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ARTICLE TYPE

Microstructured fiber@HZSM-5 core-shell catalysts with dramatic selectivity and stability improvement for methanol-to-propylene

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**We report a macroscopic stainless-steel-fiber@HZSM-5 core-shell catalyst by direct growth of 27 wt% HZSM-5 on a 3D microfibrous structure using 20-μm SS fibers, demonstrating dramatic selectivity and stability improvement in the MTP**
10 **process. The unprecedented performance is due to the promotion of olefin methylation/cracking cycle in the methanol-to-hydrocarbon catalysis.**

In recent years the methanol-to-olefins (MTO) process has been attracting particular attention as an alternative route for light
15 olefin production from non-petroleum sources such as coal, natural gas and biomass.[1] To date, large-scale implementation of the MTO process has been successful in ethylene operation mode on SAPO-34 zeolite catalyst in fluidized bed reactor.[1] However, the global demand for propylene is growing faster than for the
20 ethylene.[1] Hence, it is in particular desirable to develop catalysts that can selectively convert methanol to propylene (MTP).

ZSM-5 zeolite-based catalysts for MTO have been extensively studied to orient product selectivity toward light olefins especially propylene and to further improve the catalyst stability,
25 although Lurgi's MTP process based on the packed bed with ZSM-5 catalyst has been industrially demonstrated. Most attention has been focused on modification of the ZSM-5 zeolite, such as proper tuning of the acidity (strength and density),[2] size- and/or morphology-controllable synthesis[3] and hierarchical
30 design of pore structure.[4] In some cases, high selectivity toward propylene was obtainable with increased propylene to ethylene ratio on ZSM-5 zeolite catalysts.[3a,5] Despite these promising results, their practical use as catalyst in a fixed bed reactor is still particularly challenging, as macroscopic shape of microgranules
35 or extruded pellets a few millimeters in size are required in the real-world forms rather than as-made powders. As a result, some frustrating problems emerged in these cases including mass/heat transfer limitations, high pressure drop, non-regular flow pattern and adverse effects of the used binders, which will always reduce
40 the intrinsic catalyst selectivity and activity.

Microstructured catalyst has now been attracting growing interests in the heterogeneous catalysis due to improved hydrodynamics in combination with enhanced heat/mass transfer.[6] This recently becomes a source of inspiration for
45 attempts to develop microstructured zeolite materials[6d,7,8] by growing zeolite coatings on porous supports such as SiC foam. However, only a few studies have been reported on the synthesis
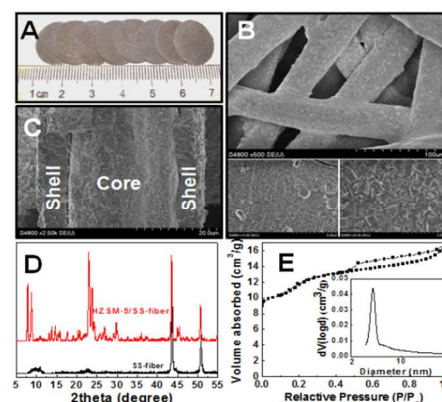
Fig. 1 All-in-one for HZSM-5/SS-fiber composite. (A) Photograph of
50 macroscopic sample; (B, C) SEM images, showing uniform and dense growth of zeolite crystals along with fiber to form electric-wire-like core-shell structure; (D) XRD patterns, showing the formation of MFI-type HZSM-5 shell; (E) N_2 adsorption-desorption isothermal and Barrett–Joyner–Halenda (BJH) mesopore size distribution (inset).

55 of ZSM-5 on SiC foam support for the MTP applications.[6d,7,8] The density of ZSM-5 zeolite in per unit volume of ZSM-5/SiC-foam catalyst is unacceptably low.[7] Uniform and large-amount growth of ZSM-5 on SiC foam are still challenging due to the disadvantageous surface tension effect near the sharp edge of
60 cellular foam struts and ligaments.[6d,7] Simulation calculation shows that microstructured design of ZSM-5 can promote the C2-C4 olefin selectivity up to 71% with high propylene selectivity of up to 49%;[9] as yet the benefits of microstructured ZSM-5 catalysts with regard to enhanced selectivity to light olefins
65 especially propylene have not been demonstrated in practice.[6d,7]

In this Communication, we present a hierarchical 3D pore ZSM-5 catalyst engineered from micro- to macro-scales. Such microstructured design exhibits dramatic selectivity and stability improvement in the MTP process in comparison with the purely
70 microporous zeolite powder, by nature, due to the increase of the propagation of olefin methylation/cracking cycle in the methanol-to-hydrocarbon (MTH) catalysis.

The microstructured HZSM-5 catalyst is obtained by direct growth of zeolite crystals onto a 3D porous network of sinter-
75 locked 20-μm stainless steel (SS) 316L fibers and subsequent ion-exchange (see ESI† for details). Fig. 1 shows the geometry, morphology, structural and textural properties of our representative HZSM-5/SS-fiber sample. The first novelty of our

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Table 1. Methanol-to-propylene (MTP), catalyzed by microstructured and powdered HZSM-5 zeolite [a].

Catalyst	$T_{React.}$ (°C)	Conv. (%)	Select.[b] (%)								C_3H_6/C_2H_4 molar ratio	Ethylene/2MB yield[c]
			CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	C_5^+		
HZSM-5/SS-fiber[d]	450	100	1.9	8.3	0.1	43.6	1.1	14.9	11.1	19.0	3.5	2.74
	480	100	2.3	9.6	0.1	45.7	0.8	14.0	10.2	17.3	3.2	2.83
HZSM-5 powder[d,e]	450	100	1.8	12.3	0.2	35.9	3.0	16.7	10.3	19.8	1.9	3.98
	480	100	3.2	11.8	0.2	37.1	1.6	15.0	8.3	22.8	2.1	4.07
Structured HZSM-5[f]	450	100	2.6	8.3	0.2	43.5	0.8	14.5	10.5	19.6	3.5	2.36
	480	100	5.8	10.0	0.3	45.3	0.6	11.9	8.8	17.3	2.6	2.48
HZSM-5 powder[g]	450	100	2.7	12.4	0.3	34.5	2.2	16.7	9.5	21.7	1.9	4.12

[a] Reaction conditions: WHSV (methanol weight flow rate to zeolite mass) =5 h⁻¹, 0.1 MPa, 30 vol% methanol in N_2, zeolite 0.4 g. [b] Data were collected in steady-state associated with the highest propylene formation; calculation was on the basis of carbon. [c] Ethylene/(2-methylbutane + 2-methyl-butene) (ethylene/2MB) yield, calculated using initial reaction results for avoiding the effect of partially coking. [d] Si/Al molar ratio of HZSM-5 zeolite in the shell was determined to be 75 by ICP-AES. [e] HZSM-5 powder was taken from the HZSM-5/SS-fiber to keep the zeolite property identical; to obtain the powder sample, the composite samples were crashed to destroy the robust core-shell structure, followed by super sonication to facilitate the separation of HZSM-5 with the fiber substrate. [f] Standing-free HZSM-5 with the monolithic 3D network structure identical to the HZSM-5/SS-fiber, obtained by directly dissolving away the SS-fiber from HZSM-5/SS-fiber using excess 10 wt% nitrohydrochloric acid followed by thoroughly washing. [g] Powdered HZSM-5 sample obtained by milling the standing-free structured HZSM-5 sample.

study is the use of entirely open porous substrates (Fig. S1†) rather than the conventional foam. This change can eliminate the surface tension effect near the sharp edge of foam struts and ligaments, which not only is unfavorable for the zeolite growth but also may cause zeolite detachment. Not surprisingly, uniform and dense zeolite shell is grown continuously along with the SS-fibers to form hierarchical 3D pore fiber@zeolite core-shell structure (Fig. 1A-C). This results from the rod feature of the fibers, which assures identity of the crystallization condition at the microfiber interface by eliminating the unfavorable characters such as the surface tension effect in the foams. A high zeolite mass of 27 wt% is achieved after undergoing a two-step synthesis cycle, showing a perfect core-shell structure with ZSM-5 shell thickness of 6~7 μm (Fig. 1C). Note that a zeolite mass of 12 wt% is achievable by only one-step synthesis cycle (Fig. S2†). Clearly, the HZSM-5/SS-fiber sample exhibits typical MFI structure, evidenced by the XRD patterns with major peaks located at ~7.9° and ~8.9° and the characteristic triplet at ~23.5° (Fig. 1D). The ²⁷Al and ²⁹Si MAS NMR spectra in Fig. S3 further confirm the presence of a zeolite framework consisting of both AlO_4 and SiO_4 tetrahedra while showing the absence of any extraframework aluminum species. The HZSM-5/SS-fiber composite presents a specific surface area (SSA) of 93 m²/g (micropore SSA: 85 m²/g; micropore volume: 0.031 cm³/g), and shows a mesopore feature (SSA of only 8 m²/g) evidenced by the step appeared at P/P_0 of 0.4-0.6 on the N_2 adsorption-desorption isothermal with a dual Barrett–Joyner–Halenda (BJH) mesopore size distribution (~4 nm (dominant) and ~5.5 nm (recessive))(Fig. 1E). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurement indicates a Si/Al molar ratio of 75 for the zeolite shell of the HZSM-5/SS-fiber.

Our fiber@zeolite core-shell structure shows excellent robustness (Fig. S4 and supplementary text, ESI†), and allows for us to flexibly design their geometric configuration on demand (*e.g.*, thin sheets of large area and/or pleated sheet to control pressure drop and contacting efficiency;¹⁰ hollow-core pillars or chips used directly as catalysts of the packed bed (Fig. S5†)). Our HZSM-5/SS-fiber composite provides a combination of large void volume and high ZSM-5 content not only in mass fraction but also in volume fraction. At a mass content of 27 wt%, the fiber-zeolite-voidage volume fractions (vol%) are estimated to be 15, 22 and 63 for the HZSM-5/SS-fiber. Clearly, larger void volume (63 vol%) can be obtained compared to the packed bed with pellets (in general <40 vol%). It is expectable that the large void volume together with the entirely open 3D pore structure of the HZSM-5/SS-fiber catalyst will offer the high permeability thereby leading to a low pressure drop within the reactor bed.⁶,¹⁰

We initially check the MTP performance of the microstructured HZSM-5/SS-fiber (27 wt% HZSM-5) core-shell catalyst as well as the corresponding HZSM-5 powder catalyst for comparison, using a weight hourly space velocity (WHSV; methanol mass flow rate divided by zeolite mass) of 5 h⁻¹ and 30 vol% methanol in N_2, with the results as shown in Table 1. Interestingly, a significant improvement on the light olefins formation, especially the propylene, is able to be achieved by only the microstructured design of the HZSM-5 without any chemical modification. Most notably, dramatic improvement of the selectivity to light olefins is also observable in the cases of using Al-fiber or Cu-fiber to replace the SS-fiber (Table S1 and supplementary text, ESI†). High propylene selectivity (43.6% at 450 °C or 46.7% at 480 °C) can be obtained with the C2-C4 olefin selectivity to 67~70%. This observation is accompanied by a visible reduction of the formation of C2-C4 alkanes (especially for the propane) and C5⁺ heavy products. In contrast, the corresponding HZSM-5 powder catalyst delivers a propylene selectivity of only 35.9% at 450 °C (or 37.1% at 480 °C) and a low C2-C4 olefin selectivity of <65%, being associated with much formation of the C2-C3 alkanes and C5⁺ products. Additionally, a higher propylene/ethylene molar ratio of ~3.5 is obtainable over the HZSM-5/SS-fiber, 1.8 times as high as that

for the corresponding HZSM-5 powder catalyst.

It is widely accepted that MTH over the HZSM-5 zeolite proceeds through the dual-cycle mechanism including both aromatic- and olefin-based hydrocarbon pools. Recently, Bhan *et al.*[11] prove that ethylene/(2-methylbutane + 2-methyl-butene) (ethylene/2MB) yield can be employed to describe the relative rates of propagation of the aromatic and olefin methylation/cracking cycles. A high ethylene/2MB yield indicates the aromatic-base cycle dominant over the olefin-based cycle and otherwise the olefin-base cycle propagates over the aromatic-based cycle. The ethylene/2MB yield is measured for both microstructured and powdered HZSM-5 catalysts and the results are listed also in Table 1. It is not surprising that a relatively low ethylene/2MB yield of only 2.74 (at 450 ^{o}C) is observed for the HZSM-5/SS-fiber, much lower than that (3.98) for the HZSM-5 power. The results indicate that our microstructured design of the HZSM-5, by growing its crystals on a 3D porous network of sinter-locked 20-μm SS-fibers, shows an ability to propagate the olefin methylation/cracking pathway, which is favorable for the propylene formation.[12] By nature, this most likely thanks to the improved hydrodynamics (*e.g.*, uniform residence times and flow patterns) and enhanced transfer accordingly.[6a,b] Actually, the standing-free structured HZSM-5, obtained by removing the SS-fiber from the HZSM-5/SS-fiber (with well-preserved disc shape and microstructure, as shown in Fig. S6†), delivers the activity and product selectivity quite comparable to those for the HZSM-5/SS-fiber (Table 1). Not surprisingly, the powdered HZSM-5 from such standing-free structured HZSM-5 shows MTP performance comparable to the other powdered one (abstracted from the HZSM-5/SS-fiber; Table 1). This again confirms that the microstructured design can improve the hydrodynamics and enhance the transfer thereby leading to the pronounced MTP selectivity enhancement.

Another advantage of the microstructured design is the dramatic improvement of the stability, which is a very important practical consideration for a heterogeneous catalyst. At 450 ^{o}C and a WHSV of 1 h^{-1}, as shown in Fig. 2, the HZSM-5/SS-fiber catalyst delivers a dramatic prolonged single-run lifetime of 210 h with very good activity and selectivity maintenance when using 30 vol% methanol in N$_2$. The methanol conversion is retained at >99% within first 160 h and then declines slowly to ~90% within another 50-h. The propylene selectivity shows a visible increase from only ~35% initially to ~43% after first 60 h running and then is sustained at it throughout the entire stability testing. The ethylene selectivity shows a reverse evolution behavior along with prolonged time on stream, being decreased slowly from ~16% (at initial) to ~10% (after 100 h) and then remained almost unchanged even within the time period of catalyst deactivation (Fig. S7†). Within the 210-h testing, no obvious change is observed on the selectivity to butene but the formation of C5$^+$ heavy products is visibly increased along with time during the catalyst deactivation stage. In contrast, the corresponding HZSM-5 powder catalyst shows a very short single-run lifetime of only 60 h; the highest obtainable selectivity to propylene is only 30% with the C2-C4 olefin selectivity no more than 60% (Fig. 2B).

The ethylene/2MB yield is detected and is also plotted against time on stream in Fig. S8. A decline evolution is observed over both the microstructured and powdered HZSM-5 catalyst samples,
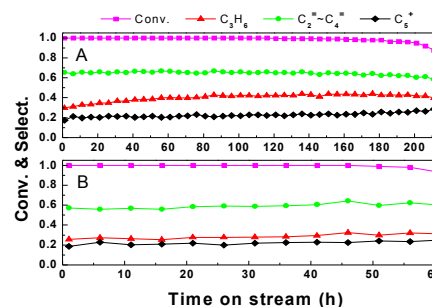
Fig. 2 Methanol conversion and product selectivity for MTP vs time on stream using (A) HZSM-5/SS-fiber and (B) HZSM-5 powder. Reaction conditions: 450 ^{o}C, WHSV=1 h^{-1}, 0.1 MPa, 30 vol% methanol in N$_2$, zeolite 0.4 g. Testing is quitted at ~90% conversion.

indicating that the aromatic-based cycle is superior initially while the olefin-based cycle propagates over the aromatic-based cycle gradually with prolonged time on stream according to Bhan *et al.*[11] Most notably, within the entire long-term testing our HZSM-5/SS-fiber catalyst always delivers lower ethylene/2MB yield than the powdered ones while the former delivers ethylene selectivity just a little higher than the latter (Fig. S7†). As widely accepted, ethylene exclusively forms from the aromatic hydrocarbon pool while the propylene forms from both the aromatic-based cycle and olefin-based cycle. We thus can say that the microstructured design of HZSM-5 provides, by nature, a pronounced enhancement of the olefin-based cycle propagation while slightly suppressing the aromatic-based cycle propagation.

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