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Preparation and Development of Porous Ceramic Membrane Supports Fabricated by Extrusion Technique

Pengmeng Fan[a, b], Kunfan Zhen[b], Zhongyang Zan[c], Zhang Chao[b], Zhang Jian[b], Junzhang Yun*[a]

[a] Key Laboratory for Liquid-Solid Structural Evolution & Processing of Materials of Ministry of Education, Shandong University, Jinan 250061, China;
[b] Shandong Guiyuan New Material CO, Ltd, Zibo 255086, China;
[c] Shandong University of Technology, Zibo 255000, China
yujunzhangcn@sdu.edu.cn

Ceramic membranes have been widely used in petroleum-chemical industry, food industry and pharmaceutical industry due to several characteristics such as high thermal and chemical stability, high filter precision, chemical resistance, and mechanical strength. Porous ceramic membrane supports are the essential part of ceramic membranes. A survey of the main preparation techniques of porous ceramic membrane supports and their characteristics was introduced in this paper. Emphasis was placed on the mechanism of the response of the support structure and performance to various technical parameters in the extrusion forming process, such as extrusion process, raw materials, additives, and sintering. In addition, the present technical issues to address and the development trends of porous ceramic membrane supports were also proposed herein

1. Introduction

Ceramic membranes emerge in recent years as a novel inorganic membrane material, which is prepared specially with inorganic materials such as $A1_2O_3$, ZrO_2, TiO_2 and SiO_2. Compared to organic membranes, ceramic membranes are featured by high thermal and chemical stability, easiness to rinse, regeneration and so on, and thus enjoy widespread application in fields of petroleum-chemical industry, food industry and pharmaceutical industry, for example (Mallada and Menendez, 2008; Bolduan and Latz, 2000; Hong and Yang, 2011; Xu et al, 2003; Debruijn et al, 2003; Jorge et al., 2015). Currently, most ceramic membranes are prepared as multi-layer asymmetric compounds, for which the sol-gel method is used to process the surface of supports so that being loaded with gradual porous transition layer and separation layer. The preparation of supports as the basis for organic membranes costs about 2/3 of the grand sum. The preparation quality is directly related to the industrialized production of inorganic membranes. In recent years, domestic and foreign companies like the DOW Chemical Company and Jiangsu Jiuwu High-tech Company have already released their ceramic membrane products on the market. Corresponding support preparation techniques are strictly confidential for the sake of their commercial interests. Given the importance of supports in the entire membrane performance and preparation cost, support itself and its preparation are a key factor of preparing and using cost-efficient inorganic ceramic membranes. In this connection, the paper intended to detail and summarize main support preparation techniques as well as its influencing factors.

2. Structural characteristics of porous ceramic membranes and requirements of support properties

As brittle thin films, porous ceramic membranes can only resist external forces generated by high-speed feed flow when they are loaded on strong porous supports. According to the diagram in Figure 1, a porous ceramic membrane is largely an asymmetric structure that is composed of support, transition layer, and membrane (Falamaki, 2004). The support provides the basis for membrane preparation and operation. To a great extent,

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membrane flux is controlled by parameters of support thickness, pore size, pore ratio, pore distribution and so on. Moreover, support properties such as wettability, flatness and smoothness impact on membrane quality, which further affects membrane performance. Therefore, apart from mechanical strength, it is a must for supports to satisfy some other performance requirements (Shqau et al, 2006) :(1) high pore ratio (30%), large average pore size (1-15 μm), and dense distribution; (2) high structural stability in the face of filtration of hot media, acids, and bases; (3) smooth and flat surface, uniform wettability; (4) parameters of chemical property, thermal expansion coefficient, and pore size.

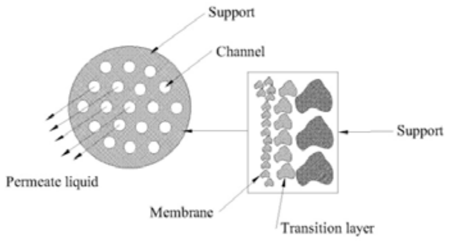

Figure 1: Schematic of the Porous Ceramic Membrane (Falamaki, 2004)

3. Major preparation methods for ceramic membrane supports

The major preparation methods for ceramic membrane supports contain slip casting, dry pressing, and extrusion forming. Each of them has its own merits and demerits. The first two approaches are mostly used for laboratory study, whilst the extrusion forming method has already been prominently applied to industrialized manufacturing.

3.1 Slip casting

Slip casting is a simple, flexible molding technology. Slurries with high solid content and good mobility are poured into cast molds, in which capillaries suck solvents until the body presents certain strength. After demolding, the body of certain thickness is sintered, which is the last process to yield an end product. The key point is slip control. A solid layer should instantly form on the contact surface between the slip and the cast mold, so that preventing the aggregate from penetrating into the mold. Support performance is closely linked to various parameters such as initial particle size, binder content, additive types and content, temperature and time of firing (Das and Maiti, 1998). Zhang et al., (1998) designed a new slip casting process of melting the inner mold core and separating the outer mold. The ceramic membrane supports they developed can be directly used in microfiltration, overcoming the shortages of demoulding difficulties, body cracking, and body deformation. With the centrifugal slip casting method, He et al., (2001) researched into factors such as pore-forming agent and sintering temperature, and accordingly prepared a yttria stabilized zirconia (YSZ) porous ceramic tube with high porosity (49.0%-64.1%). Tong et al., (2013) studied the effects of the amount of pore-forming agent, high temperature binder, sintering additive, and sintering temperature on properties of support, based on which a tubular Al_2O_3 ceramic membrane support was prepared. A higher-level slip casting improves the properties of porous ceramic membrane supports. However, multi-channel support preparation is beyond its scope. In light of other limitations such as the difficulty to control slips or pore size, pinhole problem as well as cracking, this process is seldom applied to industrial manufacturing.

3.2 Dry pressing

For this method, a fixed proportion of binder, pore-forming agent, mineralizer and the like (usually blunged well) is poured into a metal mold. After being punched or semi-punched in a given temperature, the mixture is sintered according to a certain sintering procedure. Ding et al., (2008) used dry pressing for preparation of support template, during which the influence of the initial particle size on support performance was studied. Li et al., (2012) prepared circular plate-shaped porous ceramic membrane supported by dry pressing and solid sintering. The support is with porosity above 34%, pore size between 2.26 and 6.75 μm, and the degree of acid/alkali resistance over 98%. Dry pressing is an ideal approach for preparing support template. However, its failure to prepare large-area tubular supports limits it largely to laboratorial studies.

3.3 Extrusion forming

This is the most convenient way to prepare multi-channel ceramic supports. The mixture of powder aggregate and a given amount of additives undergo vacuum smelting and aging. Then, it enters the vacuum extruder and extruded into tubular supports with fixed cross-section shapes under pressure (Figure 2). This method is allowed application to industrial scale production. The performance of supports obtained in this way rests on parameters such as powder composition, binder, additive and sintering procedure (Zhang et al, 2006; Yang and Tsai, 2008; Mongkolkachit et al, 2010). Li et al., (2012) introduced the preparation method of 19-channel hexagonal alumina support for ceramic membrane using extruding technique. The effect of particle diameter of raw material, the binder content and sintering temperature on the support was detailed by them. Isobe et al., (2007) used extrusion forming technique to prepare a multi-channel tubular alumina support, and analyzed the effect of additives on preparation techniques. Extrusion forming has been used to manufacture industrial products of various specifications by some companies and institutes, including Nanjing Tech University, the Membrane Institute under the University of Science and Technology, and Jiangsu Jiuwu Technology Company. Such industrial expansion is a great promotion to the development of domestic multi-channel inorganic membrane supports (Meng et al, 2011).

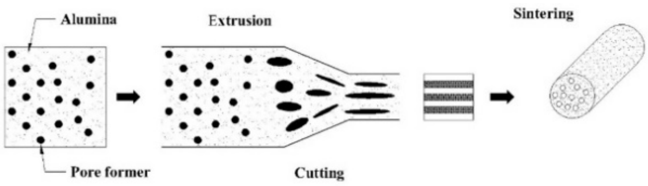

Figure 2: Schematic of the extrusion

4. Major factors influencing preparation of ceramic supports by extrusion forming technique

The low-cost technique of extrusion forming is deemed as the most suitable one among all ceramic forming techniques to produce products of constant cross sections. Nevertheless, during the complicated extrusion process, plenty of factors may affect product performance, such as technique parameters, raw materials, binders, and sintering additives. Therefore, it is necessary to discuss technique conditions required for ceramic support preparation as well as their influencing factors.

4.1 Impacts of extrusion techniques on preparation of ceramic supports

In actual production processes, the quality of body responds greatly to procedure parameters including the velocity of extrusion forming, pressure, rheological characteristics of the paste, etc. Under improper control, the body may easily distort, deform, crack or have uneven density, as shown in Figure 3. To address these problems, massive studies have been undertaken on the extrusion process, represented by the Benbow & Bridgwater (1993) model and its formula to anticipate the extrusion pressure of slips with high-content solid phase. Cai et al., (2006) analyzed the forming process, measurement methods and influencing factors in relation to screw extrusion pressure. Based on the phenomenon that the extrusion forming cracks are always perpendicular to the extrusion direction of ceramic pastes, they deducted the theoretical expression of extrusion pressure without cracks. Domantia et al., (2002) conducted systematic research on the relationship between residue stress area, die-entrance angle, extrusion rate and body surface breakage. Their theoretical proposal of the standard to predict surface damage provided basis for body quality control. Zhao (2009) used FLUENT software to numerically simulate ceramic paste of screw reamer, so that obtaining the flow characteristics and movement mechanisms of ceramic paste extruded. What is more, the relationship between velocity, pressure distribution and productivity was also expounded by them. Through a test, Kulikova Hornungb (2011) quantitatively analyzed the causes to tear failure or sharkskin-style cracks on the support surface. They further installed thin and long mold lining to mitigate surface deficient (Figure 3).

4.2 The influence of powders on preparation of ceramic supports

The pore-forming mechanism for porous ceramic supports is particle stacking, for which different particle sizes, particle size distribution modes and powder morphologies require different stacking methods. The stacking form affects particle formation significantly, and further impacts on support density, its pore distribution and mechanical strength. Existing commercialized ceramic membranes at home and abroad are mostly made from alumina. The common raw material for preparation of ceramic membranes is spherical mono-dispersive alumina with an average particle size of 30 um which is synthesized hydrothermally (Hsieh, 1996; Seyed et al., 2013). Limited by powder preparation technologies, rod-like or sheet alumina powders are usually used as the starting material in China. Figure 4 is SEM images of Al_2O_3 porous support prepared by different alumina powders. Ding et al., (2008) prepared ball-like alumina particles for extrusion use by spray granulation, and ascertained that a support may have high porosity, narrow pore size distribution, smooth surface, and whole evenness with the use of regular ball-like particles, benefiting control on ceramic membrane thickness. Li et al., (2011) used the extrusion forming technique to prepare AL_2O_3 ceramic membranes. According to their findings, under the same preparation conditions, support porosity responded little to the initial powder size but much to powder particle stacking mode. Control on the initial powder size is one of the effective ways to control support pore size, because the former one influences supports remarkably. Ding Guanbao et al. used three alumina materials with medium particle diameter D50 of (20±2) μm, (15±2) μm, (10±2) μm to prepare supports (Ding et al, 2008). In their investigation on the influence of the change of particle size distribution parameters on support pore structures, they indicated that as the parameter increased, the pore size distribution narrowed, and the most probable distribution peak mounted up, accompanied by peak moving to the direction of small pore size. Zhou et al., (2016) employed another three alumina powders (with ball-like wide pore size distribution, ball-like narrow pore size distribution, and ellipsoidal pore size, respectively) for preparation of porous supports. According to the observation result of the influence of powder particle parameters (shape and particle size distribution) on the mechanical performance, micro-structure and permeability of supports, the optimal comprehensive performance was obtained from supports prepared by ellipsoidal alumina aggregate.

4.3 The influence of binders on preparation of ceramic supports

The quality of matrix tubes prepared by extrusion technique is controlled by a large number of factors, among which physical material performance is the key one. For lean materials likeα-Al_2O_3, TiO_2, binders are often required in order to improve its mobility and stability. The type and content of binders exert significant influence on both extrusion techniques and support performance. Tong et al., (2016) studied the content of CMC on support performance. For supports with CMC of 4% mass percent, the porosity is 31.85%, the pure water flux is 5107.68 L/(m^2·h·MPa), the flexural strength is 104.429 MPa, and the mass loss due to respective acid and alkaline corrosion is 0.88% and 0.92%. Based on talc river system, Trbischel and Emrich (1946). used extrusion forming technique to evaluate the impact of five binders on support performance (Table 1). Through research, Zhang et al., (2006) concluded that PVA binder at the liquid state can better optimize alumina support performance than at the solid state, and that its usage amount exerts a direct influence on the support performance including pore size distribution, porosity and binding strength. In recent years, with the double roles as binders and sintering additives, inorganic AlOOH has received widespread attention in preparation for alumina ceramics. Ananthakumar et al., (2004) used boehmite gel as the binder to compare the respective responses of support performance to boehmite gel, the mixture of boehmite gel and additives (PVA, PEG, glycerinum) and HPMC. Finally, they acquired the recipe of ceramic pastes with good mobility and that can form under low pressure.

Table 1: Effect of the different binders on the support

Binders	Wet Strength	Water Retention During Extrusion	Extrusion Characteristics	Modulus of Rupture
flours, starches	better	fair	good	fair
gums	best	good	better	better
alcohols and ellulose	best	better	better	best
wood extracts	good	poor	poor	fair
alginates	poor	best	best	good

4.4 The influence of sintering additives on preparation of ceramic supports

To ensure high support permeability, the ceramic support on the market is mostly made from >99% Al_2O_3, which is sintered at a temperature of more than 1750°C with highly pure 20~30 μm Al_2O_3 as the raw material. However, this sintering process poses high demand to kiln equipment. What is more, due to high energy consumption in the sintering process, the supports produced in this way is costly. Given this, it is a matter of urgency to develop suitable sintering additives which can endow the output with superior performance at the same time when require lower sintering temperature. The frequently-used sintering additives (Y, Ti, Si, for example) for industrial use lower down the anti-corrosion behavior of ceramic membranes to a certain degree.

Over the past few years, some research focuses of sintering temperature reduction lie on the adoption of homogeneous nanometer or modified powder surface. For instance, according to research findings of Huang et al., (2011), the 5wt.% nano-aluminium hydroxide gel as the additive of highly pure alumina membrane support can drop the sintering temperature from 1580°C to 1350°C. Qi et al., (2010), Hu et al., (2009) coated the 22 μm alumina with 0.5 μm α-Al_2O_3 via heterocoagulation process. The support CS sintered at 1550 °C exhibited higher strength and permeability as follows: a bending strength of 34.2 MPa, a porosity of 34%, an average pore size of 2.34 μm, and a pure water flux of 205 m^3/(m^2·h·MPa). A.Kritikaki et al., obtained ceramic supports of different performances by use of two kinds of sintering additives: nano powder and gel. Their research result showed that if the sintering additive was added to the spray-dried supports in the form of gel, the finished product would be stronger with less irregular pores.

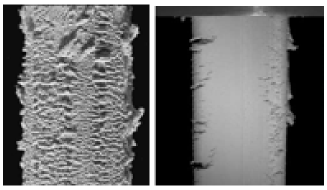

Figure 3: The common defects in extrusion process (Hsieh, 1996)

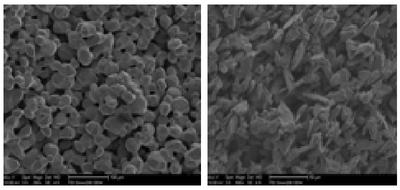

Figure 4: SEM images of Al_2O_3 porous support prepared by different alumina powders: (a) ball, (b) plate

5. Conclusion

Currently, abundant theoretical achievements and engineering experience have been accumulated in China with regard to several aspects of ceramic membrane supports, such as microstructure control, procedure control and design, corrosion resistance, durability, and cost reduction. Despite these powerful bases in ceramic membrane application, there remains the following gaps compared to foreign countries.

(1) Development of powder preparation technology fitting for ceramic membrane supports: powder types, particle size, and particle size distribution are still the key to preparation of porous ceramic supports of superior performance. Some corporations that have launched research on such powders though fail to produce powders with ideal parameters (morphologies, particle size distribution). Porous ceramic membranes with current powders cannot perform much better than before. Given this, a key factor of the quality enhancement of future ceramic supports rests on whether high-quality powders can be developed or not.

(2) Discussion of mechanism between extrusion parameters and extruded bodies: to facilitate support paste extrusion, manufacturers universally adds plenty of additives such as binders, plasticizers, oily anti-cracking agents and pore-forming additives. This measure gives rise to deficiencies brought by the dry stage and the sintering stage as well as prolonged production span. Therefore, how to adjust the proportions of organic additives and extrusion parameters so as to extrude pastes of higher hardness smoothly is a crucial research perspective.

(3) Research on highly pure α-Al_2O_3 low-temperature sintering process: the sintering cost occupies around 2/3 of the grand sum. Therefore, one follow-up research focus should be a recipe system that can produce ceramic membrane supports with good resistance to acid-alkaline corrosion, and the other should be thermal transmission mechanism of the sintering equipment and fast-ejection fast-sintering technology.

The preparation technology of ceramic membrane supports is the pillar of the development of the porous ceramic membrane industry. The paper conducted a comprehensive review of the impact mechanism of extrusion process, raw materials, additives and sintering process on ceramic membrane support structures and its performance during extrusion forming, with an attempt to provide certain reference and basis for preparation of cost-efficient supports.

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