

Supporting Information

Encapsulated Liquid Nano-droplets for Efficient and Selective Biphasic Hydroformylation of Long-Chain Alkenes

Xiaoli Zhang,^a Juan Wei,^{*b} Xiaoming Zhang^{*c}

^a Shaanxi Key Laboratory of Natural Products & Chemical Biology, College of Chemistry & Pharmacy, Northwest A&F University, 22 Xinong Road, Yangling 712100, Shaanxi, P. R. China

^b School of Chemical and Environmental Engineering, Sichuan University of Science and Engineering, Zigong 643000, P. R. China. Email: jwei@suse.edu.cn

^c School of Chemistry and Chemical Engineering, Shanxi University, Wucheng Road 92, Taiyuan 030006, P. R. China. Email: xmzhang4400@sxu.edu.cn

Experimental section

Fig. S1 SEM image of HMSN

Fig. S2 N₂ sorption of synthesized SBA-15

Fig. S3 (a) TEM image of silica nanospheres for forming Pickering emulsions; (b) microscopic images of Pickering emulsions

Fig. S4 Photograph of reaction solution before and after centrifugation

Fig. S5 Water contact angle of (a) Rh-TPPTS-0.97@C₈-HMSN and (b) Rh-TPPTS-0.97@C₁-HMSN

Fig. S6 Recycling tests of Rh-TPPTS-0.97@C₁-HMSN (left) and Rh-TPPTS-0.97@C₈-HMSN (right)

Experimental section

Chemicals and materials

All chemicals were used as received unless otherwise stated. Tetraethylorthosilicate (TEOS, AR), ammonia solution (25-28%), cetyltrimethyl ammonium bromide (CTAB) were purchased from Shanghai Chemical Reagent Company of the Chinese Medicine Group. 1, 2-bis(triethoxysilyl)ethane (BTEE, 96%) was obtained from Sigma-Aldrich. Rh(acac)(CO)₂ was purchased from Aladdin-reagent Company. Fluorescein isothiocyanate (FITC), and tris(m-sulfonatophenyl)phosphine were purchased from J&K Scientific.

Synthesis of hollow structured mesoporous silica nanospheres (HMSN)

The hollow structured mesoporous silica nanospheres were synthesized through a facile in situ generated template method in one-pot medium by utilizing the etching effects of organosilane BTEE, and the specific procedure was described as follows: 0.16 g CTAB and 0.50 ml aqueous ammonia was dissolved in a mixture of 40 ml water and 10 ml ethanol under stirring. After stirring at 50 °C for 30 min, 0.50 ml TEOS was added to the mixture. Within 1-2 min, another organic silane precursor 1, 2-bis(triethoxysilyl)ethane (BTEE, 0.16 ml) was added to the system. And the resulting mixture was firstly stirred at 50 °C and then heated up to 80 °C for 2 h. Subsequently, the mixture solution was transferred to a stainless autoclave with a Teflon container and hydrothermally treated at 100 °C for 24 h under static conditions. The solid product was collected by filtration, and then washed with water and ethanol for several times. To remove the surfactant, the as-synthesized materials (1 g) were dispersed in a solution of 440 mg ammonium nitrate and 120 ml ethanol (95 %) and heated at 60 °C for 30 min. The process was repeated for three times. After air-dried at 100 °C overnight, the final product was obtained.

Fabrication of confined homogeneous catalyst Rh-TPPTS- χ @HMSN

0.05 mmol of Rh(acac)(CO)₂ (12.9 mg) and 2.5 mmol of tris(m-sulfonatophenyl)phosphine (142 mg) were dissolved into different amounts of water to form Rh-TPPTS aqueous solution. And the final volume of catalyst solution was 0.27, 0.67, 0.97, 1.37 ml, respectively. Then, the Rh-TPPTS solution was impregnated into HMSN support (0.50 g) drop-by-drop. The yielded solid catalysts were denoted as Rh-TPPTS- χ @HMSN, where χ represents the volume of Rh-TPPTS aqueous solution. Rh-TPPTS-0@HMSN sample without water was also fabricated by oven drying Rh-TPPTS-0.97@HMSN sample at 80 °C under vacuum.

Fabrication of SBA-15 supported aqueous phase catalyst

0.05 mmol of Rh(acac)(CO)₂ (12.9 mg) and 2.5 mmol of tris(m-sulfonatophenyl)phosphine (142 mg) were

dissolved into desired amount of water to form Rh-TPPTS aqueous solution (0.97 ml). Then, the solution was impregnated into SBA-15, forming supported aqueous catalyst Rh-TPPTS/SBA-15.

Fabrication of silica stabilized Pickering emulsions

80 mg of methyl-modified silica nanospheres were added to a mixture of 2.0 ml water (containing 2.5 μmol Rh-TPPTS) and 1.5 ml toluene (containing 7.5 mmol 1-octene). After shaking for a few minutes, Pickering emulsion catalyst system was formed.

Modification process of confined homogeneous catalyst Rh-TPPTS- χ @HMSN

For the modification process, 0.50 g of Rh-TPPTS-0.97@HMSN was dispersed into 3 ml hexane, 0.5 mmol organic silane methyltrimethoxysilane or octyltrimethoxysilane and 0.5 ml triethylamine were added and stirred at 40 °C for 8 h. After centrifugation and washed with hexane for several times. The obtained solids were volatiled at room temperature, the obtained materials were donated as Rh-TPPTS-0.97@C₁-HMSN and Rh-TPPTS-0.97@C₈-HMSN, respectively.

Characterization

Nitrogen sorption experiments were carried out on micromeritics ASAP2020 volumetric adsorption analyzer. Before the measurements, samples were degassed at 373 K for 6 h. The BET surface area was evaluated from the adsorption data in the relative pressure P/P₀ range from 0.04 to 0.2. The total pore volume was estimated from the amount adsorbed at the P/P₀ value of 0.99. Pore size distributions were determined from the adsorption branches using a BJH method. Transmission electron microscopy (TEM) was performed on a HITACHI 7700 microscope at an acceleration voltage of 100 kV. Thermogravimetric analysis (TGA) was performed under an air atmosphere with a heating rate of 5 °C/min by using a NETZSCH STA-449F3 thermogravimetric analyzer. Scanning electron microscope (SEM) images were performed using a Hitachi SU 1510. The static water contact angles were measured in sessile drop mode. Confocal laser scanning microscopy images were obtained on a Carl Zeiss LSM880 instrument (Germany).

General procedures for hydroformylation of 1-octene

Anhydrous toluene (3 ml), 1-octene (840 mg, 7.5 mmol) and dodecane as internal standard were added to a test tube containing a desired amount of Rh-TPPTS- χ @HMSN catalyst (2.5 μmol Rh). The test tube was transferred into a stainless steel autoclave and sealed. After purging with CO/H₂ (1/1) several times, the pressure was adjusted to 3 MPa and left with stirring at 70 °C in an oil bath. After reaction, the CO/H₂ pressure was released, and the solid catalyst was separated by centrifugation. The conversion and aldehyde selectivity were analyzed by gas chromatography using an HP-5 capillary column (30 m \times 0.32

mm × 0.25 mm). Since the close boiling points of product (aldehydes) and by-products (alcohols), no isolated yield was provided. For the catalyst recycling, the solid catalyst obtained after centrifugation was used directly for the next catalytic reaction.

The hydroformylation reactions of 1-octene under different reaction conditions were performed with a similar procedure, except that the reaction temperature was tuned to be 60 and 80 °C, while the pressure was tuned to be 20 bar and 40 bar respectively.

The hydroformylation reactions of other long-chain alkenes were performed similar with above procedure, but with a different alkene as substrate.

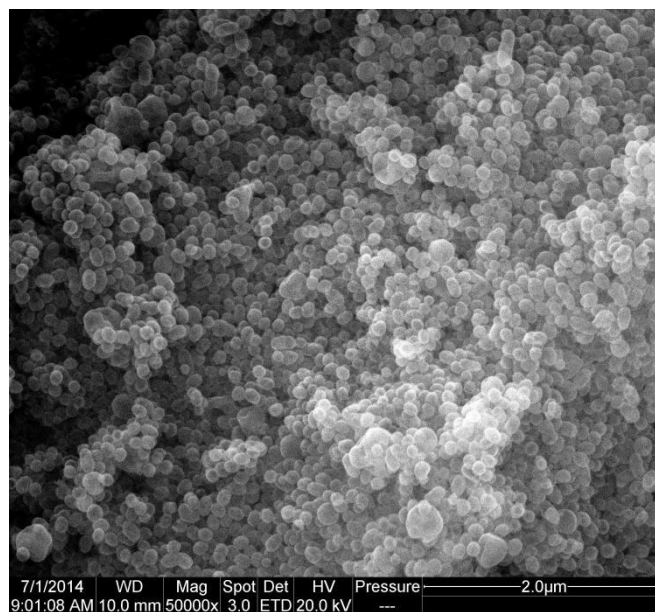


Fig. S1 SEM image of HMSN

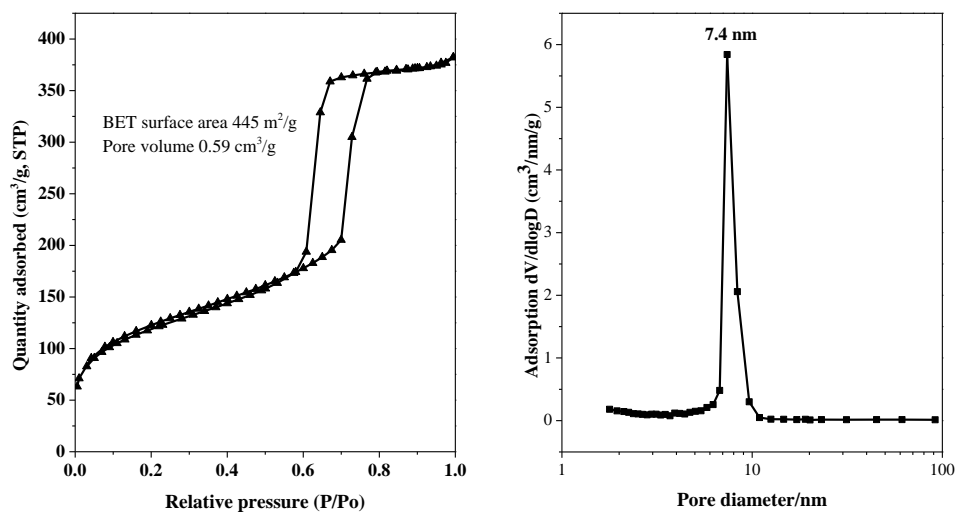


Fig. S2 N₂ sorption of synthesized SBA-15

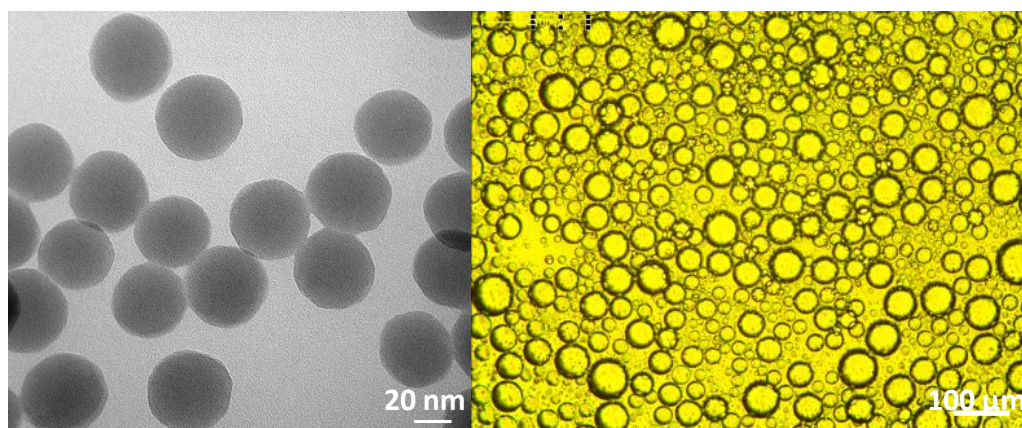


Fig. S3 (left) TEM image of silica nanospheres modified with -CH₃ groups, (right) optical microscopy image of silica nanosphere stabilized Pickering emulsion

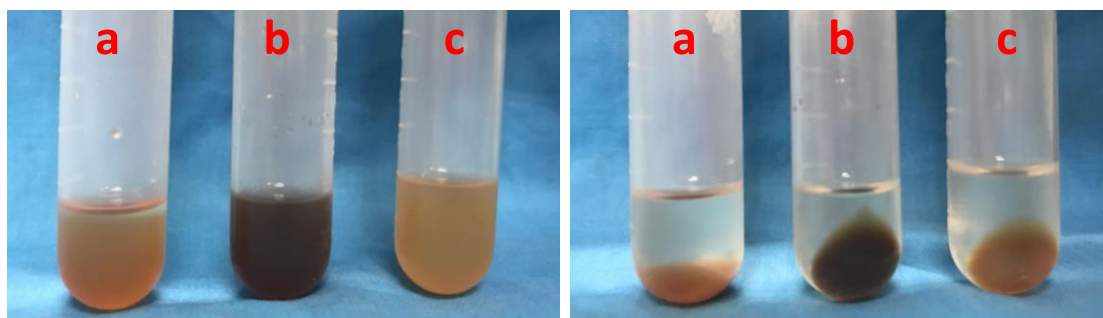


Fig. S4 Photograph of recycling reaction solution before and after centrifugation (a) Rh-TPPTS-0.97@HMSN, (b) Rh-TPPTS-0.97@C₁-HMSN and Rh-TPPTS-0.97@C₈-HMSN

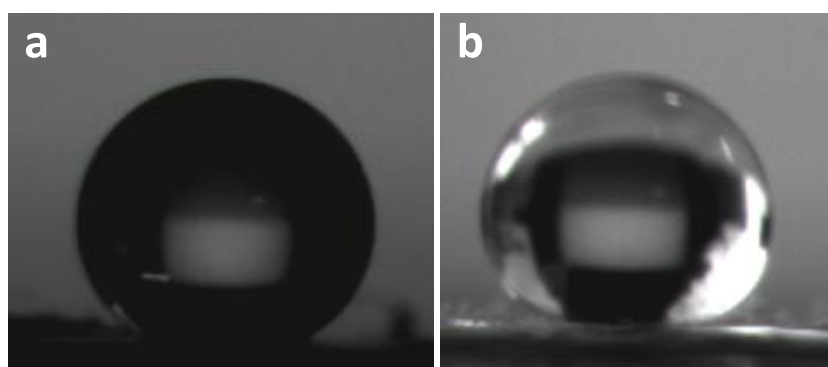


Fig. S5 Water contact angle of (a) Rh-TPPTS-0.97@C₈-HMSN and (b) Rh-TPPTS-0.97@C₁-HMSN

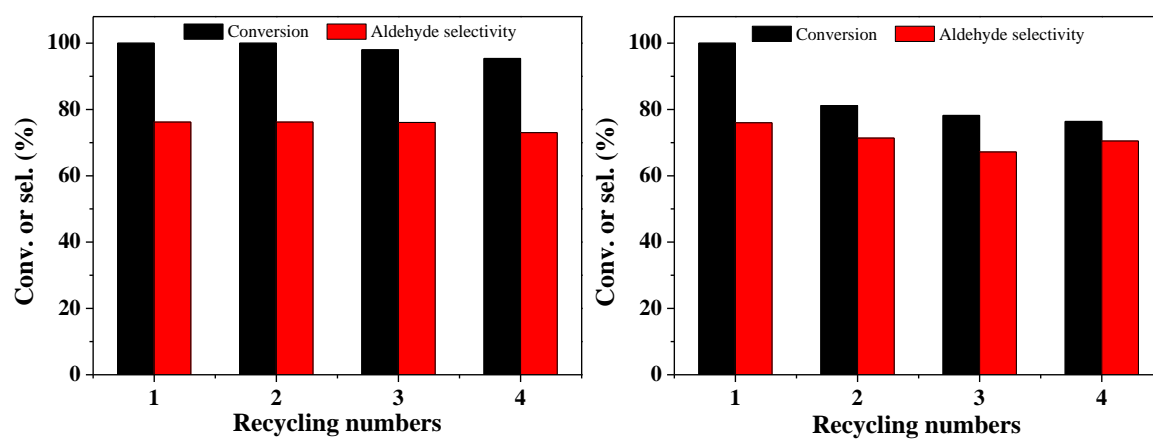


Fig. S6 Recycling tests of Rh-TPPTS-0.97@C₁-HMSN (left) and Rh-TPPTS-0.97@C₈-HMSN (right)