Supplementary information

Pd-silicalite-1 composite membrane for direct hydroxylation of benzene

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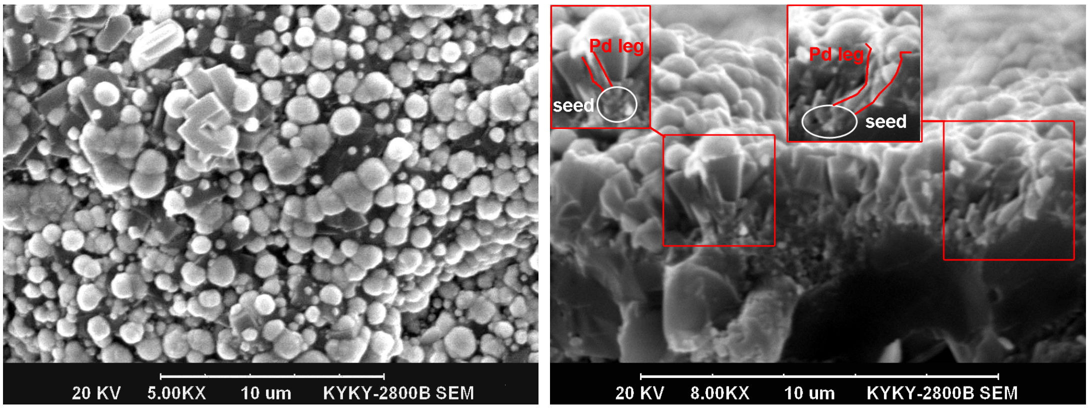
1. Preparation of Pd-silicalite-1 membrane and analysis of membrane structure.

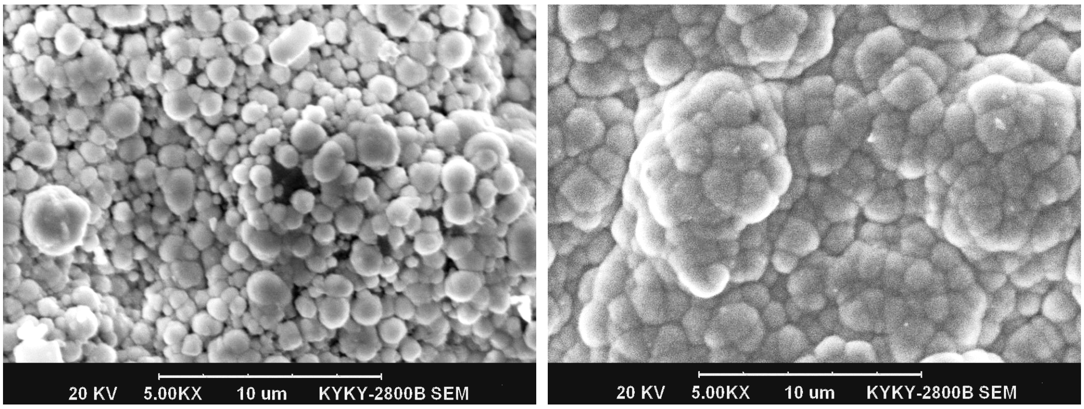
Asymmetric membrane structures are common in metal and inorganic membranes and the stability of the final membrane is dependent on the underlying support structures. The zeolites have strong adhesion on ceramic and metal surfaces [1-3] and can tolerate high temperature (up to 800 K). The thermal expansion coefficients of alumina and palladium are 0.65×10^{-5} K^{-1} and 1.17×10^{-5} K^{-1}, respectively and the expansion coefficient of zeolites are considered to be similar to that of the ceramic alumina. Zeolites have been used as supporting layer for Pd composite membrane [4-6] and there is no evidence that zeolites impair the performance of membrane.

The SEM image in Fig. 1 shows that the Pd growth starts from the zeolite seed layer, filling the inter-zeolite pores before forming a Pd film on the surface of the zeolite layer shown in Fig. 2. The Pd deposition process explains the formation of the Pd protrusions that anchors the film to the support.



(a) (b)

Fig.1 Pd deposits on the modified support at initial plating stage (10min): (a) surface and (b) cross section of Pd deposit on Sil-1 layer.



(a) (b)

Fig.2 Pd deposits on the surface of the modified support with different deposition time: (a) 30min; (b) 60min.

The Pd-Sil-1 membrane cross-section was characterized by EPMA and shown in Fig.3. It can be seen from the figure that palladium penetrates through the zeolite layer to the seed layer.

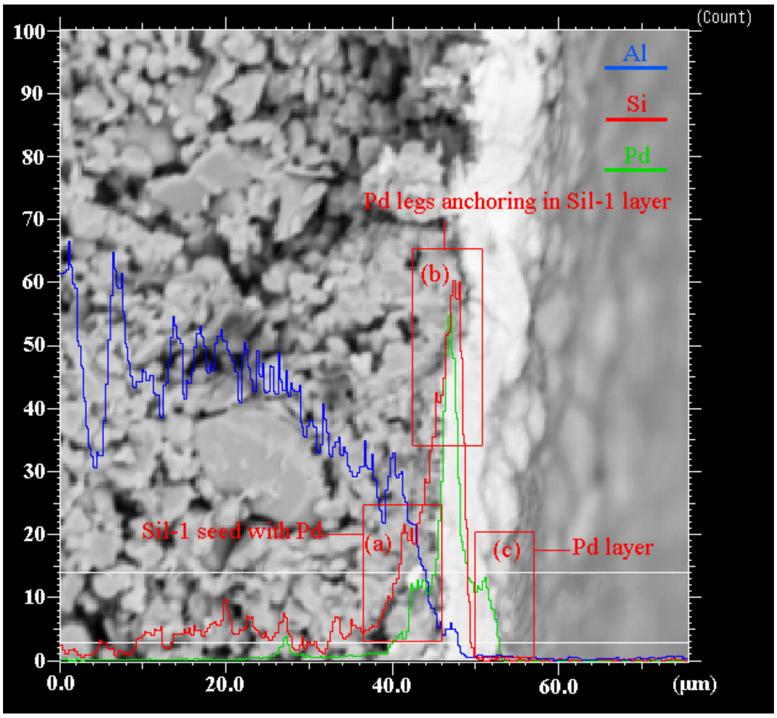


Fig.3 EPMA profiling of the Pd-silicalite-1 membrane: lining analysis

2. Pressure cycling test

The H_2 permeation performance was tested at a trans-membrane pressure gradient of 100 kPa, followed by a rapid decrease to a pressure gradient of 20 kPa and back to the original 100 kPa gradient. This was repeated 15 times at a temperature of 773K. Fig. 4 shows that hydrogen flux remained unchanged after each cycle.

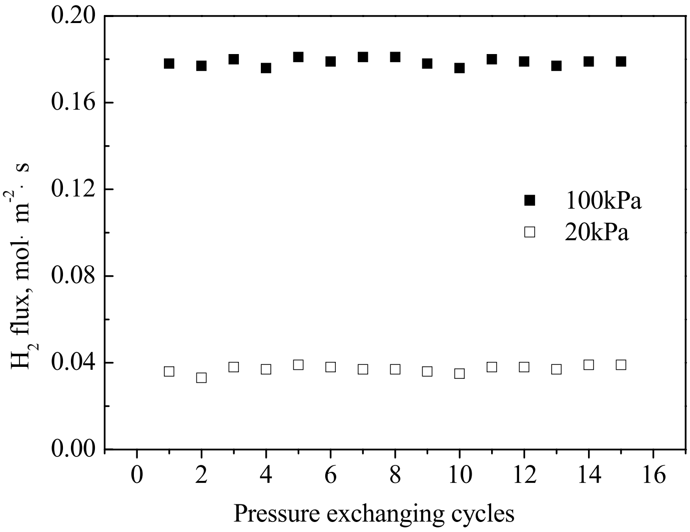


Fig.4 H_2 flux of as-prepared Pd-silicalite-1 membrane after successive pressure exchanging cycles between pressure difference of 100kPa and 20kPa at the operating temperature of 773K.

3. Gas cycling test

Fig.5 shows that the H_2 flux and ideal separation factor is constant after 200 h and 18 repeat cycles of changing between hydrogen and nitrogen gases. The Pd membrane was tested

One cycle: $H_2 \rightarrow N_2 \rightarrow H_2$

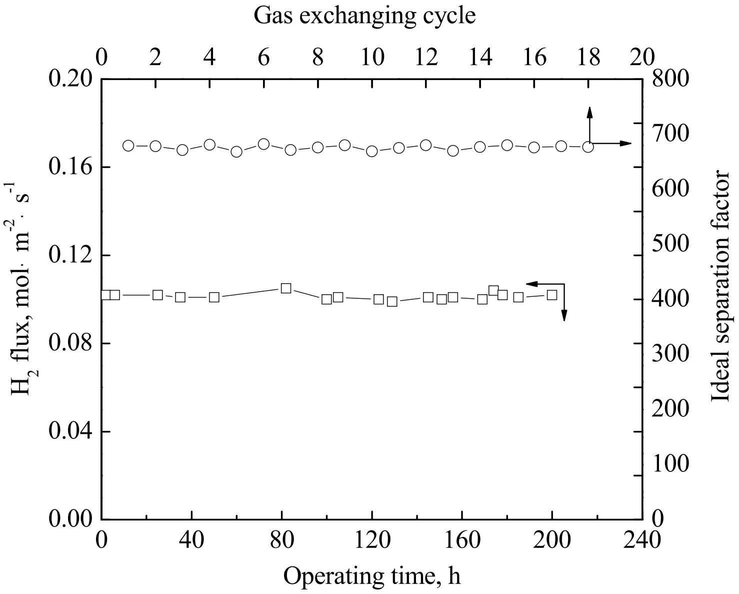


Fig.5 The stability of the Pd-silicalite-1 membrane for long term test with H_2 and N_2.

4. Temperature cycling test

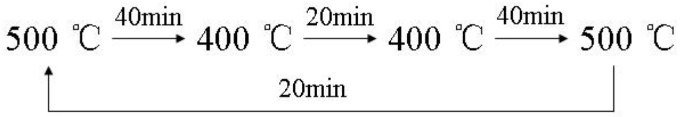


Fig.6 shows that the temperature program.

The temperature of the membrane was changed from 773 K to 673 K according the program cycle shown in Fig. 6. The H_2 was also changed to N_2 every 5 cycles during the experiment. The membrane flux and selectivity remained unchanged for the entire experiment.

5. Comparison of the Pd membrane stability reported in the literature and this work

A comparison was made for Pd/alumina, Pd/Sil-1/alumina and Pd-Sil-1 composite membranes for direct hydroxylation of benzene to phenol at 573 K. The Pd/alumina membrane suffered embrittlement at this low operating temperature. The Pd/Sil-1/alumina membrane was prepared by conventional electroless plating of Pd on seeded Sil-1 film on alumina. No anchoring legs were observed in Pd/Sil-1/alumina membrane and the membrane delaminated after 40 h of direct hydroxylation reactions (Fig. 7). On the other hand, the Pd-Sil-1 composite membranes were stable even after 120 h of reaction. Although this is in no way a measure of the membrane stability, it does give an indication as to the severity of the reaction towards the membrane.

Fig.7 Pd/Sil-1/alumina membrane after direct hydroxylation of benzene

Tables 1 and 2 compares the stability and hydrogen permeance of different Pd membranes reported in literature to the Pd-Sil-1 composite membrane prepared in this work.

Table 1 Comparison of the membrane stability of different Pd membranes

Membrane	Thickness (μm)	Stability test			
		a	b	c	d
Pd/ Al_2O_3[7]	5	170h, 773 K	40 cycles, H_2 and He	-	-
Pd-Ag/PSS[8]	84.6	500h, 773 K	-	-	-
Pd/ Al_2O_3[9]	5	470h, 773 K	10 cycles, H_2 and Ar at 753 K	10 cycles, 723-773 K	-
This work	5	200h, 623 K	10 cycles, H_2 and N_2 at 473K	15 cycles, 673-773 K	10 cycles, 20-100kPa

PSS is porous stainless steel; [a] Long term operation test; [b] Gas exchanging cycling test; [c] Thermal changing cycling test; [d] Pressure exchanging cycling test.

Table 2. Comparison of hydrogen permeation flux for Pd composite membranes

Membrane	Thickness (μm)	Temperature (K)	H_2 flux (mol m^{-2} s^{-1})	Selectivity	Ref.
Pd/SiO_2/PSS	5	773 K	0.270	300-450	[4]
Pd/ZrO_2/PSS	10	773 K	0.083	160	[10]
Pd/Al_2O_3	5	773 K	0.333	∞	[7]
Pd/Al_2O_3	3-4	773 K	0.136	1000	[11]
Pd/silicalite-1/ Al_2O_3	5	773 K	0.178	1280	This work

6. H_2 permeation test between 473~773K

The H_2 flux varies linearly with trans-membrane H_2 pressure difference and increases with temperature as shown in Fig.8.

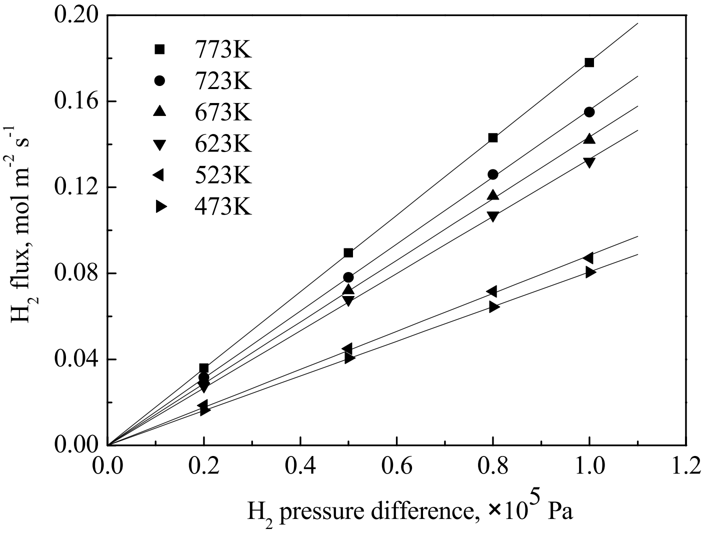


Fig.8 H_2 flux as a function of pressure difference at different temperatures

7. Hydroxylation of benzene

The direct hydroxylation of benzene was conducted with hydrogen in the tube side and the reactants oxygen and benzene as well as the nitrogen diluent in the shell side. The gases were metered by mass flow controllers and the benzene vapor was fed by bubbling nitrogen to benzene saturator. The reaction temperature was kept at 473K and the products were analyzed by two online gas chromatographs (GC-7890T; GC-7890F) as shown in Fig.9.

Prior to the reaction, the H_2 permeance for the Pd-Sil-1 membrane was measured to be 9.73×10^{-7} $mols^{-1}m^{-2}Pa^{-1}$ with an ideal separation of 520 at 473K. The permeated hydrogen and unreacted hydrogen were monitored during the reaction (Fig. 10) and it can be seen that the membrane operation is stable during the hydroxylation reaction. Also, a comparable H_2 permeance of 9.68×10^{-7} $mols^{-1}m^{-2}Pa^{-1}$ and separation factor of 515 was obtained after the reaction. The catalytic activity for the Pd-silicalite-1 membrane was stable during the prolonged reaction (Table 2).

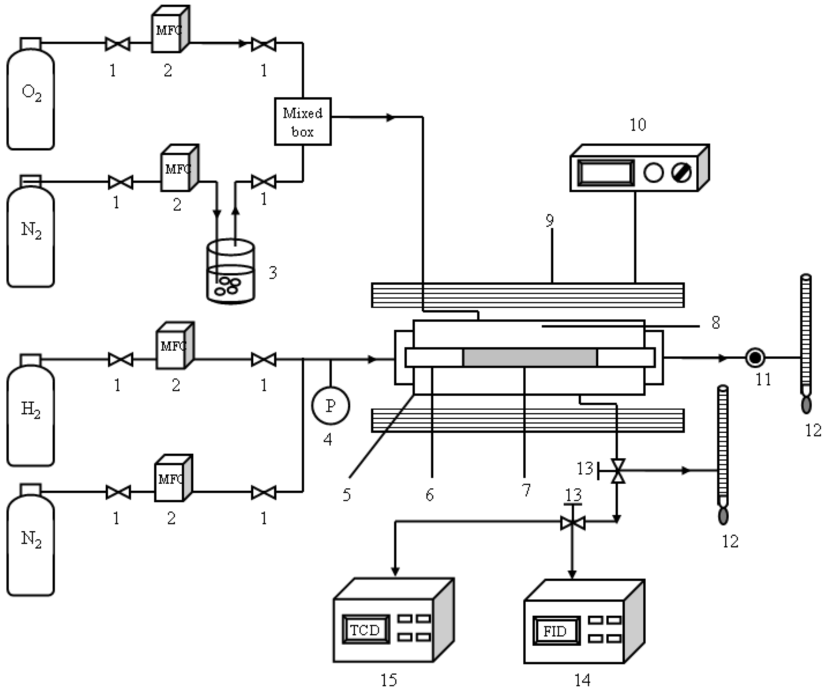


Fig.9 Apparatus used for hydroxylation of benzene

1.on/off valve; 2.mass flow controller; 3. benzene container; 4. pressure gage; 5. stainless steel reactor; 6. glass enamel; 7. Pd-silicalite-1 membrane; 8. thermocouple; 9. furnace; 10. temperature controller; 11. needle valve; 12. bubble flowmeter; 13. three way valve; 14. on-line gas chromatograph equipped with FID detector; 15. on-line gas chromatograph equipped with TCD detector.

Table 2 Comparison of the catalytic stability of different Pd-based membranes in hydroxylation of benzene

Membrane	Thickness (μm)	Hydroxylation of benzene		
		Benzene conversion (%)	Phenol yield (%)	Reaction time[a] (hour)
Pd/ Al_2O_3[12]	1	18	14.5	5
Pd / Al_2O_3[13]	4	25~30	19~23	7
Pd/Al_2O_3[14]	1	10	4	24
Pd/Al_2O_3[15]	2	3.8	0.16	-[b]
This work	5	4~6	2.5~3.5	46

[a] Reaction time is the durability for the Pd membrane with stable catalytic performance.

[b] -: unknown.

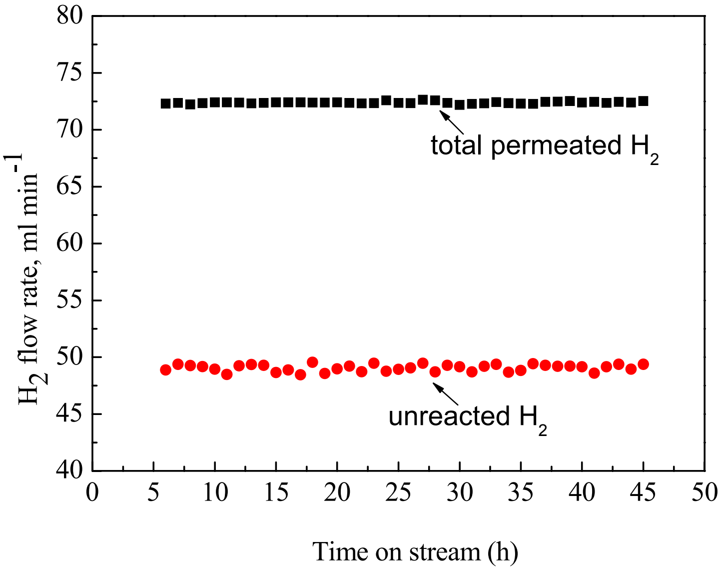


Fig.10 H_2 flow rate as function of time on stream

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