PRF #: 58598-ND10

Project TITLE: Synthesis of Hierarchically Porous Zeolites by Solid-State Crystallization and Their Catalytic Properties

P.I. and Affiliation: Shengnian Wang, Louisiana Tech University

1. Project Activities and Outcomes

1.1. Optimize the synthesis recipes of ZSM-5 zeolites

We first optimized the synthesis recipes of ZSM-5 zeolites. Different structure-directing agent (TPAOH, TEAOH, TPABr) and their adding ratios were tested and optimized. Aging solutions of various pH values and/or base types, blending of TPAOH, TEAOH, or TPABr with NaOH, were also formulated. Broad aging conditions and crystallization parameters were tested. Figs 1a & 1b show mesoporous ZSM-5 zeolites (Meso-ZSM-5) synthesized by solid crystallization method with different structure directing agents (SDAs). Both give monolithic zeolite pieces stacked up and merged by many nanoparticle subunits. The stacking of these nanocrystals creates many connected inter-lattice mesoscale space inside zeolites. The concentration of SDAs and water content in the original aging solution affect their crystal size and crystalline degree (Figs 1c & 1d). Meso-ZSM-5 zeolites of a broad Si/All ratios were successfully synthesized by this solid crystallization method, confirming with their matched X-ray diffraction patterns with typical MFI structure. Their major differences lie on the grain size of nanoparticle subunits (Fig 1e). The presence of mesopores is further confirmed with BET surface area and pore volume measurement for both type zeolites with two steep steps in BET isotherms: one at $P/P_0 < 0.02$ and the other at $0.45 < P/P_0 < 0.90$ locations, responding for micropore filling and mesopore capillary condensation, respectively.

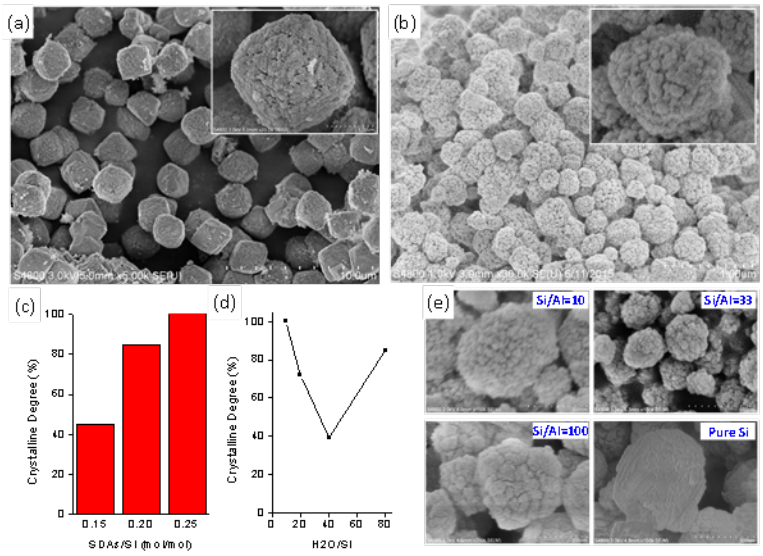

Fig 1: (a-b) SEM images of mesoporous ZSM-5 (Meso-ZSM-5) zeolites synthesized with TEAOH (a) and TEAOH (b) as the structure directing agents (SDAs); (c, d) crystalline degree with various SDAs/Si (c) and H2O/Si ratio, respectively; (e) Meso-ZSM-5 zeolites synthesized by solid crystallization under various SI/Al ratios.

1.2. Evaluate their roles as catalyst support in palladium catalyst for hydrodeoxygenation of bio-oil products

The catalytic performance of those zeolites was further evaluated as the acidic support of palladium (Pd) catalyst for hydrodeoxygenation (HDO) of lignin depolymerization products. This bio-oil upgrading process targets at oxygen removal and aromatic ring saturation with hydrogen gas. The HDO experiments were conducted over Pd catalyst loaded onto zeolites by wet impregnation. A major bio-oil compound, guaiacol (GUA, $C_7H_8O_2$ with 25 wt.% oxygen content and 0.72*0.50 nm molecule size), was tested, which has often disappointing conversion and severe coking issue over many HDO catalysts. GUA were dissolved in n-hexadecane prior to reaction and the reaction was carried out in a high-pressure batch reactor (Col-Int Tech, 400 mL). In each run, 1.0 g GUA, 0.3 g catalyst, and 150 mL n-hexadecane were loaded and the reaction temperature was chosen between 150 ºC and 250 ºC. Liquid samples were taken every hour and analyzed by a GC–MS (Agilent 7890A-5975C). The deoxygenation and hydrogenation degree are determined by calculating the percent of all non-oxygen compounds and all saturated compounds in the product, respectively. The obtained results were compared with what occurred over corresponding microporous

zeolites supports. When compared with those supported on conventional microporous ZSM-5 counterparts, this prepared Pd/Meso-ZSM-5 catalyst exhibits superior conversion and product distribution in the HDO of guaiacol. This is attributed to the improved diffusion and accessibility of active sites in these Meso-ZSM-5 zeolites. The HDO processes hold strong temperature dependence on the conversion and product distribution. As shown in Figs 2a & 2b, the guaiacol conversion reaches 84 % at 200 °C and the hydrogenation process dominates the HDO process with ring-saturated cyclohydrocarbons as major products (72 % of the total test sample). When the reaction temperature was further elevated to 250 °C, the guaiacol conversion quickly reaches 100% in 3 and 4 hours for Meso-ZSM-5 and microporous ZSM-5, respectively (Fig 2c). Different from reactions at 200 °C, deoxygenation overturns hydrogenation to become the domination reaction route with more diverse products, among which over 94% are oxygen-free compounds (Fig 2d). Additional mesopores also promote reactant/product diffusion at multiple scales to slow down the coke-leading deactivation process.

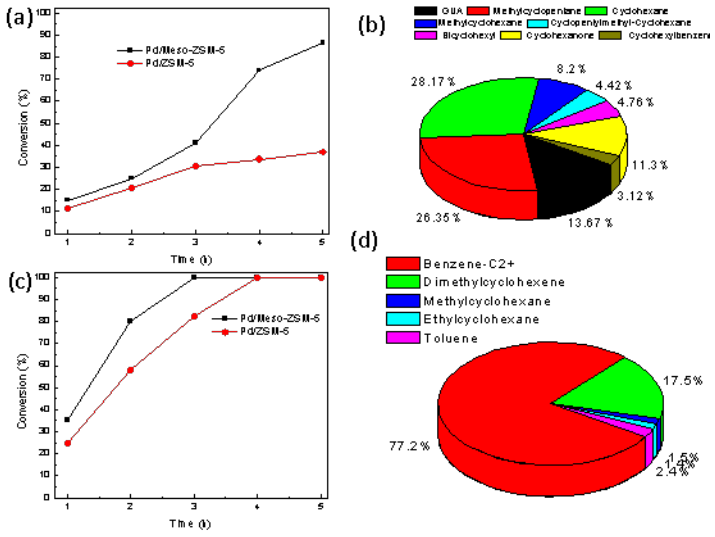

Fig 2: Guaiacol (GUA) hydrodeoxygenation over Pd/Meso-ZSM-5 at 200°C (a-b) and 250°C (c-d): GUA conversion (a,c) and HDO product distributions (b,d). The catalytic performance of Pd/ZSM-5 was also provided for comparison purpose.

2. Project Impact

The PI (Dr. Wang) is benefited from this project from multiple aspects. One post-doc and one PhD student were partially supported by this project. They received hands-on training on zeolite synthesis and catalytic reaction experiments. Two manuscripts were submitted to peer-review journals: one about guaiacol HDO over Pd/Meso-ZSM-5 by solid crystallization was submitted to Catalysis Today which is still under review [1]; the other focusing on lignin depolymerization by supercritical ethanol was just submitted [2]. Two presentations were given in the funding period: one in the 2018 annual meeting of AIChE [3] and one in the 3rd international conference of catalysis and chemical engineering (CCE) of 2019 [4]. Besides research supporting, this project also motivates collaborations with industrial researchers. This ACS petroluem funding mechanism provides a great platform to build bridges between academia and industry. Our research drew attentions of a leading chemical and material company and some initial tests were planned on their facilities. The invovled students will therefore receive experience to work in industrial environment and operate pilot scale facilities. Current technology has been filed in a patent application with an application number of 683,257, entitled "synthesis of hierarchical zeolites by solid state crystallization of nanogels" [5]. Two proposals were submitted to DOE, focusing on coupling solid crystallization of zeolites and metal catalysts to promote gas-to-liquid processes for natural gas utilization.

References

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[2] N. C. Baxter, Y. Wang, Y. Liao, S. Wang, Catalytic Ethanolysis of Lignin over Various Mesoporous Zeolites: the Importance of Acidity and Mesopore Size, submitted.
[3] Y. Wang, N. C. Baxter, Y. Liao, S. Wang, Mesoporous Zeolites Produced by Solid Crystallization and Their Catalytic Properties, Annual meeting of AIChE (Pittsburgh, PA, 2018).
[4] Y. Wang, N. C. Baxter, Y. Liao, S. Wang, Hierarchical ZSM-5 Zeolites Synthesized by Solid Crystallization of Nanogels, and Their Hydrogenation Properties, Third International Conference of Catalysis and Chemical Engineering (Houston, TX, 2019).
[5] Y. Wang, S. Wang, Hierarchical ZSM-5 Zeolites Synthesized by Solid-state Crystallization of Nanogels, US patent 62/683,257.