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Highly selective conversion of methanol to propylene: design of an MFI zeolite with selective-blockage of (010) surfaces

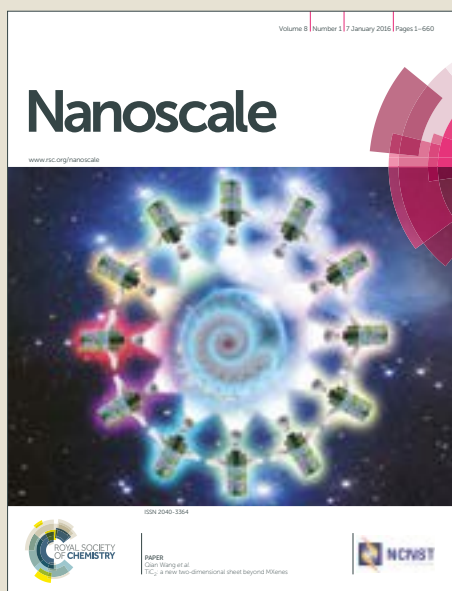
Item Type	Article
Authors	Cai, Dali; Wang, Ning; Chen, Xiao; Ma, Yunhai; Hou, Yilin; Li, Xinghua; Zhang, Chengxi; Chen, Zhaohui; Song, Wenlong; Arslan, Muhammad Tahir; Li, Yiru; Wang, Yao; Qian, Weizhong; Wei, Fei
Citation	Cai D, Wang N, Chen X, Ma Y, Hou Y, et al. (2019) Highly selective conversion of methanol to propylene: design of an MFI zeolite with selective-blockage of (010) surfaces. <i>Nanoscale</i> . Available: http://dx.doi.org/10.1039/c8nr10371b .
Eprint version	Post-print
DOI	10.1039/c8nr10371b
Publisher	Royal Society of Chemistry (RSC)
Journal	<i>Nanoscale</i>
Rights	Archived with thanks to <i>Nanoscale</i>
Download date	09/08/2022 17:39:32
Link to Item	http://hdl.handle.net/10754/631809

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Highly selective conversion of methanol to propylene: design of an MFI zeolite with selective-blockage of (010) surfaces

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DOI: 10.1039/C8NR10371B

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Abstract

As an important catalyst of methanol-to-propylene (MTP), ZSM-5 zeolite has an anisotropic diffusion path and large pore size, resulting in the formation of undesirable heavy aromatic by-products. Herein, we developed a surface-specific silica deposition method to block straight channels of nanosized ZSM-5 crystals selectively. By such coating method, we can selectively suppress the yield of aromatics from the original 13% to 2.4% at 100% conversion of methanol. Trapped hydrocarbon pool species are directly confirmed by Aberration-Corrected S/TEM for the first time. Such a method of trapping and restricting hydrocarbon pool species in multiscale zeolite with 10-membered rings would significantly benefit its catalytic efficiency and olefin diffusion. Moreover, this is providing new methodologies for zeolite structure construction and will be greatly beneficial to industrial MTP process.

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Zeolites are widely used in modern chemical processes.¹ Zeolite structures, including its pore size, topology, and connectivity, play the decisive role, especially in catalytic application.²⁻⁴ By structure modification, the selectivity of specific products can be selectively suppressed or increased.⁵⁻¹³ Methanol-to-olefin/propylene (MTO/MTP) process has attracted much attention from both industrial field and academic field, and it has been regarded as one of the central processes of methanol economy¹⁴ and modern coal chemical industry¹⁵. In China, more than 12,000,000 t per year of olefin production ability from methanol has been built up in 2017, which has become one of the largest coal-to-chemical activities ever in human history. Two types of catalysts, aluminosilicate molecular sieves, ZSM-5 (MFI topology),¹⁶ and silicoaluminophosphate molecular sieves, SAPO-34 (CHA topology),¹⁷ are used in MTO process. Although SAPO-34 has a higher selectivity to light olefins including ethylene and propylene, the large cavities in CHA structure can lead to a high coke selectivity. Coke is converted to CO₂, resulting in a low atom efficiency at last.¹⁸ In contrast, ZSM-5 zeolite has two types of 10-membered ring channels (straight channels (5.6×5.4 Å in diameters) along the b-axis and sinusoidal channels (5.5×5.1 Å in diameter) along the a-axis).¹⁹ Due to this special channel and proper size of micropores, coke with more than two aromatic rings cannot form in the pore channel of ZSM-5. Thus, the deactivation rate is much slower than SAPO-34, and the coke formation is lower than SAPO-34 by several orders of magnitude, which is quite effective given the atom economy.

As one of the 10-membered ring zeolite, however, a larger pore opening of ZSM-5 can lead to a lower selectivity for ethylene and propylene, as well as a higher selectivity of aromatic species as compared to SAPO-34. According to the mass balance, as the formation of one aromatic molecule is accompanied by the formation of three alkane molecules, a high aromatics selectivity leads to a high paraffin selectivity, resulting in a loss of olefin selectivity. Aromatics and paraffin, as by-products block the cycling attempt of C4-C8 olefins to get more ethylene and propylene. For a flow containing a high percentage of aromatics cannot be directly recycled into the reactor. From documents of Lurgi's MTP technology, the total propylene selectivity is about 66% even after olefin recycle.²⁰

Diffusion of products is critically important in MTO reaction.^{21,22} ethene and propylene show a difference in diffusion coefficient over CHA, MFI, BEA and FAU type zeolite, especially in CHA type zeolite.²³ aromatics species also show its

diffusion resistance over different channels in zeolite crystals.²⁴ The diffusion of aromatics products (benzene, toluene, and para-xylene (PX)) out of MFI zeolite is not through the sinusoidal channel, but through the straight channels.²³ So, blocking straight channels without affecting sinusoidal ones is speculated to prevent the generation of aromatics products, thereby improving the performance of the MTO reaction. Previously, much work has been done on surface modification of ZSM-5 to improve the product selectivity in relevant methanol conversion processes.²⁶ For example, in methanol-to-aromatics (MTA) reaction, by removing the surface acid sites, the isomerization reaction of xylene can be effectively suppressed.²⁷ However, a surface-selective modification can barely be achieved, facing difficulties in orientation. Recently, we found that during the MTA reaction, the (100) surfaces of spent Zn/ZSM-5 was covered with a thick coke layer, which blocked the sinusoidal channels of ZSM-5 and prevented the diffusion of paraffin and olefin out of zeolite channels, while the coke on (010) surfaces was much smaller, leading to ultrahigh aromatic selectivity (>98%).²⁸

Here, based on this interesting phenomenon, we designed a silica deposition process, which can block straight pores without affecting sinusoidal channels on ZSM-5 crystals, so the selectivity of both aromatics and paraffin were significantly suppressed.

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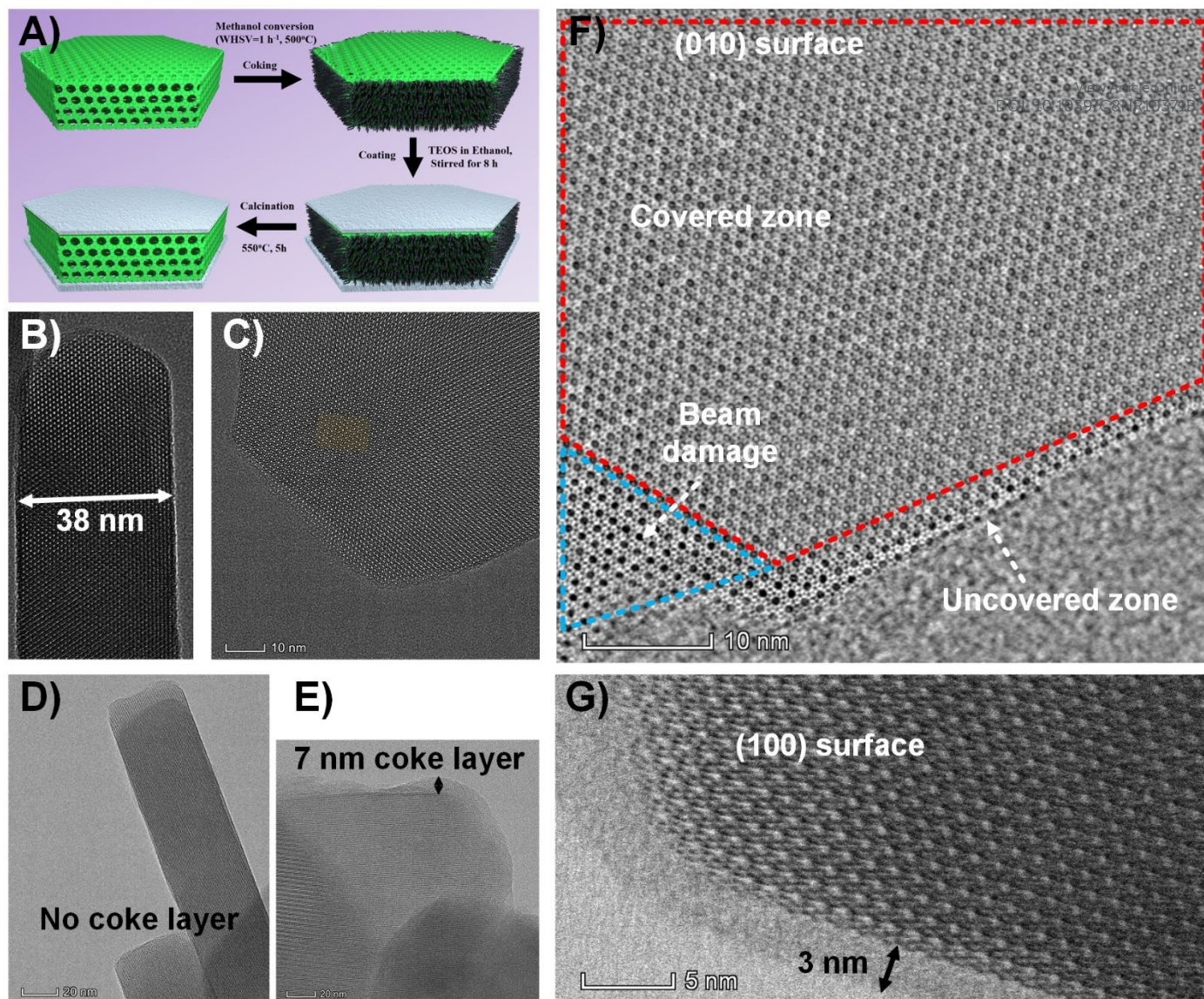


Figure 1 A) Designed scheme of the silica deposition process. Details are listed in Supporting Information. Aberration-Corrected HRTEM Images of pristine ZSM-5 (ZSM-5-P): B) (100) surface, C) (010) surface. Aberration-Corrected HRTEM images of Coked ZSM-5-P (ZSM-CP): D) (100) surface, E) (010) surface. Image of surface-selective coated ZSM-5 after reaction (coked ZSM-5-OC): F) Aberration-Corrected STEM image of (010) surface G) Aberration-Corrected HRTEM image of (100) surface.

The construction process of the surface-selective coating of silica is illustrated in Figure 1A, and the detailed procedure is described in Supporting Information. Firstly, we performed methanol-to-hydrocarbon (MTH) reaction over pristine ZSM-5 zeolites to deposit coke layers on (100) and (001) surfaces of ZSM-5 crystals. Then, by using chemical liquid deposition (CLD) method, we coated solid silica layers on clear (010) surface. Finally, the solids were separated and calcined to remove the coke and expose the (100) and (001) surfaces. In this procedure, coke performed as a protective shell, and silica preferred to deposit on the surfaces without coke.

The pristine coffin-shaped ZSM-5 zeolite with a thickness along the b-axis of ~ 50 nm (denoted as ZSM-5-P, Figure 1B and C) was synthesized based on our previous research.^{28,29} After the MTH reaction, a selectively deposited coke was formed over (100) and (001) surface of ZSM-5-P (denoted as ZSM-5-CP) (Figure 1D and E). The coke is only $\sim 0.5\%$ (wt.) but

selectively blocks the sinusoidal channels. The increasing aromatics selectivity indicates that aromatics can still diffuse out from zeolite channels. As shown in Table S1, coking process does not influence the micropore volume, while increases the external surface area. This indicates that coke only accumulates at the external surfaces of ZSM-5 crystals, which can be validated with HRTEM images. The mechanism for selective coke deposition during MTH reaction may come from the differences of surface bonding³⁰, and this is worth characterizing and discussing in the future. After surface-selective coating of silica on ZSM-5-CP and calcination, the obtained sample (denoted as ZSM-5-OC) gains a 3-nm-thick silica layer at (010) surface, which can be clearly characterized by HRTEM images (Figure 1G). In the covered zone, as outlined by the red dotted line in Figure 1F, we can observe a gray contrast as background due to the existence of the deposited silica. Almost nothing is deposited on the other surfaces. The appearance of silica can be confirmed by an additional wide peak appearing in the XRD (Figure S1). Micropore surface area decreases after silica deposition, but the major part of the surface area is maintained. And the reason comes from the amorphous silica which is occupying part of the total mass. Comparing with previous work,²⁶ we not only achieved the surface-selective silica deposition over zeolites but also achieved a much higher resolution for HRTEM imaging.

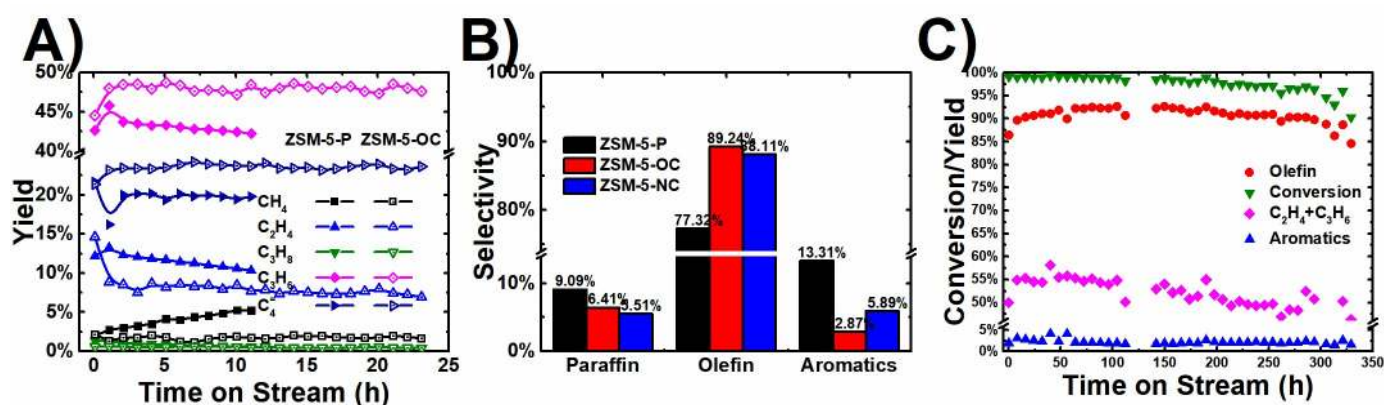


Figure 2 Comparison of catalytic performance of various ZSM-5 catalysts in the MTO reaction. A) The carbon-based yield of different species (methanol conversion keeps at 100%), B) olefins, aromatics and paraffin selectivity, (TOS=9 h) C) Lifetime test of ZSM-5-OC (WHSV=1 h⁻¹, reaction temperature: 500°C, the N₂ flow rate is 30 SCCM). Mass balance (outlet carbon/inlet carbon) was kept at about 98%.

We tested the catalytic performance of as-synthesized catalysts and found that the olefin selectivity is significantly improved (Figure 2). The propylene yield of ZSM-5-OC increased by 5%, and the ethylene yield gets a slight decrease of ~3%, compared to ZSM-5-P. With a higher propylene yield and a lower ethylene yield, the propylene-to-ethylene ratio (P/E

ratio) has reached ~ 7.4 , showing a superior performance for an MTP catalyst. Khare et al. reported a similar procedure that by suppressing aromatics diffusion they got a higher ethylene selectivity.¹² The differences from our results would come from the differences in reaction conditions. We kept the conversion at $\sim 100\%$, and the results would be different from low conversion conditions. At a low space velocity condition, more reaction paths are included, exhibiting a higher efficiency for the whole system. And product distribution is more infected by thermodynamics instead of kinetics.

As for other olefins, e.g., butene, an increment of selectivity are also observed after the surface-selective coating process. By suppressing the diffusion of aromatics, we trapped aromatic molecules in channels, resulting in a change of hydrocarbon pool percentage. More empty intersections and channels are occupied so that aromatics cannot efficiently producing ethylene, resulting in a reduction of ethylene selectivity. We also noticed a rather shorter induction period for modified catalyst than pristine. Selectivity of C4 olefins over ZSM-5-P took 2 h to reach the steady state, but for ZSM-5-OC it took only 1 h. Sun et al. reported that a co-feeding of aromatics could shorten the induction period by pre-establishing the hydrocarbon pool.³¹ Here a similar shorten induction period comes from the trapped aromatics in zeolite channels. (Figure 2A) Trapped aromatics plays the role of hydrocarbon pool species and help shorten the induction period. Before the surface-selective coating process, the total aromatics selectivity were over 13.3%, while after the surface-selective coating process, it reduced significantly to 2.4%. The selectivity of paraffin also decreased, according to both the mass balance principle and experimental results. Ethylene selectivity is also suppressed because of the limited diffusion of aromatics. As a result, olefin selectivity gains a significant increment. (Figure 2B) In order to illustrate the surface-selective pore blockage effect, ZSM-5 was treated only with the silica-coating process but without the coking process (denoted as ZSM-5-NC). The selectivity of aromatics over ZSM-5-NC can only be lowered down to about 6%, indicating invalidity of non-selective silica deposition.

In Figure 1F for the first time, we can observe the hydrocarbon pool species trapped in straight pores of ZSM-5-OC, shown as the white dots in pores in STEM image. As a 10-membered ring zeolite, straight channels of ZSM-5 has a similar diameter to aromatic rings. So all molecular confined in channels can be regarded as hydrocarbon pool species. When scanning a specific area with electron beam for a longer time, amorphous silica would be destroyed, and hydrocarbon species can be released. In the beam-damaged area labeled in Figure 1F, clear 10-membered rings without anything inside can be recognized.

Furthermore, we can notice that one or two layers of ZSM-5 channels near the edge of (010) surface cannot be covered by silica (labeled uncovered zone in Figure 1F). This may come from the electrical charge on the carbon layer which is preventing the near deposition of silica colloid. By carefully adjusting procedure of silica deposition, aromatics selectivity would be able to further suppressed.

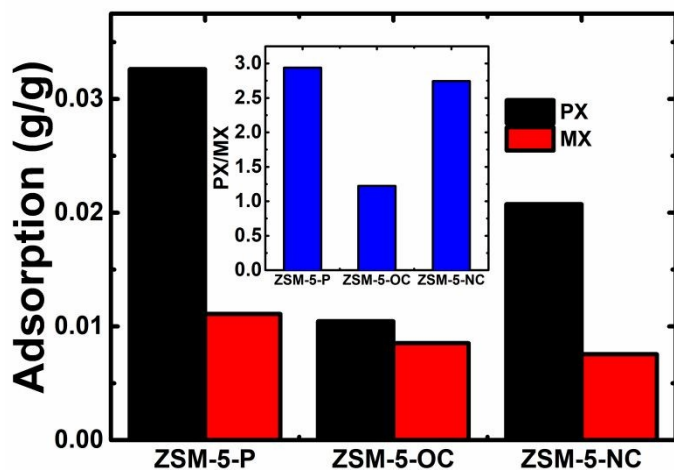


Figure 3. Adsorption results of different samples, measured with TGA. The temperature program was set to firstly evaporate free xylene and then test the weight loss for adsorption. Details are listed in Supporting Information.

In order to further verify the surface-selective pore blockage effect, we measured the adsorption amounts of PX or meta-xylene (MX) over various zeolites (Figure 3). Because of the structure difference, PX can enter the ZSM-5 crystals via straight channels,³² while MX cannot. This is the reason why the adsorption amount of PX is significantly higher than that of MX on ZSM-5-P. As both PX and MX molecule can adsorb on the external surface, the MX adsorption amount is not zero. The PX adsorption amount of ZSM-5-NC is slightly lower than ZSM-5-P, indicating that non-selective silica deposition blocked part of pore channels. The ratio of PX/MX over ZSM-5-NC keeps almost the same with ZSM-5-P, for the silica deposition is isotropic and cannot prevent PX from entering the micropore channels. Also, it cannot prevent aromatics rings from getting out the micropore channels, resulting in a high selectivity of aromatics.

However, the ZSM-5-OC sample shows a different adsorption mode to other samples. The ratio of PX/MX is close to 1. As MX molecules are adsorbed only on outer surfaces of ZSM-5 crystals, almost all the PX molecule are also adsorbed at the same sites, and no PX molecules can enter the micropore channels. With the same amount of silica deposition, a uniform distribution of silica cannot block either sinusoidal channels or straight ones, as shown in ZSM-5-NC, while directional deposition on (010) surfaces can block it completely (ZSM-5-OC). As almost no aromatic species can diffuse out of the

crystals, the aromatics selectivity shows a significantly decreasing trend.

Furthermore, ZSM-5-OC catalyst exhibited a good lifetime (Figure 2C). The ZSM-5-OC catalyst shows a lifetime of over 300 h, which is similar to some other reported results.³³ During the catalytic stability test, the aromatics selectivity can be maintained at around 3%. Under this situation, undesired products can be directly recycled and reconverted over the catalyst to get a higher ethylene and propylene selectivity. The coke over spent ZSM-5-OC tend to accumulate in micropores after the reaction, results in the obvious decrease of micropore volume (Table S1).

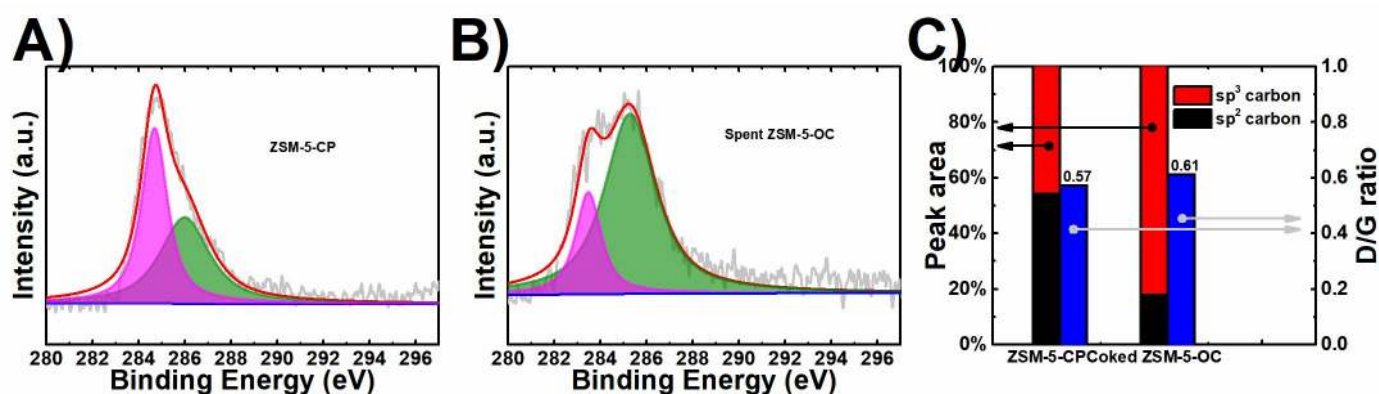


Figure 4. XPS spectra of C1 for the spent zeolite. A) ZSM-5-CP, B) ZSM-5-OC. C) Comparison of XPS peak area as well as the I_D/I_G ratio of Raman spectrum. (A commercially built XPS system (Thermo Fisher ESCALAB 250Xi) was used)

Concerned with lifetime issue, we investigated the difference between the coke on spent ZSM-5-P and spent ZSM-5-OC and found that a significantly different coking mode, as indicated in XPS results (Figure 4). On ZSM-5-P, sp^2 carbon tends to form at (100) and (001) surfaces (Figure 1D and E), while on modified zeolite, more sp^3 carbon has generated (Figure 4B). Following some previous report about graphene and other carbon-based materials, sp^3 carbon usually indicates amorphicity, which cannot prevent the diffusion of reactant and product molecules.^{34,35} According to previous work by Diaz et al.,³⁰ (010) surface on MFI zeolite tend to have a different chemical environment to (100) and (001) surface. Structural defect tends to form at (100) and (001) surface in a coffin-shape MFI zeolite crystal, while (010) surface keeps flat and perfect. In the case of ZSM-5-P, aromatic molecules diffuse out through straight channels during the MTO process, and, as coke precursors, can stuck on (100) and (001) surface for their structural imperfection and defect, but cannot stuck on (010) surface for its perfection, which can be confirmed by HRTEM in Figure 1B and C. In contrast, as the aromatic selectivity is seriously suppressed over ZSM-5-OC, the coke generated on (100) and (001) surface are mainly from olefins. According to the previous study,^{25,36,37} the carbon species formed by rapid polymerization of aromatics, such as toluene and PX, have significantly higher

graphitization degree (sp^2/sp^3 ratios) compared to that using ethylene or propylene as the precursor under the same experimental conditions.

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We can have a simple math calculation. With a simplification that we get 55% selectivity for $C_2H_4 + C_3H_6$ (E+P), 10% for paraffin + aromatics, 35% for other olefins, when we fully recycle the other olefins (mainly butene and pentene), we can expect a total E+P selectivity to $55\% / (55\%+10\%) = 84.6\%$. This has reached the level of industrial units with SAPO-34 as the catalyst. We tested the pentene conversion over ZSM-5-OC, and the conversion keeps at 47%. Similar product distribution is noticed. (Figure S2) A lower aromatics selectivity (1.1%) is obtained, and this indicates a possibility for recycling higher olefins into the reactor to get more E+P. Comparing with commercial SAPO-34 catalyst, we have a 200 times longer lifetime and a 30 times lower coke selectivity (Table S2). This will become more competitive than commercial MTO process nowadays and greatly benefit the profitability and atomic efficiency of industrial units.

In summary, for the first time, we propose a surface-selective silica deposition method over ZSM-5 zeolite. By blocking the straight channels without affecting sinusoidal channels, a significant increment of olefin selectivity is observed, and the selectivity of both aromatics and paraffin is controlled. Moreover, for the first time, we can observe the hydrocarbon species with ACTEM/STEM directly. This will benefit the industrial MTP process and give a new methodology for zeolite structure control. In the future, new host-guest interaction will be discovered and applied to modify specific pores on zeolite crystals, and this will contribute to both zeolite structure research and industrial applications.

Acknowledgments

This research is funded by the National Natural Science Foundation of China (91434122), National Key R&D Program of China (2017YFB0602204 and 2018YFB0604803). All the calculations are supported by Tsinghua National Laboratory for Information Science and Technology (National Research Center of Information Science and Technology, Beijing). We thank Prof. Yu Han at KAUST for his advice.

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