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, and Yong Lu*

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

Fax: (+86) 21-62233424, Email: ylu@chem.ecnu.edu.cn

* To whom correspondence should be addressed

Abstract:

Monolithic microstructured Al-fiber@HZSM-5 core-shell catalysts have been synthesized by direct in-situ growing the shell of HZSM-5 with varied $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio on the core of sinter-locked aluminum microfibers. Such monolithic catalysts are employed in methanol-to-propylene reaction, and the best catalyst with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 200 delivers a $\text{C}_2^+=\text{C}_4^+$ selectivity of 62% ($\sim 36\%$ to C_3^+) as well as a single-run lifetime of 160 h under industrial relevant conditions.

Keywords: *structured catalyst; core-shell structure; ZSM-5 zeolite; fiber; methanol-to-propylene*

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 acidity 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 combination of activity and selectivity with mass/heat transfer for the efficient practical MTP process is particularly desirable but 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 successfully applied microfibrinous

supports in gas-phase oxidation of alcohols [8], methane dry reforming [9], oxidative coupling of methanol to methyl formate [10], NH₃ cracking [11], and methanol steam reforming [12]. Very recently, we have reported that the stainless-steel-fiber@HZSM-5 core-shell catalysts demonstrate dramatic selectivity and stability improvement in the MTP process in comparison to the ZSM-5 powdered counterpart [13, 14]. Furthermore, Jiang et al. found that the similar ZSM-5/stainless-steel-microfiber catalyst show good catalytic performance in hydrocracking paraffin wax [15]. Considering the costly sinter-locked stainless-steel-fiber and inferior thermal conductivity compared with pure Al fiber (ten-fold higher than stainless-steel-fiber), it is worthwhile to develop microfibrinous-structured ZSM-5 zeolite catalysts using aluminum-fiber (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- μ m Al-fiber and demonstrate their catalytic performance in the MTP process. The microstructured catalyst with SiO₂/Al₂O₃ molar ratio of 200 shows an improved C₂-C₄ olefin selectivity and significantly prolonged single-run lifetime.

2. Experimental

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

A thin-sheet 3D network consisting of 15 vol% 50- μ m Al-fiber and 85% voidage was utilized as substrate, which was purchased from Shanghai Xincal Screen Manufacturing Co. Ltd. To remove any contamination, such microfibrinous-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 aluminium 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: 19.6H₂O. [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: $m\text{NaAlO}_2$: 250H₂O ($m=0.02, 0.01, 0.005, 0.0025, 0.00167, 0.00125$ or 0; corresponding to the gel $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 N₂ 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 K α ; Japan), N₂ 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 (NH₃-TPD, Xianquan TP-5080; China). The mass of ZSM-5 shell is estimated by the weight change of the seeded microfibrinous 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-microfibrinous 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 $23-25^\circ$ (Fig. 1D). We believe that such perfect core-shell structure formation is mainly attributed to the one-dimension rodlike 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 $104\text{ m}^2/\text{g}$ and a total pore volume of $0.062\text{ cm}^3/\text{g}$ (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 $86\text{ m}^2/\text{g}$ with a micopore volume of $0.040\text{ cm}^3/\text{g}$ and a mesopore surface area of $18\text{ m}^2/\text{g}$ with a mesopore volume of $0.022\text{ cm}^3/\text{g}$. This catalyst also shows a narrow Barrett–Joyner–Halenda (BJH) pore size distribution at $\sim 3\text{ nm}$ (Fig. 1E). Table S1 indicates that all samples have similar texture properties.

As shown in Table S2 for the real $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the ZSM-5 shell by ICP-AES, our Al-fiber@HZSM-5 with tunable $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio can be obtained by adjusting the synthesis gel $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio in a wide range from 50 to ∞ . All samples show a much lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio ranged from 50 to ∞ . Clearly, continuous growth of ZSM-5 shell becomes difficult with lowering the synthesis gel $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio. It is notable that the diffraction intensity at 2θ of $23\text{-}25^\circ$ weakens gradually with decrease of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $400\text{-}450^\circ\text{C}$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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

SiO₂/Al₂O₃ ratio, their acid strength looks unchanged while their amount decreases monotonously. It is generally acknowledged that the density of acid sites and the acid strength decreases with increasing SiO₂/Al₂O₃ molar ratios for HZSM-5 [19], and our results are in good agreement with this rule, except Al-fiber@HZSM-5(50) due to its low crystallinity degree.

3.2. Catalyst performance for MTP process

We initially checked the MTP performance of our Al-fiber@HZSM-5 catalysts using a WHSV of 5 h⁻¹ for feed gas of 30 vol% methanol in N₂, and the results are shown in Table 1. The Al-fiber@HZSM-5(200) is the best catalyst, delivering a total light olefin selectivity of 66.8% associated with a propylene selectivity of 35.5% at 450 °C. Moreover, this catalyst is stable at least for 23 h (till to 90% methanol conversion). With the increase of SiO₂/Al₂O₃ molar ratio from 100 to 800, the propylene selectivity increases from 35.5~35.8 to 42.7% as well as the propylene/ethylene (P/E) ratio from 1.6~1.7 to 4.5, while the acid density decreases especially for the strong acid sites (Fig. 2). This indicates that relatively weak acid strength together with low acid density is beneficial to the formation of propylene, being consistent with the previous literature report [20]. Whereas the catalyst samples with SiO₂/Al₂O₃ ratio of 400 or above all can convert methanol completely at the beginning of reaction (*i.e.*, in first hour), their stability is very poor while the deactivation is accelerated with the increase of SiO₂/Al₂O₃ ratio (Fig. S5). The main cause for this observation is the large crystallites (Fig. S3) which result in mass transfer limitation so as to bring about fast accumulation of polycyclic aromatic hydrocarbons in their pores [21]. In comparison with the best Al-fiber@HZSM-5(200), the Al-fiber@HZSM-5 with low SiO₂/Al₂O₃ ratio, such as the

Al-fiber@HZSM-5(100), is unfavorable for the formation of light olefins while facilitating the yield of C_5^+ heavy products, because of the improved acid density and strength of the strong acid sites (Fig. 2) that facilitates the hydrogen transfer and methylation of light olefins [22].

3.3. Stability

Another advantage of our microfibrinous design of the HZSM-5 for the MTP is the significantly improved stability. Fig. 3 shows the methanol conversion and light olefin selectivity for the MTP reaction against the time on stream using our Al-fiber@HZSM-5(200) catalyst under the industrial relevant conditions. Clearly, this microstructured catalyst delivers a single-run lifetime of 160 h (till to 90% methanol conversion), being 1.7-fold higher than that (~60 h) for the powdered HZSM-5 zeolite catalyst with similar characteristics such as SiO_2/Al_2O_3 ratio [13, 16]. Over the Al-fiber@HZSM-5(200) catalyst, the methanol conversion is retained at >99% within the first 105-h running and then declines slowly to ~90% within another 55 h on stream. The propylene selectivity increases from only 20.4% at the beginning to 37.3% throughout the entire stability testing with an average of 32.6%. The ethylene selectivity shows a completely opposite characteristic, decreasing from 15.4% to 5.5% over the whole test. According to “dual cycle” mechanism, aromatic-based cycle and olefin-based cycle are favorable to form ethylene and propylene respectively [23]. In accordance, we believe that the olefin-based cycle propagation is gradually enhanced while the aromatic-based cycle propagation is slightly suppressed along with the reaction time during our long-term test. The total light olefin selectivity shows a visible increase from initial 53.0% to 60.8% after 20 h running, subsequently remains almost unchanged within the following 75

h, and slightly decreases within the last 55 h. The butene selectivity increases from 17.0% to 19.5% in the first 25 h running and then slowly decreases to 12.5% within another 135 h. Furthermore, the formation of C_5^+ heavy products exhibits obvious increase along with the reaction time.

4. Conclusions

Monolithic microstructured Al-fiber@HZSM-5 core-shell catalysts are controllably synthesized by direct growth of zeolite shell on Al-fiber core, which provides a good combination of high thermal conductivity and hierarchical 3D porous metal-fiber@zeolite core-shell structure for the heat/mass transfer limited reactions. The effect of SiO_2/Al_2O_3 molar ratio on the MTP reaction was investigated, and the results show that Al-fiber@HZSM-5(200) achieves the longest single-run life-time (160 h at 450 °C and WHSV of $1\ h^{-1}$) and the highest $C_2^--C_4^-$ selectivity (>60%). In spite of above advance, further improvement of the MTP performance of the Al-microfibrous structured HZSM-5 catalysts is particularly desirable. To accomplish this goal, new synthesis strategy should be developed to avoid Al contamination from Al-fiber during the hydrothermal synthesis, which might degrade the MTP performance of our Al-fiber@HZSM-5 catalysts. The work along this line is in progress.

Acknowledgments

This work was financially supported by the “973 program” (2011CB201403) from the MOST of China and the NSF of China (21473057, U1462129, 21273075).

References

- [1] Y. Park, C.W. Lee, N.Y. Kang, W.C. Choi, S. Choi, S.H. Oh, D.S. Park, *Catal. Surv. Asia*, 14(2) (2010) 75-84.
- [2] P. Tian, Y.X. Wei, M. Ye, Z.M. Liu, *ACS Catal.* 5 (2015) 1922-1938.
- [3] S. Ivanova, C. Lebrun, E. Vanhaecke, C. Pham-Huu, B. Louis, *J. Catal.* 265 (2009) 1-7.
- [4] A.Z. Ruiz, H. Li, G. Galzaferri, *Angew. Chem. Int. Ed.* 45 (2006) 5282-5287.
- [5] C. Mei, P. Wen, Z. Liu, Y. Wang, W. Yang, Z. Xie, W. Hua, Z. Gao, *J. Catal.* 258 (2008) 243-249.
- [6] X.J. Meng, F.S. Xiao, *Chem. Rev.* 114 (2014) 1521-1543.
- [7] E. Reichelt, M.P. Heddrichb, M. Jahn, A. Michaelisa, *Appl. Catal. A.* 476 (2014) 78-90.
- [8] G.F. Zhao, Y.K. Li, Q.F. Zhang, M.M. Deng, F.H. Cao, Y. Lu, *AIChE J.* 60 (2014) 1045-1053.
- [9] W. Chen, W.Q. Sheng, G.F. Zhao, F.H. Cao, Q.S. Xue, L. Chen, Y. Lu, *Int. J. Hydrogen Energy*. 37 (2012) 18021-18030.
- [10] Q.F. Zhang, Y.K. Li, L. Zhang, L. Chen, Y. Liu, Y. Lu, *J Catal.* 317 (2014) 54-61.
- [11] Y. Liu, H. Wang, J.F. Li, Y. Lu, Q.S. Xue, J.C. Chen, *AIChE J.* 53 (2007) 1845-1849.
- [12] M. Ling, G.F. Zhao, W. Chen, M.M. Wang, Q.S. Xue, Y. Lu, *Int. J. Hydrogen Energy*. 36 (2011) 12833-12842.
- [13] X.Y. Wang, M. Wen, C.Z. Wang, J. Ding, Y. Sun, Y. Liu, Y. Lu, *Chem. Commun.* 50 (2014) 6343-6345.
- [14] M. Wen, X.Y. Wang, L.P. Han, J. Ding, Y. Sun, Y. Liu, Y. Lu, *Micro. Meso. Mater.* 206 (2015) 8-16.
- [15] J. Jiang, C. Yang, Z.J. Lu, J. Ding, T. Li, Y. Lu, F.H. Cao, *Catal. Commun.* 60 (2015) 1-4.

- [16] A.E. Persson, B.J. Schoeman, J. Sterte, J.E. Otterstedt, *Zeolites*. 14 (1994) 557-567.
- [17] Y. Jiao, C.H. Jiang, Z.M. Yang, J.S. Zhang, *Micro. Meso. Mater.* 206 (2015) 8-16.
- [18] M.A. Ali, B. Brisdon, W.J. Thomas, *Appl. Catal. A*. 252 (2003) 149-162.
- [19] N.R. Meshram, S.G. Hegde, S.B. Kulkarni, *Zeolites*. 6 (1986) 434-438.
- [20] R.C. Wei, C.Y. Li, C.H. Yang, H.H. Shan, *J. Nat. Gas. Chem*, 162 (2012) 152-158.
- [21] H.-G. Jang, H.-K. Min, J.K. Lee, S.B. Hong, G. Seo, *Appl. Catal. A*. 437-438 (2012) 120-130.
- [22] S. Müller, Y. Liu, M. Vishnuvarthan, X. Sun, A.C. van Veen, G.L. Haller, M. Sanchez-Sanchez, J.A. Lercher, *J Catal.* 325 (2015) 48-59.
- [23] M. Bjørgen, S. Svelle, F. Joensen, J. Nerlov, S. Kolboe, F. Bonino, L. Palumbo, S. Bordiga, U. Olsbye, *J Catal.* 249 (2007) 195-207.

Fig. 1. The geometry, morphology, structural and textural properties of our representative Al-fiber@HZSM-5(200) sample. (A) Macroscopic sample photograph, (B, C) SEM images, (D) XRD patterns, (E) N₂ adsorption-desorption isotherm and Barrett–Joyner–Halenda (BJH) mesopore size distribution (inset)

Fig. 2. NH_3 -TPD profiles of the Al-fiber@HZSM-5 core-shell catalysts with different synthesis gel $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of (A) 50, (B) 100, (C) 200, (D) 400, (E) 600, (F) 800, and (G) ∞ .

Table 1 MTP process catalyzed by monolithic Al-fiber@HZSM-5 catalysts with various SiO₂/Al₂O₃ molar ratio^a

Sample	Conv.	Select. ^b (%)									P/E ^c	Life time ^d
		CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ H ₈	C ₄ H ₁₀	C ₅ ⁺	C ₂ ⁼ ~C ₄ ⁼		
Al-fiber@HZSM-5 (50)	71.6	3.8	10.3	0.1	32.8	2.7	12.8	8.6	28.9	55.9	2.1	2
Al-fiber@HZSM-5 (100)	100	2.0	14.0	0.2	35.8	3.5	16.2	8.3	20.0	66.0	1.7	22
Al-fiber@HZSM-5 (200)	100	1.8	14.7	0.2	35.5	3.7	16.6	8.8	18.7	66.8	1.6	23
Al-fiber@HZSM-5 (400)	100	2.3	11.4	0.1	38.0	2.4	16.9	10.1	18.8	66.3	2.2	17
Al-fiber@HZSM-5 (600)	100	2.1	10.9	0.1	38.4	2.3	16.6	9.1	20.5	65.9	2.4	14
Al-fiber@HZSM-5 (800)	97.1	3.3	6.3	0.1	42.7	0.8	12.2	9.8	24.8	61.2	4.5	7
Al-fiber@HZSM-5 (∞)	27.9	14.4	4.6	0.2	28.3	0.4	8.4	8.3	35.4	41.3	4.1	1

^a Reaction conditions: WHSV (methanol weight flow rate to zeolite mass) = 5 h⁻¹, 0.1 MPa, zeolite 0.4 g. ^b Data are collected in the 5th hour; calculation is on the basis of carbon. ^c C₃H₆/C₂H₄ molar ratio. ^d Life time till the reaction was quitted at ~90 % methanol conversion.

Fig. 3. Conversion and product selectivity for the MTP reaction vs. time on stream using the Al-fiber@HZSM-5(200) catalyst. Reaction conditions: 450 °C, WHSV of 1 h⁻¹, 0.1 MPa, 30 vol% methanol in N₂, zeolite 0.4 g. Testing was quitted at a methanol conversion of ~90%.

Graphical Abstract

ZSM-5

Methanol-to-Propylene