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Oligomerization of lower olefins to fuel range hydrocarbons over texturally enhanced ZSM-5 catalyst

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ABSTRACT

Zeolites with various pore structures and sizes such as microporous ZSM-5, desilicated ZSM-5, Beta zeolite and ZSM-48 were investigated as catalysts in the oligomerization of propylene and 1-hexene to fuel-range hydrocarbons. Mesoporous ZSM-5 was prepared *via* a post-synthesis alkaline treatment. Physicochemical properties of the zeolite catalysts were characterized by XRD, XRF, SEM, TEM, MAS NMR, BET, and NH_3-TPD techniques to analyze the crystallinity, element composition, morphology, textural properties as well as acidity distribution. The catalyst characterization confirmed that NaOH post-treatment by mild desilication is an effective method to tune the pore structure of medium pore ZSM-5 zeolite by introducing mesoporosity without damaging the microporous structure. Enhanced activity and selectivity to jet fuel/diesel range (C_{12}) products of ˜90% and 55% respectively was achieved over a modified ZSM-5 catalyst at optimum reaction conditions of 220 °C and weight hourly space velocity (WHSV) of $4\,h^{-1}$ in the oligomerization of 1-hexene. Good selectivity to gasoline-range hydrocarbons with high octane number was achieved over modified ZSM-5 in the oligomerization of propylene. The spent catalysts were characterized by thermogravimetric and NH_3-TPD analyses which confirmed that carbonaceous deposits were prevalent inside the micropores of the catalysts but its effects were less severe on the modified ZSM-5.

1. Introduction

Catalytic oligomerization of C_3-C_6 light olefins is an industrially important process for producing high quality, eco-friendly gasoline (C_5–C_{12}) and diesel fuels (C_{11}–C_{24}) [1,2]. Light olefins are generally formed in significant quantities during petroleum processing. Primary products from the high-temperature Fischer-Tropsch (HTFT) synthesis are characterized by their high light olefins content, and integrated processes like oligomerization add value into beneficiating the "unwanted" by-product olefins [3–5]. Some commercial processes for oligomerization utilize homogeneous catalysts, but with respect to the green chemistry principles, heterogeneous catalysts potentially offer a more environmental friendly alternative, due to their ease and efficiency of recovery and potential reuse [4,6,7]. Solid acid catalysts, zeolites in particular, are the most favorable catalysts in the oligomerization reaction as a result of their cost-effectiveness and good shape-selective properties [1,3,8–10]. The process conditions and the physicochemical properties of the catalyst such as porosity and acidity have a significant effect on the oligomerization product composition [11,12]. Typical operating conditions for the Mobil olefins-to-gasoline and distillate (MOGD) process are 200–280 °C, 1–5 MPa and WHSV between 0.1 and $5\,h^{-1}$ in the employment of microporous HZSM-5 zeolite as catalyst [13,14]. There have been a number of studies on the oligomerization of light olefins higher than C_3 over H-zeolites and mesoporous catalysts amongst which C_{5+} olefins are relatively less common [2,15]. Arno de klerk [3] studied properties required for 1-hexene olefin oligomerization on MCM-41, ZSM-5 and zeolite-Y catalysts and deduced that catalysts with an average pore size of 10 nm or more showed good activity and a lower deactivation rate. Meso-structured solid acid catalysts exhibit lower hydrothermal stability and weaker acidity than those of the microporous zeolites, which strongly limit their applications in the petrochemical industry [16,17]. Since zeolites are the preferred choice of catalyst in the conversion of olefins to distillates, incentives still exists to improve their performance related to catalytic activity, selectivity and stability. However, the major drawback of microporous zeolites is their easy deactivation because the materials are connected with internal diffusion limitations. Only active sites close to the zeolite pore entrances or on their external surfaces

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which represent at most 5% of the total number of active sites are available for bulky/branched molecules [18]. Therefore, many groups have applied post-synthesis treatments such as desilication and dealumination to enhance diffusion *via* the introduction of mesoporosity. Structures that contain bi- or tri-modal pore systems are known as hierarchical zeolites. The intrinsic microporous network of pore diameters less than 2 nm imposes a limitation on intracrystalline diffusion in zeolites catalysts, especially when bulky/branched intermediates are involved [19,20]. Hierarchically-structured zeolites however, have a multi-distribution of pores, where the micropores provide a shape-selective catalytic process for guest molecules, while the meso- or macropores provide a facile diffusion pathway to and from catalytic sites in the zeolitic pores [20–23]. Nonetheless, the development of more active solid catalysts for oligomerization of light olefins C_2-C_6 is still needed and finding ways to convert straight chain olefins to more branched hydrocarbons still remains a major challenge. The activity and stability of oligomerization is reported to be most affected by mass transfer (diffusion) rather than reaction conditions [24]. The good accessibility of acid sites for ZSM-5 with hierarchical structure can be a remarkable benefit for catalytic reactions, when larger reactant molecules are involved, in which diffusion constraints and/or adsorption of reactant molecules onto the acid sites are the main concerns [18]. Recently, Moon et al. [2] have shown that oligomerization of both short and longer chain C_2 and C_6 olefins were more selective to $C_{10}+$ jet fuel range hydrocarbons over ZSM-5 with a mesoporous morphology and/or nanocrystalline structure. This was attributed to improving the diffusion limitation during the oligomerization of light olefins. Rapid catalyst deactivation may also be caused by the blocking of pores, which has a detrimental effect on the catalyst selectivity and stability. To prevent and improve these pore-constraint related problems, the generation of mesoporosity in the zeolite crystals by way of desilication using an alkaline solution has become a routine practice and been reported in the literature [25–29]. There are numerous reactions benefiting from desilication of zeolites which were recently compiled by Perez-Ramirez et al. [20,25]. Desilication is an inexpensive and easy method of obtaining hierarchical zeolites. It is a more commercially viable method of modifying textural properties of zeolites on a large scale compared to syntheses utilizing expensive templates. One of the advantages of using dual-porous zeolites is to add to the improvement of the gasoline formulation by enhancing selectivity to multi-branched hydrocarbons instead of only linear hydrocarbons to ensure a higher octane number. A more remarkable phenomenon, in relation to the hierarchically porous structure, is the significantly enhanced catalytic lifetime in some catalytic reactions that are believed to have occurred inside the zeolite micropores [30]. While desilication may enhance textural properties of a zeolite, consequently the acidity is also affected. The changes in the type, strength and density of acid sites may also affect the activity, selectivity and stability of catalysts during oligomerization. However, the role of acidity, the introduction of mesoporosity and whether a synergistic effect exists is not clearly understood and further investigations are required. In this study, the activity, selectivity and stability of ZSM-5 after modifying the physicochemical properties, *i.e.*, their porosity and acidity, using the method described above, for both propylene and 1-hexene oligomerization will be investigated. For comparison purposes, the effect of zeolites with various pore sizes, topologies and structures such as Beta zeolite (intersecting 12-ring channels, BEA topology) and ZSM-48 (10-ring channels without intersections, TON topology) were synthesized and their catalytic performances evaluated. The focus of this study was to explore the factors which mostly govern the yield/selectivity of fuel range hydrocarbons from light olefins and to optimize the catalytic properties for this reaction.

2. Experimental

2.1. Raw materials

The following chemicals are used: Colloidal silica (Ludox 40 wt.%, Sigma-Aldrich), Sodium aluminate (50–56 wt.% Al_2O_3 & 30–45 wt.% Na_2O, Sigma-Aldrich), tetrapropylammonium bromide (98 wt.%, Sigma-Aldrich), tetraethylammonium hydroxide (35 wt.% Sigma-Aldrich), Ammonium nitrate (99 wt.%, Sigma) Sodium hydroxide (98 wt.% ACE), 1-hexene (97 wt.%, Sigma-Aldrich), and Propylene (85 wt.%). Distilled water is obtained by a house supply that produces Milli-Q quality water.

2.2. Catalyst preparation

The synthesis of pristine ZSM-5 zeolite with the silica-to-alumina ratio (SAR) of 60 was synthesized following the procedure reported by Nicolaides et al. [31]. The molar gel composition used was 3 Na_2O:3 TPABr:0.5 Al_2O_3:30 SiO_2:1000 H_2O. The desilication method was adapted from previous works with slight modifications [32]. Approximately 5 g of the ZSM-5 zeolite was added to 500 ml of a 0.2 M solution of NaOH in a round bottom flask and refluxed at 65 °C for 0.5 h. The round bottom flask was subsequently cooled down to room temperature and the contents were filtered to recover the solid product. The solid was further washed with distilled water until pH 7 and dried overnight at 100 °C. Further, all H-form zeolites were prepared as follows; NH_4^+ ion-exchange was carried out with a threefold of 5 wt.% NH_4NO_3 solution at 80 °C. The dried NH_4-zeolite was calcined at 550 °C for 5 h in the presence of air. Detailed synthesis procedures for zeolite beta (referred as Beta in this study) and ZSM-48 are given in the supplementary information.

2.3. Characterization

Crystalline structure was characterized by X-ray diffraction (XRD) on a Bruker AXS D8 Advance Diffractomer (Cu-Kα radiation $\lambda K\alpha 1 = 1.5406$ Å) 40 kV in the 2θ range 5°–90°. The determination of the relative crystallinity value was based on the intensity of the characteristic reflections in the ranges 7°–10° and 22.5°–25.0°. Textural properties, *i.e.*, BET surface area measurements and porosity analysis were determined by N_2 adsorption/desorption isotherms at −196 °C using the Micromeritics TRISTAR 3000 analyzer. Prior to the measurements, samples were degassed at 400 °C for 4 h using helium. The total surface areas of the samples were calculated by the BET method, the mesopore surface areas and pore volumes were calculated by the BJH method, and the pore size distributions were derived from the BJH desorption branches. The ^{29}Si and ^{27}Al MAS NMR analysis of samples were studied using Bruker UltraShield 300 MHz/54 mm spectrometer. The MAS NMR was used to investigate the coordination of Al and Si atoms in the ZSM-5 framework. The framework silica-to-alumina ratio (SiO_2/Al_2O_3) was calculated from the ^{29}Si NMR spectra with the resolution of overlapped bands. X-ray fluorescence (XRF) was carried out on a Bruker S8 Tiger instrument to determine the bulk. The acidity of the zeolites was determined using temperature programmed desorption of ammonia (NH_3-TPD). Approximately 0.1 g of catalyst was loaded into the reactor and degassed at 500 °C for 20 min under helium flow at 30 ml/min. After cooling 120 °C under flowing helium, the sample was exposed to 5% NH_3 in balance helium and the NH_3 was adsorbed at 120 °C for 30 min at a flow rate of 15 ml/min. Helium was once again allowed to flow over the catalyst to remove any physically adsorbed NH_3. Finally, the TPD profiles were measured at a rate of 10 °C/min under He flow (25 ml/min) while the temperature increased from 100 to 700 °C. The signal was detected using a thermal conductivity detector (TCD) and the outputs recorded on a computer. Scanning electron microscopy (SEM) micrographs were obtained using a high resolution-SEM EHT 5.00 kV. All samples were carbon coated before imaging.