Vapor-Phase Strategy to Pillaring of Two-Dimensional Zeolite

Lu Wei,†‡ Kechen Song,‡§ Wei Wu,‡ Scott Holdren,‖ Guanghui Zhu,‖ Emily Shulman,‡ Wenjin Shang,‡ Huiyong Chen,‡ Michael R. Zachariah,‖‡ and Dongxia Liu‡§†

†College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, P. R. China
‡Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, Maryland 20742, United States
§School of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing, 100083, China
∥Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, United States
‖School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States
§School of Chemical Engineering, Northwest University, Xi’an, Shanxi 710069, China

Supporting Information

ABSTRACT: Two-dimensional (2D) layered zeolites are new forms of 3D zeolite frameworks. They can be pillared to form more open porous structures with increased access for reactants that are too big for the micropores of zeolites. The current pillaring procedure, however, requires intercalation of pillaring precursors by dispersing 2D zeolite in an alkoxide liquid and hydrolyzing entrapped alkoxide to form inorganic oxide pillars in an aqueous alkaline solution. Both steps use excess solvents, generate significant waste, and require multiple synthesis and separation steps. Here we report a vapor-phase pillarization (VPP) process to produce pillared zeolites from 2D layered zeolite structures. The VPP process has ∼100% efficiency of alkoxide usage in the intercalation step, requires less (and, in some cases, zero) water addition in the hydrolysis step, does not require separation for product recovery, and generates no liquid waste. Furthermore, synthesis of pillared zeolites via the VPP process can be accomplished within a single apparatus with one-time operation. The pillared zeolite prepared by the VPP method preserves the zeolitic layered structure as well as acidity and showed enhancement in catalytic activity and diverse structures.

Two basic chemical processes, exfoliation and pillarization, have been used to modify 2D zeolites into diverse structures. The exfoliation process separates the stack of 2D zeolite nanosheets into self-standing independent entities by breaking down the interlayer interactions. The exfoliated zeolite nanosheets can be used as a base material for the fabrication of membranes or used directly as hierarchical catalysts. Rather than breaking down the stack of 2D zeolites in the exfoliation process, the pillarization process transforms the 2D zeolites into hierarchical materials with the retention of the stacked layer structure. The pillarization often involves subsequent expansion of interlayer space by swelling with long chain polar molecular molecules, intercalation of the swollen materials in an alkoxide liquid, hydrolysis of entrapped alkoxide in an aqueous alkaline solution, and removal of organics as well as transformation of alkoxide liquid into permanent oxide pillars between zeolitic layers by calcination. The current pillaring procedure requires multiple discrete steps, uses excess solvents in both intercalation and hydrolysis treatments, and generates waste.

Here, we report on a vapor-phase pillarization (VPP) process to produce pillared zeolites from 2D layered zeolite materials. The experimental setup (Figure 1) is similar to that used in steam-assisted zeolite crystallization in a Teflon-lined autoclave. A glass vial containing 2D layered zeolite is

Figure 1. Schematic of the formation of pillared zeolite from 2D layered zeolite in the VPP process.

Received: March 31, 2019
Published: May 22, 2019
placed in the Teflon cup. The pillaring precursor (i.e., liquid alkoxide) is dropped into the Teflon cup and separated from the 2D layered zeolite by the glass container. After heating the autoclave to evaporate alkoxide for intercalation, the same setup is used to evaporate water for hydrolysis of intercalated alkoxide (Section S1). The mass ratios of alkoxide/zeolite and water/zeolite are controlled as 0.5 and 10 in the intercalation and hydrolysis steps, respectively. The 2D layered zeolite is calcined in a furnace to form the pillared zeolite. In comparison to pillaring of 2D layered zeolites in liquid solvent/solution reported previously, \(^{16-19,22}\) the VPP method requires up to \(\sim10\) times less alkoxide in the intercalation step, uses less (and even zero, to be discussed below) water addition in the hydrolysis step, does not require product recovery from the liquid solvent/solution, and generates no liquid waste.

As a prominent representative of 2D layered zeolite, multilamellar MFI (M-MFI), \(^{31}\) synthesized by hydrothermal crystallization of a synthetic gel comprising zeolite precursor materials and a diquaternary ammonium template (Section S1.2), was used as the precursor (M-MFI(P)) to form pillared MFI (PMFI) zeolite using the VPP process. Tetraethyl orthosilicate (TEOS) and deionized water (DI \(\text{H}_2\text{O}\)) were used in the intercalation and hydrolysis steps, respectively, to form silica (\(\text{SiO}_2\)) pillars in PMFI. Figure 2a shows the XRD patterns of M-MFI(P) and M-MFI(P) after TEOS intercalation and PMFI synthesized using the VPP process. The disappearance of diffraction peaks in the low-angle XRD region of the quartz tube from \(2\theta \sim 13.5^\circ\) indicates preservation of the 2D layered structure since the \(\text{SiO}_2\) pillars formed using TEOS concentrations were insufficient to maintain the layered structure integrity upon organic template removal via calcination. The TEOS/M-MFI(P) ratio of 0.50 and 0.10 produced PMFI with high crystallinity, ordering of zeolitic nanosheet layers, and high mesoporosity (isotherm data in Figure S3 and Table S1). The intercalation temperature did not influence PMFI formation significantly under investigated conditions. The XRD patterns (Figure S4) and \(\text{N}_2\) isotherms (Figure S5) of PMFI synthesized at intercalation temperatures of 363, 383, 403, and 423 \(\text{K}\) with the VPP process are very similar.

The effects of water in the hydrolysis step on PMFI formation were examined by varying the mass ratio of water to M-MFI(P) (\(\text{H}_2\text{O}/\text{M-MFI(P)}\)) from 0 to 10 in the VPP process. In all cases, PMFI was synthesized successfully, as confirmed by both XRD (Figure S6) and \(\text{N}_2\) isotherm (Figure S7) data. The formation of PMFI can be completed even with no water added, which is unexpected since water is considered a required material for TEOS hydrolysis to form the pillars. \(^{35}\) However, since the M-MFI(P) was dried in a convective oven at 343 \(\text{K}\) for 12 h after the hydrothermal crystallization, it is likely that adsorbed water remained in the porous zeolite structures. Alkali ions and diquaternary ammonium template molecules trapped in M-MFI(P) from the hydrothermal synthesis provide sufficient basicity for TEOS hydrolysis, since a \(\text{pH}\) of 8 (by \(\text{NaOH}\) solution) is commonly used in the liquid-phase pillization in previous methods. \(^{16-19,22}\) The thermogravimetric analysis (TGA) (Figure S8) shows that M-MFI(P) contains \(\sim 16\% \text{H}_2\text{O}\), which closely corresponds to the water amount required for complete hydrolysis of TEOS in the intercalation step (calculation details see Section S2.3). This is consistent with the fact that the pillared structure was unable to form when the M-MFI(P) sample was dried in a vacuum oven at 393 \(\text{K}\) for 12 h (absence of low-angle XRD peaks in Figure S9).

The zero water addition in the VPP process suggests an option to further simplify the zeolite pillization protocol. In this case, we eliminated the TEOS hydrolysis step and integrated TEOS intercalation and zeolite calcination steps into one apparatus to realize a one-time operation for the synthesis of PMFI zeolite. In the new VPP protocol, the apparatus contains a furnace containing a quartz “U”-shaped tube (Figure 3, for details refer to Section S1.3). The 2D layered zeolite is added into the “bulb” region of the quartz tube from...
one opening, while liquid alkoxide solvent is dropped from the other opening. A quartz frit isolates the 2D layered zeolite from direct contact with alkoxide liquid before the VPP process starts. After operating the furnace according to the temperature profile shown in Figure 3, PMFI (confirmed by XRD (Figure S10) and N2 isotherm (Figure S11) in the Supporting Information) was formed along with complete TEOS consumption. Therefore, the entire VPP process only requires a single apparatus and one-time operation and does not require further separation for product recovery or generate liquid waste; this process can achieve ~100% efficiency in zeolite and TEOS utilization for the formation of pillared zeolite.

The composition, acidity, and catalytic performance of PMFI synthesized from the VPP process was characterized. The silicon (Si) and aluminum (Al) contents of PMFI are nearly identical to those calculated using M-MFI(P) and TEOS quantities, assuming all TEOS was consumed during the transformation into SiO2 pillars (Table S2). This confirms the complete consumption of alkoxide liquid in the VPP process, which is consistent with visual observation. FTIR spectra of the OH-stretching mode (\(\nu(OH)\)) and adsorbed pyridine in PMFI and M-MFI (Figure 4a,b) were recorded to understand their acidity properties. In Figure 4a, three peaks centered around 3739, 3674, and 3614 cm\(^{-1}\) are associated with terminal silanol (Si–OH) groups, extra-framework Al–OH species, and Bronsted acid site (Si–O(H)–Al) groups,\(^{36–38}\) respectively, on both M-MFI and PMFI. Both samples showed comparable characteristic peaks for Bronsted (1545 cm\(^{-1}\)) and Lewis (1450 cm\(^{-1}\)) acid sites\(^{36,38,39}\) in the FTIR spectra of adsorbed pyridine (Figure 4b). These results indicate acidity properties of the 2D zeolites were not destroyed during the VPP process. Solid state NMR (Figure 4c) was employed to investigate the local bonding environment of Si and Al species in the PMFI zeolite by recording the \(^{29}\)Si single pulse (SP) and \(^{27}\)Al NMR spectra. In the top panel, the peak (–113 ppm) corresponding to the crystallographically nonequivalent \(Q^1\) tetrahedral sites (\(Q^1\) stands for \(X_4=Si-\{OSi\}_3\))\(^{34,40,42}\) is much stronger than that of \(Q^0\) sites (–103 ppm) arising from the silanol groups. In the bottom panel, the peak at 55 ppm is due to the tetrahedrally coordinated framework aluminum (\(Al_{TE}\)), whereas the peak around 0 ppm is due to an octahedral coordination typical of extra-framework Al (\(Al_{EF}\))\(^{19,31}\). The NMR spectrum of PMFI prepared via the VPP process is similar to that of M-MFI\(^{31}\) and PMFI synthesized by the liquid phase pillarization method.\(^{34}\) The catalytic conversion of benzyl alcohol in mesitylene, a reaction that requires mesoporosity in MFI to enable high activity,\(^{25,42–44}\) shows that PMFI had higher benzyl alcohol conversion than M-MFI and conventional MFI (Figure 4d; for experimental details, see Section S1.5), suggesting the successful formation of a pillared hierarchical zeolite structure for space-demanding catalytic reactions. The catalytic performance of PMFI prepared by the VPP process is comparable to that synthesized by the conventional liquid-phase pillarization approach (Figure S12).

In conclusion, we demonstrate that the pillarization of 2D layered zeolite can be accomplished by the VPP method that integrates three discrete operation steps (intercalation, hydrolysis, and calcination, typically practiced in zeolite pillaring) into a single operation using only one apparatus. The VPP protocol has ~100% efficiency in usage of alkoxide liquid as well as zeolite materials and does not generate liquid waste. The pillared zeolite prepared using the VPP process has preserved the structural integrity (both framework crystallinity and ordering of zeolitic nanosheet layers), acidity, and catalytic performance of the zeolite framework in comparison to 2D zeolite prepared using direct calcination. The VPP process is scalable, easy to operate, remarkably simple, and highly efficient compared to the previous liquid-phase pillarization method, which could pave a new avenue toward pillaring additional 2D zeolites and new types of layered materials.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b03479.

Experimental details for synthesis and characterization of M-MFI(P), M-MFI and PMFI; catalyst preparation for catalysis study and details in catalysis tests; additional XRD and N\(_2\) isotherm and TGA analyses (PDF)
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

L.W. and K.S. are thankful for fellowship support from the China Scholarship Council. This work was supported by the U.S. National Science Foundation (CBET-1706059). This work was supported as part of the Catalysis Center for Energy Innovation, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award No. DE-SC0001004. The authors acknowledge the support of the Maryland NanoCenter and its NispLab. The NispLab is supported in part by the NSF with a method of preparing a pillared layered oxide material (Mobil Oil Corporation). WO Patent 92/01935, 1992.


