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Controllable Fabrication and Catalytic Activity of Highly *b*-Oriented HZSM-5 Coatings

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Significance

Multilayer b-orientated HZSM-5 catalytic coating is controllably synthesized by repeated growth of zeolite layer on Ti—OH-modified surface of sublayer. The as-prepared zeolite coating shows performance enhancement up to 110% in catalytic cracking of n-dodecane ascribed to enhanced mass transfer in its straight and short pathway along the b-axis.
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Structured catalysts have generated considerable research during the past few decades.[1,2] Since the introduction of monolithic catalysts in the mid-1970s, they have been recognized as one of the most promising candidates for environmental applications due to its excellent pressure-drop, mass-transfer ratio and high thermal conductivity.[3] Along with the increased interest in structured catalysts, another member of this family, zeolite structured catalysts, also have become a subject of extensive research. MFI-type zeolites, in particular, have received much attention for a number of reactions including selective catalytic reduction of NO_x,[4] disproportionation of toluene,[5] and methanol to olefins.[6]

In MFI zeolite crystals, 0.53×0.56 nm^2 straight channels (*b*-axis) are interconnected with the 0.51×0.55 nm^2 sinusoidal channels (*a*-axis).[7] The *b*-axis channel with straight and short transport path has been recognized as the fastest diffusion pathway.[8,9] Great progress has been made on synthesis of *b*-oriented MFI zeolite membranes, typically by *in situ* growth method[10,11] or secondary (seeded) growth method,[12,13] to improve the flux and selectivity for potential of gas or liquid separation. Thereby, *b*-oriented HZSM-5 catalytic coatings may offer particular advantages for the diffusion-limited reactions attributed to the faster mass-transfer rates of reactants or products in its straight channels.[14,15] However, to the best of our knowledge, almost all the *b*-oriented MFI zeolite membranes reported in the literatures were silicalite-1 monolayers (pure-silica phase) without any framework aluminum due to great challenges in preparing *b*-oriented HZSM-5 catalytic coating (containing aluminum). First of all, the presence of aluminates in the synthesis mixtures will make it more difficult to control the crystal orientation and coating continuity even for the *b*-oriented HZSM-5 monolayers.[16–18] Moreover, up to now, little work has been done on the fabricating *b*-oriented HZSM-5 (containing aluminum) bilayer or multilayer coatings due to extreme difficulties in controlling the *b*-orientation of MFI crystals on the top or secondary layers,[16] while sufficient zeolite loadings are basically required to provide enough catalytic active sites for application of structured zeolite coatings in various catalytic processes. In this work, attempts were made to develop a facile method for preparing bilayer *b*-oriented HZSM-5 catalytic coatings, and to further examine their catalytic performance using a model reaction, that is, catalytic cracking of *n*-dodecane (550°C, 4 MPa; see Supporting Information, SI).

Our previous article focused on the synthesis of *b*-oriented HZSM-5 zeolite monolayer (HZ-M) on stainless steel tube (SST) using a synthesis gel with a composition of 1TEOS: $0.01Al(NO_3)_3$:0.32TPAOH:$165H_2O$, which was the same as that for the synthesis of *b*-oriented silicalite-1 membrane but adding $Al(NO_3)_3$.[10,17] Here, we prepare bilayer *b*-oriented HZSM-5 catalytic coating. In this work, we found that direct growth on HZ-M gave a bilayer with much amounts of

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Additional Supporting Information may be found in the online version of this article.

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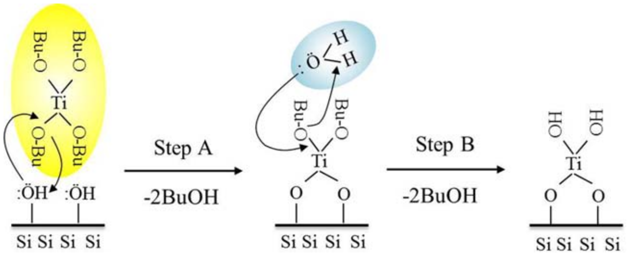

Scheme 1. The schematic illustration of the TBOT modification process.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a-oriented crystals on the top layer (HZ-B-D). Considering the positive effects of Ti-OH in controlling the *b*-oriented crystal orientation,[17] we developed two methods to introduce Ti-OH on HZ-M for the preparation of the bilayer *b*-oriented HZSM-5 coatings. First, TiO_2 coating was prepared with sol-gel method using different mass ratio of ethanol to titanium dioxide solution, and then the *b*-oriented bilayers (HZ-B-C series) were synthesized. However, we found the additional mass-transfer resistance was brought in by the TiO_2 coating when the coating thickness was higher to achieve the full coverage and higher orientation. To solve this problem, Ti—OH groups were then introduced by tetra *n*-butyl *ortho*-titanate (TBOT)-modified HZ-M as illustrated in Scheme 1. TBOT was first tethered on the HZ-M surface through a nonaqueous condensation reaction to form the Si—O—Ti linkage (Step A), and then aqueous hydrolysis of the adsorbed titanium alkoxide to generate the terminal Ti—OH groups (step B). More details on the two methods can be found in Supporting Information.

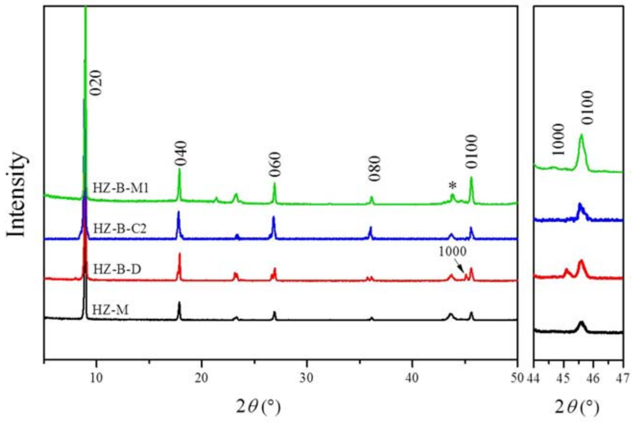

Figure 2. XRD patterns of the as prepared coatings.

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Figure 1a shows the highly *b*-oriented HZ-M on the inner surface of SST as evidenced by the only (0*k*0) diffraction peaks on XRD pattern (Figure 2). As shown in Figure 1b, direct secondary growth on the HZ-M results in a top layer of *a*-oriented twin crystals (HZ-B-D) as evidenced by double peaks of (*h*00/0*k*0) on XRD pattern (Figure 2). As expected, a highly *b*-oriented HZSM-5 bilayer (HZ-B-C2, Figure 1c) was successfully prepared by coating a 200-nm thick TiO_2 layer on HZ-M, with evidence of the only (0*k*0) peaks on XRD pattern (Figure 2). According to the (*h*00) peak and (0*k*0) peak of XRD patterns (Supporting Information, Figure S1), an index of F_b was defined to quantitatively describe the degree of *b*-orientation of the coatings (see notation in

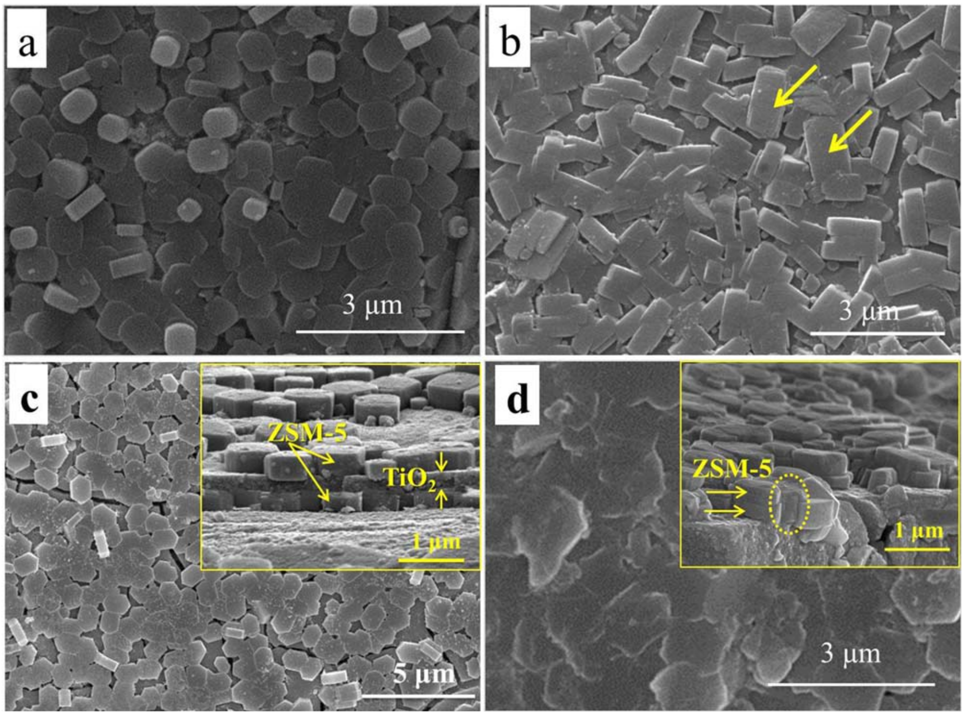

Figure 1. SEM images of (a) HZ-M; (b) HZ-B-D; (c) HZ-B-C2; and (d) HZ-B-M1.

Inserted SEM image in (c) and (d) is the cross-section view of the HZ-B-C2 and HZ-B-M1, respectively.

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Table 1. The Properties and Catalytic Performances of Zeolite Coatings

Samples[a]	F_b[b] (%)	Si/Al Ratio	Zeolite Loading (mg cm^{-2})	Conversion (%)	P_e[c] (%)	TOF[d] (mmol g^{-1} s^{-1})
Blank	–	–	–	12.5 ± 0.4	0	–
HZ-M	88.8	62.5	0.17 ± 0.04	19.8 ± 1.0	58.6 ± 8.0	16.8
HZ-B-D	38.5	61.5	0.46 ± 0.10	14.4 ± 1.3	15.6 ± 8.5	1.6
HZ-B-C1	89.7	68.9	0.30 ± 0.05	20.2 ± 0.6	61.9 ± 4.4	10.1
HZ-B-C2	78.4	64.0	0.31 ± 0.04	22.2 ± 1.0	78.0 ± 7.7	12.3
HZ-B-C3	48.4	69.7	0.37 ± 0.04	17.1 ± 0.6	37.1 ± 4.5	4.9
HZ-B-M1	89.7	67.2	0.33 ± 0.03	26.2 ± 0.5	110.4 ± 4.4	16.3
HZ-B-M2	76.4	63.5	0.32 ± 0.06	23.7 ± 0.3	90.2 ± 2.3	13.7
HZ-B-M3	46.7	67.9	0.39 ± 0.02	17.9 ± 0.7	44.0 ± 5.7	5.4

[a] HZ-M refers to HZSM-5 monolayer; HZ-B-D, bilayer with direct growth; HZ-B-C, bilayer with coating of TiO_2 interlayer; HZ-B-M, bilayer with modification method.

[b] $F_b = \frac{I'(0k0)/[I'(0k0)+I'(h00)] - I(0k0)/[I(0k0)+I(h00)]}{I(0k0)/[I(0k0)+I(h00)]} \times 100$, where I' is intensity of XRD peaks on a test sample, and I is that on a randomly oriented sample (Supporting Information, Figure S1).

[c] $P_e = (X' - X)/X \times 100\%$, where X′ is the *n*-dodecane conversion of a catalytic coating, and X is that from a blank tube.

[d] TOF (turn-over frequencies): mmol *n*-dodecane catalytically converted per second per g zeolite.

Table 1). A higher F_b suggests a larger amount of *b*-oriented crystals. Table 1 listed the F_b of the coatings.

For catalytic cracking of supercritical *n*-dodecane (550°C, 4 MPa), those coatings exhibit different performances in terms of performance enhancement (P_e, see notation of Table 1). P_e of HZ-B-D coating with large amounts of *a*-oriented crystals (F_b of 38.5%) is only 15.6%, which is even lower than that of the HZ-M monolayer (58.6%). In contrast, P_e of HZ-B-C2 coating with highly *b*-oriented crystals (F_b=78.4%) increases to 78.0% which is five times higher than that of the HZ-B-D coating, but with lower total amount of acidic sites due to the similar acidic properties, Si/Al ratio, and lower solid loading (Table 1). Thus, the diffusion limitation of reactants ascribed to the top layer of *a*-oriented crystals may lead to the poor catalytic activity of HZ-B-D to a certain degree, as evidenced by the fact that turn-over frequency of HM-B-D coating (1.6 mmol g^{-1} s^{-1}) is only one-tenth of that for HM-Z (16.8 mmol g^{-1} s^{-1}), and about 13% of that for HM-B-C2 (12.3 mmol g^{-1} s^{-1}). However, with further increase of F_b to 89.7% with a TiO_2 interlayer thickness of 580 nm (HZ-B-C1 coating, Supporting Information, Figure S2), P_e does not increase as expected but slightly drops to 61.9%, which may result from the increased diffusion resistance brought by the thicker TiO_2 interlayer. Meanwhile, lower average conversion (18.8%) of HZ-M coated with 508 nm TiO_2 layer might further confirm the above assumption in contrast with 19.8% conversion for HZ-M.

To further show the possible high catalytic activity for high F_b in absence of additional diffusion resistance by TiO_2 coating, bilayers *b*-oriented HZSM-5 coatings (HZ-B-M, M refers to modification) were synthesized on the TBOT-modified HZ-M.[18] After modifications, surface Si—OH on HZ-M was gradually replaced by Ti—OH groups, as evidenced by the gradually decreased Si—O peak (532.4 eV-533 eV) and increased Ti—O peak (ca. 529.9 eV).[19] in the x-ray photoelectron spectroscopy (Figure 3). After several cycles of modifications, the coverage of Ti—OH reaches 71.85%, but coverage of Si—O decreases to 12.31% (Supporting Information, Figure S4, Table S1). With the 71.85% coverage of Ti—OH groups, a highly *b*-oriented HZSM-5 bilayer (Figure 1d, HZ-B-M1) was then hydrothermally synthesized with F_b as high as 89.7% (XRD pattern in Figure 2), which is equivalent to that of HZ-B-C1. For lower

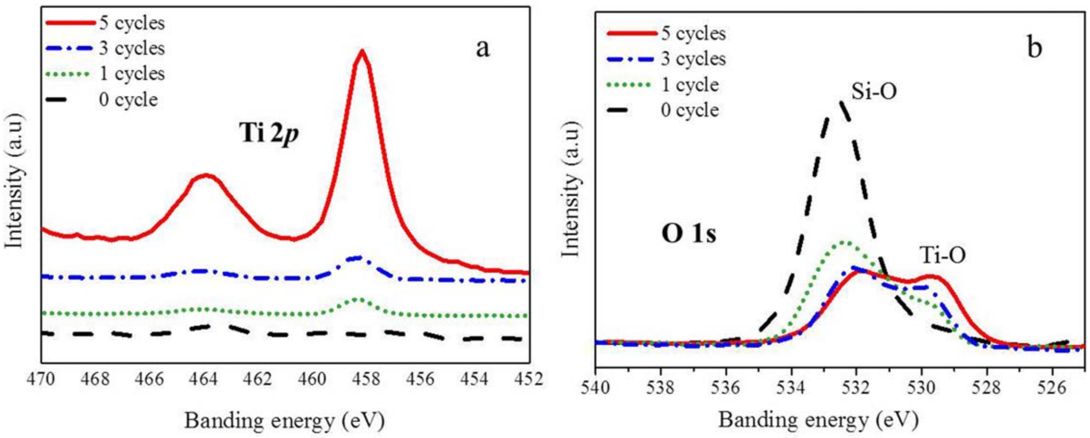

Figure 3. High-resolution XPS spectra of the (a) Ti 2p and (b) O 1s of the HZ-M modified with TOBT solution.

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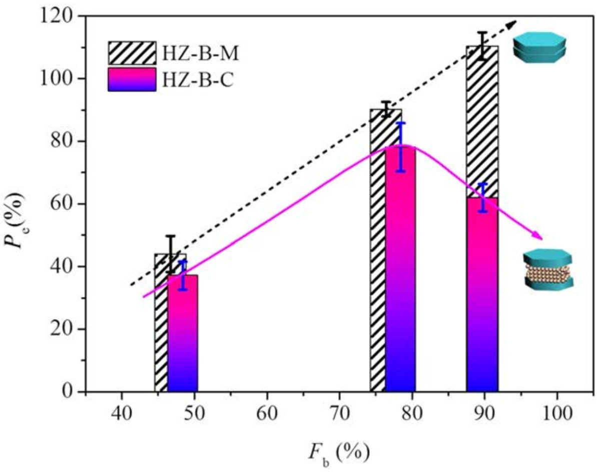

Figure 4. The plot of P_e vs. F_b for the zeolite bilayers (HZ-B-C series and HZ-B-M series).

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coverage of Ti-OH groups, such as 67.85% or 43.31% (Supporting Information, Table S1), the F_b of the corresponding coatings obviously drop to 76.4% (HZ-B-M2) and 46.7% (HZ-B-M3) (Table 1), indicating the crucial roles of Ti—OH groups in controlling orientation of secondary HZSM-5 layer. More details of the HZ-B-M2 and HZ-B-M3, including SEM characterization and XRD patterns shown in Supporting Information, Figure S3.

With high *b*-orientation and negligible thickness, HZ-B-M1 indeed exhibited the best catalytic activity (P_e =110.4%), which is about 50% higher than that of HZ-B-C1 (P_e=61.9%) with the same F_b (89.7%). Similar results were also observed for the F_b around 45–50% and 75–80% (Figure 4). Moreover, an approximate linear relationship between P_e and F_b for the HZ-B-Ms samples (see Figure 4) was also observed as expected, indicating that *b*-oriented coatings significantly overweight the *a*- or *c*-oriented coatings for the catalytic cracking of hydrocarbons by enhancing the diffusion rate of reactants in straight channels of HZSM-5 crystals. Meanwhile, differences of P_e between HZ-B-C and HZ-B-M coatings at similar F_b also increase sharply from about 7% to 48% with the increasing F_b from 45–50% to 89.7%. All those facts indicated that the diffusion resistance of TiO_2 interlayer depends on its thickness, and that the Ti—OH from TBOT modification is more favorable for performance enhancement by remarkably reducing the thickness of TiO_2 interlayer.

In summary, *b*-oriented HZSM-5 multilayer was synthesized with TiO_2-coated and TBOT-modified HZ-M to avoid the formation of *a*-oriented crystals. The catalytic performances of these coatings strongly depend on the HZSM-5 crystals orientation, the number of zeolite layers, and the thickness of the TiO_2 interlayer. HZ-B-M1 coatings exhibit excellent catalytic cracking activities attributed to the enhanced mass transfer of reactants in the *b*-axis straight channels. This work suggests a possibility to the synthesis of highly *b*-oriented zeolite multiple layers that could find great potential application as structured catalysts in the diffusion-limited catalytic processes.

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