

ศึกษาการหาค่าความน่าจะเป็นของการเติบโตของโซ่ของการเกิดโค้กบนโลหะและบนตัวรองรับ
ของ Pt/ γ -Al₂O₃ โดยใช้ทฤษฎีการกระจายตัวแบบพูลซ์-ฟลอรี

นางสาวสุนีย์ ศรีหิรัญพัลลภ



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DETERMINATION OF PROBABILITY OF CHAIN GROWTH OF COKE
FORMATION ON METALS AND ON SUPPORTS OF Pt/ γ -Al₂O₃ BY USING THE
SCHULZ-FLORY DISTRIBUTION THEORY

Miss Sunee Srihiranpullop

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for the Degree of Doctor of Engineering in Chemical Engineering

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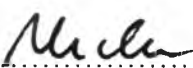
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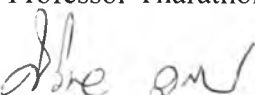

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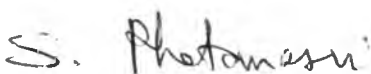
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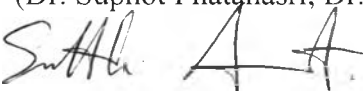

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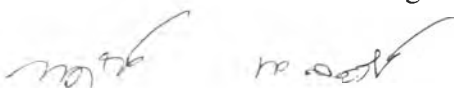

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สุนีย์ ศรีหิรัญพัลลภ: ศึกษาการหาค่าความน่าจะเป็นของการเติบโตของโซ่ของการเกิดโค้กบนโลหะและบนตัวรองรับของ Pt/ γ -Al₂O₃ โดยใช้ทฤษฎีการกระจายตัวแบบซูลซ์ฟลอรี (DETERMINATION OF PROBABILITY OF CHAIN GROWTH OF COKE FORMATION ON METALS AND ON SUPPORTS OF Pt/ γ -Al₂O₃ BY USING THE SCHULZ-FLORY DISTRIBUTION THEORY) อ. ที่ปรึกษา : ศ.ดร.ปิยะสาร ประเสริฐธรรม, อาจารย์ที่ปรึกษาร่วม: ผศ.ดร.ชราธร มงคลศรี และ ดร.ศิริพล คุณาธิปพงษ์, 196 หน้า ISBN 974-346-969-9.

งานวิจัยนี้มีจุดมุ่งหมายเพื่อศึกษาการกระจายตัวและความน่าจะเป็นของการเติบโตของโซ่ของโค้กบนโลหะและบนตัวรองรับ โดยในตอนแรกทำการศึกษาโดยใช้ Pt/SiO₂ เป็นตัวแทนของโลหะและใช้อะลูมินาเป็นตัวแทนของตัวรองรับ พิจารณาค่าการเปลี่ยนแปลงไปเป็นผลิตภัณฑ์จำนวนโซ่ของโลหะ ปริมาณไฮโดรเจน ธรรมชาติและปริมาณของโค้ก พบว่าการใช้ Pt/SiO₂ ขนาด 100-120 เม็ชและอะลูมินาขนาด 60-80 เม็ชจะมีพฤติกรรมการเกิดโค้กเหมือนกับ Pt/ γ -Al₂O₃ จากนั้นนำมาใช้ในการศึกษาการเกิดโค้กโดยใช้เทคนิคของ TPO, ESR, IR, BET, XRD, TEM และการสกัดโค้กโดยวิธีการสกัดแบบ Soxhlet แล้วนำมาวิเคราะห์ด้วยแก๊สโครมาโตแกรม 14B พบว่าผลของเวลา อุณหภูมิ อัตราส่วนไฮโดรเจนต่อไฮโดรคาร์บอน และการปรับปรุงของตัวเร่งปฏิกิริยามีผลอย่างมากต่อการลดปริมาณและความน่าจะเป็นของการเติบโตของโซ่ของโค้ก เมื่อเปรียบเทียบโค้กบนโซ่โลหะและโค้กบนโซ่ตัวรองรับ พบว่าความน่าจะเป็นของการเติบโตของโซ่ของโค้กบนโซ่ทั้งสองมีค่าเท่ากัน อย่างไรก็ตามพบว่ามีการสะสมของโค้กอย่างมากบนตัวรองรับ ซึ่งเกิดขึ้นเนื่องจากการถ่ายเทอิเล็กตรอนมีเดียของโค้กที่สร้างจากโซ่โลหะแล้วถ่ายเทไปยังโซ่ตัวรองรับในรูปของแก๊สเฟสตามแบบจำลองของการเกิดโค้กที่ได้เสนอไว้ ส่งผลให้บนโซ่โลหะมีดีกรีในการพอลิเมอไรเซชันที่ต่ำกว่าดังนั้นจึงทำให้ได้โค้กที่มีมีอัตราส่วนของไฮโดรเจนอยู่มากกว่า

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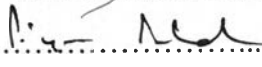

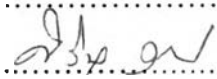
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#3972172821 : MAJOR CHEMICAL ENGINEERING

KEY WORD: coke/ a physically mixed catalyst/ distribution and probability of chain growth of coke

SUNEE SRIHIRANPULLOP: DETERMINATION OF PROBABILITY OF CHAIN GROWTH OF COKE FORMATION ON METALS AND ON SUPPORTS OF Pt/ γ -Al₂O₃ BY USING THE SCHULZ-FLORY DISTRIBUTION THEORY. THESIS ADVISOR: PROF. PIYASAN PRASERTHDAM, Dr.Eng., THESIS COADVISOR: ASSISTANT PROF. THARATHON MONGKHONSI, Ph.D., and Dr. SIRIPOLN KUNATIPPAPONG, Dr. Eng., 196 pp. ISBN 974-346-969-9.

In this thesis, the main goal was to study the distribution and probability of chain growth of coke on the metal sites and on the support sites. At the beginning, the combination of Pt/SiO₂ representing the metal sites and Al₂O₃ representing the acid sites was investigated. Considering conversion, metal site, H₂ uptake and the nature and amount of coke, interestingly, it was found that Pt/SiO₂ with 100-120 mesh mixed with Al₂O₃ 60-80 mesh has coking behavior similar to Pt/ γ -Al₂O₃. TPO, ESR, IR, BET, XRD, TEM and Soxhelt extraction analyzed with GC-14B were employed for characterization. It was obvious that the effects of time, temperature, H₂/HC ratio and modification of catalysts greatly affected reducing of the amount and probability of chain growth of coke. By considering coke formation on the metal sites and on the support sites, it was found that probabilities of chain growth on both sites were the same. However, the greater accumulation was occurred on the support. This offered the transformation on gas phase of coke intermediates from the metal, which was primarily responsible for producing the coke precursors, to the support as proposed in this model of coke formation. Since coke on the metal had a lower degree of polymerization, the coke was rich in hydrogen.

Department...Chemical Engineering..... Student's signature.....
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5. The influence of Sn and K addition on the coke formation

The main theories put forward to account for the improved properties of multi-metallic catalysts tend to involve either geometric or electronic effects [2, 7, 15, 24, 32, 89, 92, 98, 99, 109, 111, 135, 192]. Coke formation is known to require relatively large clusters or ensembles of adjacent metal atoms. For the Sn addition, the presence of Sn improved the diluting of the active metal surface into smaller ensembles (see Figure 5.49), which enhanced the catalysts' resistance to deactivation. The addition of Sn to Pt catalyst forms substitute surface alloys and it was shown that Sn interacts with platinum on silica to form a Pt/Sn alloy. Thus, carbon intermediates cannot readily form multiple carbon-metal bonds. Furthermore, it inhibits the formation of highly dehydrogenated surface species that are intermediates for coking. According to the earlier work [26, 91], one reason is that coke deposits bind more strongly to the Pt catalyst than to the Pt-Sn catalyst.

From TPO profiles and ESR spectra of the metallic sites, the adsorbed species attached less strongly to the metal surface would be explained by the significant minimization of coke on these sites and promotion of the migration of coke precursors to the support. The change in the peak height in the TPO profiles and ESR spectra evidenced for this idea.

The addition of K into bimetallic Pt-Sn catalyst decrease significantly the catalyst deactivation as shown in Figure 5.51 illustrating the conversion of hexane as a function of time. The decline in conversion was slower for catalysts containing tin and potassium than for catalysts containing platinum only because less amount of coke was formed on the modified catalysts. From Figure 5.51 and Table 5.14, it is obvious that Pt catalyst deactivated quickly and a considerable amount of coke was formed. It may be related to the incorporation of tin into the platinum surface through the formation of a substituted alloy, while potassium may be presented on the top of the platinum surface. As described elsewhere [29, 31, 111, 114, 132, 147, 193-195], it was found that K-doped catalyst significantly decreased the activation energy of HC dehydrogenation and the potassium diminished the interaction between Pt and Sn.

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