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รองรับบนเหล็กกล้าไร้สนิมพูน

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DRY REFORMING OF METHANE USING DENSE PALLADIUM MEMBRANE
SUPPORTED ON POROUS STAINLESS STEEL

Mr. Sutheerawat Samingprai

A Dissertation Submitted in Partial Fulfillment of the Requirements
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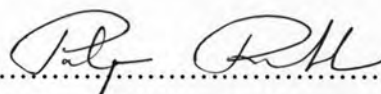
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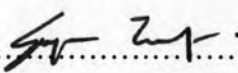
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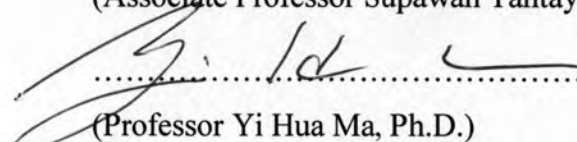
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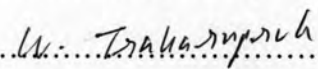
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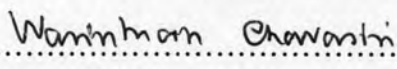
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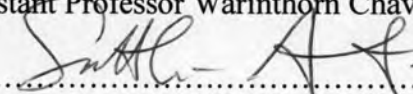
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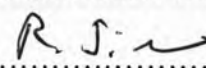
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ในงานวิจัยนี้ได้เคลือบแพลเลเดียมบนเหล็กกล้าไร้สนิมพอรุนด้วยเทคนิคการเคลือบแบบไม่ใช้
กระแสไฟฟ้าได้ศึกษาสภาวะการเคลือบโดยใช้ชั้นเหล็กกล้าไร้สนิมชนิดธรรมดาและชนิดมีรูพอรุน พบว่าสภาวะ
การเคลือบที่เหมาะสมคือ อุณหภูมิ 60°C เป็นเวลา 90 นาทีและวัดความหนาของชั้นแพลเลเดียมโดยการชั่ง
น้ำหนักและเปรียบเทียบกับผลที่ได้จากเอสซีเอ็ม ได้ตรวจพบการแพร่ของโลหะจากเหล็กกล้าไร้สนิมพอรุนไปยัง
ชั้นแพลเลเดียมเมื่ออุณหภูมิสูงกว่า 500°C ด้วยวิธีเอสซีเอ็ม-อีดีเอสได้เตรียมท่อแพลเลเดียมเมมเบรนสองท่อที่มี
พื้นที่ผิวที่มีประสิทธิภาพขนาด 20 ตารางเซนติเมตร และมีขนาดรูเฉลี่ย 0.1 ไมครอน ได้แก่ ท่อหมายเลข 1 (ความ
หนา 19.3 ไมครอน) และท่อหมายเลข 2 (ความหนา 17.5 ไมครอน) ได้ตรวจสอบสมบัติการใช้งานของท่อทั้งสอง
โดยประกอบอยู่ในเตาปฏิกรณ์ แล้ววัดฟลักซ์ของฮีเลียมและฟลักซ์ของการแทรกผ่านของไฮโดรเจนที่อุณหภูมิ
350-450°C และที่ความแตกต่างของความดัน 1-3 บรรยากาศไม่มีฟลักซ์ของฮีเลียมสำหรับท่อหมายเลข 1 และ
ตรวจพบฟลักซ์ของฮีเลียมเล็กน้อยสำหรับท่อหมายเลข 2 ดังนั้นจึงพิสูจน์ได้ว่าแพลเลเดียมเมมเบรนของทั้งสอง
ท่อเป็นแบบแน่น พบว่าการเปลี่ยนของมีเทนและคาร์บอนไดออกไซด์มีค่าสูงขึ้นเมื่อใช้เตาปฏิกรณ์แบบท่อ
แพลเลเดียมเมมเบรนที่มีท่อหมายเลข 1 เปรียบเทียบกับเตาปฏิกรณ์แบบท่อธรรมดาโดยใช้ 1.0%PvAl₂O₃ เป็น
ตัวเร่งปฏิกิริยาที่สภาวะปฏิกิริยาเดียวกัน ซึ่งติดตามด้วยเทคนิคแก๊สโครมาโทกราฟี เมื่ออุณหภูมิของเตาปฏิกรณ์
เพิ่มขึ้นการเปลี่ยนเพิ่มขึ้นด้วย ยิ่งกว่านั้นเมื่อใช้อาร์กอนเป็นสวิตช์แก๊สค่าการเปลี่ยนสูงขึ้นเมื่ออัตราการไหลของ
สวิตช์แก๊สเพิ่มขึ้น เพื่อป้องกันการแพร่ของโลหะ ได้ใช้วัสดุหลายชนิดเป็นกันชั้นเพิ่มขึ้นบนชั้นเหล็กกล้าไร้สนิม
พอรุนก่อนเคลือบแพลเลเดียม ได้แก่ เงิน-ทังสเตน ซิลิกา โครเมียม และโครเมียมออกไซด์ หลังจากปล่อยให้ใน
ฮีเลียมที่อุณหภูมิ 500°C เป็นเวลา 24 ชั่วโมง ได้ตรวจสอบการแพร่ของโลหะระหว่างชั้นด้วยเอสซีเอ็ม พบว่าไม่มี
การแพร่ของโลหะระหว่างชั้นในกรณีของชั้นโครเมียมออกไซด์ ได้เตรียมท่อแพลเลเดียมเมมเบรนที่มีความหนา
ของชั้นแพลเลเดียม 3.2 ไมครอน คือท่อหมายเลข 3 ซึ่งมีชั้นโครเมียมออกไซด์เป็นชั้นกันการแพร่ของโลหะ
ระหว่างชั้นซึ่งมีความหนา 2.0 ไมครอน ได้รับรองว่าท่อหมายเลข 3 มีแพลเลเดียมเมมเบรนแบบแน่นด้วยการวัดฟ
ลักซ์ของฮีเลียมพบว่าฟลักซ์ของการแทรกผ่านของไฮโดรเจนไม่ลดลงที่อุณหภูมิ 500°C ซึ่งตรงข้ามกับผลก่อน
หน้านั้นเมื่อใช้ท่อแพลเลเดียมเมมเบรนที่ไม่มีชั้นโครเมียมออกไซด์ แสดงว่าโครเมียมออกไซด์เป็นชั้นป้องกันการ
แพร่ของโลหะระหว่างชั้นที่ดี

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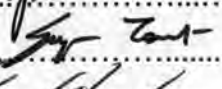
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In this research, the electroless plating technique had been used for palladium plating on porous stainless steel. The plating condition was determined using normal and porous stainless steel disks. The appropriate plating condition was at 60°C for 90 minutes and palladium layer thickness was measured gravimetrically and compared with the results from SEM. By using SEM-EDS, the metal diffusion from stainless steel to palladium layer was found when the temperature was higher than 500°C. Two palladium membrane tubes with effective surface area of 20 cm² and average pore size 0.1 μm, Tube 1 (19.3 μm thickness) and Tube 2 (17.5 μm thickness), were prepared. The performance testing of these tubes were investigated by assembling it in the reactor. Helium flux and hydrogen permeation flux were then measured at 350-450°C and pressure differences 1-3 atm. The helium flux was not detected for Tube 1 and only a trace of helium flux was found for Tube 2. Therefore, palladium membranes of both tubes were proved to be dense. Higher conversion of methane and carbon dioxide using palladium membrane tube reactor containing Tube 1, comparing to conventional tube reactor utilized 1% Pt/Al₂O₃ as the catalyst at the same reaction condition was resulted which was monitored by gas chromatographic technique. It was also found that higher conversions were obtained when the temperature of reactor increased. Furthermore, when argon was used as a sweep gas, higher conversion was obtained and increased with increasing sweep gas flow rate. To prevent the metal diffusion, several kinds of materials as the incremental layer on porous stainless steel disks were generated before palladium plating, i.e. silver-tungsten, silica, chromium, and chromium oxide. After the exposure at 500°C for 24 hours in helium, the intermetallic diffusion of these disks was investigated by SEM. It was found that no intermetallic diffusion was observed in case of Cr₂O₃ layer. The palladium membrane tube with palladium layer thickness of 32μm, Tube 3, was then prepared with Cr₂O₃ intermetallic diffusion barrier at the thickness of 2μm. It was confirmed to have dense palladium membrane by helium flux measurement. Its hydrogen permeation flux at 500°C was not declined, which was in contrast to the previous result when the other palladium membrane tube without Cr₂O₃ layer was used, implying that Cr₂O₃ acted as the good intermetallic diffusion barrier.

Field of studentPetrochemistry.....Student's signature.....

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List of Abbreviation and signs

C_{H_2}	Hydrogen concentration [mol/cm^3].
C_{pi}	Heat capacity [$\text{J}/\text{mol}\cdot\text{K}$].
D_i	Diffusion coefficient of the component I [cm^2/s].
E_a	Activation energy [kJ/mol].
F	Gas permeance [$\text{mol}/(\text{m}^2\cdot\text{s}\cdot\text{Pa}^n)$ or $\text{m}^3/(\text{m}^2\cdot\text{h}\cdot\text{atm}^n)$].
G	Gibbs free energy [J]
H	Enthalpy [J/mol]
J	Gas peameation flux [$\text{mol}/(\text{m}^2\cdot\text{s})$ or $\text{m}^3(\text{STP})/(\text{m}^2\cdot\text{h})$].
J_i	Gas peameation flux of the component i [$\text{mol}/(\text{m}^2\cdot\text{s})$ or $\text{m}^3(\text{STP})/(\text{m}^2\cdot\text{h})$].
k_i	Reaction rate constant of the reaction i [$\text{kmol K}^m/(\text{kg}\cdot\text{h}\cdot\text{bar}^n)$ (for k_1 and k_2 , $m=0$, $n=1$; for k_3 and k_5 , $m=0$, $n=2$; for k_4 , $m=0$, $n=1.5$; for k_6 , $m=3$, $n=3$)] or rate constant of the sissolution of hydrogen in palladium [$\text{mol}/(\text{m}^2\cdot\text{s})$].
k_a	Adsorption rate constant [$\text{mol}/(\text{cm}^2\cdot\text{s}\cdot\text{atm})$].
k_d	Desorption rate constant [$\text{mol}/(\text{cm}^2\cdot\text{s})$].
k_o	Rate constant of reverse dissolution of hydrogen in paladium [$\text{mol}/(\text{m}^2\cdot\text{s})$].
K_p	Reaction equilibrium constant.
L	Thickness of the palladium layer [m]; length of the reactor [m].
M	Molecular mass of the gas [kg/mol or g/mol].
n	Exponent of pressure or n is the atomic H/Pd ratio.
n_i	Mole of the component i.
P	Upsteam pressure [atm or Pa].
P_{ave}	Average pressure across the membrane [atm or Pa].
P_o	Downsteam pressure[atm or Pa].
P^s	Total pressure in the shell side [atm or Pa].
P^t	Total pressure in the tube side [atm or Pa].
P_i^s	Partial pressure of the component i in the shell side [atm or Pa].
P_i^t	Partial pressure of the component i in the tube side [atm or Pa].
P_i	Partial pressure of the component i [atm or Pa].

P_T	Total pressure [atm or Pa].
Q	Permeation coefficient, or permeability [mol·m/(m ² ·s·Pa ⁿ) or m ³ m/(m ² ·h·atm ⁿ)].
R	Gas constant [J/mol K], R=8.315
T	Temperature [K].
X_i	Mole fraction of component i in the shell side.
X	Ethylbenzene conversion.
Y_i	Mole fraction of component i in the tube side.
α^*	Selectivity of coefficient
θ	Separation factor or the surface hydrogen coverage.
θ_k	Refection factor for Knudsen mechanism of diffusion.
J	Flux of permeated gas through the palladium membrane, m ³ /m ² h
Q	Permeability, m ³ cm/m ² h atm ^{0.5}
F	Permeance, m ³ /m ² h atm ^{0.5}
L	Palladium membrane length, cm
(J_{He})	Helium flux
(J_{H_2})	Hydrogen flux
$\alpha_{H_2/He}$	Selectivity
PSS	Porous Stainless Steel