



## Short Communication

## Yield of gasoline-range hydrocarbons as a function of uniform ZSM-5 crystal size

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## ABSTRACT

Uniform ZSM-5 nanocrystals were synthesized by a single-templating procedure. The samples were then characterized by a variety of physical techniques such as XRD, SEM, BET, ICP and TPD. The dehydration of methanol over synthesized ZSM-5 zeolite was studied in a fixed-bed continuous flow reactor at 370 °C and WHSV of 2.6 gg<sup>-1</sup> h under ambient pressure. The effect of crystal size of zeolite catalysts on product distribution in methanol dehydration reaction was investigated. Good correlation was observed between catalytic performance, product distribution and size of ZSM-5 crystals. It was found that the decrease in crystal size significantly influences light olefins (ethylene and propylene) and paraffins (C<sub>1</sub>–C<sub>4</sub>) selectivity in methanol dehydration reaction. Furthermore, nanocrystal ZSM-5 showed long-term catalytic stability compared with conventional ZSM-5 provided that the reaction activity is strongly dependent on the crystal size in methanol dehydration process. The results indicated that crystal size significantly affects the catalyst lifetime and hydrocarbon distributions in product stream. Based on the obtained results, it is concluded that the use of uniform ZSM-5 nanocrystals improves the yield of propylene and alkyl aromatics in methanol conversion reaction at mild conditions.

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## 1. Introduction

Gasoline, an important derivative of oil, is widely used as a transportation fuel all over the world [1]. However, the increasing energy demand can be based only so heavily on liquid petroleum because non-renewable resource will last for only a few more years. Thus, establishing non-petroleum pathways to fuels such as renewable resources (biomass) is critical for the production of transportation fuels and chemicals. In the wake of the global energy crisis, alternatives to fuels derived from crude oil became a major research focus during the past few years.

An alternative pathway to produce fuel from biomass-derived synthesis gas (CO + H<sub>2</sub>) is to first convert synthesis gas to methanol over a mixed metal oxide catalyst (Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>) and then convert the methanol to gasoline (MTG) over ZSM-5 [2,3]. However, biomass thermochemical-derived syngas needs to be utilized to form compatible liquid hydrocarbon molecules that could be either a direct feed into current petroleum refineries or direct replacements of diesel, gasoline, or chemical products. ZSM-5 zeolite is well known as a promising class of porous materials which has demonstrated its potential in the conversion of fossil and biomass resources to fuels and chemicals in recent years [4,5]. Chemical and physical properties of zeolite (*i.e.*, crystal size, pore size, channel structure and acidity) and

operating conditions strongly influence the selectivity to alkane, alkene and aromatics [6,7]. Although higher resistance to coke poisoning and shorter diffusion paths are the important advantages of mesoporous and small crystallite size of zeolites for their successful applications in catalytic reaction processes [8,9], due to the presence of narrow channels (*i.e.* micropores) in their structures, the mass transfer limitations and the catalytic stability still remain important challenges [10,11].

In recent years, the effect of zeolite crystal size has been recognized as an important factor in alkylation of aromatics, methanol to hydrocarbons (MTH) and methanol to gasoline (MTG) processes [9–12]. Recently, several strategies for preparing nanocrystals zeolites have been proposed [13]. Even though some of these approaches are effective and result in improved catalytic performance in various reactions, the high cost of carbon template or troublesome preparation is still unavoidable in most cases. Therefore, a developed route is highly desired in terms of simplicity, reproducibility and large-scale applicability. Herein, we propose a facile and low cost route to synthesize high Al-content ZSM-5 nanocrystals.

In this study, we report the first comparative investigation of the performance of conventional ZSM-5 and uniform ZSM-5 nanocrystals in the conversion of methanol to gasoline-range hydrocarbons. More specifically, catalyst lifetime and product distribution in methanol conversion are accordingly investigated over a uniform nanocrystals and conventional ZSM-5 crystals. We clearly observed the difference of catalytic performance and product selectivity according to both suggestions summarized earlier.

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## 2. Experimental

### 2.1. Catalyst preparation

In this study, two different ZSM-5 zeolites were synthesized and used in the experiments, which are denoted by Nano-ZSM-5 and Con-ZSM-5. The Nano-ZSM-5 was synthesized hydrothermally from clear colloidal synthesis mixtures. Tetraethylorthosilicate (TEOS, 98%, Aldrich) and aluminum isopropoxide ( $\text{Al}(\text{O}-i\text{-Pr})_3$ , Aldrich) were used as Si source and Al source, respectively. Concentrated tetrapropylammonium hydroxide (TPAOH, 40 wt.% aqueous solution, AppliChem) was used as template. The starting mixtures were formed using the following procedures:  $\text{Al}(\text{O}-i\text{-Pr})_3$  and sodium hydroxide pastilles were first dissolved in water and part of template to get solution A. After the addition was completed, the solution mixture was stirred for at least 120 min to get a clear solution. Solution B consisted of second part of template and TEOS. Solution A was added to solution B while stirring. However, the molar composition of the synthesis mixtures was  $3\text{TPAOH}:0.5\text{Na}_2\text{O}:0.5\text{Al}_2\text{O}_3:25\text{SiO}_2:1500\text{H}_2\text{O}:100\text{EtOH}:3\text{PrOH}$ . After the addition was completed, the gel was stirred for at least 15 min to get a homogenous gel, and then the gel was transferred to a stainless-steel vessel that included liners, and the sealed autoclave was placed in an oil bath maintained at 120–180 °C for 24 h. After, this treatment, the solid product was separated by centrifugation, washed four times with distilled water, and then the products were dried by freeze-drier. The removal of organic template was carried out at 550 °C for 16 h under air. The samples were treated three times in a 10 wt.%  $\text{NH}_4\text{NO}_3$  solution at 100 °C for 1 h, rinsed and then calcined in air at 500 °C for 16 h, prior to catalytic experiments. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of synthesis solution was 50. A conventional zeolite (Con-ZSM-5) was synthesized following the procedure described elsewhere [14].

### 2.2. Catalyst characterization

XRD was performed to determine the bulk crystalline phases of the catalysts using a Siemens diffractometer model D 5000 running in Bragg-Brentano geometry employing  $\text{CuK}\alpha$  ( $\lambda = 1.54439 \text{ \AA}$ ) radiation to generate diffraction patterns from powder crystalline samples at ambient temperature. The spectra were scanned at a rate of  $2.0^\circ/\text{min}$  in the range  $2\theta = 2\text{--}70^\circ$ .

Nitrogen adsorption/desorption isotherms at  $-196^\circ\text{C}$  were recorded using a Micromeritics ASAP 2010 instrument. Before the measurements, the samples were heated to 350 °C in a vacuum for at least 12 h. The Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area ( $S_{\text{BET}}$ ) using adsorption data at  $p/p_0 = 0.05\text{--}0.25$ . The mesopore size distribution was derived from the adsorption branch by using the Barrett–Joyner–Halenda (BJH) method. The micropore volume was determined from a  $t$ -plot.

SEM images were recorded using a FEI Magellan™ 400L instrument. Zeolite crystals were deposited on a silicon wafer from dispersion and the sample was calcined in air at 500 °C. SEM images were recorded without any coating. The average crystal length was determined by measuring the length of 20 crystals for each sample.

$\text{NH}_3$ -TPD measurements were performed to determine the acid strength and the amounts of the acidic sites on the catalyst by using ThermoFinnigan TPD/R/O 1100 Series instrument.

The bulk compositions of the crystals were determined using a Perkin-Elmer Emission Spectrometer Model Plasma 1000 inductively coupled plasma-atomic emission spectrometer (ICP-AES). A 0.1 g sample is digested with 0.375 g  $\text{LiBO}_2$  and dissolved in  $\text{HNO}_3$ . Loss on ignition was conducted at 1000 °C.

### 2.3. Catalytic activity measurements

The catalytic measurements were made at atmospheric pressure in adjustable nitrogen flow saturated with methanol in a fixed-bed reactor connected to a Gas Chromatograph (GC). The feed ( $\text{N}_2$ ) was saturated

with methanol (99.9%) in a bubble saturator at 30 °C. The structure temperature was maintained by a constant temperature bath. The inlet flow rate was adjusted using a mass flow controller (MFC). The reaction was carried out in a fixed-bed flow reactor containing a standard mass of catalyst (i.e., 0.50 g) at 370 °C with various ranges of weight hourly space velocity (WHSV) of  $2.6 \text{ gg}^{-1} \text{ h}^{-1}$ . For each test, the powder ZSM-5 catalyst was sieved to 250–300  $\mu\text{m}$  and diluted with inert quartz sand, then loaded to the reactor. The maximum temperature variation along the bed was  $\pm 1^\circ\text{C}$ . The catalyst and sand were mixed in a 1:10 mass ratio. Soda glass beads and quartz glass were used as catalysts beds in the catalytic test. The catalysts were loaded in a tubular reactor with an internal diameter of 17 mm and a total length of 250 mm. Soda glass beads and quartz glass were placed on the top and bottom of the catalysts. A thermocouple was positioned in the center of the catalyst bed in order to monitor the temperature. The catalyst was then pretreated *in situ* at a heating rate of  $5^\circ\text{C}/\text{min}$  under a flow of air (30 mL/min). When the reactor temperature reached 500 °C, it was maintained at that temperature for 4 h. The temperature was then decreased to the reaction temperature in flowing air. To avoid possible condensation of hydrocarbons, the temperature of the effluent line was constantly maintained at 100 °C. An on-line Varian 3800 Gas Chromatograph with a flame ionization detector (GC-FID) equipped with a capillary column (CP-Sil PONA CB fused silica WCOT) analyzed the reaction products with hydrogen as carrier gas. The first sampling of the product gas was done 1 h after the reactant feed started. During a typical run, subsequent samplings and analyses were done with 1 h sampling periods. To simplify the discussion, we defined the light olefins as the sum ethylene and propylene, alkyl aromatics as the sum of  $\text{C}_6\text{--}\text{C}_{10}$  aromatics, the paraffins as the sum of  $\text{C}_1\text{--}\text{C}_4$  *i*-paraffins and paraffins, and the other hydrocarbons as the sum of  $\text{C}_5^+$  (alkane and alkene).

## 3. Results and discussion

### 3.1. Catalyst characterization

The powder XRD patterns of both ZSM-5 catalysts are given in Fig. 1, all in good agreement with previously reported data in the literature [15]. Both samples displayed ZSM-5 XRD patterns and no other peak could be observed in the patterns. Nano-ZSM-5 showed higher peak intensity than Con-ZSM-5 sample, indicating the strong influence of synthesis conditions on zeolite crystallization. It therefore follows that the crystallinity of the zeolite is dramatically enhanced in the case of uniform Nano-ZSM-5. In addition, inspection of Fig. 1 reveals that the XRD pattern of Nano-ZSM-5 is strongly affected by preferred orientation phenomena caused by relative large and well formed crystallites.

The SEM images clearly show the crystal morphology and size of the synthesized ZSM-5 crystals. As shown by SEM images in Fig. 2, synthesis method significantly affects ZSM-5 morphology and crystal size. From

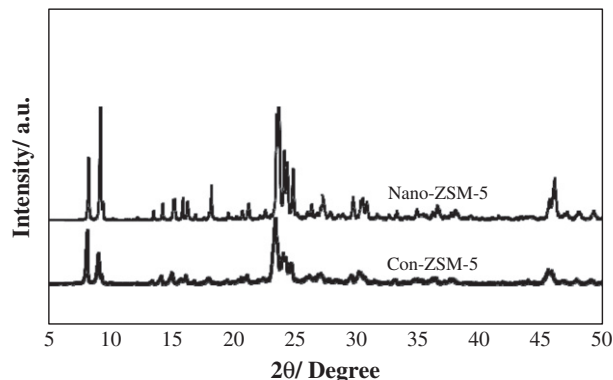


Fig. 1. Powder XRD patterns of uniform ZSM-5 nanocrystals (Nano-ZSM-5); and conventional ZSM-5 crystallite (Con-ZSM-5) derived by hydrothermal reaction.

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