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สาขาวิชาเคมี ภาควิชาเคมี

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PROTON EXCHANGE AND DEGRADATION OF ALKANES IN ZSM-5

Miss Kanjarat Sukrat

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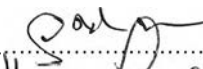
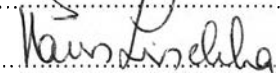
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ในงานวิจัยนี้ได้ศึกษาการดูดซับและกลไกปฏิกิริยาการถ่ายโอนโปรตอน ปฏิกิริยาการตั้งไฮโดรเจนและปฏิกิริยาการแตกพันธะของแอลเคนที่มีคาร์บอน 2 ถึง 4 อะตอม ได้แก่ อีเทน โพรเพน ไอโซบิวเทน และนอร์มัลบิวเทน ซึ่งเร่งปฏิกิริยาด้วยกรดบรอนสเตทในซีเอสเอ็ม-5 ด้วยวิธีทางเคมีควอนตัม โดยใช้แบบจำลองคลัสเตอร์ที่มีขนาด 5T, 20T, 28T, 38T, และ 96T (T อ้างถึงหน่วยของเตตระฮีดรอลของในโครงสร้างซีเอสเอ็ม-5) และแบบจำลองฟิสิกส์ โครงสร้างทรานซิชันสเตทและพลังงานก่อกัมมันต์ทั้งหมดคำนวณด้วยระเบียบวิธี DFT โดยใช้ฟังก์ชันัล PBE และเบซิสเซตเชิงอะตอมแบบสเปลลิทเวเลนซ์โพลาริเซชัน (SVP) พลังงานการดูดซับที่คำนวณได้มีผลสอดคล้องอย่างดีกับค่าที่ได้จากการทดลอง โดยมีค่า 7.1, 10.5, 8.0, และ 11.5 กิโลแคลอรีต่อโมล สำหรับอีเทน โพรเพน ไอโซบิวเทน และนอร์มัลบิวเทนตามลำดับ พลังงานการดูดซับสัมพันธ์กับขนาดของคลัสเตอร์ที่เพิ่ม และกับจำนวนของอะตอมคาร์บอนในสายไฮโดรคาร์บอน นั่นคือ นอร์มัลบิวเทน > โพรเพน > อีเทน พบว่าโครงสร้างที่สภาวะทรานซิชันของปฏิกิริยาการถ่ายโอนโปรตอนและการตั้งไฮโดรเจนเป็นแบบเพนตะ-โคออร์ดิเนท คาร์โบเนียม ไอออน ปฏิกิริยาถ่ายโอนโปรตอนดูเหมือนเป็นปฏิกิริยาตั้งต้นสำหรับปฏิกิริยาตั้งไฮโดรเจน ได้นำวิธีการประเมินค่า ที่พิจารณาถึงผลกระทบของขนาดคลัสเตอร์, พลังงานที่ศูนย์องศาสัมบูรณ์, สหสัมพันธ์อิเล็กทรอนิกส์, และเบซิส เซต มาใช้ในการคำนวณเขตขวางกั้นปฏิกิริยา จากวิธีการประเมินค่าพบว่า เขตขวางกั้นปฏิกิริยาที่คำนวณได้มีค่าต่ำเกินไปสำหรับปฏิกิริยาการถ่ายโอนโปรตอน ในขณะที่มีค่าสูงเกินไปสำหรับปฏิกิริยาการตั้งไฮโดรเจน และให้ผลที่สอดคล้องกับการทดลองสำหรับปฏิกิริยาการแตกพันธะ ค่าพลังงานที่ต่ำเกินไปสำหรับปฏิกิริยาการถ่ายโอนโปรตอนมีความเป็นไปได้ว่าจะเกิดจากสภาวะพลวัตของไฮโดรเจนอะตอม ในขณะที่ปฏิกิริยาการตั้งไฮโดรเจนมีค่าสูงเกินไปแสดงว่า น่าจะมีโครงสร้างทรานซิชันอื่นที่มีพลังงานต่ำกว่าอยู่ การผนวกผลของพลังงานที่ศูนย์องศาสัมบูรณ์, เบซิส เซต, สหสัมพันธ์อิเล็กทรอนิกส์, และเฉพาะอย่างยิ่งขนาดคลัสเตอร์มีความสำคัญและจำเป็นอย่างมาก

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Quantum chemical methods were used to study the adsorption and the mechanism of proton exchange, dehydrogenation, and cracking reactions of C2-C4 alkanes, such as ethane, propane, iso-butane, and n-butane, which were catalyzed by Brønsted acid site of ZSM-5 zeolite. The cluster approach employing 5T, 20T, 28T, 38T, and 96T models (T referring to the tetrahedral unit of the zeolite structure) and the periodic model were used. All transition state structures and corresponding activation energies were determined using DFT with PBE functional and atomic basis set of the split valence polarization (SVP) embedded in the Turbomole program. The obtained results showed that using the periodic model computed adsorption energies are in good agreement with the experimental values. They are 7.1, 10.5, 8.0, and 11.5 kcal/mol for ethane, propane, iso-butane, and n-butane, respectively. The adsorption energies are functions of the cluster-size and proportionally increase with the number of carbon atoms in the hydrocarbon chain, *i.e.* n-butane > propane > ethane. The penta-coordinated carbonium ions have been observed for the transition state structures of the proton exchange and dehydrogenation reactions. The proton exchange seems to be the precursor for the dehydrogenation reaction. An extrapolation scheme for estimating the reaction barrier which takes into account effects of cluster-size, zero-point energy, electron correlation, and basis set has been proposed. Using the extrapolation scheme computed reaction barriers for proton exchange reactions are underestimated while they were overestimated for dehydrogenation reactions and shows good agreement with experiments for the cracking reaction. The underestimation for the proton exchange reaction is probably due to the dynamic nature of H atom, while the overestimation for dehydrogenation reaction suggests that there might exist another TS structures with lower energy. Inclusion of corrections such as ZPE, basis-set, electron correlation, and especially cluster-size deem to be very important and necessary.

Department : ..... Chemistry .....

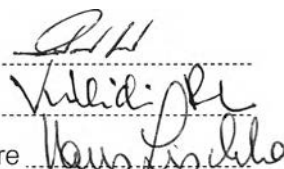
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