

Supporting Information

for

Pilot-scale cyclohexanone production through phenol hydrogenation over Pd/CN in a continuous ceramic membrane reactor

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Pilot-scale membrane reactor system

The pilot-scale membrane reactor system mainly included feed system, reaction system and membrane separation system. Twenty 40 L hydrogen cylinders (Yangzhou Weisheng Industrial Gas Co., Ltd., China) were used to provide the hydrogen, and the hydrogen inlet was below the liquid level. The mixing tank and feed tank, which were made of stainless steel, had the volume of 1500 L and 150 L, respectively. The feed pump was a metering pump, which could control the flow of the reactants at the set value. The three reactors in series were made of stainless steel with a working volume of 60 L, and the reaction temperature in each reactor could be controlled up to 150 °C by an industrial steam with about 0.5 MPa of steam pressure. A catalyst feed port was located at the top of each reactor. Especially for the reactor A, the port was connected with the reaction mixture returning pipeline. The circulating pump was a centrifugal pump, which could provide a higher cross-flow velocity for reducing the membrane fouling. The membrane separation unit was made of stainless steel and the sealing O-ring was made of perfluoroelastomer (Dupont, Wilmington, DE). A 19-channel porous ceramic membrane tube (Jiangsu Jiuwu High-Tech Co., Ltd., China) with a length of 1 m and outer diameter of 30 mm was used as the separation medium. The asymmetric ceramic membrane was composed of a fine membrane layer of α -Al₂O₃ with a pore size of 200 nm on the inside of the multichannel tubular α -Al₂O₃ porous support with an average pore size of 3000 nm. Pneumatic valves A and B were attached to the rear of the membrane module, which could be opened or closed automatically in a specific frequency. The permeate tank and distillation still, which were made of stainless steel, had the volume of 200 L and 3000 L, respectively. The recycled cyclohexane and crude products were packed in the galvanized barrels.

Continuous phenol hydrogenation

1500 L of 10 wt.% phenol (Yangzhou Shiyou Chemical Co., Ltd., China)-cyclohexane (Jiangsu Yangnong Chemical Group Co., Ltd., China) solution was prepared in the mixing tank and kept at about 30 °C to avoid solidification, and parts of the mixture flowed into the feed tank. 60 L of 20 wt.%, 60 L of 15 wt.% and 60 L of 10 wt.% phenol-cyclohexane solutions were added in the reactors A, B and C, respectively, and 1.2 kg of Pd/CN catalysts (prepared according to our previous works^{1,2}) were added in each reactor simultaneously. After purging with N₂ and H₂ for three times respectively, the three reactors were all heated to 140 °C. The stirring rate and hydrogen pressure were tuned to the expected values and the batch hydrogenation started to ensure a high phenol conversion in the system at the beginning of the continuous operation. After 2 hours, the reactants were fed into the reactor A by the feed pump at a flow rate of 20 L/h, and the reaction mixture overflowed from the reactor A to the reactor B and then to the reactor C. The reaction mixture in the reactor C was fed and recycled in the membrane separation system by the circulating pump. The circulating flow rate was high to ensure a high cross-flow velocity across the membrane surface and reduce the membrane fouling. When the membrane separation system was filled with the reaction mixture, the outlet valve was opened to keep a balance between the flows of the inlet and outlet. The Pd/CN catalyst particles were retained in the reactor system by the ceramic membrane, and the liquid-phase reaction mixture permeated through the membrane and flowed into the permeate tank. In the first 5 hours, 3.0 kg of Pd/CN catalysts were added into the system gradually, and the valve A was kept open and the valve B was closed. The reaction mixture was concentrated in the membrane separation system. After the addition of Pd/CN catalysts, the valve B was opened and the valve A was closed to return the reaction mixture with

high catalyst content to the reactor A at a certain frequency to ensure a constant catalyst concentration in the reaction system. The components in the reactor A and permeated products were analyzed every two hours. When sufficient amount of reaction mixture was collected in the distillation still, the crude cyclohexanone products were obtained by distillation, and the recovered cyclohexane was reused in the feed system as the solvent. During the continuous operation, when additional catalysts were needed, the catalysts were firstly mixed with cyclohexane. The valve C was opened after the valves B and D were closed. The catalysts-cyclohexane mixture was added in the pipeline between the valves C and D. The valve C was closed and the valve D was opened, and then the catalysts-cyclohexane mixture flowed into the reactor A. After the continuous reaction process, the hydrogen was discharged and the reactors were cooled to about 30 °C, and then the system was purged with nitrogen for three times. A metal sintered tube filter with a pore size of about 5 μm was installed at the bottom of the reactor A to recover the Pd/CN catalysts from the reaction mixture. The whole system was washed by cyclohexane to recover the residual catalysts. And then the system was cleaned by deionized water thoroughly and dried by nitrogen at above 100 °C. Lastly, the used membrane was replaced by a fresh one. The used membrane was cleaned by scouring with cyclohexane.

Characterization of Pd/CN catalysts and membranes

To investigate the distribution of the Pd nanoparticles on the support, the transmission electron microscope (TEM) images were taken on a JEM 1200 microscope. To obtain the Pd loading on the support, the inductively coupled plasma emission spectroscopy (ICP-AES, Optima 7000 DV) was employed.

The morphology changes of the membrane surface and cross-section during the continuous

phenol hydrogenation were estimated by using a field-emission scanning electronic microscopy (FESEM, S-4800 II, Hitachi).

Analytical methods

The components of the products were analyzed by gas chromatography (Agilent 7890B). Notably, except the solvent cyclohexane, the reactant phenol and the product cyclohexanone, only the cyclohexanol as the by-product was detected (Figure S1). Cyclohexane, cyclohexanone, cyclohexanol and phenol could be completely separated under the analysis conditions. The peaks were sharp and the base line leveled off, and the measurement error was negligible. Based on the analysis, the phenol conversion (X), cyclohexanone selectivity (S), and cyclohexanone yield (Y) could be calculated according to the equations.^{1, 2}

$$X = \frac{n_{none} + n_{nol}}{n_{none} + n_{nol} + n_{phenol}} \times 100\% \quad (S1)$$

$$S = \frac{n_{none}}{n_{none} + n_{nol}} \times 100\% \quad (S2)$$

$$Y = X \cdot S \quad (S3)$$

where n_{phenol} , n_{none} and n_{nol} are the amounts of phenol, cyclohexanone and cyclohexanol (mol) in the sample, respectively.

The filtration resistance was estimated by the Darcy's law.³

$$R = \frac{\Delta P}{\mu J} \quad (S4)$$

where R, ΔP , J and μ are the filtration resistance (m^{-1}), transmembrane pressure (Pa), membrane flux ($m \cdot s^{-1}$) and permeate viscosity ($Pa \cdot s$), respectively.

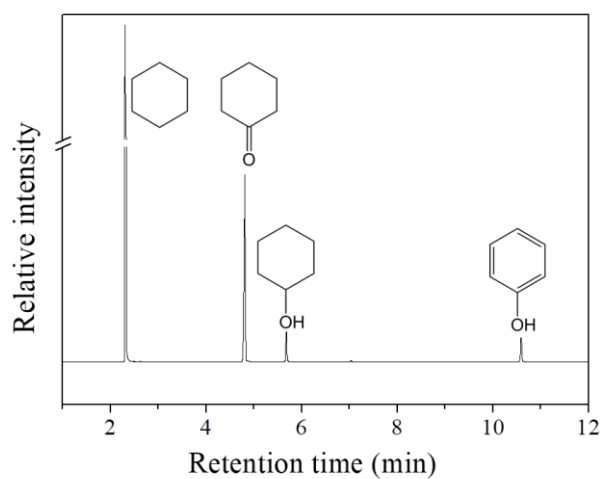


Figure S1. Typical products analysis by GC

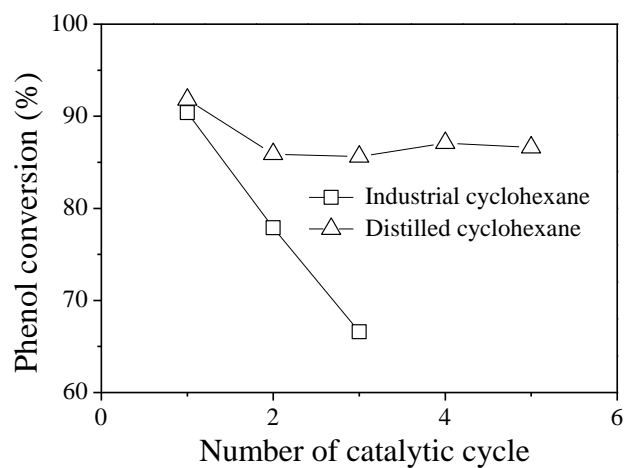


Figure S2. Effects of industrial cyclohexane and distilled cyclohexane on the reaction stability

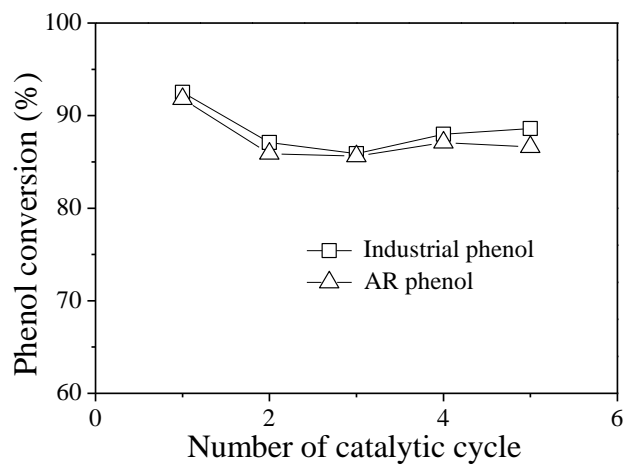


Figure S3. Effects of industrial phenol and analytical reagent phenol on the reaction stability

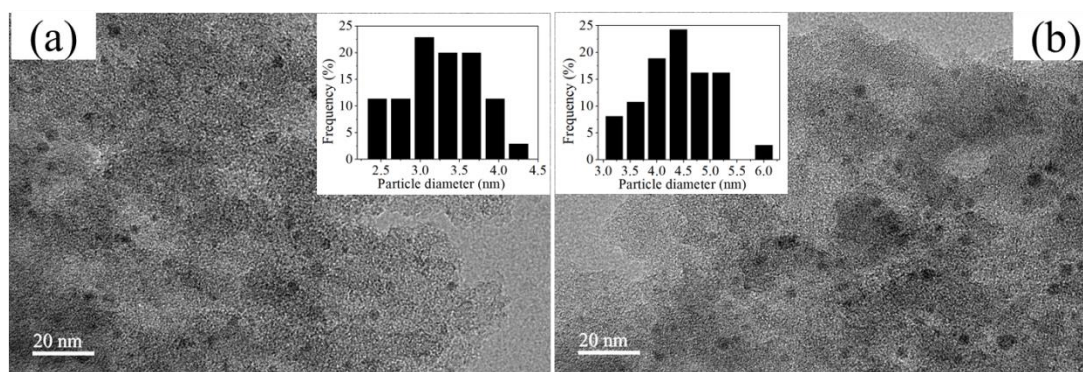


Figure S4. TEM images of (a) fresh Pd/CN and (b) recovered Pd/CN

REFERENCES

1. Jiang, H.; Qu, Z. Y.; Li, Y.; Huang, J.; Chen, R. Z.; Xing, W. H. One-step semi-continuous cyclohexanone production via hydrogenation of phenol in a submerged ceramic membrane reactor. *Chem. Eng. J.* **2016**, *284*, 724-732.
2. Qu, Z. Y.; Hu, S.; Jiang, H.; Liu, Y. F.; Huang, J.; Xing, W. H.; Chen, R. Z. A side-stream catalysis/membrane filtration system for continuous liquid-phase hydrogenation of phenol over Pd@CN to produce cyclohexanone. *Ind. Eng. Chem. Res.* **2017**, *56*, 11755-11762.
3. Masoodi, R.; Tan, H.; Pillai, K. M. Darcy's law-based numerical simulation for modeling 3D liquid absorption into porous wicks. *AIChE J.* **2011**, *57*, 1132-1143.