number of publications per year was plotted in Fig. 2 vs. the year itself. The results enlighten a remarkable increase in the last decade which does not seem to have reached its peak, yet. From the authorship of these papers, it is clear that the membrane-reactor research community is not only