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Efficient recovery of ultrafine catalysts from oil/water/solid three-phase system by ceramic microfiltration membrane

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Abstract−A submerged ceramic membrane filtration system was constructed for the filtration of oil/water/solid three-phase mixture, where hexane acted as the oil phase and beta zeolite as the solid phase. The effects of the phase composition and transmembrane pressure on the filtration performance of ceramic membrane were investigated. The liquid composition in the feed and transmembrane pressure greatly affected the filtration rate and the proportion of oil/water in the permeate. Only aqueous phase passed through the membrane at lower pressures, both water and oil phases could permeate through the membrane with a lower water yield at higher pressures, and the lower water content in the feed promoted the earlier discharge of oil. The hydrophilic nature of ceramic membrane should be responsible for the filtration behavior. A combined process applying low pressure for water permeation and high pressure for oil permeation was proposed for the filtration of oil/water/solid three-phase mixture, and an efficient separation of oil/water/solid three phases was achieved.

Keywords: Ultrafine Catalysts, Recovery, Oil/Water/Solid Three-phase, Ceramic Membrane, Fouling

INTRODUCTION

Heterogeneous catalysis plays an important role in the development and progression of chemical and petrochemical production processes. Heterogeneous catalysts with ultrafine particle size often exhibit excellent reaction performance [1]. Nevertheless, their large-scale applications are often limited by the difficulties of separating the ultrafine catalyst particles from the reaction mixture and recycling them into the reactor [2]. Generally, ultrafine catalysts are immobilized on supporting materials to prevent particle agglomeration and make them easy to recover afterwards [3-5], but at the expense of a reduction of the effective surface area of the catalyst and masstransfer limitations of reactants to the catalyst surface. Membrane reactors, in which a process that integrates the membrane separation with the heterogeneous catalysis, have emerged as an effective means of retaining the ultrafine catalysts in situ that makes the reaction process continuous [1]. Recently, many types of membrane reactors have been developed by our group [6-10]. For example, a submerged ceramic membrane reactor, where membranes positioned in a "flooded" tank, was constructed for the hydroxylation of phenol to dihydroxybenzene over TS-1 (average particle size, 200 nm), in which the ultrafine particles could be recovered completely [9]. In these works, ceramic membranes were mainly used to retain the ultrafine catalysts from the solid-liquid two-phase catalysis system. However, some heterogeneous catalytic reaction systems may be a liquid-liquid-solid three-phase slurry, where the aqueous phase or oil phase can appear through the external introduction or catalytic reaction itself [11,12]. Due to the differentiations of physical properties and components between the aqueous phase and oil phase, as well as the difference of surface properties of membrane such as surface wettability and surface charge, the membrane filtration performance of three-phase mixture could be more complicated than that of a solid-liquid two-phase system. However, to the best of our knowledge, there is no report on the application of membrane for the recovery of ultrafine catalysts from the oil/water/solid three-phase reaction mixture.

In fact, membrane separations for the treatment of oil/water two-phase mixture especially for the oily wastewater have been developed greatly over the last 40 years and are becoming a promising technology [13-17]. This technology has several advantages, including low capital cost and stable effluent quality compared with traditional separation techniques. Many studies of membrane separations for oil/water two-phase mixture have been reported using organic/inorganic membranes [18-22]. Particularly, ceramic membranes have been widely used depending on their superior mechanical, thermal, and chemical stability [19,20]. Unfortunately, the present studies mainly focused on the filtration system mostly composed of water [13-20]. Membrane separations for the treatment of oil/water two-phase mixture mostly composed of oil still remain a great challenge.

We constructed a submerged ceramic membrane filtration system for the filtration of oil/water/solid three-phase mixture. Beta zeolite was used as the solid phase due to its wide application in heterogeneous catalysis, especially in alkylation reactions [23,24], and hexane acted as the oil phase because of its insolubility in water. To investigate the feasibility of the process, the effect of transmembrane pressure on the filtration performance of ceramic membrane was investigated. Great emphasis was given to study the relation-

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ship between the mixture composition and filtration performance. Then, an effective strategy by varying the transmembrane pressure for the efficient separation of oil/water/solid three-phase mixture was developed.

EXPERIMENTAL

1. Materials

Beta zeolite catalyst (average particle size 570 nm, measured by MasterSizer 2000) was supplied by SINOPEC Shanghai Research Institute of Petrochemical Technology, China. Hexane was purchased from Shanghai Shisihewei Chemical Co., Ltd., China. Sodium hydroxide was provided by Shantou Xilong Chemical Co., Ltd., China. Deionized water (electrical conductivity <12 $\mu s \cdot cm^{-1}$) was homemade. All materials were of analytical grade and used without further treatment.

2. Submerged Ceramic Membrane Filtration System

A submerged ceramic membrane filtration system as shown in Fig. 1 was developed for the filtration of oil/water/solid three-phase mixture. The system mainly consisted of an autoclave, a ceramic membrane module and nitrogen resource. The autoclave was made of stainless steel with a working volume of 2.0 L, which was equipped with an internal thermocouple and an external heater for temperature control and a pressure gage for pressure monitoring. The ceramic membrane was made up of a fine layer of ZrO_2 (nominal pore size of 50 or 200 nm) or α-Al_2O_3 (nominal pore size of 500 nm) on the outer wall of a tubular α-Al_2O_3 porous support, and was provided by Nanjing Jiusi High-Tech, China. The membrane with an outer diameter of 12 mm, an inner diameter of 8 mm and a length of 8 cm, was connected with the liquid outlet valve at one end and the other end was sealed with glaze.

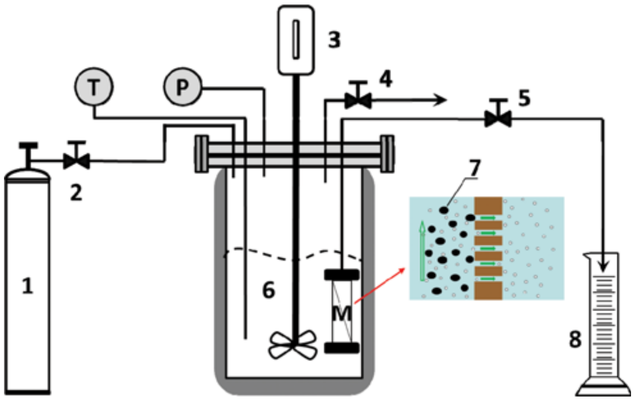

Fig. 1. Schematic diagram of the submerged ceramic membrane microfiltration system.

1. Nitrogen source
2. Gas inlet valve
3. Stirrer
4. Exhaust valve
5. Liquid outlet valve
6. Autoclave
7. Solid catalyst
8. Liquid storage tank

M. Membrane module
T. Thermocouple
P. Manometer

3. Evaluation of Filtration Performance

In the preliminary work, the effect of membrane pore size on the membrane filtration performance was investigated using ceramic membranes with pore sizes of 50, 200 and 500 nm. The membrane with a pore size of 200 nm exhibited satisfactory filtration performance, with a better membrane flux and a complete retention of beta zeolite catalyst (data not shown here). Thus, a ceramic membrane with a pore size of 200 nm was selected for the filtration of oil/water/solid three-phase mixture.

The feed suspensions were composed of hexane and water with different volume ratios (0 : 100, 50 : 50, 70 : 30, 90 : 10 and 100 : 0) and fixed dose of beta zeolite (catalyst concentration 5.0 g/L). Prior to a filtration experiment, the initial pure water flux of the ceramic membrane was measured to ensure the similar value for each experiment. A typical experimental procedure was as follows: certain amounts of hexane, water and beta zeolite were first introduced into the autoclave, respectively, and the total volume of suspension was 1.0 L. Then the autoclave was sealed and purged with N_2 for five times to completely remove the air in the reactor and subsequently heated to a desired temperature of 50 °C under a stirring rate of 600 rpm. In this work, a feed suspension was not formed the oil-in-water emulsion. After reaching the desired temperature, N_2 was fed into the reactor to adjust the pressure to the set value, and then the filtration process was started. The liquid passed through the membrane pore while the beta zeolite particles were retained in the reactor. The permeate was collected in a measuring cylinder, and the membrane filtration rate was calcu-

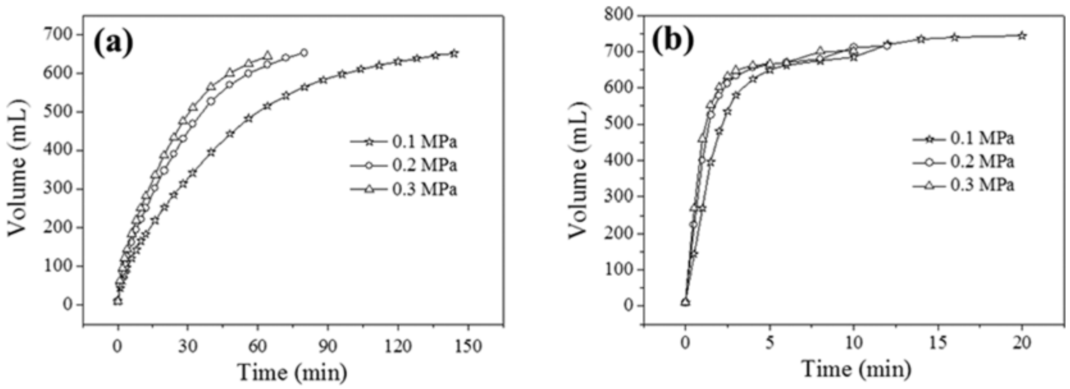

Fig. 2. Variation of filtration volume with time under different transmembrane pressures for different suspensions: (a) 100% water+5.0 g L^{-1} catalyst and (b) 100% hexane+5.0 g L^{-1} catalyst.

lated by the filtration volume per time. After each experiment, the used membrane was taken out and first rinsed with sodium hydroxide (1 wt%) at 30 °C and then with deionized water, and the system was thoroughly rinsed with deionized water for the subsequent experiments.

RESULTS AND DISCUSSION

1. Effect of Phase Composition on the Filtration Performance

To study the relationship between the mixture composition and filtration performance, we designed and carried out five groups of filtration experiments by adjusting the volumetric ratio of hexane and water (0 : 100, 50 : 50, 70 : 30, 90 : 10 and 100 : 0) as presented in the Experimental section.

Fig. 2 shows the filtration performance at different transmembrane pressures for the suspension made up of pure water or oil phase. In each case, the filtration volume first increases significantly with time and then gradually levels off, because of the reduction of effective membrane filtration area and the formation of cake layer on the membrane surface during the filtration process [25]. As expected, the filtration rate increases with the increase of transmembrane pressure from 0.1 to 0.3 MPa, which indicates that a higher pressure can promote the filtration. However, excessively high filtration pressure may have negative effects on the permeate flux due to the rapid adsorption of catalyst particles on the membrane surface to form a thicker cake layer [26]. Comparing Figs. 2(a) and 2(b) shows that the filtration rate for the suspension consisting of

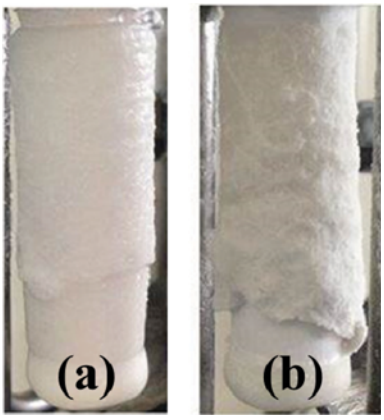

Fig. 3. Photographs of ceramic membranes after the filtration for different suspensions: (a) 100% water+5.0 g L^{-1} catalyst and (b) 100% hexane+5.0 g L^{-1} catalyst.

hexane and beta zeolite is much higher than that of water and beta zeolite, which may be attributed to the lower viscosity of hexane than that of water [27]. In addition, the loose cake layer formed on the membrane surface as shown in Fig. 3(b) is another reason for the higher filtration rate of the former, which is caused by the weak affinity of oily hexane on hydrophilic catalyst particles [28] and the prevention of oil phase between catalyst particles and hydrophilic membrane surface [15].

The filtration performance for the suspensions with different

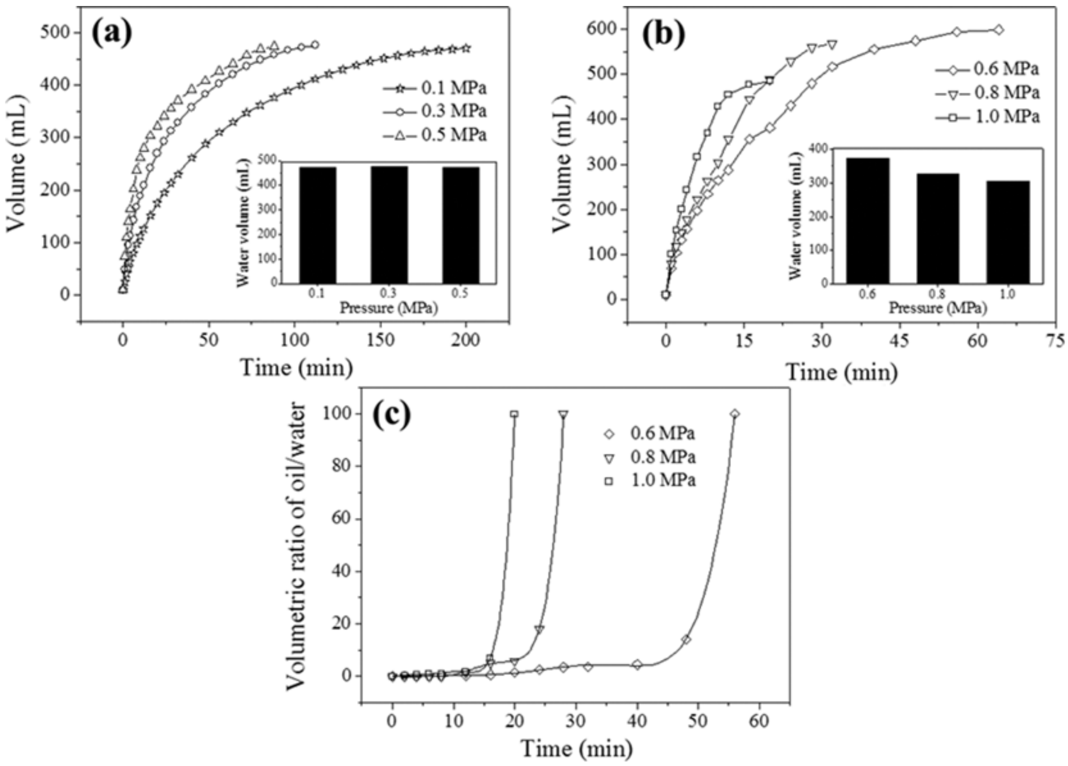

Fig. 4. The filtration performance of ceramic membrane in the filtration of oil/water/solid three-phase mixture with an oil/water volumetric ratio of 50 : 50: variation of filtration volume with time under (a) low transmembrane pressures and (b) high transmembrane pressures, (c) change of oil/water volumetric ratio in the permeate with time. Insets give the water yield versus transmembrane pressure.

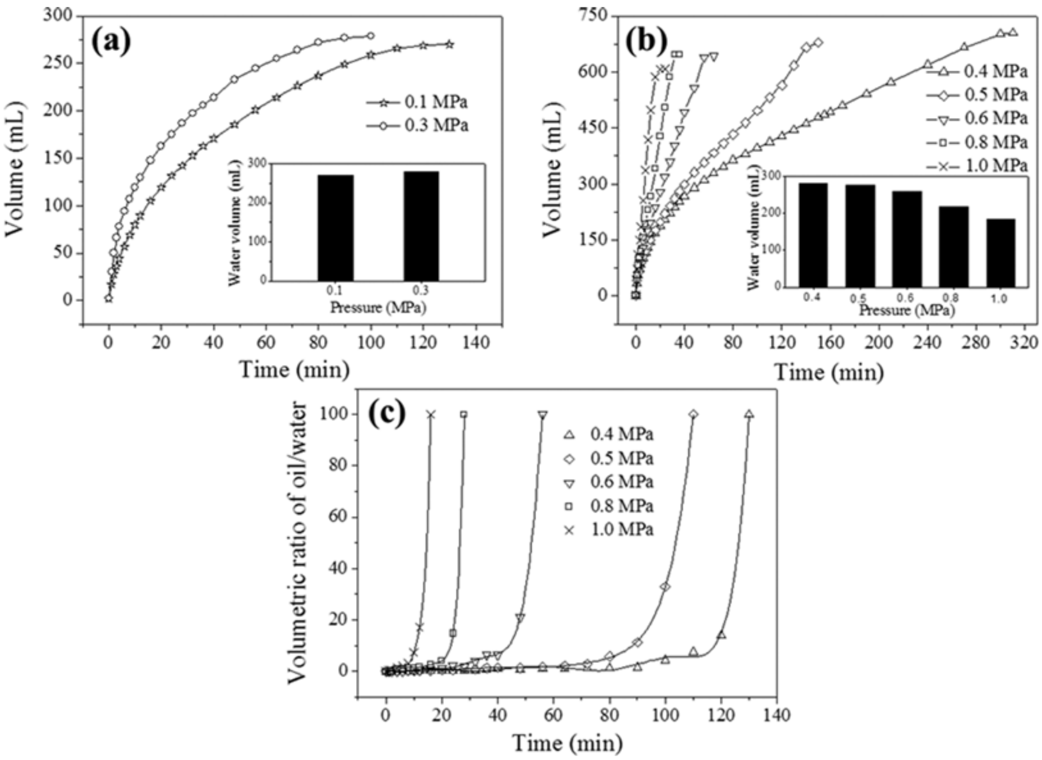

Fig. 5. The filtration performance of ceramic membrane in the filtration of oil/water/solid three-phase mixture with an oil/water volumetric ratio of 70 : 30: variation of filtration volume with time under (a) low transmembrane pressures and (b) high transmembrane pressures, (c) change of oil/water volumetric ratio in the permeate with time. Insets give the water yield versus transmembrane pressure.

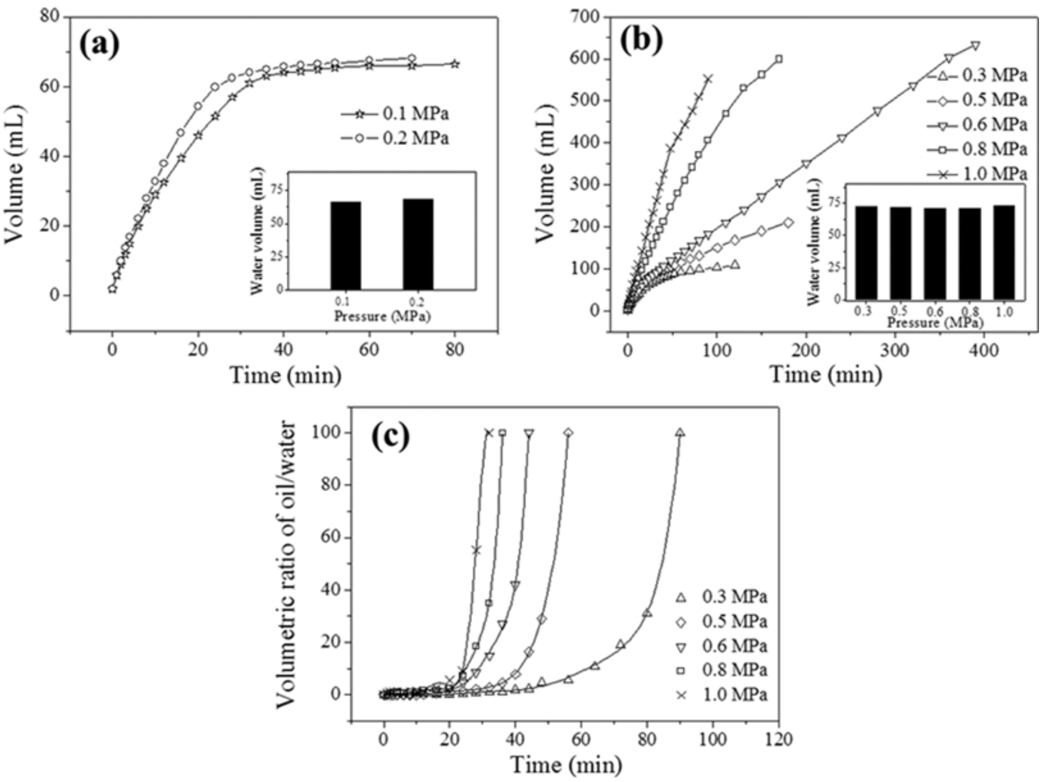

Fig. 6. The filtration performance of ceramic membrane in the filtration of oil/water/solid three-phase mixture with an oil/water volumetric ratio of 90 : 10: variation of filtration volume with time under (a) low transmembrane pressures and (b) high transmembrane pressures, (c) change of oil/water volumetric ratio in the permeate with time. Insets give the water yield versus transmembrane pressure.

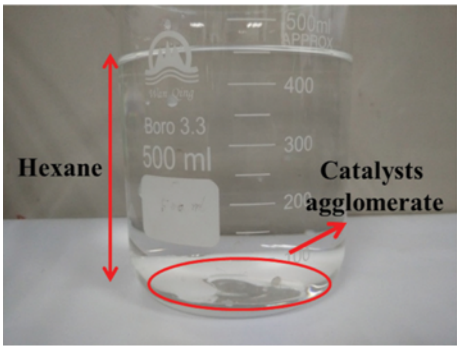

Fig. 7. Photograph of the concentrated solution in the filtration of oil/water/solid three-phase mixture with an oil/water volumetric ratio of 50 : 50 at a transmembrane pressure of 0.5 MPa.

oil/water volumetric ratios of 50 : 50, 70 : 30 and 90 : 10 is shown in Figs. 4-6, respectively. Similar to the results in Fig. 2, the filtration volume first increases rapidly with time and tends to be stable, and a higher transmembrane pressure is beneficial for the filtration. Interestingly, the composition of permeate varies with the transmembrane pressure. For example, for the suspension with an oil/water volumetric ratio of 50 : 50, when the transmemrbane pressure is less than 0.5 MPa, only aqueous phase is filtered out in the permeate, while the oil phase is retained in the system. In addition, almost all the water in the suspension can be filtered out with a volume of about 480 mL (insert in Fig. 4(a)), and a small residue adsorbs on the beta zeolite catalyst particles due to the hydrophilic of catalyst and only hexane can be observed in the top layer in the concentrated solution as presented in Fig. 7. When the transmembrane pressure reaches a boundary of 0.6 MPa, the oil phase can be observed in the permeate during the filtration process. Moreover, the water yield in the permeate displays very little dependence at low transmembrane pressures (≤0.5 MPa) (insert in Fig. 4(a)), while higher transmembrane pressures (≥0.6 MPa) lead to a lower water yield (insert in Fig. 4(b)), which indicates that the water yield can be controlled by the transmembrane pressure. The results of oil/water volumetric ratios in the permeate with time at higher transmembrane pressures (≥0.6 MPa) are presented in Fig. 4(c). Clearly, only water phase is first obtained in the permeate at the initial stage of filtration, then both water and oil phases are filtered out and the proportion of oil gets higher, and finally clean oil phase permeates through the ceramic membrane. In addition, the moment that the oil phase permeates through the ceramic membrane is found to be different with the transmembrane pressure. The higher the transmembrane pressure, the faster the oil phase appears. Similar results are observed for the suspensions with oil/water volumetric ratios of 70 : 30 and 90 : 10 (Figs. 5 and 6).

The great influence of phase composition on the filtration performance of ceramic membrane is mainly related to its surface properties. Since the ceramic membrane is hydrophilic, preferential water adsorption on the membrane surface rather than the oil is encountered. A certain thickness of water-rich layer covers on the ceramic membrane surface while the oil-rich layer is retained above the water-rich layer, making the oil not able to permeate through the ceramic membrane comfortably. To achieve the objective of the permeation of oil, increasing the applied transmembrane pressure ($P_{applied}$) is a necessary means. A limiting factor in separation arises from the breakthrough pressure ($P_{breakthrough}$) [21,29], which is required to push the oil phase through the membrane pores already saturated by the aqueous phase. When $P_{applied}<P_{breakthrough}$ is applied, only the aqueous phase permeates through the membrane. And as $P_{applied}>P_{breakthrough}$ is provided, both water and oil can easily permeate through the membrane. Relevant data from Figs. 4-6 are summarized in Table 1. It is evident that the breakthrough pressure greatly depends on the composition of three-phase mixture, and decreases with the decrease of water content. Fig. 8 depicts the change of oil/water volumetric ratio in the permeate with time at the pressure greater than the breakthrough pressure (e.g., 0.6 MPa) for the feeds with different volumetric ratios of oil/water. As can be seen, the lower content of water can promote the permeation of oil. Lower water content contributes to the thinner water layer on the surface of ceramic membrane under the same operation conditions, resulting in the easy breakdown of aqueous layer by oil layer.

Table 1. Breakthrough pressure in the membrane filtration of suspensions with different three-phase composition

Three-phase composition	$P_{breakthrough}$ (MPa)
Oil/water, 50 : 50 (v : v) +5.0 g L^{-1} catalyst	0.5-0.6
Oil/water, 70 : 30 (v : v) +5.0 g L^{-1} catalyst	0.3-0.4
Oil/water, 90 : 10 (v : v) +5.0 g L^{-1} catalyst	0.2-0.3

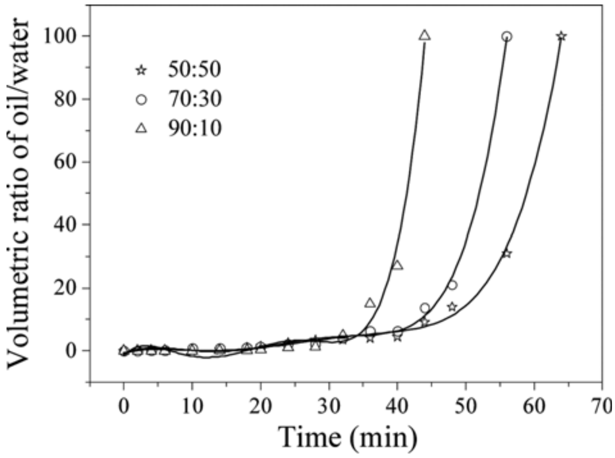

Fig. 8. Change of oil/water volumetric ratio in the permeate with time in the filtration of oil/water/solid three-phase mixture with different oil/water volumetric ratios.

2. Efficient Filtration of Three-phase Mixture

The investigation on the membrane filtration of oil/water/solid three-phase system has indicated that only water phase passes through the membrane, while the oil and solid phases are retained at lower pressures, and as the pressure is larger the breakthrough pressure both water and oil phases can permeate through the membrane. Although two distinct phases can be filtered out under higher pressures, lower water yield is obtained and thus part of water still remains in the reactor. It is unreasonable for the oil/water/solid three-phase separation in heterogeneous catalysis, because the composition change of reaction mixture may affect the cata-

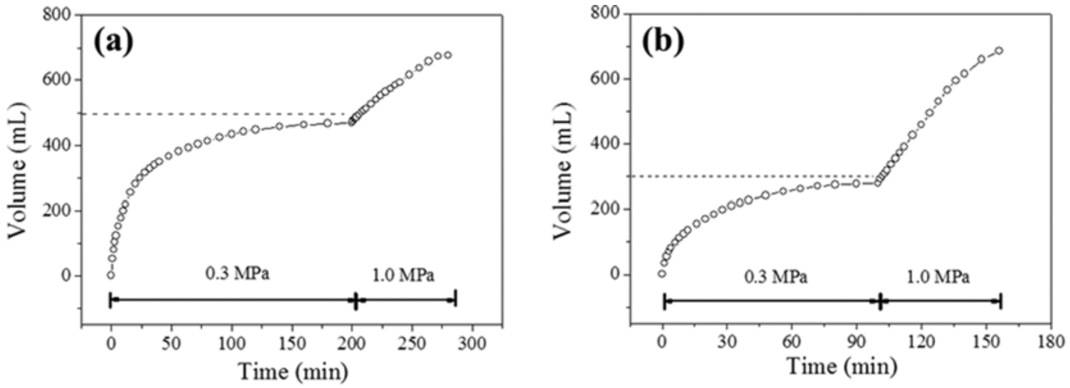

Fig. 9. The membrane filtration performance of ceramic membrane in the filtration of oil/water/solid three-phase mixture with oil/water volumetric ratios of (a) 50 : 50 and (b) 70 : 30 by varying the filtration pressure.

lytic properties. Therefore, a combination process applying variable pressures is proposed to guarantee the efficient separation of oil/water/solid three phases. Fig. 9 shows the membrane filtration performance of ceramic membrane for the suspensions with oil/water volumetric ratios of 50 : 50 and 70 : 30 by varying the filtration pressure. The permeate volume evidently grows with increasing the transmembrane pressure, and almost all water phase is filtered out at 0.3 MPa, while the oil phase passes through the membrane continuously by raising the pressure to 1.0 MPa as expected. However, unfortunately, part of oil still remains in the reactor due to the limitation of experimental conditions. In this study, a tubular ceramic membrane was used for the filtration of oil/water/solid three-phase mixture, and one end of the ceramic membrane was sealed with glaze as presented in Experimental section. Thus, part of oil is inevitably retained in the reactor, and it is not easy to completely separate the oil and solid phases.

CONCLUSIONS

Separation of oil/water/solid three-phase suspension was performed in a submerged ceramic membrane filtration system. The filtration rate and the proportion of oil/water in the permeate significantly depended on the composition in the feed and the transmembrane pressure. Efficient separation of oil/water/solid three-phase mixture was achieved by integration of low and high transmembrane pressures during the filtration. The present work demonstrates that the developed separation strategy is feasible for the oil/water/solid three-phase system, and would aid the development of heterogeneous catalysis over ultrafine catalysts.

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