

Original papers

PREPARATION OF ALUMINA MEMBRANES
FOR MICROFILTRATION

PAVEL FELLNER, MIROSLAV HAVIAR*, MARIÁN KOMAN, MARTA CHOVCANOVÁ

*Department of Inorganic Technology, Slovak Technical University, Radlinského 9, 812 37 Bratislava
Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta, 842 36 Bratislava

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Porous α -Al₂O₃ ceramics for microfiltration membranes can be obtained by calcination of Al(OH)₃ in the temperature interval 1150–1400° C followed by milling and sintering. Calcination at 1150° C provides Θ -Al₂O₃ whose sintering leads to approx. 8 % higher porosities comparing to α -Al₂O₃. Milling of calcined powder has significant influence on decreasing of the mean pore size which is accompanied by the 20–25 % decreasing of porosity.

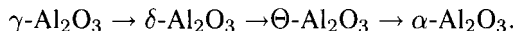
INTRODUCTION

Recently there is an increasing demand for using of inorganic membranes for filtration purposes. For microfiltration (pore size 0.1 to several μm) mainly alumina membranes are used and current research is focused on ultrafiltration membranes (pore size 1 to 10 nm). The selected properties of ceramic membranes are exploited at the separation in food industry (purification of various drinks, separation of milk), in waste water cleaning. Use of these membranes in separation of gases in bioreactors is tested.

The principal advantage of ceramic membranes comparing with polymer ones, which are used for years in praxis [1] is their thermal and chemical stability. This allows the membranes to work at higher temperature and because of lower viscosity at higher temperature to increase the efficiency of the filtration process. With certain applications also their chemical stability against non aqueous solvents in wide pH range is beneficial. The tube modules, which are advantageous for efficient filtration can be easily fabricated and such membranes can work for up to 5 years.

In connection with the use of ceramic membranes also their main disadvantage, that is higher price should be discussed. This depends on the type of membrane, but is typically ten times higher comparing to polymer membrane. Second disadvantage is their brittleness, specially in the case of thin tube membranes. This is also the reason for construction of more complex membranes where the body with higher strength and larger pore size is covered with the layer of fine-pore material. Special field is the production of ultrafiltration membranes where the long term stability and permeability should be improved.

Calcination of Al(OH)₃ is a complex and intensively studied process. Toropov et al. [2] have described the phase transformation sequence as



Iler [3] suggests that the transformation $\Theta\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ requires the presence of transient liquid phase. McLeod [4] describes various possibilities at the decomposition of Al(OH)₃. These are depicted in Fig. 1. The way *a* is favoured by increased pressure, higher humidity, higher heating rate ($>1^\circ\text{C}/\text{min}$) and for

the grain size over $100\mu\text{m}$. It is obvious that various calcination conditions will provide various Al_2O_3 powders with various morphology and sintering behaviour.

The aim of the present paper is to discuss the preparation of $\alpha\text{-Al}_2\text{O}_3$ membranes for the purification of waste water from galvanic plants.

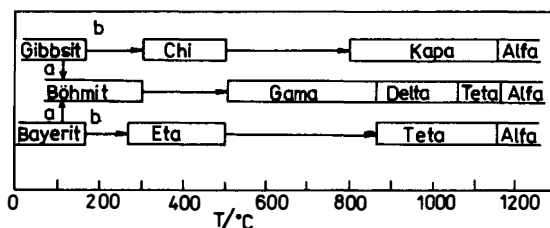


Fig. 1. Schematic diagram of the decomposition of $\text{Al}(\text{OH})_3$ after McLeod [4].

EXPERIMENTAL

The properties of ceramic membranes depend first of all on the powders used for their preparation. Aluminum oxide, used for preparation of the membranes was prepared by the calcination of aluminum hydroxide. This was prepared by the calcination of aluminum hydroxide. This was prepared by the precipitation of sodium aluminate by the carbon dioxide. The quality of the product is significantly controlled by 6 parameters:

- concentration of sodium aluminate,
- the way and amount of CO_2 entering the reactor,
- reaction temperature,
- duration of the reaction and of the product storing,
- the filtration and washing-out procedure,
- surface activation, if any.

The reaction medium can be varied by the partial or total substitution of water by alcohol. All these aspects are discussed in details in [5–8].

For the preparation of starting $\text{Al}(\text{OH})_3$ wide spectrum of experimental conditions was tested. It was found, that suitable product can be in laboratory scale prepared by following procedure:

The reactor with diameter of 10 cm contained 600 cm^3 of sodium aluminate solution, having concentration $50\text{ g} \cdot \text{dm}^{-3}$. Carbon dioxide was introduced by the two jets ($\Phi = 1\text{ mm}$) located 2 cm over the bottom with the volume speed $50\text{ dm}^3 \cdot \text{h}^{-1}$. The temperature was held at 25°C . The reaction mixture was intensively mixed by the paddle mixer (300 rpm). After approx. 15–20 min of introducing CO_2 aluminum hydroxide began to precipitate, while pH decreased from the value of 12 to 10. After ceasing of $\text{Al}(\text{OH})_3$ precipitation (approx. 20 minutes after beginning of precipitation) the solid phase was separated by the S4 frit. Obtained aluminum hydroxide was washed in distilled water. The product was dried on the frit and later in the dryer at 120°C .

After drying the $\text{Al}(\text{OH})_3$ powder was milled in agate mortar and calcined in the chamber furnace Netzsch at temperatures of 1150–1400° C. Milling of the calcination product was performed in agate planetary mill for 60 min. The pellets with $\Phi = 12$ mm and 3 mm height were pressed using the pressure 100 MPa in steel double acting die before sintering. The porosities of these were in the range 50 to 70 vol %. The pellets were sintered in a platinum wound tube furnace at the temperatures of 1300 to 1450° C with various dwells at working temperature. The porosities of sintered pellets were measured in Carlo Erba 1500 porosimeter, microstructure was observed in Tesla 400 scanning electron microscope.

RESULTS AND DISCUSSION

Morphology of the starting $\text{Al}(\text{OH})_3$ can be seen from Fig. 2. The first sample was calcined at 1300° C for 60 min. Result of the calcination was $\alpha\text{-Al}_2\text{O}_3$ labeled as A1 having specific surface $4.94 \text{ m}^2 \cdot \text{g}^{-1}$. Its morphology is shown in Fig. 3. Parameters of the microstructure of the powder A1 sintered at 1400° C for 60 minutes are given in Table I. It is clear that this porous material has high porosity, but unfortunately also high mean pore size (maximum in the pore distribution function). The sintering process did not cause significant neck growth what is indicated by the very low decrease of specific surface to $4.44 \text{ m}^2 \cdot \text{g}^{-1}$. Corresponding grain size (assuming spherical shape of the grains) is $0.31 \mu\text{m}$ and this is in agreement with the grain size determined from Fig. 3. In the sintered body having approx. 50 % porosity and narrow range of coordination numbers of the powder particles the mean pore size should be approximately equal to the mean grain size. In the case of the sample sintered from powder A1 this assumption is fulfilled (0.23 resp. $0.31 \mu\text{m}$). Particles in the powder A1 form clusters (Fig. 3) which consist of great number of grains. The existence of these does not influence the space distribution of the grains in the pellet and we can conclude that they are destroyed during pressing.

Table I
Porosity parameters of the powder A1 calcined at 1300° C for 60 min

Sintering temperature $t/^\circ\text{C}$	Dwell time τ/min	Specific surface $S/\text{m}^2 \cdot \text{g}^{-1}$	Porosity	Mean pore size r/nm
1400	60	4.44	0.612	232

The powder A1 was (with the intention to decrease the mean pore size) milled 60 min in the planetary agate mill. The obtained powder, labeled as A2 had specific surface $8.25 \text{ m}^2 \cdot \text{g}^{-1}$. Its morphology is shown in Fig. 4, the parameters of microstructure are in Table II and the microstructure of the sintered pellet can be seen from Fig. 5. The microstructure is porous and relatively homogeneous, the sample consists of approx. equal sized grains.

The milling had significant influence on the sinterability of the powder, which resulted in lower porosities comparing with powder A1. The mean pore size was also significantly decreased from approx. 230 to 80 nm. It seems reasonable that

except of aggregates also the grains with more complex shape were destroyed (compare Figs 3 and 4). The increasing temperature and temperature dwell results in decreasing of porosity and specific surface, however, this is not very important. The influence of increasing temperature on the decreasing of porosity is in accordance with increasing role of sintering mechanisms, contributing to shrinkage in the sintering process [9, 10].

Table II
Porosity parameters of the powder A2 calcined at 1300° C for 60 min and milled for 60 min

Sintering temperature $t/^\circ\text{C}$	Dwell time τ/min	Specific surface $S/\text{m}^2 \cdot \text{g}^{-1}$	Porosity	Mean pore size r/nm
1400	30	4.03	0.342	78
1400	60	3.51	0.326	78
1450	30	3.06	0.284	77
1450	60	2.46	0.211	76

From the results in Table II it follows that sintering process does not have significant influence on porosity parameters at temperatures lower than 1450° C. This depends, first of all, on the morphology of the Al_2O_3 grains which are formed during calcination process.

Messing [11] observed that addition of $\alpha\text{-Al}_2\text{O}_3$ nuclei to the $\Theta\text{-Al}_2\text{O}_3$ powder significantly increases the shrinkage kinetics. The nucleation is thus the rate limiting step in the sintering process. Because shrinkage of the sintering system is not desired process during preparation of porous bodies, the starting aluminum hydroxide was calcined at 1150° C for 60 min. The result was $\Theta\text{-Al}_2\text{O}_3$ powder, labeled as A3. The parameters of the microstructure, obtained by the sintering of this powder are in Table III. These samples show, comparing to the samples obtained by sintering of powder A2 higher mean pore size (120 vs. 80 nm) as well as higher porosities (in the range 40 vol%). From the fact that there is an increase in the mean pore size while the total porosity does not decrease significantly during the sintering process we can conclude that the grain growth process is more active than densification. This suggests higher rate of surface diffusion during sintering of $\Theta\text{-Al}_2\text{O}_3$, which is in agreement with the works of Iler [3] and Messing [11].

Table III
Porosity parameters of the powder A3 calcined at 1150° C for 60 min and milled for 60 min

Sintering temperature $t/^\circ\text{C}$	Dwell time τ/min	Specific surface $S/\text{m}^2 \cdot \text{g}^{-1}$	Porosity	Mean pore size r/nm
1400	30	4.99	0.421	119
1400	60	4.89	0.387	118
1450	30	4.39	0.396	119
1450	60	4.20	0.381	117

CONCLUSIONS

Aluminum hydroxide was calcined at various temperatures and at various sintering regimes. It was found that calcination is the most important step from the point of view of resulting porosity. Preparation of Θ - Al_2O_3 as the starting material for sintering leads to higher porosity in the final product, but also to the increase of mean pore size. The milling of the calcined powder results in lower mean pore size, but the product has also lower total porosity.

References

- [1] Lloyd D. R. (ED): *Materials Science of Synthetic Membranes*, Amer. Chem. Soc., Washington DC, 240 (1985).
- [2] Toropov N. A., Barzakovskij V. P., Bondar I. A., Udalov J. P.: *Diagramy sostoyania silikatnykh sistem*, Spravochnik, Vol. 2, Nauka – Leningrad 27 (1970).
- [3] Iler R. K.: *J. Amer. Ceram. Soc.* 44, 618 (1961).
- [4] McLeod C. T., Kastner J. W., Carbone T. J., Starr J. P.: *Ceramic Engineering and Science Processing* 6, 1233 (1985).
- [5] Lajner A. I.: *Proizvodstvo glinozema*, Moskva, Metalurgizdat, 89 (1961).
- [6] Šulc J.: *Chem. Prům.* 32, 1–5, 61–63 (1982).
- [7] Chýlček S.: *Slinování korundové keramiky III*. Research report VUEK, Hradec Králové Z-854 (1971).
- [8] Šulc J.: *Kinetika vylučování hydroxidu hlinitého z alkalického roztoku hlinitanu*. Thesis, VŠCHT Praha (1980).
- [9] Šajgalík P., Haviar M., Pánek Z.: *Ceram. Int.* 14, 63 (1987).
- [10] Šajgalík P., Pánek Z., Uhrík M.: *Mater. Sci.* 22, 4460 (1987).
- [11] Messing G. J.: *Science of Ceramic Chemical Processing*, (Hensch L. C., Ulrich D. R. Eds.), John Wiley and Sons, NY 265 (1986).

PRÍPRAVA MEMBRÁN NA BÁZE Al_2O_3 PRE MIKROFILTRÁCIU

Pavel Fellner, Miroslav Haviar*, Marián Koman, Marta Chovancová

Katedra anorganickej technológie CHTF STU, Radlinského 9, 812 37 Bratislava
**Ústav anorganickej chémie SAV, Dúbravská cesta, 842 36 Bratislava*

Z hydroxidu hlinitého pripraveného laboratórne zrážaním roztoku hlinitanu sodného oxidom uhličitým boli pripravené porézne keramické materiály na báze α - Al_2O_3 s celkovou pórovitosťou v rozsahu 20 až 60 % a so strednou veľkosťou pórov v oblasti 76–230 nm.

Bolo zistené, že mletím kalcinátu dôjde k zníženiu strednej veľkosti pórov, sprievodným javom však je zníženie celkovej pórovitosti materiálu. Na výslednú mikroštruktúru keramiky majú podstatný vplyv podmienky kalcinácie. Naproti tomu spekanie nemá na parametre porozity, pokiaľ sa neprekročí teplota 1450 °C, podstatný vplyv. Pre udržiavanie vyššej celkovej pórovitosti je výhodné, ak je východiskový prášok pre prípravu filtračných membrán Θ - Al_2O_3 .

Obr. 1. Schéma rozkladu $\text{Al}(\text{OH})_3$ podľa McLeodovej [11].

Obr. 2. Prášok A ($\text{Al}(\text{OH})_3$).

Obr. 3. Prášok A1 (α - Al_2O_3).

Obr. 4. Prášok A2 (α - Al_2O_3 , mletý).

Obr. 5. Mikroštruktúra vzorky A2 spekanej pri 1400 °C 60 minút.

ПРИГОТОВЛЕНИЕ МЕМБРАН НА БАЗЕ Al_2O_3 , ПРЕДНАЗНАЧЕННЫХ ДЛЯ МИКРОФИЛЬТРАЦИИ

Павел Феллнер, Мирослав Гавиар*, Мариан Коман, Марта Хованцова

Кафедра неорганической технологии химико-технологического факультета Словацкого политехнического университета, 812 37 Братислава,

** Институт неорганической химии САН, 842 36 Братислава*

Из гидроксида трехвалентного алюминия, приготовленного лабораторным путем осаждением раствора алюмината натрия оксидом четырехвалентного углерода получили пористые керамические материалы на базе $\alpha-Al_2O_3$ с общей пористостью в пределах 20–60 % и со средним размером пор в области 76–230 нм.

Было установлено, что измельчением кальцината вызывается понижение среднего размера пор, однако сопровождаемым явлением является понижение общей пористости материала. На окончательную микроструктуру керамики оказывают существенное влияние условия кальцинации. Наоборот, спекание не оказывает существенное влияние на параметры пористости в случае, когда температура не выше 1450 °С. Для сохранения более высокой пористости оказывается удобным, когда исходный порошок, предназначенный для приготовления мембран $\Theta - Al_2O_3$

Рис. 1. Схема разложения согласно Мек–Леоду (11).

Риц. 2. Порошок А ($Al(OH)_3$)

Риц. 3. Порошок А1 ($\alpha - Al_2O_3$)

Рис. 4. Порошок А2 ($\alpha - Al_2O_3$, молотый).

Рис. 5. Микроструктура образца 12, спекаемого при температуре 1400 °С во время 60 минут.

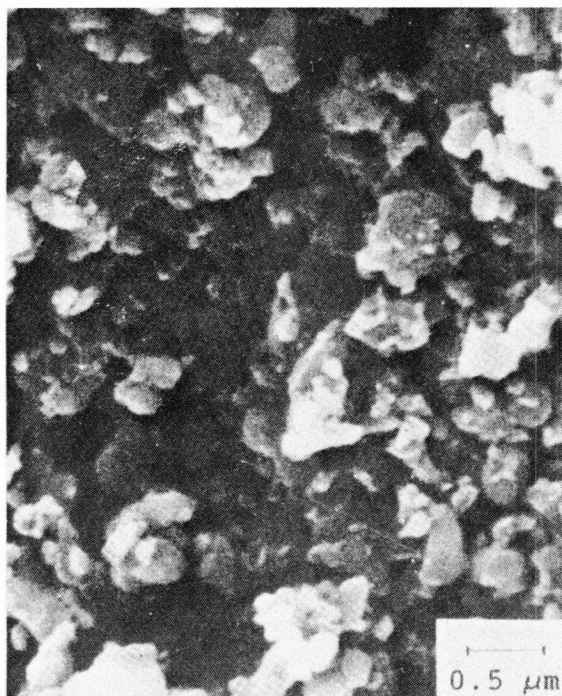


Fig. 4. Powder A2 (α - Al_2O_3 , ground).

Preparation of alumina membranes for microfiltration



Fig. 5. The microstructure of specimen A2 sintered at 1400° C for 60 minutes.



Fig. 2. Powder A ($\text{Al}(\text{OH})_3$).

Preparation of alumina membranes for microfiltration

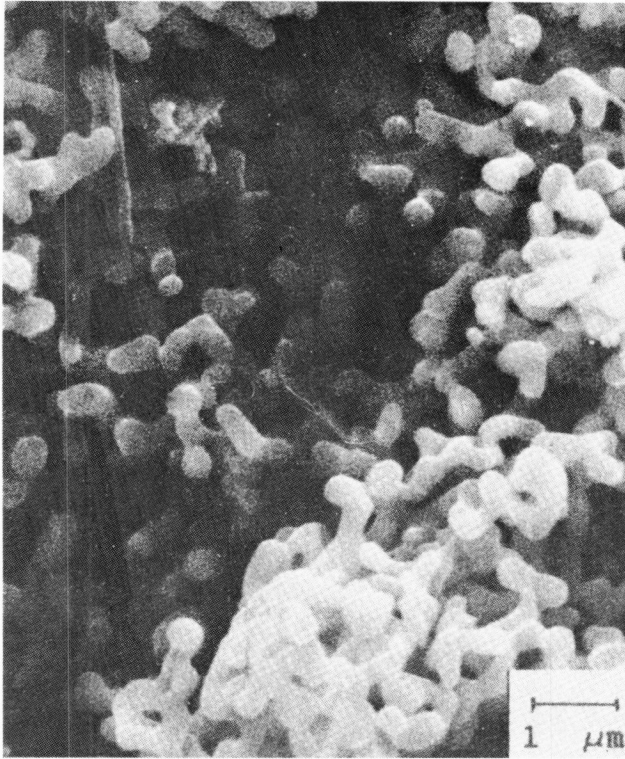


Fig. 3. Powder Al (α -Al₂O₃).