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Synthesis of phosphorus-containing HZSM-5 zeolite particles: Control of phosphorus incorporation through a hydrophobic external-surface Shell[☆]

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ABSTRACT

Selective blocking of external surface HZSM-5 zeolite (Si/Al of 11.5) silanol sites followed by impregnating the zeolite with phosphate leads to changes in the zeolite acidity and catalytic performance for *n*-butane cracking. A monolayer of organosilane capping the zeolite external surface by chemisorption of 3-cyanopropyltrimethylchlorosilane formed a hydrophobic shell consisting of 0.36 cyano groups/nm². Partial hydrolysis of the shell by wetting of the zeolite by water allowed tuning of the transport/chemical reaction tradeoff during aqueous impregnation of the zeolite with phosphate, facilitating efficient distribution of the phosphorus in the internal pore space. The procedure led to a higher degree of framework aluminum retention and a higher total Brønsted acid-site density than was observed with phosphorus-modified HZSM-5 prepared by conventional aqueous wet impregnation. Correspondingly, the phosphorus-modified catalyst had a higher activity for *n*-butane cracking than the phosphorus-modified catalyst prepared conventionally.

1. Introduction

Chemical engineers have long been motivated to understand the methods of preparation of supported catalysts and to improve them by control of the reaction and transport processes by which metals and other components are introduced into porous supports. Several excellent books provide summaries of the preparation methods [1–3]. The various preparation methods typically involve contacting aqueous solutions of the salt of a metal or of an additive with porous support particles in a slurry; the common supports are metal oxides and zeolites. Control of the metal or additive uptake is influenced by the contacting methods, which range from equilibration of the salt solution with the support particles (leaving some salt in the external solution) (called wet impregnation) to techniques such as incipient wetness impregnation (called dry impregnation)—whereby just enough solution is provided to fill the pores, incorporating essentially all of the precursor in the support

and consuming all of the added solution. Some preparations involve contacting the support with liquid-filled pores, on the one hand, or with air-filled (or even empty (evacuated)) pores on the other, with correspondingly different resistances to flow and transport of the precursor solution into the interior of the support and various tradeoffs between transport and reaction of the precursors with the support surface. Components are sometimes added to the solution with the salt (e.g., citrate) to affect the metal-support or additive-support surface chemistry, providing other variables for control of the deposition. Optimizing the preparation conditions may lead to optimized locations of the species in the supports, giving, for example, egg-yolk catalysts or egg-shell catalysts [1].

The egg-shell catalysts are the best-known examples of core-shell catalysts, and an extensive literature of such catalysts has emerged recently, providing many opportunities for adjusting the reaction/transport tradeoffs in catalyst operation [4–6]. Now we report how to

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use a hydrophobic shell surrounding zeolite particles to control the transport of a phosphorus-containing precursor into the particles, elucidating how to control the resulting catalytic species. The results presented below show how the shell was synthesized, and then modified, to control the wetting of the particles in an aqueous impregnating solution and thereby control the transport of the phosphorus-containing precursor into the zeolite particles.

Post-synthetic phosphorus modification of the zeolite HZSM-5 is widely used to improve the properties of this catalyst for hydrocarbon cracking to enhance light-olefin selectivity [7,8]. The phosphorus modifiers influence the densities of strong-acid sites [9–16] and afford increased hydrothermal/steaming stability [12,17–20], which improves the catalyst performance [12,21,22], for example, increasing the propene or propene plus ethene selectivity in cracking of *n*-butane (*n*-C₄) [23–27] and naphtha (C₅–C₁₂ *n*-alkanes) [28].

Although the overall physical and chemical effects on the zeolite structure and composition are similar for various phosphorus-containing precursors and incorporation methods [29], the method of introducing phosphorus affects the distribution of phosphorus in the zeolite particles: conventional wet impregnation has been observed to lead to a higher proportion of phosphorus localized on the zeolite outer surface than in the bulk [9,15,30–33], whereas it has been claimed that treating a zeolite with an aqueous phosphate precursor under hydrothermal conditions involving high temperature and pressure results in more phosphorus within the pores [25,34]. Precursors such as ammonium dihydrogen phosphate (NH₄H₂PO₄), tetrabutyl phosphonium chloride (TBPCl; serving as an organic structure-directing agent (OSDA)), and phosphoric acid (H₃PO₄), have all been applied for modification of the zeolite HZSM-5 [16,35,36]. The presence of phosphorus inside the HZSM-5 zeolite micropores rather than on the external zeolite surface was demonstrated in a recent contribution in which tetrapropylphosphonium hydroxide served as the OSDA [37]. This catalyst, P@HZSM-5, had triple the lifetime and higher propene selectivity than a conventional P/HZSM-5 catalyst prepared by conventional wet impregnation; this comparison illustrates a significant potential benefit of controlling the phosphorus placement within the zeolite micropores.

In the work reported here, we modified the external surface chemistry of HZSM-5 (which was obtained by calcining ammonium-type ZSM-5 zeolite at 550 °C for 5 h prior to any capping and/or phosphate modification) via shell capping to control the transport/reaction trade-offs in the incorporation of phosphate species by wet impregnation. Our rationale was that formation of a shell capping the external zeolite surface silanol sites with 3-cyanopropyldimethylchlorosilane (in the presence of an excess of non-coordinating base 2,6-di-*tert*-butylpyridine to neutralize the hydrochloric acid released in the synthesis) could block the surface, preventing condensation with phosphate groups there and decreasing the rate of phosphate penetration into the zeolite pores. We hypothesized that this blocking could be accomplished (i) by preventing Si – O – P bonds from forming on the external surface because the capping group was already there and (ii) by preventing Al – O – P bonds from forming on the external surface by virtue of steric hindrance associated with the capping groups on nearby silanols. The goal was thus to form, after calcination, a material with phosphate modification excluded from the exterior surface and present only within the interior pores where it would be most beneficial (Scheme S1, Supporting Information).

We thus capped zeolite external-surface silanol groups prior to phosphate aqueous impregnation. A 3-cyanopropyl-functionalized capping group was chosen because it has both polar and aprotic character and lacks OH groups that could condense with the phosphorus-containing precursor in the later impregnation step [38]—and at the same time its local cyano-group polarity [38] could potentially facilitate wetting of the zeolite by water, as needed for aqueous wet impregnation. We avoided capping the HZSM-5 with groups that could become protonated at the pH of the solution used in phosphate modification, such as amino-functionalized capping groups, because such protonated groups

would electrostatically anchor phosphate to the external surface, leading to undesired phosphate condensation there. However, our 3-cyanopropyl-functionalized capped material became hydrophobic and was not wetted by aqueous solutions containing phosphate, so that transport of phosphate into the interior of these capped particles became blocked. Therefore, we proceeded by partially decapping the surface before phosphorus wetness impregnation, seeking conditions to facilitate the transport of phosphate into the pores while blocking its condensation on the external surface.

An essential result of this work is evidence that capping of the external HZSM-5 surface does not prevent phosphorus condensation on the external surface. Moreover, our data demonstrate a benefit of the capping group in synthesizing a catalyst that has an increased proportion of aluminum sites preserved within the zeolite framework, leading to higher catalytic activity than that characterizing the unmodified zeolite—and we were led by the results to investigate samples in which the zeolite capping was partially removed, thus allowing a comparison of two separate classes of phosphorus-modified catalysts, each of them modified by wet impregnation to afford a phosphorus content of 1.0 wt % (a value chosen because it has been reported to provide the highest propene selectivity in *n*-butane cracking on HZSM-5 with a Si/Al ratio of 12.5) [23,29].

To characterize the catalysts (and the phosphorus-containing species in them) we used powder X-ray diffraction (PXRD), N₂ physisorption, ²⁷Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy, ³¹P MAS NMR spectroscopy, ³¹P cross-polarization (CP) MAS NMR spectroscopy, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, and pyridine-probe thermogravimetric analysis (Py-TGA). All the data determined with these methods provide evidence of the role of surface capping on the properties of the catalysts, which were also characterized by their performance in *n*-butane cracking. The results show that the wetting properties of the surfactant-coated material are essential, with a partially decapped support giving a catalyst that is effectively wetted and allows incorporation of phosphorus within the zeolite particles, which exhibit a higher total Brønsted acid site (BAS) density and a higher *n*-butane cracking activity than the conventionally made impregnated catalyst in the absence of a capping layer.

2. Results and discussion

Our approach to controlling the tradeoff between transport and reaction in phosphate modification of HZSM-5 with an organic capping layer initially led us to investigate fully capped HZSM-5 particles (details in the Supporting Information), and a central result is that these particles were not wetted with an aqueous precursor solution containing phosphorus, so that transport of phosphate into the interior of these capped particles was prevented; rather, the particles floated to the top of the water meniscus during attempts at aqueous impregnation (Fig. S1, Supporting Information). The lack of water wettability remained even after extensive methanol washing of the capped zeolite and after vacuum drying at 150 °C at a pressure < 20 mTorr (Fig. S2, Supporting Information), which removed residual toluene solvent that could otherwise have influenced the hydrophobicity. We conclude that the hydrophobicity of the capping layer prevented water wettability and phosphate transport into the HZSM-5 zeolite—and that a modification of the preparation method was needed.

We thus further modified the shell capping the HZSM-5 particles with the goal of facilitating the transport of phosphate into the pores—by hydrolyzing a small fraction of the condensed capping groups on the external surface, as shown in Fig. 1. This partial decapping was accomplished simply by stirring the zeolite in a slurry in an excess of water at room temperature—nitrogen elemental analysis data demonstrate a loss of 18 ± 7 wt% of the capping groups (Table S1, Supporting Information), leading to the same fraction of silanol groups being available and accessible for water wettability. The treatment succeeded

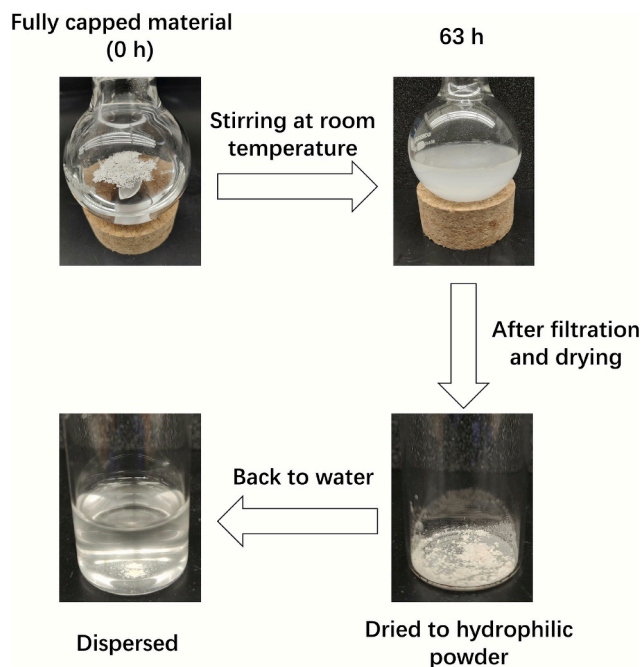


Fig. 1. Evolution of wetness properties of the fully capped material after stirring for 63 h in water at room temperature.

in producing a material that (after evacuation and drying) was fully dispersible in water. In view of the hydrothermal stability of HZSM-5 during routine procedures such as aqueous ion exchange [39–41], we do not anticipate that the mild room-temperature aqueous treatment during decapping would alter the catalyst in any substantial way. Similarly, we do not anticipate any substantial effect on the HZSM-5 catalyst resulting from capping in organic (toluene) solution, in the presence of a sterically bulky base (which is too large to enter the micropores).

Using this partially decapped material, we synthesized phosphorus-modified material (1.0 wt% phosphorus) by wet impregnation, resulting in a catalyst, after calcination, called the partially decapped catalyst. For comparison, the parent HZSM-5 was tested as a control (resulting in a catalyst, after calcination, called the conventional impregnated catalyst), as shown in Fig. 2a and b (Scheme S2, Supporting Information).

To have a sense of the representative timescales for transport and phosphate modification by reaction with our HZSM-5, we followed the reaction of this zeolite with ammonium phosphate dibasic solution at various contact times by using a conductance probe in the solution to determine the uptake of the precursor. The data demonstrate that 15 min of mixing was sufficient to achieve solution/solid equilibrium (Table X1, Supporting Information). Next, we compared the amount of phosphate condensation that occurred on HZSM-5 with that on amorphous silica. Considering that silanol groups in HZSM-5 are present only on the external surface, our data demonstrate that the large majority (~95%) of phosphate condensation occurring during the wet impregnation involved aluminum sites in the bulk zeolite rather than on surface silanols under our conditions (Table X2, Supporting Information). The data lead to the estimate that, during the 15-min contact time, more than 99% of the phosphate added to the impregnation solution reacted with aluminum sites on the zeolite (calculations in Supporting Information).

PXRD patterns of the wet-impregnated catalysts (Fig. 2c) exhibit essentially no difference from those of the parent HZSM-5 zeolite, consistent with the expected retention of zeolite crystallinity after phosphate incorporation [42]. N_2 physisorption data recorded at 77 K demonstrate lower N_2 uptakes for each catalyst after phosphorus modification than for the unmodified parent HZSM-5 (Fig. S3 and Table S2, Supporting Information), consistent with trends reported for

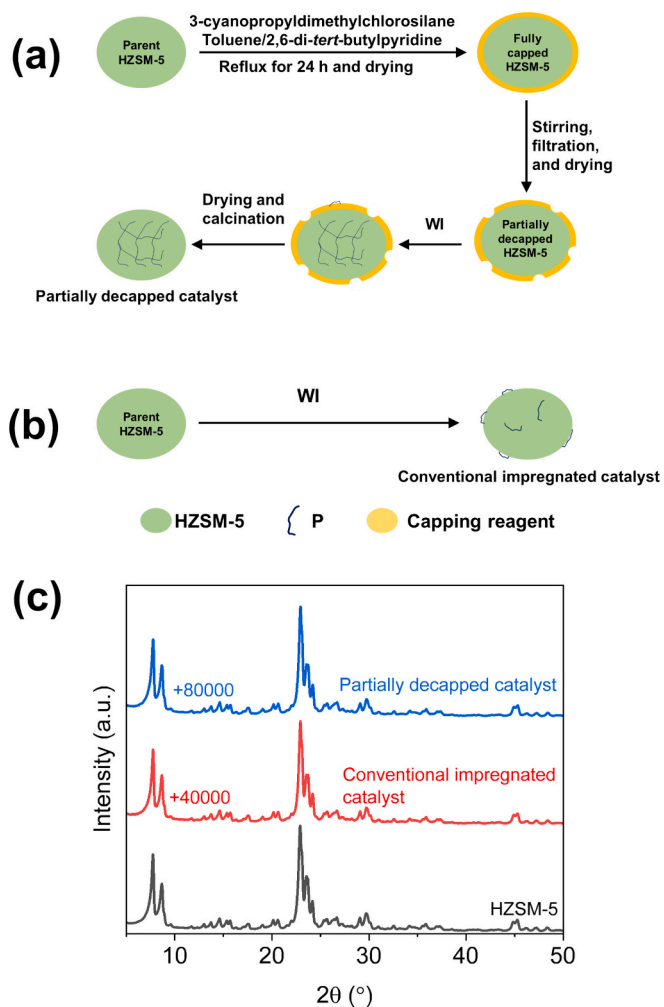


Fig. 2. (a) Scheme representing phosphorus wet impregnation (WI) by converting the fully capped material to partially decapped material; (b) representation of conventional phosphorus WI using parent HZSM-5; (c) PXRD patterns of 1.0 wt% phosphorus-modified catalysts and the parent HZSM-5. Stacked PXRD patterns are offset for visual clarity. The magnitude of the offset of PXRD patterns is indicated on the left just above the pattern (no offset is shown for HZSM-5).

other phosphorus-modified HZSM-5 catalysts [13,19,42–44]. A decrease in micropore volume was observed as a result of the phosphate impregnation, but it does not reflect the amount of intrapore phosphate in our catalysts, because there was micropore blockage that affected the N_2 uptake.

Scanning electron microscopy (SEM) images shown in Fig. 3 (also see Figs. S4 and S5, Supporting Information) demonstrate that phosphorus modification of both the partially decapped and parent HZSM-5 supports led to no observable change in the zeolite particle morphology or crystallite size distribution. These data thus confirm that the onset of water wettability observed with the partially decapped catalyst was not the result of breakage of zeolite crystallites (which would otherwise exhibit a smaller crystallite size and expose hydrophilic silanol-rich native uncapped surfaces); rather, it was the result of hydrolysis of a critical fraction of the chemisorbed capping groups on the external surface.

We tested for the presence of phosphorus species on the external surfaces of the catalysts before and after calcination, following wet impregnation, by using XPS (the energy scales of the collected data were corrected using the O 1 s signal for each sample individually). Data in Fig. 4a and b show P_{2p} peaks at approximately 133 eV, which are consistent with reported assignments characterizing phosphorus species

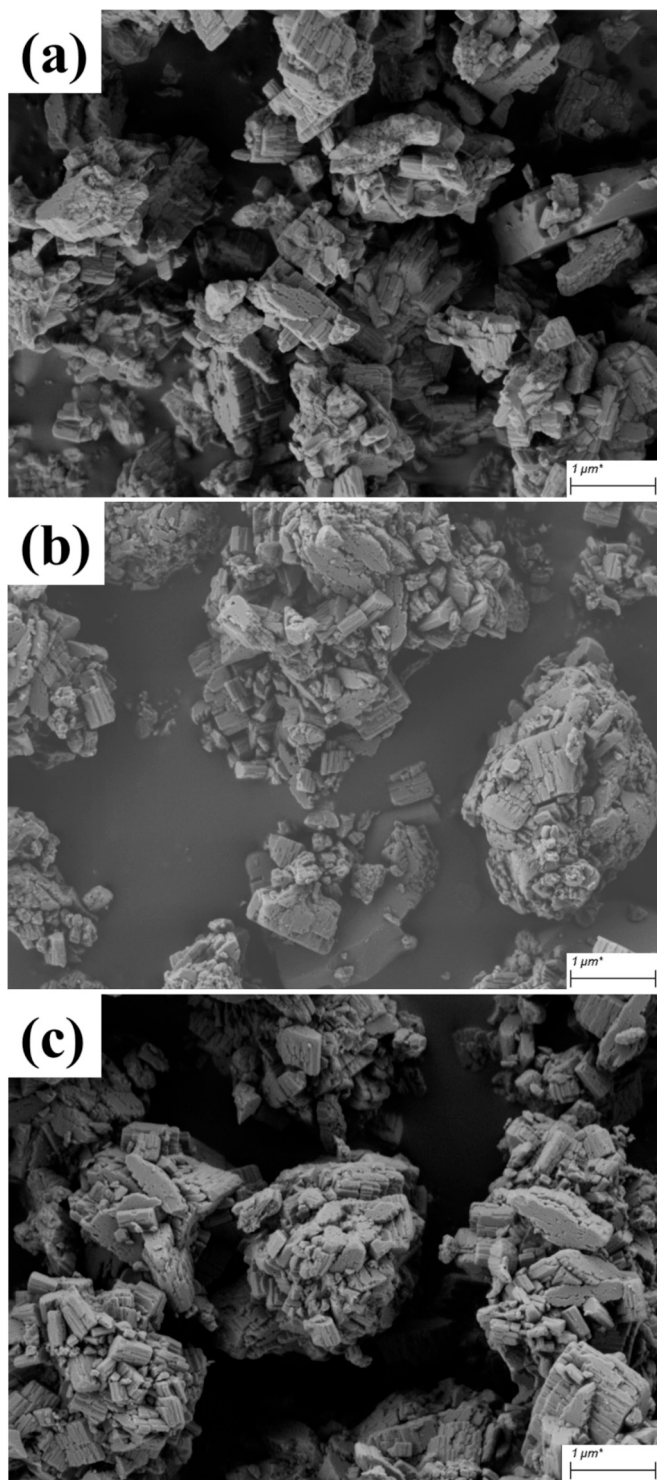


Fig. 3. SEM images of the catalysts at the length scale of 1 μm : (a) HZSM-5; (b) partially decapped catalyst; (c) conventional impregnated catalyst.

on the external surface of HZSM-5 catalysts [15,37,45]. However, the corresponding XPS data representing the partially decapped catalysts (Fig. 4a, before calcination and Fig. 4b, after calcination) also show the presence of a $\text{P}_{2\text{p}}$ peak. Our XPS experiment was similar (in terms of experimental conditions and X-ray source, which controls the penetration depth) to a previously reported experiment for an HZSM-5 catalyst in which phosphorous placement was strictly inside the zeolite particles (accomplished with organophosphonium OSDA) [37]. In view of the results of this latter experiment, not showing any phosphorous signal

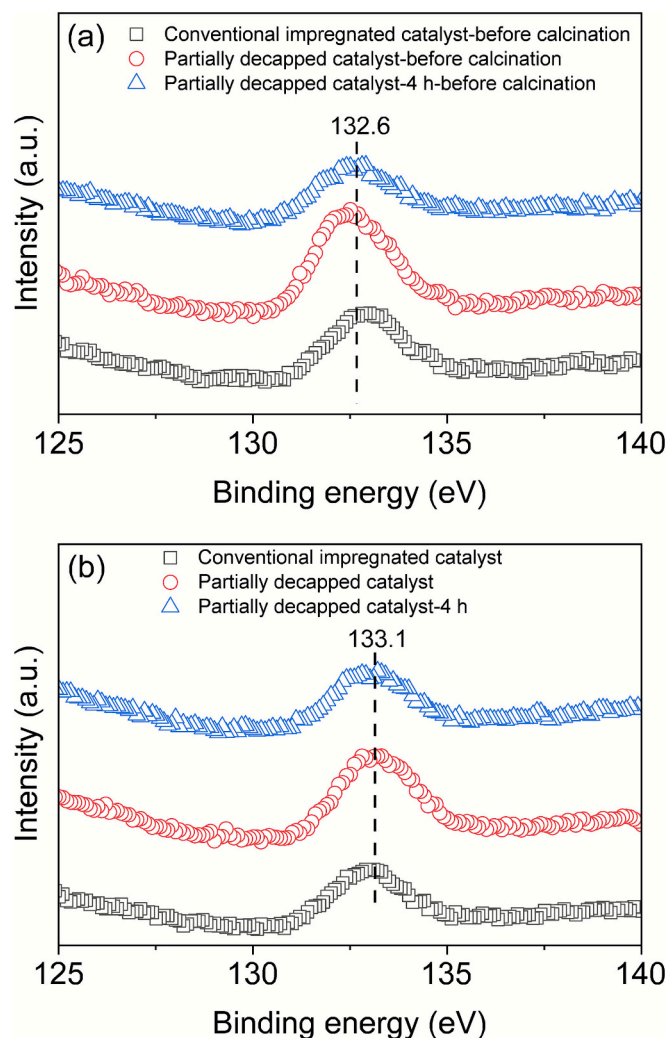


Fig. 4. $\text{P}_{2\text{p}}$ XPS data characterizing phosphorus-modified catalysts (a) before and (b) after calcination (calcination conditions: 550 $^{\circ}\text{C}$ for 5 h in dry air at ambient pressure).

[37], and the result that our samples are all characterized by similar oxygen-normalized phosphorous XPS intensities (Table S3, Supporting Information), we conclude that phosphorous in our samples must have been localized on the external surface. We thus conclude that phosphate reacted with external surface sites during the wet impregnation, even for the catalyst containing the capping organosilane functional groups. Because there is no evidence of phosphate scrambling between the interior and external surfaces during calcination [37], we conclude that the hydrophobic capping groups in our partially decapped catalyst did not prevent external surface sites from reacting with phosphate species during wet impregnation.

In an effort to further increase the capping coverage, we synthesized an additional variant of the partially decapped catalyst, by following a procedure similar to the one illustrated in Fig. 2a—but this time involving stirring in water for only 4 h for decapping (instead of 63 h as in the preparation of the original partially decapped catalyst). As shown in Fig. 5, although 4 h of stirring at room temperature allowed dispersal of the material in water (indicating a partial decapping), this material was not wetted in water after drying. We conclude that, in contrast to 63 h of decapping in water, 4 h of decapping in water hydrolyzed a significantly smaller fraction of the capping groups in the initially fully capped material. The partially decapped catalyst after 4 h was then used to synthesize samples by phosphate wet impregnation (by the procedure represented in Fig. 2a), followed by drying and calcination, as before.

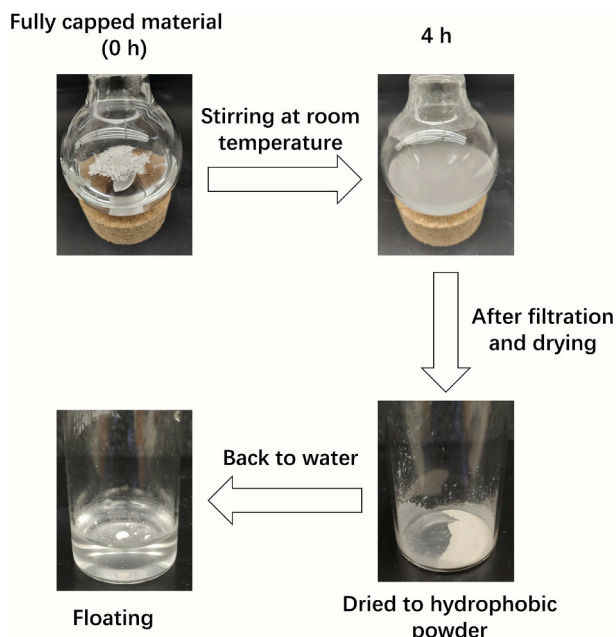


Fig. 5. The evolution of wetness properties of the fully capped material after stirring for 4 h in water at room temperature.

However, this partially decapped sample (treated for only 4 h) still incorporated phosphate species on the external surface, both before and after calcination, as shown by the XPS data in Fig. 4. To summarize, we conclude that a capping followed by a partial decapping procedure (either for 63 h or 4 h) does not prevent phosphorus condensation on the external surface of the zeolite.

With the understanding that phosphorus was present on the external surface in both our partially decapped catalyst as well as the conventional HZSM-5 used as a control, our attention turned to elucidating the effect of the capping group on the chemical environment of phosphorus in the impregnated catalyst. Our hypothesis was that the capping group would influence the competition between transport and reaction of phosphate in the zeolite during impregnation, thereby allowing control of its environment in the partially decapped catalyst (expected to be different from that in the control catalyst, HZSM-5 modified with phosphate in the absence of a capping layer).

We thus characterized the partially decapped and conventional impregnated catalysts with solid-state NMR spectroscopy. We first investigated the reproducibility of our data by repeating the synthesis and spectroscopic investigation of the conventionally impregnated catalyst. The two ^{31}P MAS NMR spectra representing two different synthesis batches show essentially no differences, within the expected error, confirming the reproducibility of both the NMR analysis approach as well as our wet impregnation synthesis approach (Fig. S6, Supporting Information).

As shown in Fig. 6a, the ^{31}P MAS NMR spectra of both phosphorus-modified catalysts exhibit resonances at -8.1 , -16.1 , -25.1 , -33.0 , and -38.7 ppm. In comparison with the conventional impregnated catalyst, the partially decapped catalyst exhibits more intense resonances at -8.1 and -25.1 ppm, characterizing phosphate groups (Fig. 6a). ^{31}P CPMAS NMR spectra (Fig. 6b) also show higher intensity of resonances at -7.5 and -15.3 ppm in the partially decapped catalyst compared with the conventional impregnated catalyst. A recent solid-state NMR spectroscopic investigation [46] of phosphorus-modified ZSM-5 zeolite catalysts ascribes the resonance at -25.6 ppm to framework-bound $\text{Si}-\text{OH}-\text{Al}-\text{O}-\text{P}$ groups, which are adjacent to crystalline AlPO_4 clusters (represented by a ^{31}P MAS NMR resonance at -33.0 ppm). The framework-bound nature of this site suggests the preservation of framework aluminum sites, which are representative of

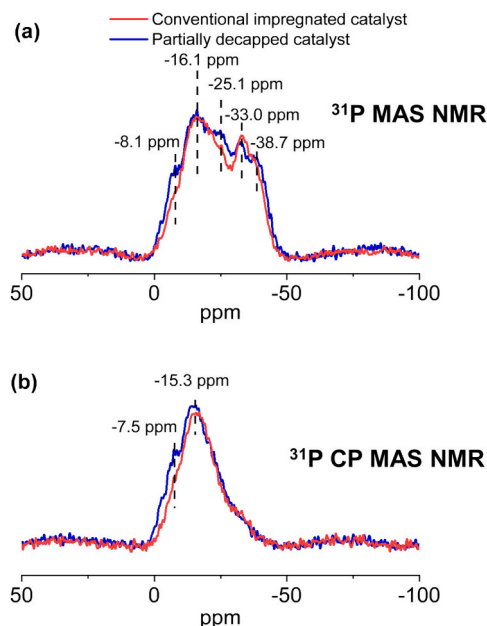


Fig. 6. (a) ^{31}P MAS NMR spectra, (b) ^{31}P CPMAS NMR of phosphorus-modified catalysts: conventional impregnated (red) and partially decapped catalyst (blue).

Brønsted acid sites [46]. We conclude that the higher intensity of the resonance of -25.1 ppm in the spectrum of the partially decapped catalyst, compared with that of the conventional impregnated catalyst, indicates a greater retention of framework aluminum in the former, which, as a result, is expected to result in a higher Brønsted acid-site density in the partially decapped catalyst. This greater retention of framework aluminum is confirmed by solid-state ^{27}Al MAS NMR spectra (Fig. S7, Supporting Information), which exhibit resonances previously described for phosphorous-modified HZSM-5 catalysts [12,21,24,31,32,42].

The different phosphate speciation outcomes among the calcined catalysts have consequences for the acidity and therefore the catalytic activity for cracking, as demonstrated below.

To investigate the acidic properties of the phosphorus-modified catalysts and the parent HZSM-5, we recorded IR spectra of the three catalysts (partially decapped, conventionally impregnated, and unmodified parent HZSM-5), using pyridine as a probe molecule. A summary of total Brønsted to Lewis acid site ratios measured by the respective band areas characterizing adsorbed pyridine is shown in Table 1 (bands at 1543 and 1454 cm^{-1} correspond to Brønsted and Lewis acid sites, respectively [47,48]). At a desorption temperature of 150°C , the partially decapped catalyst is characterized by a Brønsted to Lewis acid site (B/L) ratio of 2.99, which is approximately 17% higher than that observed for the conventional impregnated catalyst (B/L ratio of

Table 1

B/L ratio (ratio of Brønsted to Lewis acid sites) measured by the integrated peak areas of the respective band areas determined by IR spectroscopy at the pyridine desorption temperature of 150°C , and the total pyridine acid-site count determined by pyridine thermal desorption data.

Sample	B/L ratio measured by the respective band areas	Total pyridine acid-site count determined by pyridine thermal desorption analysis ($\mu\text{mol g}^{-1}$)
HZSM-5	3.47	966
Conventional impregnated catalyst	2.56	635
Partially decapped catalyst	2.99	680

2.56), and both catalysts exhibit at least 16% lower B/L ratios than the parent HZSM-5 zeolite (Fig. S8, Supporting Information). The total acid-site counts characterizing these catalysts determined by pyridine thermal desorption analysis are shown in Table 1 (also see Fig. S9, Supporting Information). The highest total acid-site count was observed for the parent HZSM-5 zeolite, but we also observed 1.06-fold more total acid sites per unit of zeolite mass in the partially decapped catalyst than in the conventional impregnated catalyst. Thus, taken together, the pyridine adsorption data demonstrate a slightly higher total Brønsted acid-site density of the phosphorus-modified, partially decapped catalyst than of the phosphorus-modified HZSM-5 catalyst used as a control.

We expected that the higher Brønsted acid-site density characterizing the catalyst synthesized by partial decapping compared with the phosphorus-modified HZSM-5 control would lead to greater alkane cracking activity in the former, because Brønsted acid sites are known to be the active sites for this reaction [14,49–52]. We therefore compared the calcined catalysts after phosphorus modification, as well as the parent HZSM-5, for *n*-butane cracking as a simple probe reaction, using a once-through flow reactor operated at 550 °C and 1 atm. Initial activities extrapolated to zero time on stream were calculated from data recorded at conversions below 11% and are shown in Fig. 7 for all three catalysts (Fig. S10, Supporting Information). There was no difference in selectivity among the catalysts (Fig. S11, Supporting Information), but the data demonstrate a 1.14-fold (± 0.04) increase in the initial activity of the partially decapped catalyst compared with the conventional wet-impregnated HZSM-5 control catalyst. We attribute this activity increase in the partially decapped catalyst to the altered phosphate speciation in the latter, reflecting its higher density of framework-aluminum Brønsted acid sites compared with that of the conventional wet-impregnated HZSM-5 control catalyst.

However, our catalytic data also reflect 1.5 times higher initial activities of both phosphorus-modified catalysts in our *n*-butane cracking reaction than of the parent HZSM-5 zeolite, notwithstanding the higher BAS density of the parent HZSM-5 zeolite (Table 1). To support our observation, we refer to reports of phosphorus modification without steaming leading to more active alkane cracking catalysts, for HZSM-5 zeolites having high aluminum contents (Si/Al ratios of 15 and less) [23,28]. Our parent HZSM-5 zeolite Si/Al ratio of 11.5 falls into this category, whereby there is a catalytic benefit of phosphorus incorporation even without steaming for alkane cracking. We do not have an explanation for why the parent HZSM-5 is less active in our case than the phosphate-modified HZSM-5 catalysts, but, taken together, the data show that the higher BAS density in our partially decapped catalyst is responsible for its higher *n*-butane cracking initial activity than that of the conventional impregnated catalyst.

3. Conclusions

We report a synthetic strategy involving incorporation of a hydrophobic shell (capping layer) on the external surface of HZSM-5 particles for controlling the tradeoff between transport and reaction when introducing phosphate species by wet impregnation into the pores of this zeolite. The procedure, with modification to remove part of the capping layer, leads to a higher degree of framework aluminum retention and a higher total Brønsted acid-site density than observed with phosphorus-modified HZSM-5 prepared by conventional aqueous wet impregnation. The phosphorus-modified partially decapped catalyst reported here was found to have a higher initial activity for *n*-butane cracking than the phosphorus-modified, conventionally impregnated HZSM-5 catalyst, demonstrating a catalytic benefit of this synthetic approach.

Personal acknowledgment

We are pleased to contribute to this special issue in honor of Professor Harold Kung. Some of us authors have had fruitful discussions and interactions with Professor Kung over many years, having benefited

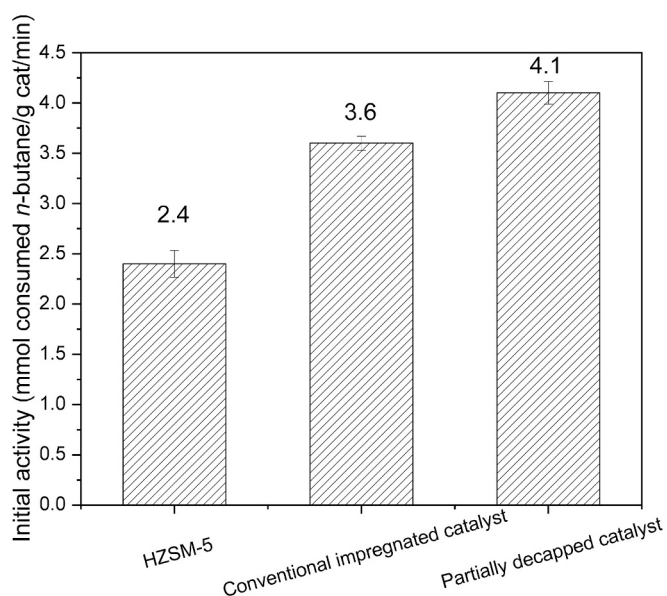


Fig. 7. (a) Initial activity (extrapolated to zero time on stream) comparison among the parent HZSM-5 and phosphorus-modified catalysts (P loading of 1.0 wt% in phosphorus-modified catalysts). Reaction conditions: once-through flow reactor operated at 550 °C; *n*-butane flow rate of 10 mL(NTP)/min, with 40 mL (NTP)/min N₂ at ambient pressure.

from his many insightful contributions, his keen insights, and his kind collaboration and strong leadership in the catalysis community.

CRedit authorship contribution statement

Xuemin Li: Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Kaan Yalcin:** Investigation, Data curation. **Abraham Martinez:** Investigation, Data curation. **Kanan Shikhaliyev:** Investigation, Data curation. **Oleksandr Trybrat:** Investigation, Data curation. **Finn Babbe:** Investigation, Data curation. **Heng Dai:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Ke Zhang:** Writing – review & editing, Supervision, Methodology, Conceptualization. **John Yang:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Xuezhen Wang:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Son-Jong Hwang:** Investigation, Data curation. **Coleman X. Kronawitter:** Supervision, Funding acquisition. **Ron C. Runnebaum:** Supervision, Funding acquisition. **Bruce C. Gates:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. **Alexander Katz:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix B

This includes experimental procedures, physisorption isotherms, SEM images, NMR spectra, pyridine desorption FTIR spectra, Py-TGA plots, and product distribution data characterizing *n*-butane cracking. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.173346>.

Data availability

Data will be made available on request.

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