

**ADSORPTIVE REMOVAL OF SULFUR COMPOUNDS FROM
TRANSPORTATION FUELS BY USING ZEOLITIC ADSORBENTS**

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ABSTRACT

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This research work was conducted to study the modification of NaY zeolite by ion-exchanging with selected transition metal ions (Cu^{2+} , Ni^{2+}) in order to enhance the capacities of adsorbents for adsorptive removal of refractory sulfur compounds which are difficult to remove by using conventional methods. The efficiencies of the Cu(II)Y and NiY zeolites in removing model sulfur compounds (3-methylthiophene, benzothiophene and dibenzothiophene) from simulated transportation fuels such as isooctane and decane were examined and systematically related to type and amount of metal loading by batch method at ambient conditions. The amount of metal loading on both CuY and NiY zeolites was varied by using different amount of metal solution to NaY zeolite ratio. The results showed that the adsorption isotherms were well fitted with Langmuir isotherm. From the results, CuY zeolite showed markedly high adsorptive capacities in adsorbing 3-MT, BT and DBT than NiY and NaY zeolites. The adsorption capacity of CuY zeolite was directly proportional to the amount of Cu^{2+} loading instead of NiY zeolite which had low Ni^{2+} dependency. The difference in adsorption capacities was probably due to the effect of pore size of zeolite after exchanged with transition metals.

บทคัดย่อ

ทรงพล พริ้งประยงค์ : การกำจัดสารประกอบกำมะถันออกจากร้ำมันเชื้อเพลิงโดยการดูดซับบนใช้ซีโอไลต์เป็นตัวดูดซับ (Adsorptive Removal of Sulfur Compounds from Transportation Fuels by Using Zeolitic Adsorbents) อ. ที่ปรึกษา : ผศ. ดร. ปมทอง มาลากุล ณ อยุธยา และดร. โชฟี จูเลียน 82 หน้า

งานวิจัยนี้จัดทำขึ้นเพื่อมุ่งเน้นในการศึกษาการปรับปรุงโซเดียมวอยซีโอไลต์โดยใช้การแลกเปลี่ยนไอออนกับโลหะทรานซิชัน เช่น โลหะนิกเกิล และโลหะคอปเปอร์ เพื่อเพิ่มประสิทธิภาพของตัวดูดซับในการกำจัดสารประกอบกำมะถัน ที่กำจัดได้ยากโดยใช้กระบวนการที่ใช้อยู่ในปัจจุบัน โดยประสิทธิภาพของคอปเปอร์วอยซีโอไลต์ (CuY zeolite) และ นิกเกิลวอยซีโอไลต์ (NiY zeolite) ในการกำจัดแบบจำลองสารประกอบกำมะถัน เช่น 3-เมทิลไทโอเฟน เบนโซไทโอเฟน และไคเบนโซไทโอเฟน ออกจากแบบจำลองน้ำมันเชื้อเพลิงแก๊ซโซลีน และดีเซล เช่น ไอโซออกเทน และเดเคน ตามลำดับ จะทำการศึกษาจากผลของชนิดของโลหะทรานซิชัน และปริมาณของโลหะทรานซิชันที่แลกเปลี่ยนกับโซเดียมวอยซีโอไลต์โดยใช้การทดลองแบบกะ (batch method) ที่สภาวะบรรยากาศ ผลของปริมาณสารละลายโลหะทรานซิชันต่อปริมาณตัวดูดซับปริมาณที่ส่งผลต่อปริมาณของโลหะทรานซิชันที่ทำการแลกเปลี่ยนกับโซเดียมไอออนของโซเดียมวอยซีโอไลต์จะทำการศึกษา โดยกราฟแสดงผลของปริมาณกำมะถันที่ถูกดูดซับที่อุณหภูมิคงที่สามารถทำนายได้โดยใช้สมการของแลงเมียร์ (Langmuir isotherm) โดยคอปเปอร์วอยซีโอไลต์สามารถดูดซับ 3-เมทิลไทโอเฟน เบนโซไทโอเฟน และไคเบนโซไทโอเฟน ได้สูงกว่านิกเกิลวอยซีโอไลต์และโซเดียมวอยซีโอไลต์ และความสามารถในการดูดซับของคอปเปอร์วอยซีโอไลต์เป็นสัดส่วนโดยตรงกับปริมาณคอปเปอร์บนตัวดูดซับ ซึ่งแตกต่างกับนิกเกิลวอยซีโอไลต์ที่ไม่ได้ขึ้นอยู่กับปริมาณนิกเกิลบนตัวดูดซับ ความสามารถในการดูดซับที่แตกต่างกันอาจจะมีผลมาจากขนาดของรูพรุนของซีโอไลต์หลังจากทำการแลกเปลี่ยนไอออน

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LIST OF SYMBOLS

SYMBOL

a, b	parameter in the equation of state
B	Langmuir constant
C_e	equilibrium concentration (mol/l)
E_A	equivalent fraction of metal ion in zeolite
$E_{A(S)}$	equivalent fraction of metal ion in solution phase
f	fugacity
h_2^{IG}	molar enthalpy of ideal gas
\bar{h}_2^m	infinite-dilution partial molar enthalpy of solute in the mobile phase
\bar{h}_2^s	infinite-dilution partial molar enthalpy of solute in the stationary
phase	
K_2	adsorption equilibrium constant of solute (m^3/mol)
k_{ij}	binary interaction parameter
l_{ij}	binary interaction parameters in the Peng-Robinson equation of state
N_0	avogadro's number
ND	number of data points
n	total number of moles
n_i	number of moles of i th species
OBJ	objective function
p	pressure (bar)
p_c	critical pressure (bar)
q	equilibrium adsorption capacity (mol/l)
q_2^*	solid-phase concentration of species adsorbed in the stationary phase (mol/l)
q_{max}	saturation capacity (mol/l)
R	universal gas constant

RMSD	root-mean-squared relative deviation
S_g	specific surface area (m^2/kg)
T	temperature (K)
T_c	critical temperature (K)
V	molar volume (m^3/mol)
x_i, x_j	partial molar of component i and j

GREEK LETTERS

ρ_B	bulk density of the solid phase as packed (g/cm^3)
ρ_m	molar density of the mobile phase as packed (g/cm^3)
ε	bed porosity
α^m	volume expansivity
κ^m	isothermal compressibility
\bar{v}_2^m	infinite-dilution partial molar volume of solute in the mobile phase