

Supporting Information

High temperature oil-water separation based on superwetable membranes for removing water from condensation reactions

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DOI: 10.1039/x0xx00000x

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Experimental Procedures

Materials

Unmodified porous glass membranes with pore size 50–70 μm (Grade 1) were commercial products. Ethyltrichlorosilane (ETCS) was purchased from TOKYO Chemical Industry (Tokyo, Japan). Oil red, methylene blue, xylene, *o*-xylene, *m*-xylene, *p*-xylene, hexanoic acid, octylamine and octanol were purchased from Macklin Co., Ltd (China). Toluene (Sinopharm Chemical Reagent Co., Ltd., AR) was used as received. All organic solvents used were analytical grade without any further purification. Deionized water was used for all experiments.

Characterization

SEM investigations were performed by a SEM (Zeiss Sigma 300, Germany). Prior to observation, all samples were fixed onto aluminum stubs and coated with a thin layer of platinum. Contact angles, advancing contact angles and receding angles were measured using a LAS100 contact angle measuring instrument (LAUDA LSA100, Germany). For each measurement, 5 μL -sized droplets were used, and an average value was calculated based on at least 5 tests. High temperature θ_w measurements involved heating both the materials and water to a specific temperature. Water content in oil was determined by utilizing a Karl Fisher Titration (831 KF, Metrohm, Switzerland). ^1H NMR spectra were obtained at room temperature in CDCl_3 using a Bruker Avance III 400 MHz NMR spectrometer.

Fabrication of heat-resistant and superhydrophobic/superoleophilic porous glass (HR-SPG) membranes

A HR-SPG filter was created using ethyltrichlorosilane as a precursor (unless otherwise specified) for vapor phase deposition. The process involved several steps: first, the raw glass membrane was soaked in sodium hydroxide solution for 4 hours and then washed with deionized water. Second, the drying modified glass membrane was placed in a desiccator and equilibrated at a specific relative humidity for one hour, which was measured using a hydrometer with a thin probe inserted into the reaction chamber's neck. Finally, 1.5 mL of ethyltrichlorosilane was injected into the sealed reactor via rubber plug to initiate coating reaction that proceeded overnight at room temperature.

Oil-water separation under high temperature

The flask was filled with a 100 mL oily mixture consisting of 10% water and 90% toluene. The system was then heated at a specific temperature for a certain duration, while measuring the water content in the oil at different intervals. This process generated curves depicting the variation of water content in oil over time at different temperatures.

When there are visible water droplets in the flask, we would calculate the water content in oil by using:

$$\text{Water content in oil} = m_1 * 10^6 / m_2 \text{ (ppm)}$$

Where the m_1 is the mass of the remaining water in the flask and the m_2 is the total mass of liquid mixture in the flask. When there were no visible water droplets in the flask, we would use the Karl Fisher Titration to measure the water content in oil and each measurement was repeated for 3 times.

Oil-water separation for high viscosity oils

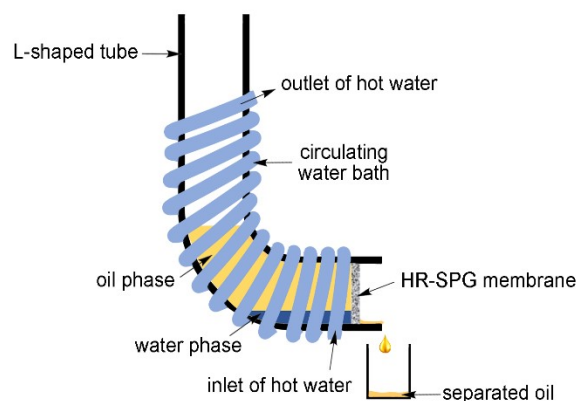


Fig. S1 Schematic diagram of the experimental set-up based on the HR-SPG (heat-resistant superhydrophobic/superoleophilic porous glass) membrane for high viscosity oil-water separation.

The separations of sunflower oil/water and mineral oil/water mixtures (produced by mixing 80 mL oil with 10 mL water) were performed at 25 and 80 °C using a home-made device (Fig. S1). A filter crucible bearing the HR-SPG membrane (diameter = 3.6 cm) was connected to an L-shaped tube; and the temperature of the oil-water mixture was controlled by the circulating water bath. The mixture was added to the separator and the separation experiment started. The separation flux was calculated when ca. 5 g oil was separated and the purity of the oil filtrate was also measured.

Synthesis

A flask was filled with 0.5 mol of hexanoic acid, 0.5 mol of octylamine and 81 mL of toluene. The reaction mixture was heated at 150 °C while the byproduct water was collected using the device equipped with an inclined HR-SPG filter and the toluene was able to return to the flask. The progress of the reaction was monitored by ¹H NMR at regular intervals.

The esterification reaction takes the same approach. 0.5 mol hexanoic acid, 0.5 mol octanol, toluene (81 mL) and the catalyst (0.05% concentrated sulfuric acid) were added into a flask. The reaction was fluxed at 150 °C and was monitored by ¹H NMR at certain intervals.

Mechanical stability of HR-SPG membrane measurements

The home-made elegant device which was embedded an inclined HR-SPG membrane was filled with 50 g of 80–100 sand and was fixed onto a rotary mixer rotating at 50 rpm. Each rotation was considered one abrasion cycle. After varying numbers of cycles, we conducted an oil-water separation experiment using the treated HR-SPG membrane and measured the water content in the flask after heating for 3 hours.

The mechanical stability of the HR-SPG membrane (diameter = 3.6 cm) against sandpaper friction was tested by placing a 100 g weight on top of the membrane above a big piece of sandpaper (1000 mesh) and pulling it along a distance of 10 cm back and forth (named as one cycle). The contact angle of the membrane was measured after each cycle.

Thermal stability of HR-SPG membrane measurements

Place the home-made elegant device with an inclined HR-SPG filter in an oven at temperatures of 160 °C, 180 °C, 200 °C, 220 °C and 240 °C for three hours. Subsequently, use the treated device to perform an oil-water separation experiment heating for 3 hours and measure the water content in the flask.

Cycle stability of HR-SPG membrane measurements

The flask was filled with a 100 mL oily mixture consisting of 10% water and 90% toluene. The reaction mixture was heated at 150 °C for 3 h and then the water content in the flask was measured. Each oil-water separation was considered one cycle, and then repeating this operation. It was important that no additional washing step was needed between each oil-water separation.

Additional Results and Discussion

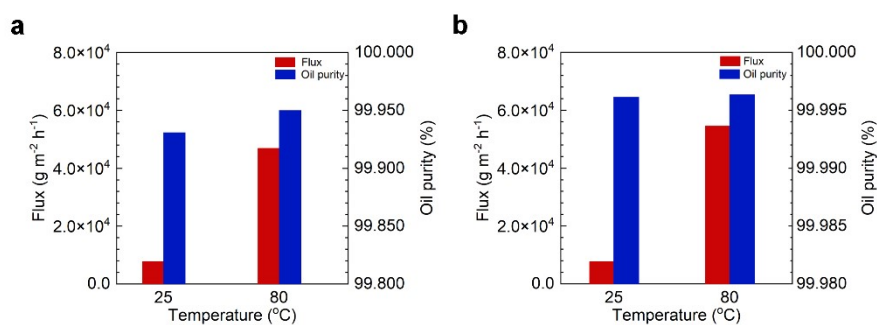


Fig. S2 The oil flux and oil purity for high viscosity oil-water separation composed of (a) sunflower oil (b) mineral oil at 25 and 80 °C.

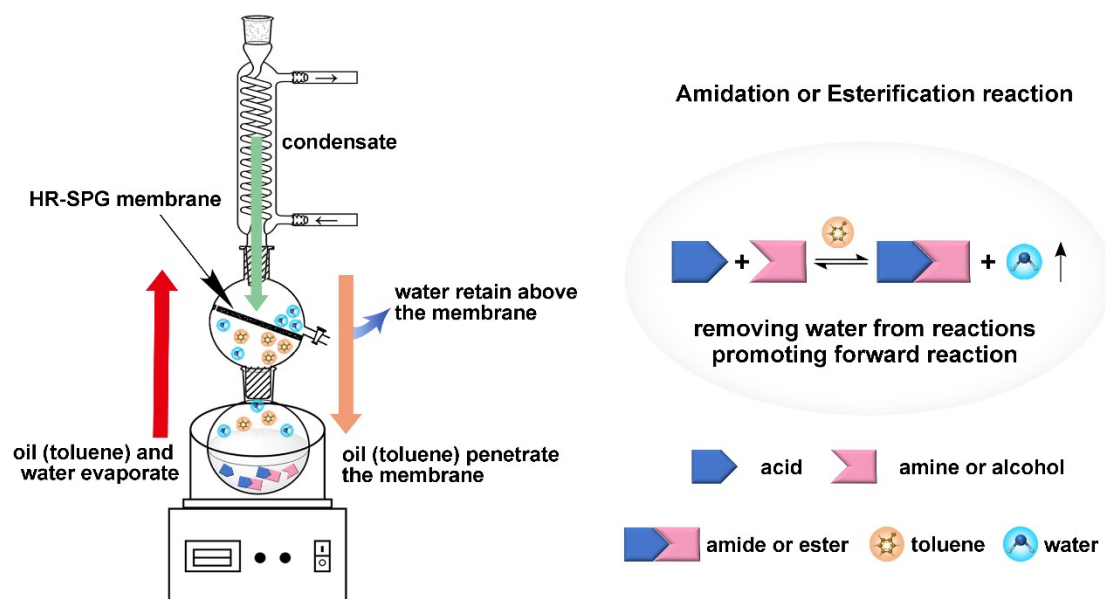


Fig. S3 Schematic diagram of the experimental set-up for the synthesis of amides and esters based on the HR-SPG (heat-resistant superhydrophobic/superoleophilic porous glass) membrane.

Hexanoic acid and octylamine were fluxed at 150 °C, and the conversion was monitored by ^1H NMR. As shown in Fig. S4, the characteristic peak *i* of the octylamine shifted towards the characteristic peak *ii* of the product over time. However, even after 40 hours, the conversion rate (P) has not reached 50% without the HR-SPG membrane.

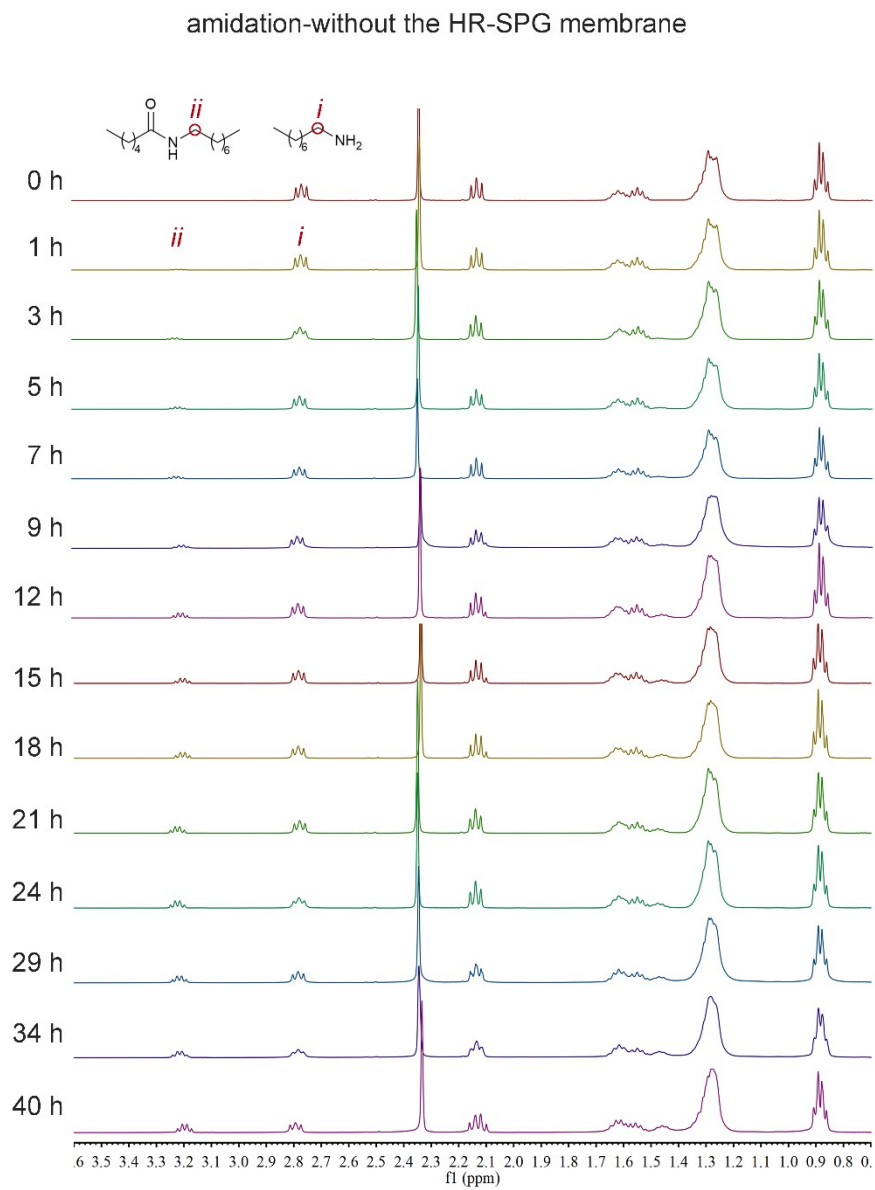


Fig. S4 The ^1H NMR of the amidation reaction without the HR-SPG membrane at different periods.

Hexanoic acid and octylamine were heated at 150 °C with a HR-SPG membrane while monitoring the conversion through ^1H NMR. As shown in Fig. S5, the characteristic peak *i* of the octylamine shifted towards the characteristic peak *ii* of the product over time. It was noteworthy that after 18 hours, the characteristic peak of the raw material disappears from the ^1H NMR spectra, leaving only peaks corresponding to solvent (toluene) and product. These results demonstrated that using a HR-SPG filter effectively enhanced amidation reaction rate and conversion, paving the way for large-scale commercial production of amides.

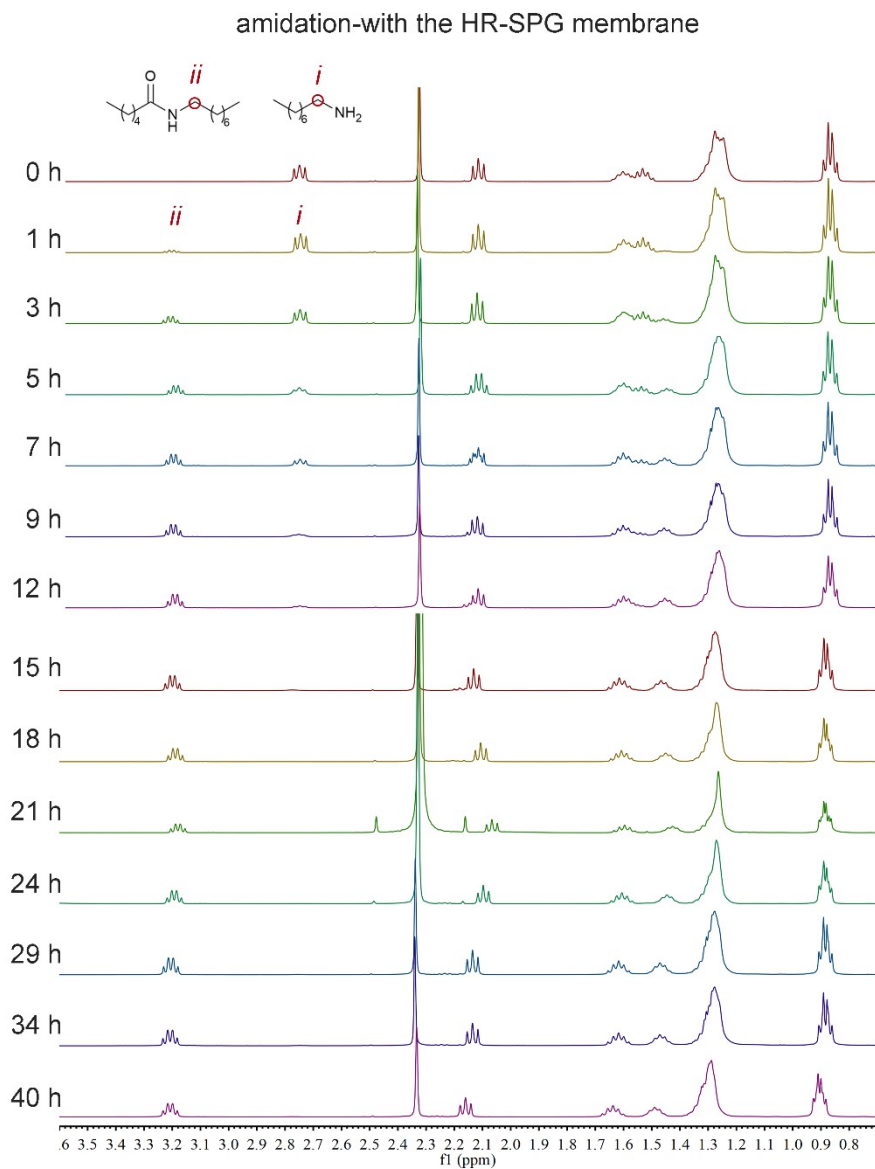


Fig. S5 The ^1H NMR of the amidation reaction with the HR-SPG membrane at different periods.

Hexanoic acid, octanol and 0.05% concentrated H₂SO₄ were fluxed at 150 °C, and the conversion is monitored by ¹H NMR. As shown in Fig. S6, the characteristic peak *i* of the octanol shifted towards the characteristic peak *ii* of the product over time. However, even after 12 hours, the conversion rate (P) has not reached 100% without a HR-SPG membrane.

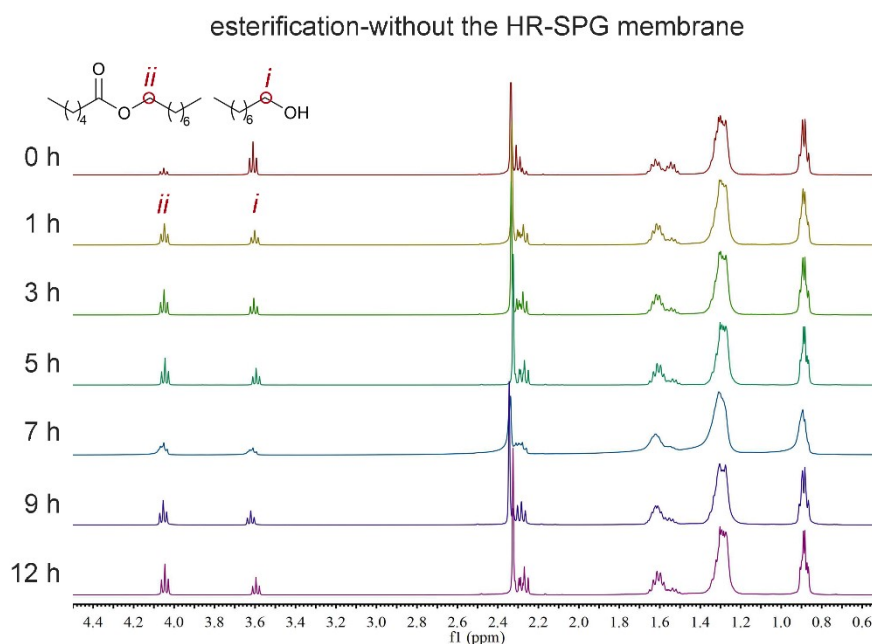


Fig. S6 The ¹H NMR of the esterification reaction without the HR-SPG membrane at different periods.

Hexanoic acid, octanol and 0.05% concentrated H₂SO₄ were heated at 150 °C with a HR-SPG membrane while monitoring the conversion through ¹H NMR. As shown in Fig. S7, the characteristic peak *i* of the octanol shifted towards the characteristic peak *ii* of the product over time. It was noteworthy that after 1 hours, the characteristic peak of the raw material disappears from the ¹H NMR spectra, leaving only peaks corresponding to solvent (toluene) and product. These results demonstrated that using a HR-SPG filter effectively enhanced esterification reaction rate and conversion, paving the way for large-scale commercial production of esters.

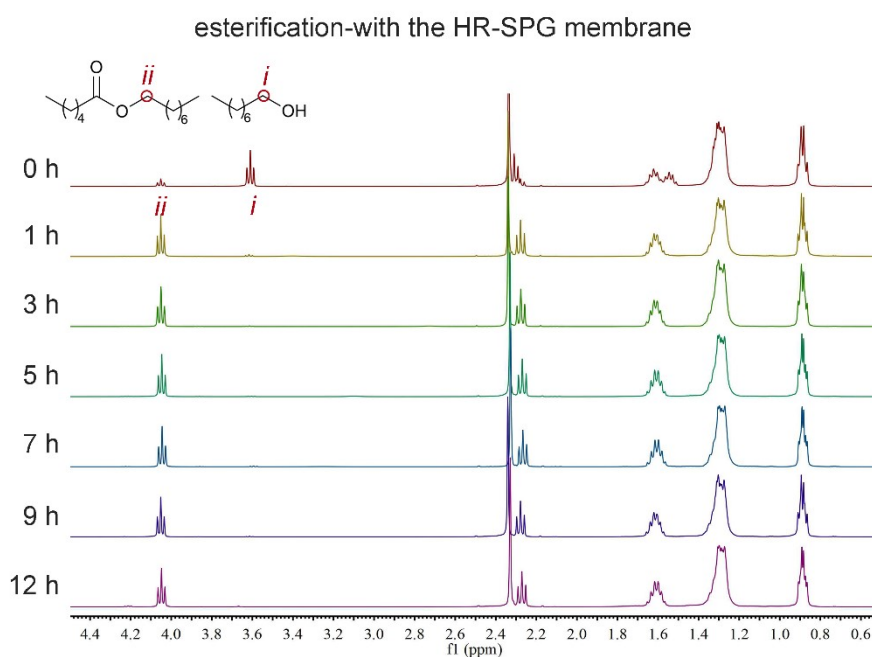


Fig. S7 The ¹H NMR of the esterification reaction with the HR-SPG membrane at different periods.

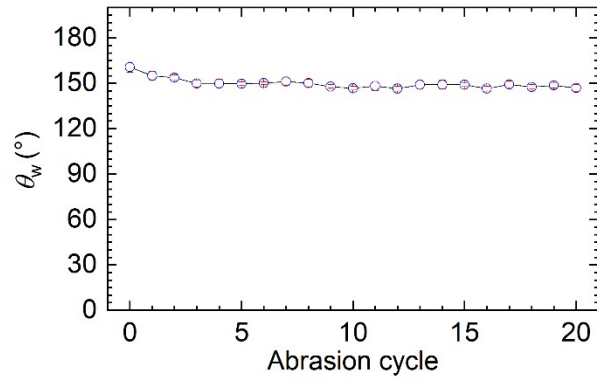


Fig. S8 The water contact angle of the HR-SPG membrane underwent sandpaper abrasion for 20 cycles.