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Enhanced Surface Activity of MWW Zeolite Nanosheets Prepared via a One Step Synthesis

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ABSTRACT: The synthesis of 2-dimensional (2D) zeolites has garnered attention owing to their superior properties for applications that span catalysis to selective separations. Prior studies of 2D zeolite catalysts demonstrated enhanced mass transport for improved catalyst lifetime and selectivity. Moreover, the significantly higher external surface area of 2D materials allows for reactions of bulky molecules too large to access interior pores. There are relatively few protocols for preparing 2D materials owing to the difficultly of capping growth in one direction to only a few unit cells. To accomplish this, it is often necessary to employ complex, commercially-unavailable organic structure-directing agents (OSDAs) prepared via multistep synthesis. However, a small subset of zeolite structures exist as naturally layered materials where post-synthesis steps can be used to exfoliate samples and produce ultrathin 2D nanosheets. In this study, we selected a common layered zeolite, the MWW framework, to explore methods of preparing 2D nanosheets via a one-pot synthesis in the absence of complex organic templates. Using a combination of high-resolution microscopy and spectroscopy, we show 2D MMW-type layers with an average thickness of 3.5 nm (ca. 1.5 unit cells) can be generated using the surfactant cetyltrimethylammonium (CTA), which operates as a dual OSDA and exfoliating agent to affect Al siting and eliminates the need for post-synthesis exfoliation, respectively. We tested these 2D catalysts using a model reaction that assesses external (surface) Brønsted acid sites and observed a marked increase in the conversion relative to 3-dimensional MWW (MCM-22) and 2D layers prepared from post-synthesis exfoliation (ITQ-2). Collectively, our findings identify a facile and effective route to directly synthesize 2D MWW-type materials, which may prove to be more broadly applicable to other layered zeolites.

INTRODUCTION

Zeolites are widely used as absorbents and heterogeneous catalysts in a number of industrial applications.¹⁻⁷ The micropores of zeolites, among other unique properties such as their (hydro)thermal stability and tunable acidity, provide confined environments for molecular reactions, leading to shape-selective catalysis with products and associated transition states determined by the cage and channel geometries of a particular crystal structure.^{4, 8-10} Zeolites with small-to-medium sized pores $(3 \sim 7 \text{ Å})$ often encounter mass transport limitations with limited access of bulky molecules.¹¹⁻¹⁴ Two-dimensional (2D) zeolites, on the other hand, possess properties that enhance mass transport within pores while providing accessible acid sites on external surfaces for molecules sterically restricted from accessing internal sites.¹⁵⁻¹⁷ MCM-22 (MWW type) is one of the most investigated 2D zeolites due to its unique crystallographic structure comprised of stacked, thin layers (ca. 2.5 nm thick).¹⁸⁻¹⁹ The MWW layers have thicknesses equal to a single unit cell dimension, and are aligned perpendicular to the c-axis (Scheme 1). The internal pores of MWW are comprised of supercages (boxed area of Scheme 1A) connected by 10-membered ring (MR) apertures. These cages are surrounded by sinuosoidal channels with narrower 10-MR openings located in close proximity to each corner of the supercage. The exterior surfaces of MWW layers are comprised of 12-MR pockets (or cups) equal to approximately one-half the volume of a supercage. Distinct from surface acid sites on many zeolite catalysts, the acid sites in the external cups of MWW-type zeolite exhibit strong acidity, similar to sites within the micropores,²⁰ which has generated interest for their use in catalytic reactions involving bulky molecules with steric restrictions for accessing interior cages/channels such as Friedel–Crafts alkylation²¹⁻²², hydrocracking²³, and acetalization of aldehydes²⁴. The MWW structure is comprised of eight unique tetrahedral (T) sites, which are illustrated in Scheme 1B and C.

Post-synthetic approaches have been developed to exfoliate MCM-22P, where P is used to denote layered precursors that are not covalently connected. Calcination of the



Scheme 1. MWW framework with its network of pores consisting of (A) 12-MR pockets on the exterior surface, 10-MR windows accessing internal supercages (indicated by the black box), and narrower 10-MR pores that give access to sinusoidal channels. (B) Top down view of an

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precursors leads to the direct condensation of MWW layers, which can be avoided via post-synthesis processes to exfoliate the layers, thereby producing disorder nanosheets with a high surface area exposing 12-MR pockets. A notable example is ITQ-2 prepared by swelling MCM-22P with an exfoliating agent (e.g. surfactant) and subsequently exfolieated via sonication.²⁵ Calcined ITQ-2 exhibits very high external surface area (\sim 700 m²/g), indicating the material is composed of disordered MWW layers.²⁶⁻²⁷ It has been reported that ITQ-2 shows superior catalytic activity as compared to conventional MCM-22 zeolites in various applications, such as cracking of vacuum gas oil.25 The original procedure and conditions used to prepare ITQ-2 involved the use of harsh conditions (i.e., high pH and temperature), leading to partial amorphization.²⁸ Several methods were established since the initial reports of ITQ-2 synthesis to overcome these problems. For example, post-synthesis swelling can be performed at room temperature (compared to 353 K).²⁹ Similarly, the separation of MWW layers can be achieved without the use of sonication.³⁰ Potential amorphization of MWW layers can be avoided when operating under pH 9 and via the use of tetraalkylammonium ions to avoid energy-intensive sonication.³¹ Roth et al. obtained the first pillared zeolitic material, MCM-36, where swollen layers are intercalated by silica species.³² Recently, Liu et al. developed a novel vaporphase pillarization (VPP) process to produce pillared 2D zeolite materials with ~100% efficiency.33 Interestingly, postsynthetic processes have been extended to borosilicates, where single-step exfoliation along with isomorphous substitution of boron with aluminum has been demonstrated ERB-1 (MWW type; borosilicate counterpart).³⁴ on Exfoliation has also been used in a related processes referred as ADOR (assembly-disassembly-organizationto reassembly) to construct new frameworks.35-39 In these processes, building units consisting of a chemical weakness (i.e. Ge heteroatoms) are used to exfoliate (or disable) and then reassemble via silica bridges to construct new frameworks that are otherwise difficult to prepare directly. Moreover, layered zeolites can be used as seeds for the topotactic conversion between different 2D zeolitic precursors through a 3-dimensional germanosilicate intermediate.40

It is highly desirable from both an economic and practical standpoint to develop one-pot synthesis methods to yield zeolite MWW nanosheets with large external surface areas, while simultaneously avoiding loss of structure that is often the result of post-synthesis treatments. To our knowledge, there are few strategies reported in literature to achieve disordered MWW-type materials with properties similar to ITQ-2. Several approaches that come close include the preparation of UZM-8,⁴¹ MCM-56,⁴²⁻⁴⁶ EMM-10,⁴⁷ and ITQ-30.48 Despite the fact these materials exhibit some degree of disordered MWW layers, their relatively low mesoporosity indicates MWW layers are not highly separated with respect to a fully exfoliated MWW-type zeolite. Multiple groups have reported⁴⁹⁻⁵¹ the preparation of MWW-type materials with single layers using a one-step method; however, these methods required the use of custom organic structuredirecting agents (OSDAs) that were not commercially available, and required multi-step synthesis. To this end, it has remained elusive to design a one-step synthesis of exfoliated MWW type zeolite through more practical pathways.

In this study, we report a one-pot synthesis of disordered MWW zeolite using a conventional route that is modified through the addition of a commercial surfactant, cetyltrimethylammonium (CTA). Our findings reveal CTA acts as a secondary OSDA to alter Al siting without impacting the overall Si/Al ratio of the final product. Parametric studies of growth conditions identify regions of growth solution composition resulting in disordered MWW. Textural analysis reveals the final product exhibits a degree of disorder and corresponding external surface area comparable to ITO-2. while solid state ²⁷Al NMR reveals materials prepared by direct synthesis contains fewer Al defect sites. We also report the catalytic performance of these materials relative to 3D MWW (MCM-22) using a model reaction to verify that higher surface area leads to greater access to external acid sites (i.e., greater initial conversion), while the intrinsic activity (when normalized by the number of external acid sites) of the disordered MWW is identical to MCM-22. Collectively, these studies highlight a potentially new, facile route to generate 2D zeolites from naturally layered frameworks that may prove relevant to a broader class of microporous materials.

RESULTS AND DISCUSSION

Preparation of disordered MWW-type nanosheets. We use a modified protocol for conventional MCM-22 synthesis that employs hexamethyleneimine (HMI) as an ODSA. To the growth mixture we add a commercially available quaternary ammonium surfactant, cetyltrimethylammonium (CTA). Established post-synthesis methods (top-down approaches) of MCM-22 exfoliation employ CTA as an exfoliating (or swelling) agent, where it is presumed that the hydrophobic tails of the surfactant aid in the separation of layers. Here, we use a bottom-up approach where the surfactant, with its positively-charged head group, has the ability to associate with negatively-charged aluminates in solution and/or Al tetrahedral sites within the MWW framework, thus creating opportunities for CTA to act as a secondary OSDA. The primary OSDA (HMI) is neutral in alkaline growth mixtures, but prior studies have indicated HMI can adopt a positive charge in confined channels of MWW zeolite, thereby acting as an extra-framework cation to counterbalance the negative charge of Al framework sites.⁵² Through parametric analysis of synthesis mixtures prepared with a combination of HMI and CTA, we explore the putative role of the latter as a cooperative OSDA and dual exfoliating agent in the synthesis of MWW type materials.

Powder X-ray diffraction (PXRD) patterns were used to validate the successful synthesis of MWW type materials and qualitatively assess differences in the degree of layer disorder, which was specifically evaluated within the range $2\theta = 6 - 10^{\circ}$ based on common practice in literature⁴⁷ to differentiate interlayer distances along the c direction. As-synthesized MCM-22 (Figure *i*) contains four peaks in this range. The position of the (002) inter-layer reflection, purely related to the layer thickness in the *c* direction, is located at 6.5° . Due to the presence of inter-layer reflections, (101) and (102), two discrete peaks appear at 7.8 and 9.6°, respectively. After calcination, the (002) reflection of the MCM-22 sample (Figure 1, *i-c*) shifts to 7.0° and overlaps with the (100) reflection due to condensation of individual layers. As the CTA concentration in the growth mixture is increased to 5.5 wt% (Figure 1, ii) and 8.0 wt% (Figure 1, iii), the intensity of the (002) peak correspondingly decreases and the bands

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assigned to the (101) and (102) peaks gradually coalesce into a single broad peak. Both changes reflect the loss of longrange order in the *c* direction. When the quantity of CTA is further increased (e.g. 10 wt%),



Figure 1. PXRD patterns of MWW type materials (gel Si/Al = 15) prepared with (i) 0, (ii) 5.5, and (iii) 8 wt% CTA. The top (grey) lines are as-synthesized solids extracted from growth solutions, whereas the bottom (black) lines are the corresponding calcined (*c*) materials. The MWW framework has a hexagonal crystal structure (*P6/mmm*) with unit cell parameters a = 1.421, b = 1.421, and c = 2.495 nm.⁵³

the PXRD pattern reveals a purely amorphous phase (Figure S1), thus indicating an upper limit of CTA that seemingly disrupts the nucleation of the MWW zeolite. For calcined samples prepared with CTA concentrations below this threshold (Figure 1, *ii-c* and *iii-c*), the single broad band at $2\theta = 7.8 - 9.6^{\circ}$ is preserved, which confirms the disordered layer arrangement of CTA-derived materials (herein referred to as *d-MWW_x* where *x* = weight percentage of CTA).

To further investigate the degree of disorder of MWW type materials, scanning electron microscopy (SEM) and adsorption/desorption measurements nitrogen were performed. Scanning electron micrographs of MCM-22 (Figure 2A and B) show aggregates of plate-like crystals. In comparison, the disordered material d-MWW (Figure 2C and D) is an interpenetrating network of nanosheets with apparent uniform thickness, consistent with PXRD patterns indicating CTA alters crystal morphology. Textural analysis (Table 1) can be used to quantify the degree of disorder for which we define a *disorder index* as the ratio between the external and total surface areas. We introduce this parameter here as an approximate measure of MWW layer exfoliation. The addition of CTA from 0 to 8 wt% increases the disorder index from 0.2 to 0.6, respectively, thus indicating CTA quantitatively improves the separation of layers in MWW type materials. Nitrogen physisorption on calcined MCM-22 reveals a type I isotherm (Figure S4) whereas d-MWW samples exhibit a type IV isotherm. At the highest concentration of CTA (8 wt%), the isotherm is characteristic of a mesoporous material with a sharp increase in N₂ uptake at higher relative pressures and a large hysteresis loop, indicating the presence of high external surface area and mesoporosity (consistent with SEM images in Figure 2). At low relative pressure in the isotherms (i.e. the micropore filling region), the d-MWW materials prepared with 5.5 and 8 wt% CTA exhibit lower N2 uptake compared to MCM-22. This is expected due to the loss of 10-membered ring (MR)

channels and 12-MR supercages along the c direction (see Scheme 1) with an increasing percentage of disordered layers.

Textural details and statistically-relevant measurements of the thickness of MCM-22 and d-MWW were assessed with cryogenic transmission electron microscopy (cryoTEM). The



Figure 2. Scanning electron micrographs of calcined MWW type materials (gel Si/Al = 15): (A and B) MCM-22; (C and D) d-MWW_{8.0}. All scale bars are equal to 1 μ m.

collection of TEM images with the MWW samples cooled to liquid nitrogen temperatures enabled high-resolution imaging and long-time imaging of single samples to collect data over hundreds of nanosheets to quantify average thickness statistics. Contamination and radiation damage were suppressed significantly due to the low temperature and the use of the Falcon 3 direct electron detector, which allowed observation at low electron dose. Figure 3 is a summary of images collected with cryoTEM for the d-MWW₈₀ sample. Figure 3A is a bright field high-resolution TEM (HRTEM) image collected at liquid nitrogen (LN2) temperature of d- MWW_{80} zeolite sheets randomly oriented. The sheets, which are visualized "edge-on" ([001] direction perpendicular to the electron beam), appear dark and narrow. Figure 3B shows two of these sheets at higher magnification. The one on the lefthand side is a single unit cell thick, while the sheet on the right is two unit cells thick. Both high resolution images of the zeolite crystal structure in Figure 3B are along a low indexed zone axis, type (xy θ). A small deviation (~1°) from the observed zone axis would destroy the high resolution pattern. Therefore, these sheets are oriented nearly edge-on, which makes thickness measurements of the sheets accurate. The brightest areas in Figure 3A are "flat" sheets where the (001) normal is oriented parallel to the electron beam. A flat area at higher magnification (Figure 3C) shows a high-resolution image of the crystal structure of MWW zeolite in the (001) orientation. In Figure 3D, a model of the zeolite structure is superimposed on a detail from Figure 3C under the conventional assumption that the bright areas are identical with the cages in the zeolite. A fast Fourier transform (FFT) of a single crystalline portion

Table 1. Properties of MWW materials produced with and without CTA

sample	DIa	BET S _A ^b (m ² /g)	External $S_A^b (m^2/g)$	V _{micro} ^b (ml/g)
MCM-22	0.2	634	149	0.19
d-MWW _{5.5}	0.3	558	164	0.16



surface areas, which are calculated using the BET method; ^b. BET S_A

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(surface area), External $S_{\rm A}$ (external surface area) and $V_{\rm micro}$ (micropore volume) calculated from N_2 adsorption isotherms.



Figure 3. HRTEM images of disordered MWW (gel Si/Al = 15, 8 wt% CTA). (A) Bright field image of a typical cluster of d-MWW₈ nanosheets with a large number of sheets viewed edge-on and suitable for thickness measurements. (B) Magnified detail of panel A with two very thin sheets which are one unit cell and two unit cells thick. (C) High resolution image of a sheet whose surface normal (001) is oriented parallel to the electron beam (a projection of the (001) plane). (D) Model of MWW structure superimposed on a portion of the image from panel C. Scale bar equals 1 nm. (E) Defocus and information limit can be calculated from the Fourier transformation of the image in panel C. The rings coincide with the maxima of contrast transfer as a function the reciprocal vector g. Most of the diffraction spots are located close to these maxima, thereby maximizing image contrast.

of the sample (Figure 3E) shows information transfer better than 0.2 nm.

Detailed analysis of HRTEM images was performed to quantify the average thickness of d-MWW nanosheets and to ascertain the statistical distribution of sizes among samples prepared with varying CTA concentration. Measurement of the thickness of MWW nanosheets as a function of sample treatment (wt% CTA) requires a substantial number of measurements to be statistically significant, since the spread in thickness for each sample is rather high. Selection of the sample area investigated had to be done without bias. A possible bias from a TEM study is to select the thinnest area(s) where image quality (contrast and resolution) is at an optimum. This bias ultimately excludes sheets thicker than a few unit cells. To avoid this situation, we employed two methods to measure nanosheet thickness: (i) electron energy loss spectroscopy (EELS) based thickness measurement using the mean free path of electrons λ in the sample and (ii) measuring the thickness of sheets whose (001) basal surface is oriented perpendicular to the electron beam, as observed in a number of micrographs (see Figure 3A). The latter method is equivalent to edge-on imaging of the sheets and measurement of sheet thickness does not require high resolution, enabling quantification of thicker areas. Method (ii) resulted in a greater number of measurements than method (i), which requires high resolution to detect areas where multiple nanosheets are in line-of-sight. These areas have to be excluded because the thickness measurement results from more than one sheet; therefore, method (i) is limited to very thin areas, excluding thicker sheets and thus creating a biased selection of results. All thickness data presented here have been obtained with method (ii), a complete description of the

procedure for measuring the thickness of edge-on oriented sheets is provided in the Supporting Information.

Figure 4 represents the histograms of sheet thickness for MCM-22 and all d-MWW_x samples. Each histogram is composed of at least 150 independent measurements. For each sample, the mean thickness (in nm) are 23.3 (MCM-22), 13.0 (d-MWW_{5.5}), 7.5 (d-MWW_{7.5}), and 3.5 (d-MWW_{8.0}). It is apparent from the images the spread of measured thicknesses is skewed to the left (i.e. a skewness parameter⁵⁴ ranging



Figure 4. Histograms of layer thickness from HRTEM analysis of (A) MCM-22 and (B - D) d-MWW_x samples (gel Si/Al: 15) prepared with

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the following CTA concentrations: (B) 5.5 wt%, (C) 7.5 wt%, and (D) 8.0 wt%. A histogram consisting of more than 700 individual thickness measurements of d-MWW_{8.0} is plotted in Figure S2, where it is apparent that neither the skewed left nature of the histogram nor the average thickness change with increased number of measurements.

from 2.3 to 4.8). Skewness describes an asymmetry from the mean of the thickness distribution, where left skewness represents an imbalance with most of the data shifted to values smaller than the mean. We plotted histograms using a bin size of 2.5 nm, which represents a thickness equal to one unit cell of MCM-22 in the *c*-direction. Therefore, the thickness is discretized and any reported value deviating from multiples of 2.5 nm are likely errors associated with the measurement of edge-on oriented particles due to edge effects and orientation of the nanosheets relative to the beam, which is not perfectly parallel (*i.e.*, the orientation is off from the [001] zone axis). On this basis, the mean thickness should be interpreted as ca. 6 (MCM-22), 3 - 4 (d-MWW_{5.5}), 2 (d-MWW_{7.5}), and 1 (d-MWW_{8.0}) unit cell dimensions. Further analysis of the histogram demonstrates the mode (thickness value encountered most often in data set) of each sample is 5 (MCM-22), 8 (d-MWW_{5.5}), 1 – 1.5 (d-MWW_{7.5}), and 0.5 – 1 $(d-MWW_{80})$ unit cells. The data (obtained from a large sample number) demonstrate single unit cell nanosheets form in all syntheses (including MCM-22), but the distribution is skewed more heavily to single unit cell or a few unit cell thick nanosheets with the addition of CTA. Indeed, the statistics demonstrate for d-MWW_{8.0} that out of the 186 nanosheets measured, 85% are 1-2 unit cells thick. For the remaining samples, the corresponding percentages are 25% (MCM-22), 42% (d-MWW₅₅), and 67% (d-MWW₇₅).

Putative role of CTA as an OSDA. We examine the impact of CTA on Al siting using solid-state ²⁷Al NMR measurements of MCM-22 and d-MWW samples. Elemental analysis of samples prepared with identical gel Si/Al ratio reveal CTA addition has a marginal effect on the product (solid) Si/Al ratio (Table 3). To discern potential differences in the spatial distribution of Al sites among samples, the local environments of Al(III) atoms were investigated by ²⁷Al Multi-Quantum Magic Angle Spinning (MQMAS) NMR spectroscopy. The MWW framework consists of eight unique tetrahedral sites for Al occupancy (Scheme 1). Prior studies⁵⁵⁻ ⁵⁶ have shown high-field (17.6 T) ²⁷Al MAS is capable of distinguishing between three groups of tetrahedral (T) sites occupied by framework Al (FAl) at specific chemical shifts: Group A ($\delta = 50$ ppm) refers to T₆ + T₇; Group B ($\delta = 56$ ppm) refers to $T_1 + T_3 + T_4 + T_5 + T_8$; and Group C ($\delta = 61$ ppm) refers to T₂. A fourth species detected at $\delta = 0$ ppm (Group D) is octahedral-coordinated Al, which is often considered as extra-framework Al (EFAl). With known chemical shifts corresponding to different Al species, the deconvolution and curve fitting of 1-dimensional ²⁷Al NMR spectra were performed on both ordered MCM-22 (Figure 5A) and disordered d-MWW₇₅ (Figure 5B) using the previous assignments of FAl species.

The integrated areas of deconvoluted peaks in Figure 5 are presented in Table 2 for MCM-22 and d-MWW_{7.5} samples after ion exchange with NH₄⁺ and calcination to generate Hform zeolites (i.e. catalysts used for studies discussed later). Similar measurements were performed on H-ITQ-2; however, the post-synthesis method involving exfoliation at high pH and temperature leads to the dissolution of framework Si, irrespective of crystal Si/Al ratio, which generates defective FAl that renders NMR spectra too noisy for analysis (Figure S3), consistent with prior reports indicating a loss of crystallinity during post-synthesis exfoliation.²⁹ Comparing the results of NMR analysis in Table 2, we observe the fraction of Al sites in Groups A, B, and D is similar for both ordered and disordered materials. Interestingly, the quantity of Al in Group C (assigned to the T_2 site) increases from 15 to 25%

 Table 2. Relative peak areas of ²⁷Al MAS NMR spectra.

δ (ppm)	$Al_{(A)}$	$Al_{(B)}$	$Al_{(C)}$	$Al_{(D)}$
	50	56	61	-1
MCM-22 ^a	14%	54%	15%	17%
d-MWW _{7.5} ^{a,b}	12%	48%	25%	15%

^a H-form samples; ^b prepared with 7.5 wt% CTA

with CTA addition. According to the distribution of T sites in Scheme 1, the T₂ site is located on the exterior surface of 2D nanosheets close to the outer rim of the 12-MR cup. The appreciable increase in T₂ content of d-MWW suggests CTA acts as an OSDA to alter the distribution of Al sites, and specifically place FAl species on the exterior surfaces where they are more accessible to bulky adsorbates. Although T₁ and T₃ (part of Group B) are also located at the exterior surface, Ivanova et al.⁵⁷ argued that the substitution of Al atom in eight T sites of MCM-22 took place in the order of $T_4 \approx T_2 > T_6 \approx$ $T_8 \approx T_3 > T_7 > T_5 > T_1$ Thus, the 5% reduction of Al content in Group B can be attributed to the loss of T4 site. We also observe the one-pot process using combinations of CTA and HMI does not alter the occlusion of FAI species (i.e. both have similar Si/Al ratios; see Table 3), and both samples contain approximately the same quantity of EFAl species (Al_(D) in Table 2).

We performed a parametric analysis of synthesis conditions to determine the compositional range where d-MWW_x can be prepared without appreciable loss of crystallinity. Syntheses were first performed in the absence of CTA at varying gel Si/Al ratios where we observed a systematic reduction in the disorder index of MCM-22 with increasing silicon content (Table S1). The quantification of percent crystallinity is difficult to extract from PXRD patterns owing to the broad peaks that overlap the region of amorphous product. To this end, we used textural analysis to evaluate changes in both total BET surface area and micropore volume (Table S1). The disorder index increases with CTA concentration, irrespective of the gel Si/Al ratio; however, in more siliceous growth solutions the presence of CTA appears to stabilize an amorphous product. This is evident in syntheses using a gel Si/Al ratio of 45 where the PXRD patterns clearly show the presence of an amorphous peak (Figure S1) and the micropore volume correspondingly decreases well below 0.1 ml/g (Table S1) while the overall BET surface area monotonically decreases with increasing CTA concentration (Figure 6). At the lowest gel Si/Al ratio of 15, it is possible to prepare d-MWW over a relatively broad range of CTA concentration without a significant reduction in total BET surface area. Under these conditions, we observe an anticipated reduction in micropore volume (from 0.2 to 0.1 ml/g) and increasing disorder index (from 0.2 to 0.6) owing to the loss of supercages and channels with the formation of 2D nanosheets. For syntheses at intermediate silica content (gel Si/Al of 30), the determination of d-MWW formation is more convoluted. Based on the trend in total BET surface area (Figure 6), it appears d-MWW with a disorder index of 0.3

can be prepared with 4 wt% CTA, while higher surfactant concentration leads to lower total surface area and micropore volume less than 0.1 ml/g (Table S1). From these studies it is evident the ability of CTA to generate d-MWW is influenced

by the Al content of the growth medium wherein it is possible to prepare disordered nanosheets with gel Si/Al ratios spanning from 15 to 30, outside the range of ITQ-2 (gel Si/Al = 50) reported in literature. We posit the



Figure 5. Two-dimensional ²⁷Al MQ MAS NMR spectra of H-form (A) MCM-22 and (B) d-MWW_{7.5} samples (gel Si/Al = 15) acquired at 11.7 T and 12.5 kHz. Deconvolution of these two samples were performed on one-dimensional ²⁷Al MAS NMR spectra using Dmfit program.



Figure 6. Parametric analysis of d-MWW synthesis at varying gel Si/Al ratios: 15 (triangles), 30 (diamonds), and 45 (circles). The total BET surface area measured from N₂ adsorption/desorption isotherms (Figure S1) is reported (solid symbols) for syntheses at varying CTA concentration (0 - 8 wt%). The dashed lines are linear regression. For additional details of textural analysis see the Supporting Information and Table S1.

upper limit is attributed to the need for a sufficient number of Al sites occupying the surface of disordered layers to electrostatically interact with adsorbed CTA molecules. This would imply a minimum coverage of adsorbed CTA is required for disoriented layers along the *c*-axis and concomitant stabilization of surface Al species, which is favored at low Si/Al ratios.

Here we hypothesize the role of CTA in the synthesis of d-MWW (Figure 7). For the preparation of ordered layered precursors at high gel Si/Al ratio, it has been postulated ⁵⁸ neighboring layers interact via hydrogen bonding between opposing silanol groups and interstitial HMI molecules (Figure 7A). As the gel Si/Al ratio decreases, there is an

increased probability of Al atoms becoming incorporated at surface sites on the layers. A higher surface density of Al sites leads to enhanced electrostatic interactions between the negative charges of framework Al and Na⁺ counterions, which act as an inorganic structure-directing agent (Figure 7B). As the gel Si/Al ratio decreases from 45 to 15, the disorder index concomitantly increases from 0.13 to 0.24 (in the absence of CTA), suggesting the presence of Na⁺ ions on layer surfaces impede layer alignment. In the presence of CTA, the positively-charged head group of the surfactant can also act as a counterion to balance framework Al atoms, which is consistent with the results of NMR analysis (Table 2) that demonstrate the ability of CTA to act as an OSDA (i.e. alter Al siting). Residual CTA in extracted solids after multiple steps of isolation involving extensive washing with water was confirmed by thermogravimetric analysis (TGA) where we observe two different peaks (Figure S5), which we attribute to surface species and those occluded within pores (or between the interstitial regions of neighboring nanosheets).55, 59 Moreover, we observe an appreciable reduction in the quantity of occluded HMI that accompanies an increased amount of CTA and Na⁺ (Table S2) measured from TGA and elemental analysis (ICP), respectively. This trend agrees with prior studies showing MCM-56 (partially disordered MWW) contains a higher content of Na⁺ and lower amount of HMI compared to conventional MCM-22P.60 For syntheses with CTA, we posit the long hydrocarbon tail of the surfactant can separate layers (Figure 7C), similar to the proposed mechanism of post-synthesis exfoliation.²³ The accumulation of CTA at exterior surfaces may impede layer-layer interactions, thus maximizing layer separation along the cdirection to generate disordered materials that are maintained even after the removal of organics by calcination.

Enhanced surface catalytic activity. A comparison of MWW type materials was performed using a model reaction to assess differences in catalyst lifetime and selectivity with increasing degree of layer disorder. For comparison, we tested

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our material against a conventional disordered MWW material. The two most commonly reported disordered MWW type materials, MCM-56 and ITQ-2, have surface areas of ca. 211 and \geq 700 m²/g, respectively.^{23, 42} Given the higher degree of disorder in ITQ-2, we used this material as a reference and we prepared a sample following a reported post-synthesis exfoliation protocol²³ (with the Si/Al gel ratio reduced to match the Al content of d-MWW). All assynthesized samples were converted to H-form by standard NH₄⁺ ion exchange and calcination. The internal and external

acidity of H-MCM-22, H-d-MWW_x, and H-ITQ-2 was determined by a method reported in literature for MWW-type materials based on the adsorption of two molecules, a less bulky trimethylphosphine oxide (TMPO) and a more bulky tributylphosphine oxide (TBPO), using solid-state ³¹P NMR spectroscopy. The ³¹P NMR spectra for TMPO and TBPO adsorption on MWW type samples reveal complex spectra composed of a number of distinct species (deconvoluted spectra for TMPO and TBPO can be found in Figures S6 and S7, respectively).



Figure 7. Putative roles of organic (HMI and CTA) and inorganic (Na⁺) structure-directing agents during the one-pot synthesis of MWW type materials. Idealized schematics depict MCM-22P (where *P* refers to the precursor, prior to calcination) at (A) high and (B) low gel Si/Al ratio, and (C) disordered d-MWW-P at low gel Si/Al ratio in the presence of CTA surfactant. The illustrations shown here are adapted from schemes reported by Roth et al.^{15, 60} Reproduced with permission from ref 15 and ref 60. Copyright 2014 and 2015 American Chemical Society.

Prior studies discussed the sites accessible by each of the phosphine oxide probe molecules used in this study. Zhao and co-workers⁶¹ stated TMPO can access acid sites in both the 10-MR channels (internal acid sites) as well as the external acid sites present in the 12-MR pockets. Therefore, the total amount of titrated TMPO represents the total number acid sites accessible on MWW-type zeolites. More recently, Luo and co-workers ⁴⁹ have utilized the same probe molecules to probe internal and external acid sites on MIT-1; their assignments agreed with those used by Zhao. TBPO is presumed to only access the 12-MR pockets on the exterior surfaces.⁶² Here, like the previous groups, we posit TMPO is capable of accessing the same sites as TBPO given that its size is less restricted; therefore, it can be assumed that the amount of adsorbed TMPO constitutes the total number of H⁺ sites, while the amount of adsorbed TBPO is a measure of external active sites. Luo conducted DFT calculations to confirm the ³¹P chemical shifts at 85, 72, 68 and 63 ppm are associated with Brønsted acid sites present in the 10-MR and 12-MR channels of MCM-22.49 Luo also suggested the peak at 53 ppm is associated with Lewis acid sites; which appears to be a controversial assignment. Since the fraction of TMPO assigned to a 53 ppm chemical shift is small and no peak at 53 ppm was observed for any sample using TBPO, we opt not to make any definitive statement regarding the presence of Lewis acid sites on the MWW-type zeolites.

Table 3 summarizes the measured TMPO and TBPO adsorbed concentrations for all catalysts. A total of ten resonance peaks at chemical shifts of $\delta = 82$, 78, 69, 66, 58,

53, 48, 42, 36, and 33 ppm (Table S3) were identified for samples with adsorbed TMPO. The peaks at $\delta = 82$, 78, 69, 66, 58, and 53 ppm correspond internal acid sites present in the 12-MR pockets and 10-MR pores; and the peaks at 48 and 42 correspond to physisorbed TMPO and the peaks at 36 and 33 ppm correspond to crystalline TMPO (not associated with the zeolite).⁴⁹ Six resonances at chemical shifts $\delta = 75$, 71, 62, 57, 50, and 46 ppm (Table S3) were identified for adsorbed TBPO. Peaks at $\delta = 75$, 71, and 62 ppm correspond to TBPO bound to external acid sites, whereas the peak at 57 ppm corresponds to physisorbed TBPO and the peaks at 50 and 46 ppm correspond to crystalline TBPO. The total quantity of acid sites (both internal and external) was measured using spectra integration coupled with ICP-OES elemental analysis of P.^{49,61}

A comparison of acid site densities in Table 3 reveals discrepancies between the total amount of Al sites measurement by ICP-OES, labeled as [Al], and that of TMPO adsorption that presumably represents the total number of Al sites. The comparison of ²⁷Al MAS NMR spectra for all samples indicates an average 15 - 20% extra-framework Al (Table 2), which likely accounts for some (but not all) of these differences. Additional considerations may include steric constraints that limit the number of accessible sites for TMPO adsorption. For example, Al sites located at the bottom of 12-MR pockets on the external surfaces may be too confined for TMPO adsorption. This would also be true for the bulkier TBPO probe molecule, which may be unable to efficiently bind to Al sites in external pockets. The latter hypothesis may

explain why the number of external acid sites, [H⁺]_{ext}, does not appreciably increase with higher CTA concentration (counter to the increased external surface area from BET analysis (Table 1)). Collectively, our data seems to highlight inherent problems with the conventional use of TMPO and TBPO as probe molecules and has prompted ongoing studies in our groups to identify alternative methods of acid site titration (outside the scope of this study).

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Another interesting observation is that H-d-MWW_{5.5} and H-ITQ-2 exhibit markedly lower acid density than the other samples. The H-ITQ-2 sample has a notably higher Si/Al ratio than other samples, which partially explains this observation;

however, ²⁷Al MAS NMR analysis reveals defective Al in this material (Figure S3), which may influence the measurements in Table 3. For the case of H-d-MWW_{5.5}, the reasoning for low acid site density is less intuitive. It appears intermediate concentrations of CTA, which correspond to the transition between ordered and disordered MWW-type materials, has an apparent impact on Al siting that is not well understood. This suggests an optimal CTA concentration (ca. 6 - 8 wt%) where values below this range lead to seemingly defective materials, while values above this range result in an amorphous product. The exact mechanism for this effect remains elusive.

Table 3. Summary of Al content and ad	dsorbed probe (TMPO and TBF	PO) amounts in H-MWW samples
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Sample	S:/A1 c	[Al]	[TMPO]	[TBPO] or [H ⁺] _{ext}	[H ⁺] _{int}
	51/AI *	(mmol g ⁻¹)	(mmol g ⁻¹) ^d	(mmol g ⁻¹) ^d	(mmol g ⁻¹)
H-MCM-22 ^a	11.2	0.76	0.43	0.05	0.38
H-d-MWW _{5.5} ^a	12.7	0.68	0.18	0.07	0.11
$H\text{-}d\text{-}MWW_{8.0}^a$	12.7	0.67	0.44	0.06	0.38
H-ITQ-2 ^a	20.3	0.48	0.19	0.10	0.09
H-ITQ-2 ^b	45.0	0.20	0.11	0.06	0.05

a. sample prepared with gel Si/Al = 15; b. sample prepared with gel Si/Al = 45; c. determined by ICP-OES; d. determined from ICP-OES and ${}^{31}P$ NMR spectroscopy.

To assess the catalytic performance of our materials, we selected the Friedel-Crafts alkylation of benzyl alcohol (BA) with benzene as a model reaction^{49, 63-64} employing bulky molecules (Figure 8A) that can only access external sites on MWW-type catalysts. Liquid-phase batch reaction was performed at 80°C using a large excess of benzene. Aliquots of the reaction mixture were removed at periodic times to analyze the products by gas chromatography (Figure S8). A comparison of BA conversion at a fixed reaction time (9 h) is shown in Figure 8B (left axis) based on an equivalent mass of catalyst. As shown in Table 3, the Si/Al ratios of H-MCM-22 and H-d-MWW_x (with x = 5.5 and 8 wt% CTA) are approximately equal, whereas H-ITQ-2 has a slightly higher Si/Al ratio. At equivalent mass, the H-d-MWW₈₀ catalyst exhibits much higher conversion among these four catalysts owing to its larger external surface area and increased density of Al sites in external 12-MR pockets (as inferred from Table 2). Notably, the conversion for H-d-MWW_{8.0} catalyst is ca. 30% higher than that of H-MCM-22. Normalization of reacted BA by the total number of external acid sites reveals H-MCM-22 and H-d-MWW₈₀ have comparable turnover number (TON) (Figure 8B, right axis), and similar activity evaluated after 9 h (Figure S8). Conversely, the TON of H-d-MWW_{5.5} and H-ITQ-2 are markedly lower, reflecting a lower activity. For H-ITQ-2, we attribute this observation to its high percentage of defective (or non-framework) Al sites, which is evident in ²⁷Al MQMAS NMR spectra (Figure S3). To confirm that the preparation of ITQ-2 with increased Al content did not impact its structural integrity, we also prepared a sample according to the original recipe (with a higher gel Si/Al ratio of 45)⁶⁵ and observed a similar, albeit slightly lower, turnover number as the ITQ-2 sample prepared with a gel Si/Al ratio of 15 (Figure S8). This indicates that postsynthesis exfoliation has a negative impact on zeolite structure, irrespective of the crystal Si/Al ratio. For H-d-MWW_{5.5}, the lower catalytic activity is more difficult to rationalize. As previously discussed, the incorporation of Al

in d-MWW at intermediate CTA concentrations is less effective, which correlates with decreased BA conversion.



Figure 8. (A) Model reaction used to assess the performance of MWWtype catalysts. (B) Benzyl alcohol (BA) conversion (blue, left axis) at 80 °C for a fixed catalyst loading (30 mg catalyst per 8.86 g reaction mixture; benzene/BA = 196 mol mol⁻¹). The turnover number (yellow, right axis) was calculated as the moles of reacted BA normalized by the moles of external [H⁺] acid sites. Data are listed for the following H-form MWWtype samples: H-MCM-22, H-d-MWW_x (x = 5.5 and 8 wt% CTA), and H-ITQ-2. The results are shown for a single time point (9 h). See the Supporting Information for a comparison of conversion at different reaction times (Figure S8) and corresponding product selectivity (Table S4).

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CONCLUSION

In summary, we present a direct route to prepare disordered MWW type nanosheets (d-MWW) without the need for post-synthesis exfoliation or the use of elaborate organic structure-directing agents. The one step approach is accomplished through the addition of a commercial surfactant, cetyltrimethylammonium, to a conventional MCM-22 growth mixture. A combination of powder X-ray diffraction and N₂ desorption/adsorption analyses reveal high surface area nanosheets are generated within a narrow range of growth mixture composition (Si/Al = 15 - 30) and quantity 10 of added surfactant (6 - 8 wt% CTA). These studies indicate 11 CTA behaves as an *in situ* exfoliating agent wherein we posit 12 that the positively-charged amine groups of the surfactant 13 associate with negatively-charged Al sites on the surfaces of 14 d-MWW nanosheets; however, solid state ²⁷Al NMR spectra 15 of d-MWW reveals that CTA also behaves as a structure-16 directing agent by virtue of its ability to alter Al siting, placing 17 additional acid sites within the 12-membered ring pockets lining the exterior surfaces. The number of Brønsted acid sites 18 within the interior and exterior of MWW type materials was 19 scrutinized through a combination of elemental analysis and 20 ³¹P MAS NMR using two titrants – trimethylphosphine oxide 21 and tributylphosphine oxide. The size disparity between these 22 molecules allowed for the former to access both internal and 23 external sites, whereas the latter is only able to access external 24 sites owing to its large size relative to the 10-membered ring 25 pores granting access to the interior supercages and sinusoidal 26 channels. 27

A combination of high surface area and increased number of external Brønsted acids for d-MWW compared to its 3dimensional analogue, MCM-22, results in greater access to surface sites for reactions involving bulky organic molecules. To this end, we tested the catalytic performance of several MWW type materials using Friedel-Crafts alkylation of benzyl alcohol with benzene as a model reaction. Our findings reveal the conversion of benzyl alcohol is markedly faster. Comparisons of turnover number reveal d-MWW exhibits similar activity as MCM-22; however, preparation of 2D nanosheets through post-synthesis exfoliation reveals that the resulting catalyst, ITQ-2, is highly defective (e.g. extraframework or distorted Al sites) and exhibits poor catalytic performance in the Friedel-Crafts alkylation reaction. Collectively, our findings indicate the direct incorporation of long-chain surfactant into syntheses of MWW type materials can lead to disordered 2D materials. It remains to be determined if this approach can be used as a generalized methodology for other layered zeolites to generate high surface area nanosheets. It is evident, however, the success along these lines could have practical implications for the rational design of zeolite catalysts for a broad range of applications.

EXPERIMENTAL SECTION

Chemicals. The following reagents were purchased from Sigma-Aldrich: benzene (99.9%), benzyl alcohol (anhydrous, 99.8%), isopropylamine (99%), hexamethyleneimine (HMI, 99%), hexadecyltrimethylammonium bromide (CTAB, 99.9%), hydrochloric acid solution (HCl, 1.0N) and sodium hydroxide (NaOH, 98%). Sodium aluminate (technical grade), tetrapropylammonium hydroxide (TPAOH, 40%) and trimethylphosphineoxide (99%) was purchased from Alfa Aesar. Tributylphosphineoxide (90%) was purchased from

Tokyo Chemical Industry (TCI). Fumed silica (Cab-o-Sil, M-5, scintillation grade) was purchased from Spectrum Chemical. Anhydrous dichloromethane (99.9%) was purchased from Fisher Scientific. Deionized (DI) water was produced with an Aqua Solutions RODI-C-12A purification system (18.2 M Ω). All reagents were used as received without further purification.

Synthesis of MWW materials. Synthesis of MWW type zeolite was performed based on a reported protocol in literature with slight modifications.¹⁸ MCM-22 zeolites (gel Si/Al = 15, 30, and 45) were synthesized using growth solution with a nominal composition of 0.49 HMI : 0.09 Na₂O : $1 \operatorname{SiO}_2$: x Al₂O₃: 43.9 H₂O, where x = 0.033, 0.017, or 0.011. The initial procedure involved the addition of sodium aluminate to a solution of HMI, NaOH and DI water. The mixture was aged at room temperature overnight under continuous stirring. Fumed silica was then added and the growth solution was heated at 150 °C for 7d in a Teflon-lined autoclave (Parr Instruments) with rotation. The solution was then removed from the oven and immediately cooled to room temperature.

Disordered MWW material was prepared by modifying the MCM-22 synthesis to include the addition of cetyltrimethylammonium bromide (CTAB). A small quantity of CTAB (0.55 - 1.38 g, or 4 - 10 wt%) was added in a mixture of 1M sodium hydroxide solution (2.41 g), DI water (9.55 g), sodium aluminate (0.03 - 0.09 g), and 0.74 g of organic structure-directing agent, hexamethyleneimine (HMI). After stirring this mixure overnight at room temperature, 0.9 g of fume silica was added to give a gel molar composition of 0.49 HMI : 0.09 Na₂O : 1 SiO₂ : x Al₂O₃ : yCTA : 43.9 H₂O, where x = 0.033, 0.017, or 0.011 and y =0.10-0.25 . The solution was heated at 150 $^{\circ}\mathrm{C}$ for 7d in a Teflon-lined autoclave with rotation. The solid product (zeolite crystals) were collected by vacuum filtration, washed thoroughly with DI water, and dried at 60 °C. Samples were calcined in a Thermo Fisher Lindberg Blue furnace under constant flow of dried air (Matheson Tri-Gas) at 550 °C for 10 h with a temperature ramp/cooling rate of 1 °C/min.

ITQ-2 was synthesized by exfoliation of MCM-22P using a method reported in literature,65 with minor modifications to increase the Al content of the final product. The procedure involved the mixing of MCM-22P (1g) with DI water (25 g), CTAB (1.42 g), and TPAOH (3.75 g of 40 wt% reagent) to achieve a starting gel Si/Al ratio of 15. The mixture was stirred at 80 °C under reflux for 16 h. After cooling to room temperature, the mixture was sonicated (110 W, 40 KHz) for 2 h. The pH of the mixture was dropped below 2 by the addition of stock HCl solution, and subsequently, the mixture was centrifuged to recover the solids. The exfoliated product was dried in air and calcined at 550 °C for 8 h. A second ITQ-2 sample synthesized from a starting gel of Si/Al ratio of 45 was prepared according to the same procedure with the following modifications: 1g MCM-22P (gel Si/Al = 45) was added into a mixture containing 12.22 g DI water, 1.13 g CTAB, and 2.50 g TPAOH (40 wt% reagent).Samples for catalytic testing were converted to their H⁺ forms by ion exchange wherein calcined zeolite was mixed with 1.0 M ammonium nitrate solution to obtain a 2 wt % suspension. This mixture was heated to 80 °C for 2 h to allow the exchange of Na⁺ with NH₄⁺. This process was performed three times with centrifugation/washing between each ion exchange cycle, using a Beckman Coulter Avanti J-E centrifuge at 5 °C and 13000 rpm for 10 min per cycle. The final NH₄-zeolite samples were washed thrice with DI water before they were calcined once again at 550 °C for 5 h with a temperature ramping/cooling rate of 1 °C/min (leading to the generation of H-form zeolites).

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Characterization. MWW type zeolite samples were characterized by powder X-ray diffraction (PXRD), nitrogen adsorption/desorption, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), cryo-transmission electron microscopy (crvo-TEM), inductively coupled plasma-optical emission spectroscopy (ICP-OES), and solidstate NMR. PXRD patterns were acquired from 5 to $50^{\circ} 2\theta$ with a step size of 0.02° at 40 kV and 44 mA using a Rigaku Smartlab X-ray Diffractometer. Analysis of surface area by the BET method was performed on N₂ adsorption/desorption isotherms obtained using a Micrometrics ASAP 2020 instrument. Crystal morphology and size were measured by a FEI Nova NanoSEM 230 instrument after Pt coating (ca. 5 nm Thermogravimetric analysis (TGA) was thickness). performed in flowing air (20 mL min⁻¹) on a TG 209 F3 Tarsus instrument with a heating rate of 10 °C min⁻¹. The temperature was ramped up to 850 °C to assess the weight percentage of occluded organics in MWW type materials.

A Thermo Fisher Krios G3 Cryo-TEM with an image aberration corrector and customized Gatan BioQuantum electron-energy loss spectrometer was used for all measurements. The samples were cooled to liquid nitrogen temperature. During the entire TEM investigation, no contamination or radiation damage effects were observed. Images were detected with a Falcon 3EC direct electron detector in counting mode. An acceleration voltage of 300 kV was used for all imaging. The system is capable of a spatial resolution of better than 0.14 nm. Additional details of cryo-TEM sample preparation and thickness analysis are provided in the Supporting Information.

Solid-state ²⁷Al NMR experiments were performed at 11.7 T on a JEOL ECA-500 spectrometer, equipped with a 3.2mm Field Gradient Magic Angle Spinning Probe. ²⁷Al MAS NMR spectra were obtained at a spinning frequency of 12.5 KHz with a $\pi/12$ pulse width of 1.25 µs and a recycle delay of 0.8 s. The number of scans was 4096 for all measurements. ²⁷Al MQMAS measurements were performed using the same instrument, where the experiment details can be found elsewhere.⁶⁶ The percentages of framework and extra-framework Al species (FAl and EFAl, respectively) were determined using the Dmfit program. The broad peak (ca. 56 ppm) in ²⁷Al MAS NMR spectra was deconvoluted into three peaks at 50, 56, and 61 ppm (represented as Al_(A), Al_(B), and Al_(C), respectively). The ²⁷Al chemical shift was referenced using 1M Al(NO₃)₃ aqueous solution.

Solid-state ³¹P NMR experiments were carried out on a Bruker AVANCE III HD solid state 500 MHz NMR with a quadruple tuned 4 mm CPMAS probe or a Bruker AVANCE solid state 300 MHz NMR with a double-resonance 4 mm HX probe spectrometers at room temperature (298 K). ³¹P NMR spectra were acquired at the frequency of 202.5 MHz using a single-pulse sequence with a pulse width of 1 µs, a recycle delay of 5 s in AVANCE III HD solid state 500 MHz NMR and a pulse width of 2.5 µs, a recycle delay of 10 s in Bruker AVANCE solid state 300 MHz NMR. The sample spinning frequency is 12 kHz with 2-10 k scans. CaHPO₄.2H₂O was used as an external reference. ICP-OES was obtained using an Agilent ICP-OES 700 to determine the total P content of the zeolite after being titrated by TMPO or TBPO. Procedures for the adsorption of the phosphine oxides are provided in the Supporting Information.

Catalytic measurements. Friedel-Crafts alkylation of benzene with benzyl alcohol reactions were carried out in septum-sealed, round-bottom flask with magnetic stirring. A fixed quantity of catalyst (30 mg) was added in a mixture of 0.54 g benzyl alcohol and 8.32 g benzene. Both reactants and catalyst were sealed into the flask and placed in an oil bath at 80 °C. Reaction mixtures were collected at a certain time period after cooling the flask to room temperature. The solution was evaluated using a gas chromatograph (Agilent 7890B) equipped with a FID detector and an Agilent HP-5 capillary column. Benzene was used as an internal standard. Both reactants, benzene and benzyl alcohol (BA), and products, diphenylmethane (DPM) and dibenzyl ether (DE), were calibrated, and their response factors were obtained. Benzyl alcohol are considered as reactant with the conversion (X_{BA}) defined as

$$X_{BA} = \frac{N_{BA,o} - N_{BA}}{N_{BA,o}} = \frac{N_{DPM} + N_{DE}}{N_{BA} + N_{DPM} + N_{DE}}$$
(1)

where $N_{BA,o}$ is the mole amount of benzyl alcohol in the feed and N_{BA} , N_{DPM} , and N_{DE} are the mole amount of benzyl alcohol, diphenylmethane, and dibenzyl ether in the reaction mixture. The yield (Y_i) of product, i, is defined as

$$Y_i = \frac{N_i}{N_{BA} + N_{DPM} + N_{DE}}$$
(2)

where N_i is the mole amount of product in the reaction mixture.

ASSOCIATED CONTENT

SUPPORTING INFORMATION

Additional details of materials characterization are provided, including XRD patterns, TEM images, TGA profiles, elemental analysis, nitrogen adsorption measurements, solid state NMR, and catalytic results including conversion and yield (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interests.

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All authors have given approval to the final version of the manuscript.

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