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Conversion of ethanol to hydrocarbons on hierarchical HZSM-5 zeolites

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ABSTRACT

This study reports synthesis, characterization, and catalytic activity of the nano-size hierarchical HZSM-5 zeolite with high mesoporosity produced via a solvent evaporation procedure. Further, this study compares hierarchical zeolites with conventional HZSM-5 zeolite with similar Si/Al ratios for the ethanol-to-hydrocarbon conversion process. The catalytic performance of the hierarchical and conventional zeolites was evaluated using a fixed-bed reactor at 360 °C, 300 psig, and a weight hourly space velocity of 7.9 h^{-1}. For the low Si/Al ratio zeolite (~40), the catalytic life-time for the hierarchical HZSM-5 was approximately 2 times greater than the conventional HZSM-5 despite its coking amount deposited 1.6 times higher than conventional HZSM-5. For the high Si/Al ratio zeolite (~140), the catalytic life-time for the hierarchical zeolite was approximately 5 times greater than the conventional zeolite and the amount of coking deposited was 2.1 times higher. Correlation was observed between catalyst life time, porosity, and the crystal size of the zeolite. The nano-size hierarchical HZSM-5 zeolites containing mesoporosity demonstrated improved catalyst life-time compared to the conventional catalyst due to faster removal of products, shorter diffusion path length, and the migration of the coke deposits to the external surface from the pore structure.

1. Introduction

Recently, in the wake of projected crude oil depletion and the negative environmental effects of crude oil usage, a great deal of research has focused on the development of renewable energy resources. Renewable fuels (e.g., methanol, ethanol, butanol, and biodiesel) are generated through thermochemical and biological routes. Though ethanol generated from renewable resources through fermentation is currently the dominant biofuel as a blend component to gasoline, several properties make ethanol undesirable as standalone transportation fuel (e.g., low energy density and high water solubility). In the near future, the production a capacity of biomass-derived ethanol and other small oxygenates are projected to rise beyond the blending needs [1]. For the successful implementation of the biomass conversion processes in the transportation fuel market, it is imperative to maximize the carbon yield from the biomass feed stocks in the final biofuel product and to produce biofuel products that closely resemble the properties of fuels derived from crude oil. One of the viable solutions for next-generation biofuels is conversion of biomass-derived ethanol and other oxygenates to hydrocarbon compounds similar to those in gasoline, diesel, and jet fuel [2].

Since the invention of the Mobil's methanol-to-gasoline (MTG) process [3], considerable research has been done on the catalytic transformation of alcohols, with respect to the reaction mechanism and the catalyst deactivation mechanism, to obtain liquid hydrocarbon fuels and light olefins from the HZSM-5 zeolite [4]. The HZSM-5 zeolite catalyzed deoxygenation of methanol accompanied by chain growth is well understood under moderate reaction conditions [5,6]. Among all the zeolite catalysts tested, the HZSM-5 zeolite provides a suitable compromise among activity, shape selectivity to produce hydrocarbons smaller than carbon number C_{10} (gasoline range), slow deactivation by coke formation from alcohol functional group as well as better hydrothermal stability [7]. The HZSM-5 zeolite is also amenable to regeneration by simply burning the catalyst at around 500 °C in air or oxygen [O_2] atmosphere to remove the coke deposits in the pore system and on the surface without altering the inherent nature of its catalytic properties [8]. These same characteristics make HZSM-5 zeolite an interesting catalyst to investigate for the conversion of other alcohols and oxygenates to hydrocarbon compounds. In addition to the MTG technology, several methanol-to-hydrocarbon processes are currently being developed, including Lurgi's methanol to propylene (MTP) process [9], Topsøe integrated gasoline synthesis (TIGAS) process [10], and hydro/UOP's methanol to olefins (MTO)

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process [11]. In addition to studying methanol, research has been conducted, to a limited extent, on the conversion of higher alcohols, $\geq C_2$ (e.g., ethanol, propanol, and butanol) to hydrocarbons [4].

Zeolites are well-defined crystalline microporous (<2 nm) aluminosilicate materials containing a one-, two-, or three-dimensional pore structure system. Zeolites are made up by SiO_4 tetrahedra, which are interconnected via oxygen atoms. Pure siliceous zeolites are electrically neutral. An ion-exchangeable cationic site in the lattice is created by the substitution of a tetrahedrally coordinated silicon atom with charge of 4^+ (Si^{4+}) by an atom with a charge of 3^+ (Al^{3+}) [12]. These sites are locations for redox and acid/base chemical reactions, depending on the nature of the charge balancing cations. The three-dimensional network in HZSM-5 is created by 10 ring channels running parallel (5.6 Å × 5.3 Å) intersected by 10 ring sinusoidal channels (5.5 Å × 5.1 Å) with an internal pore space of 6.36 Å [13]. An outstanding feature of the microporous HZSM-5 is that it converts alcohol compounds to hydrocarbons. However, the same microporous structure causes the product selectivity discrimination to limit the carbon number to $\sim C_{10}$.

Bulk conventional zeolite crystals are often several orders of magnitude larger than the pore diameter. Only a fraction of zeolite active sites in the bulky crystal might actually participate in the catalytic reaction in this diffusion-controlled regime, leading to low overall catalyst utilization. Diffusion, the main mechanism of mass transfer in the porous catalytic material, is of essential importance for their application in catalysis, because the molecular mobility ultimately determines the rate of the overall catalytic processes [14,15]. Slow diffusion or longer residence time can lay foundation for the intermediate and products to grow to the steric limitation of the pore structure or the intersecting tunnel, causing deactivation via pore blocking mechanisms. The high rate of coking requires frequent high temperature catalyst regeneration. The high temperature treatment can potentially lead to the irreversible loss of catalytic activity and ultimately reduce the overall catalyst lifetime [16].

In addition, the diffusion of molecules in zeolite pores plays an important role in the shape selective process. HZSM-5 zeolite with secondary mesoporosity (i.e., pores with diameters ranging between 2 and 50 nm) and structural microporosity (hierarchical zeolites) in nano–size crystals could increase both the catalytic activity toward hydrocarbon and the diffusion rate (i.e., short residence time inside the pores), which could reduce the rate of coke formation and increase the catalyst life-time.

Several efforts have been made to produce a hierarchical zeolite catalyst to minimize the limitations of microporous structure. Approaches taken to synthesize hierarchical zeolites fall into three categories: (1) synthesis of zeolites materials with extra-large micropores structure [17]; (2) synthesis of zeolites in the form of small nanoparticles [18]; and (3) obtaining zeolite samples with intracrystalline mesopores, generating mesopores during zeolite crystallization using a solid templating [19], supramolecular [20] and indirect templating [21], or post-synthetic treatment using acid or base [22,23]. As previously mentioned, the HZSM-5 zeolite can be easily regenerated after deactivation due to coke deposition. However, long catalytic life-time is still advantageous in negating the cost of frequent interruption for catalyst regeneration or replacement and the permanent loss of catalytic activity due to dealumination or other irreversible structural damage from frequent high-temperature regeneration conditions.

A wealth of open literature is available regarding measurement of the catalytic activity of various chemical conversions on the hierarchical mesoporous zeolite and regarding comparison of the hierarchical mesoporous zeolite to its conventional counterpart [24–26]; however, limited information is available regarding the conversion of ethanol to liquid-range hydrocarbon on the nano-size hierarchical mesoporous HZSM-5 zeolite. In this study, we investigated the conversion of ethanol-to-hydrocarbon over the conventional and nano-size hierarchical HZSM-5 zeolite at two different Si/Al ratios to understand the zeolite crystal size and the presence of mesoporosity on the catalytic activity in generating liquid range hydrocarbons compared to the conventional HZSM-5.

2. Experimental

2.1. Catalyst preparation

Hierarchical mesoporous nano-size zeolite generated via hydrothermal treatment using the dry gel procedure, is labeled here as HTS. The HTS synthesis procedure was adapted from Zhu et al. [27]. Typically, for the synthesis of the ZSM-5-HTS used in this study, 3.12 g of tetraethylorthosilicate (TEOS), 0.21 g of hexadecyltrimethoxysilane (HTS), and given amount of aluminum tritert butoxide (ATTB) were dissolved in 10 mL of ethanol under stirring. This mixture was stirred for 30 min to form a solution, and then another solution of 2 g of tetrapropylammonium hydroxide (TPAOH) in 2 g of ethanol was added under vigorous stirring. Hydrolysis occurred at this stage and a clear solution was produced. The clear solution was stirred for 1 h before being transferred to a Petri dish where the solvent was allowed to evaporate overnight. The transparent dry gel produced during solvent evaporation was placed in a 100 mL Teflon cup. The cup was placed in a Teflon-lined autoclave, and 5 g of water was added outside the cup to create steam for the hydrothermal synthesis conditions. The autoclave was then placed in an oven set at 180 °C and kept up to 5 days for moisture-assisted hydrothermal crystallization. The final solid was filtrated and washed with water and then calcined at 500 °C for 20 h in a static air atmosphere [27]. Then, the synthesized hierarchical mesoporous catalyst was pelletized and sieved between 60 and 100 mesh size for uniformity. Two different Si/Al ratios were synthesized, HTS 48 and HTS 120–the numbers represent the Si/Al ratio of the catalyst (i.e., 48:1 and 120:1, respectively). The chemical compositions listed in the hierarchical synthesis procedure are those used in the synthesis of HTS 48.

The conventional zeolite used in this study was purchased from Zeolyst International, Inc. in ammonium form (NH_4ZSM-5), labeled here as COM. Two different Si/Al ratios, similar to those in the hierarchically synthesized catalyst, were purchased: COM 40 and COM 140. The purchased catalyst was calcined in a static air atmosphere at 500 °C for 4 h to convert it into the proton form (HZSM-5) and to burn off impurities carried over from zeolite catalyst synthesis or from treatment and handling processes. Then, the powder HZSM-5 catalyst was pelletized and sieved between 60 and 100 mesh size for uniformity.

2.2. Catalyst characterization

X-ray powder diffraction (XRD) was used to verify the crystallinity of the zeolite catalyst. The diffraction patterns were recorded on a Siemens diffractometer model D 5000 running in Bragg–Brentano geometry and employing Cu Kα (k = 1.54439 Å) radiation to generate diffraction patterns from powder crystalline samples at ambient temperature. The spectra were scanned in the range of 5–50°. Nitrogen (N_2) adsorption/desorption isotherms at 196 °C were recorded using a Micromeritics ASAP 2010 instrument. Before the measurements, fresh samples were degassed to 300 °C in a vacuum for 1 h; spent catalysts were degassed at 150 °C under vacuum for 2 h. The Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area using adsorption data at p/p_o = 0.05–0.25. The pore volume was determined using the Barrett–Joyner–Halenda (BJH) method. Ammonia-TPD (NH_3-TPD)