Catalysis Communications 72 (2015) 156–160

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Synthesis of monolithic Al-fiber@HZSM-5 core-shell catalysts for methanol-to-propylene reaction

Jia Ding, Lupeng Han, Ming Wen, Guofeng Zhao, Ye Liu, Yong Lu *

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China

ARTICLE INFO

Article history:
Received 10 May 2015
Received in revised form 9 August 2015
Accepted 28 September 2015
Available online 30 September 2015

Keywords:
Structured catalyst
Core-shell structure
ZSM-5 zeolite
Fiber
Methanol-to-propylene

ABSTRACT

Monolithic microstructured Al-fiber@HZSM-5 core-shell catalysts have been synthesized by directly growing the shell of HZSM-5 with varied SiO_2/Al_2O_3 molar ratio on the core of sinter-locked aluminum microfibers. Such monolithic catalysts are examined in the methanol-to-propylene reaction, and the best microstructured catalyst of HZSM-5 with SiO_2/Al_2O_3 molar ratio of 200 delivers a $C_2^{=}$–$C_4^{=}$ selectivity of 62% (~36% to $C_3^{=}$) as well as a single-run lifetime of 160 h under industrial relevant conditions.

1. Introduction

Propylene as a very important commodity compound in the petrochemical industry is widely used to produce polypropylene, acrylonitrile, epoxy propane, etc. Usually, propylene comes from petroleum resource with naphtha as the main raw material [1]. However, with the ever-increasing demand for propylene and the depletion of petroleum resource, it is urgent to seek alternative technologies to realize the sustainable production of propylene. Hence, methanol-to-propylene (MTP) process has been attracting great interests since methanol can be readily generated from abundant non-petroleum sources such as coal, natural gas, and especially renewable biomass [2].

In recent years, ZSM-5 zeolite-based catalysts have been widely investigated due to their desirable performance for this acid-catalysis-dependant reaction. Most attention is focused on proper tuning of the acid strength and density, size and/or morphology-controllable synthesis and fabrication of hierarchical pore structure [3–6]. Despite high selectivity toward propylene is obtainable on ZSM-5 zeolite, its practical use in a fixed bed reactor still faces severe problems like poor mass/heat transfer, high pressure drop, non-regular flow pattern and even adverse effects of the used binders, which reduces the intrinsic catalyst selectivity and activity. Accordingly, to develop advanced catalysts with improved activity and selectivity integrated with enhanced mass/heat transfer is particularly desirable for the MTP process but it still remains significantly challenging.

The structured catalyst and catalytic reactors (SCRs) are promising strategies to overcome these major drawbacks due to enhanced heat/mass transfer, good mechanical stability and improved hydrodynamics [7–12]. Our previous efforts have demonstrated successful applications of microfibrous supports in development of many structured catalysts for gas-phase oxidation of alcohols [8], methane dry reforming [9], oxidative coupling of methanol to methyl formate [10], NH_3 cracking [11], and methanol steam reforming [12]. Very recently, we have reported a stainless-steel-fiber@HZSM-5 core-shell catalyst that demonstrates dramatic selectivity and stability improvement in the MTP process in comparison to the ZSM-5 powdered counterpart [13,14]. Furthermore, Jiang et al. showed that Pt/ZSM-5/stainless-steel-microfiber catalyst delivers good catalytic performance in hydrocracking paraffin wax [15]. Considering the costly sinter-locked stainless-steel-fiber and its inferior thermal conductivity in contrast to thepure Al-fiber (ten-fold higher than stainless-steel-fiber), it is worthwhile to develop microfibrous-structured ZSM-5 zeolite catalysts using Al-fiber to replace the stainless-steel-fiber.

In this work, we illustrate the fabrication of the monolithic Al-fiber@HZSM-5 core-shell catalysts by direct growth of ZSM-5 crystals onto a thin-sheet 3-dimensional (3D) network using 50-μm Al-fiber and demonstrate their catalytic performance in the MTP process. The microstructured catalyst of HZSM-5 with SiO_2/Al_2O_3 molar ratio of 200 shows an improved C_2-C_4 olefin selectivity and significantly prolonged single-run lifetime.

---

* Corresponding author.
E-mail address: ylu@chem.ecnu.edu.cn (Y. Lu).

http://dx.doi.org/10.1016/j.catcom.2015.09.026
1566-7367/

2. Experimental

2.1. Macroscopic synthesis of Al-fiber@HZSM-5

A thin-sheet 3D network consisting of 15 vol.% 50-μm Al-fiber and 85% voidage was utilized as substrate, which was purchased from Shanghai Xincai Screen Manufacturing Co. Ltd. To remove any contamination, such microfibrous-structured substrate was sonicated in acetone for 30 min, thoroughly washed using deionized water, and then dried at 100 °C overnight. Tetraethylorthosilicate (TEOS, A.R.), tetrapropylammonium (TPAOH, 25 wt%, Sinopec Co., Ltd.), sodium hydroxide (NaOH, C.P.), and sodium aluminate ($NaAlO_2$, C.P.) were used as silica source, structure-directing agent, alkali source and aluminum source. Chemicals except TPAOH are all taken from Sinopharm Chemical Reagent Co., Ltd.

Silicalite-1 (MFI-type) seeds were prepared by hydrothermal synthesis at 90 °C for 96 h, using a synthesis gel in molar ratio of TEOS: 0.35TPAOH: $19.6H_2O$. [16] As-made seeds were aggregated by adding NH_4Cl, separated by filtration, and washed thoroughly. An aqueous suspension consisting of 2 wt.% silicalite-1 (50–100 nm) was prepared and its pH was adjusted to 10 by adding 25 wt.% ammonium hydroxide. The circular chips (16.1 mm in dia. by 2 mm in thickness) of Al-microfibrous substrate were then immersed into the above seeding suspension for 30 min under ultrasonic processing, followed by drying overnight to obtain the silicalite-1 seeded Al-microfibrous substrates.

Fifteen circular chips seeded with silicalite-1 were placed vertically in a 100 mL autoclave filled with 70 mL synthesis gel. The molar composition of precursor gel was TEOS: 0.25TPAOH: 0.18NaOH: $mNaAlO_2$: $250H_2O$ ($m = 0.02$, 0.01, 0.005, 0.0025, 0.00167, 0.00125 or 0; corresponding to the gel SiO_2/Al_2O_3 molar ratio of 50, 100, 200, 400, 600,800 or ∞). After hydrothermal synthesis at 180 °C for 48 h, the as-synthesized samples were rinsed thoroughly with water, and then dried at 100 °C overnight. After three cycles of crystallization, the Al-fiber@ZSM-5 products were calcined in air to remove the organic template and transferred into their H-form by ion-exchange method as described in detail previously [14]. The catalyst products were denoted as Al-fiber@HZSM-5(n), where “n” represents the SiO_2/Al_2O_3 molar ratio in the synthesis gel used in this work.

2.2. MTP reaction evaluation

The MTP reaction testing was performed at 450 °C with methanol weight hourly space velocity (WHSV, to ZSM-5 zeolite mass) of 1 (or 5) h^{-1}, using a fixed-bed quartz tube reactor (i.d., 16 mm; reactor length of 300 mm) under atmospheric pressure as described in detail elsewhere [13,14]. Circular chips of the Al-fiber@HZSM-5 catalysts were packed layer-up-layer into the tube reactor to an HZSM-5 mass of 0.4 g, and a gaseous mixture of 30 vol.% MeOH in N_2 outflowed from the evaporator was fed into the catalyst bed. The effluent gas at outlet of the reactor is quantitatively analyzed by an on-line Shimadzu 2014C gas chromatography-flame ionization detector (GC-FID) with a 30-m HP-Plot Q capillary column (Agilent).

2.3. Characterization

The catalyst samples were characterized by X-ray diffraction (XRD, Rigaku Ultima IV, Cu Kα; Japan), N_2 adsorption-desorption (BET-MAX; Japan), inductively coupled plasma-atomic emission spectroscopy (ICP-AES; ICP Thermo IRIS Intrepid II XSP; USA), Scanning electron microscopy (SEM, Hitachi S-4800; Japan), and temperature-programmed desorption of ammonia (NH_3-TPD, Xianquan TP-5080; China). The mass of ZSM-5 shell is estimated by the weight change of the seeded microfibrous substrates before and after the hydrothermal synthesis.

3. Results and discussion

3.1. Microstructure and features of the Al-fiber@HZSM-5

Fig. 1 shows the geometry, morphology, structural and textural features of our representative Al-fiber@HZSM-5(200) catalyst samples. In comparison with the pristine Al-microfibrous structure (Fig. S1), it is clear that a uniform and dense ZSM-5 zeolite shell grows continuously along with the Al-fiber to form hierarchical 3D porous fiber@zeolite core-shell structure (Fig. 1A–D). A high ZSM-5 zeolite loading of 25 wt.% is achieved after three synthesis cycles, showing a ZSM-5 shell thickness of 4–5 μm (Fig. 1C). The ZSM-5 shell of Al-fiber@HZSM-5(200) exhibits typical MFI structure, being evidenced by XRD patterns with major diffraction peaks located at 2θ of 7.9° and 8.9° and the characteristic quintet at 23–25° (Fig. 1D). We believe that such perfect core-shell structure formation is mainly attributed to the one-dimension rod-like feature and homogeneously seeded surface of the Al-fiber (Fig. S2). This approach assures the identity of crystallization condition at the microfiber surface and avoids the edge stress effect that is innate in monolith structures such as SiC foams and is not favorable for continuous growth of ZSM-5 shell [17]. The Al-fiber@HZSM-5(200) catalyst presents a specific surface area (SSA) of 104 m^2/g and a total pore volume of 0.062 cm^3/g (including the Al-fiber mass), and shows a mesopore feature evidenced by the appearance of a clear capillary condensation step at a P/P_0 region of 0.4–0.6 on the N_2 adsorption-desorption isothermal. The zeolite shell contributes a micropore surface area of 86 m^2/g with a micopore volume of 0.040 cm^3/g and a mesopore surface area of 18 m^2/g with a mesopore volume of 0.022 cm^3/g. This catalyst also shows a narrow Barrett–Joyner–Halenda (BJH) pore size distribution at ~3 nm (Fig. 1E). Table S1 indicates that all samples have similar texture properties.

As shown in Table S2 for the real SiO_2/Al_2O_3 ratio of the ZSM-5 shell by ICP-AES, our Al-fiber@HZSM-5 with tunable SiO_2/Al_2O_3 molar ratio can be obtained by adjusting the synthesis gel SiO_2/Al_2O_3 molar ratio in a wide range from 50 to ∞. All samples show a much lower SiO_2/Al_2O_3 molar ratio in zeolite shell as compared to that of the synthesis gel, most likely due to the aluminum contamination from Al-fiber during ZSM-5 synthesis. It should be noticed that the SiO_2/Al_2O_3 molar ratio of the ZSM-5 zeolite is also crucial for a uniform and dense ZSM-5 shell growth on the Al-fiber surface. Fig. S3 shows the morphology of zeolite shell against the synthesis gel SiO_2/Al_2O_3 molar ratio ranged from 50 to ∞. Clearly, continuous growth of ZSM-5 shell becomes difficult with lowering the synthesis gel SiO_2/Al_2O_3 molar ratio, and meanwhile the crystallite shape evolves from coffin-like single-crystalline to spherical accumulation. For the Al-fiber@HZSM-5(50) sample, the zeolite shell looks discontinuous and irregular along with Al-fibers. Fig. S4 shows the XRD patterns of Al-fiber@HZSM-5 core-shell catalysts with varied SiO_2/Al_2O_3 molar ratio. It is notable that the diffraction intensity at 2θ of 23–25° weakens gradually with decrease of the SiO_2/Al_2O_3 ratio from 200 to 50 even though all samples have similar zeolite content. The above observation is in good agreement with the fact that high Al content is adverse to the ZSM-5 crystallization [18].

Effect of the SiO_2/Al_2O_3 molar ratio on the acidity of our Al-fiber@HZSM-5 catalysts was investigated by NH_3-TPD technique with the results as shown in Fig. 2. All catalyst samples offer dual-peak NH_3-TPD profiles, indicating the existence of two types of acid sites. The low-temperature desorption peak centered at 230 °C is attributed to the interaction of NH_3 with the weak acid sites in the HZSM-5 shell, and the high-temperature desorption peaking at 400–450 °C is attributed to the strong acid sites. Acid strength (indicated by NH_3 desorption temperature) of the strong acid sites shows a decrease trend with the increase of the SiO_2/Al_2O_3 ratio, associated with similar acid amount evolution here except the Al-fiber@HZSM-5(50) (Table S3). Regarding the weak acid sites, with the increase of the SiO_2/Al_2O_3 ratio, their acid strength looks unchanged while their amount decreases monotonously. It is generally acknowledged that the density of acid sites and the acid