Electronic Supplementary Information (ESI) for

Pd-TSH composite membrane reactor for one-step oxidation of benzene to phenol

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1. Experimental details

1.1 Preparation of TSH zeolite

Titanium silicalite-1 (TS) zeolite was synthesized using the method that described in our previous works [1-4]. In a typical synthesis procedure, the TEOS (tetraethyl orthosilicate) was slowly added into the TPAOH (tetrapropylammonium hydroxide) solution under vigorous stirring followed by the dropwise addition of TBOT (tetrabutyl orthotitanate) dissolved in dry IPA (isopropyl alcohol) with a molar composition of 1 SiO_2: 0.02 TBOT: 0.45 TPAOH: 19.2 H_2O. The mixture was heated to 363 K in a water bath for 40 min to remove the alcohols. After that, distilled water was added to make up for the lost water during the heating process. The mixture was aged for 24 h at room temperature and then the solutions were placed inside a Teflon-lined stainless steel autoclave and heated at 398 K for 8 h. The TS zeolite was recovered by a sequence of centrifugation and washing with distilled water. After drying at 383K and calcined at 823K, the prepared TS zeolite was post-treated with 0.5mol/L TPAOH solution in an autoclave at 448K for 24h. The treated TS zeolite denoted as TSH was then washed with distilled water, dried at 383K and calcined at 823K for 6h to remove organic templates.

1.2 Preparation of Pd-TSH composite membrane

The α-Al_2O_3 composite hollow fibers were prepared by phase inversion technique followed by high temperature sintering as described in our previous work [5]. 1.0wt.% $PdCl_2$ (palladium chloride) was uniformly dispersed into a mixture of γ-AlOOH sol and polyvinyl alcohol (PVA) under vigorous stirring. Then the γ-AlOOH sol containing Pd^{2+} was deposited on the α-Al_2O_3 hollow fibers through dip-coating method. The γ-AlOOH sol containing Pd^{2+} seeds would deposit on the outer and inner surfaces of hollow fibers. The sol could also enter the inside of hollow fiber along the pores and large finger-like channels (with size 30-50 μm). After that, the hollow fibers were calcined at 723 K in air followed by activation at 723 K for 3h under H_2 atmosphere to convert Pd^{2+} to Pd^0 seeds. The activated hollow fibers were deposited with Pd using the electroless plating solution containing $PdCl_2$,

$Na_2EDTA{\cdot}2H_2O$ ($C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$), $NH_3{\cdot}H_2O$ and N_2H_4 (hydrazine) at 318 K. The Pd/Al_2O_3 composite membranes were carefully rinsed with distilled water and then dried at 393K in an oven. The use of embedded Pd seeds avoids the time consuming sensitization and activation steps involved in conventional electroless plating method. After that, the TSH zeolite was deposited on the surface of Pd membrane (inner surface) via a novel APTS-assisted method as reported in our recent work [1]. The procedure involved the grafting alkoxysilane moieties on the Pd membrane followed by the attachment of TSH zeolite on the Pd membrane.

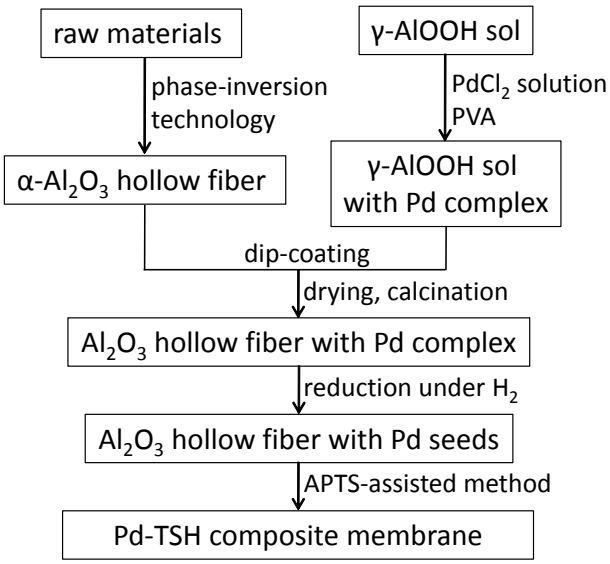

Fig. S1 The preparation procedure for the Pd-TSH composite membrane.

1.3 One-step oxidation of benzene to phenol

The schematic structure of the Pd-TSH catalytic membrane reactor is shown in Fig. S2. Benzene and O_2 were fed into the tube side facing TSH catalyst, while H_2 was flowed into the shell side (i.e., outside surface of hollow fiber). Benzene was fed as vapour by bubbling N_2 through benzene saturator. All of gases were metered by mass flow controllers and the reaction was conducted at 473K. The pipeline between furnace and chromatograph was heated by temperature controller to avoid the condensation of products. The reaction was monitored using two online gas chromatographs (GC-7900 and GC-6890N). The organic compounds were analyzed by a flame ionization detector (FID) with a 50m SE-30 capillary column. The temperature of sampler and detector was set at 260 °C and 280 °C, respectively.

In order to detect all possible products, the column temperature was controlled by third-order temperature programmed process. Inorganic products were determined by a thermal conductivity detector (TCD) with a 13X molecular sieve and a GDX molecular sieve packed columns. The benzene conversion and phenol selectivity were calculated by the following equations (1) and (2). The phenol yield was obtained by the product of benzene coversion and the phenol selectivity.

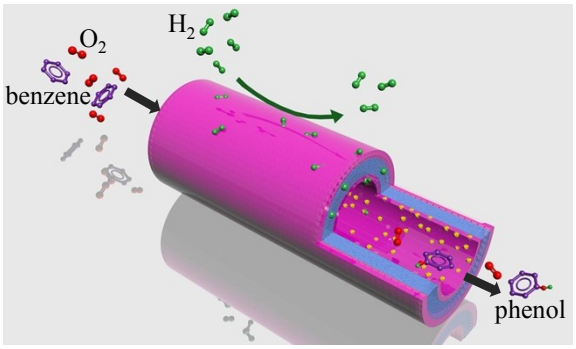

Fig. S2 Reaction scheme of Pd-TSH composite membrane reactor.

$$X_{benzene} = \frac{mol\ (reacted\ benzene)}{mols\ (unreacted\ benzene + generated\ products)} \quad (1)$$

$$S_{phenol} = \frac{mol\ (phenol)}{mols\ (phenol + other\ products)} \quad (2)$$

2. EDX analysis

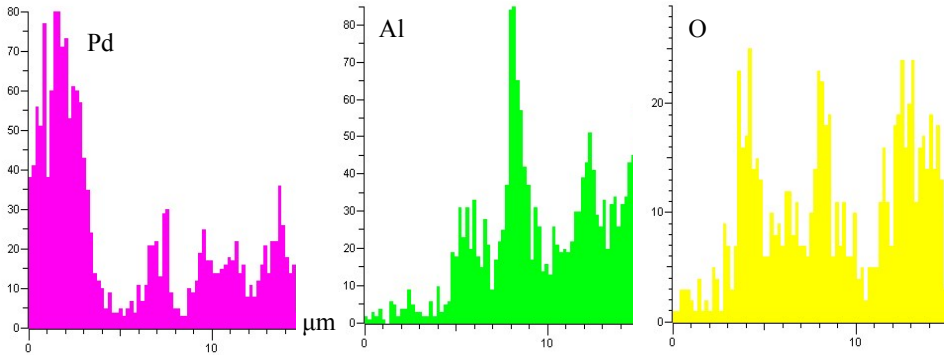

Fig. S3 EDX analysis of Pd, Al and O.

3. XRD patterns of TS and TSH zeolite

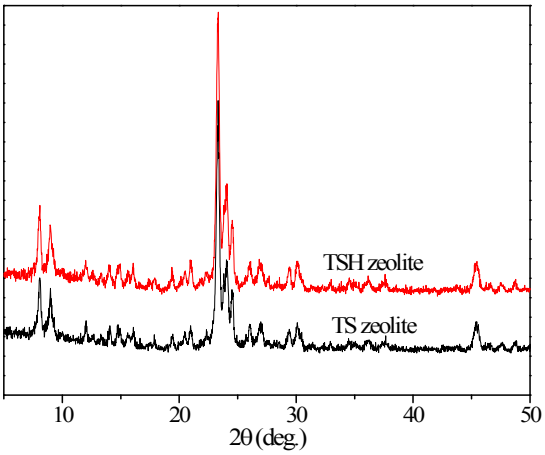

Fig. S4 XRD patterns of TS and TSH zeolite.

4. The comparison of H_2 fluxes through different Pd membranes

Table S1 The comparison of H_2 fluxes thourgh Pd membranes.

Substrate	Method	Thickness (μm)	T (K)	H_2 flux ($mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$)	Ref.
Al_2O_3 tube (o.d.=3mm, i.d.=2.3mm)	CVD	2-4	573	3.33×10^{-6}	[6]
Al_2O_3 hollow fibre (o.d.=2.9mm, i.d.=2.2mm)	Modified ELP	5	773	3.30×10^{-6}	[7]
Al_2O_3 tube (o.d.=13mm, i.d.=8mm)	Modified ELP	2.4	773	3.8×10^{-6}	[8]
Al_2O_3 tube (o.d.=11mm, i.d.=9.5mm)	VELP	6	753	9.0×10^{-7}	[9]
Al_2O_3 tube (o.d.=13mm, i.d.=9mm)	Modified ELP	5	773	1.78×10^{-6}	[10]
Al_2O_3 tube (o.d.=2.9mm, i.d.=2.2mm)	Modified ELP	0.9	733	3.81×10^{-6}	[11]
Al_2O_3 hollow fibre (o.d.=2.72mm, i.d.=1.83mm)	ELP	1.0	723	5.27×10^{-6}	[12]
Capillary α-Al_2O_3 (o.d.=2.8mm, i.d.=1.9mm)	ELP	5	773	3.51×10^{-6}	[13]
Al_2O_3 hollow fibre (o.d.=2.2mm, i.d.=1.5mm)	Modified ELP	1-2	773	5.99×10^{-6}	This work
Al_2O_3 hollow fibre (o.d.=2. 2mm, i.d.=1.5mm)	Modified ELP	1-2	723	4.99×10^{-6}	This work
Al_2O_3 hollow fibre (o.d.=2. 2mm, i.d.=1.5mm)	Modified ELP	1-2	573	1.99×10^{-6}	This work

ELP: electroless plating, CVD: chemical vapour deposition, VELP: vaccum assisted electroless plating.

5. The long-term stability test

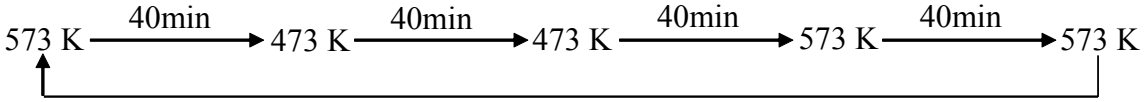

Fig. S5 The temperature program for thermal stability test.

The temperature of the membrane was changed from 573 K to 473 K as shown in Fig. S5. Each temperature cycle consists of a cooling-down process from 573 K to 473 K, heating-up process from 473 K to 573 K and two constant temperature processes at 473 K and 573 K. The heating rate and cooling rate were set at 2.5 K/min. Each thermostatic process at 473 K and 573 K lasted for 40 min, respectively.

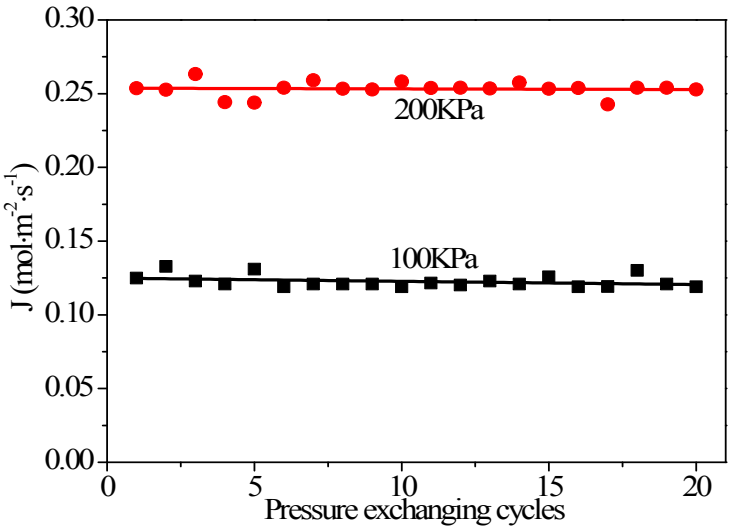

Fig. S6 Stability of Pd-TSH membrane for the pressure changing test at 473K.

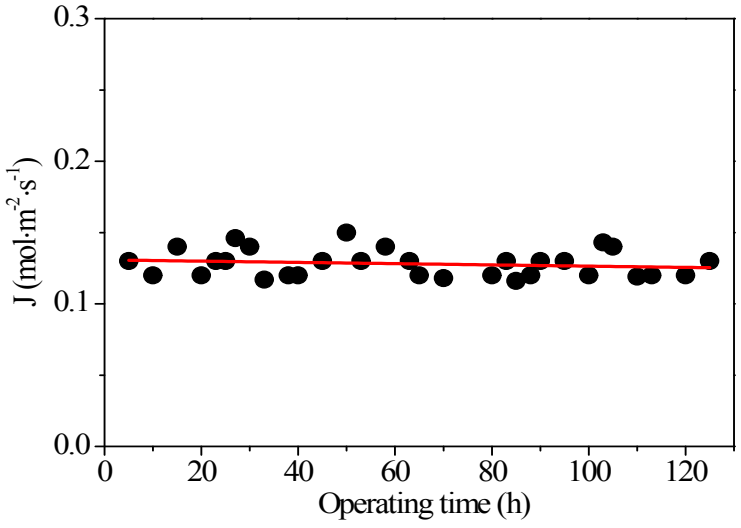

Fig. S7 Long-term operation for H_2 flux at 473 K and 100 kPa.

Table S2 Comparison of membrane productivity on different Pd membranes.

Phenol (kg/kgPd/h)	H_2O/phenol ratio	Benzene conversion (%)	Phenol selectivity (%)	Ref.
1.5	500	13.25	85.3	[14,15]
0.1	120	3.8	4.1	[16]
1.33	153	22.71	94.79	[1, our previous work][a]
1.04	122	18.87	86.35	[17, our previous work]
1.68	118	21.9	97.6	This work

a: the phenol production and H_2O/phenol ratio were not shown in the paper.

6. The reaction pathway in Pd-TSH composite membrane

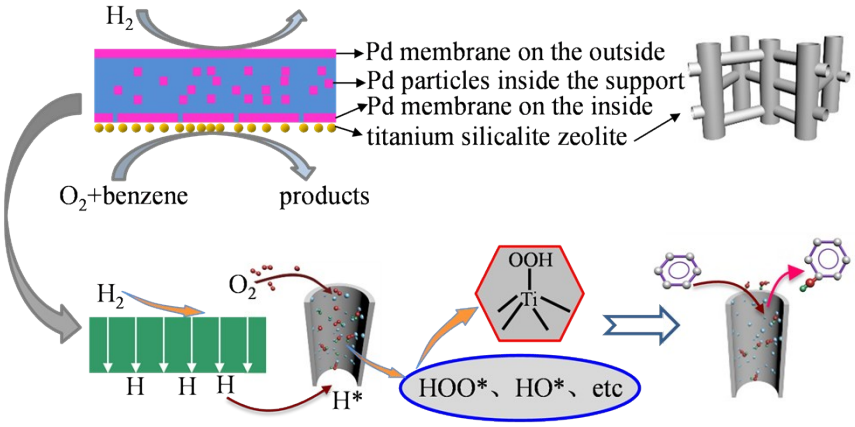

Fig. S8 The reaction pathway in Pd-TSH composite membrane.

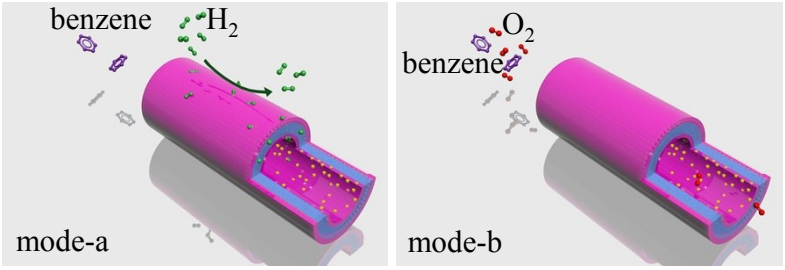

Fig. S9 Modes of reaction scheme with Pd-TSH composite membrane.

Reactor mode-a, the benzene was fed to the TSH zeolite side (tube side) and H_2 was fed to the outside of Pd membrane (shell side). Reactor mode-b co-fed the benzene and O_2 mixture to the TSH zeolite side (tube side).

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