Journal of Undergraduate Chemistry Research, **2020**,19(2), 6

EFFECT OF SYNTHESIS PARAMETERS ON TMA$^+$-FREE MICROPOROUS VANADOSILICATE AM-6

Joie Ann Mastandrea[*], Bianca Boschetti[*], Kayla Kilduff[*], Mariam N. Ismail[†]

Chemistry and Physics Department, Simmons University, Boston, MA 02116

Abstract

Hydrothermal synthesis of tetramethylammonium cation (TMA$^+$)-free vanadosilicate AM-6 was carried out with molar composition of $1.44Na_2O : 0.20K_2O : ySiO_2 : 0.10V_2O_5 : zH_20 : 0.35F$; where y = 1.1-2.2, and z = 35-250 w at 503 K and 473 K. Low Si content and high H_2O content resulted in larger crystals with accompanied quartz impurities. Synthesis with y = 2.2 and z = 35 at 473 K resulted in pure, nano-sized AM-6 products. This was evidenced by both XRD and SEM analyses. UV-Vis spectroscopic analysis of the pure product showed the typical broard absorption in the 200 - 350 nm region, as well as the visible light absorption features around 400 nm and 595 nm, indicative of AM-6.

[†]*Corresponding author*: ismailm@simmons.edu
Key words: AM-6; vanadosilicate; photocatalyst; hydrothermal synthesis; visible light

Introduction

The shortage of clean water is arguably one of the biggest challenges facing the world today. With an estimated one in nine people worldwide not having access to safe and sanitary drinking water, it is paramount that methods for water purification are developed to ease this burden on society.[1] Photocatalysis is one means for water purification that is both cost-effective and environmentally friendly.[2] A semiconductor photocatalyst absorbs light to excite an electron from its valence band to conduction band, generating electron-hole (e^--h^+) pairs. These e^--h^+ pairs partake in a series of oxidation and reduction reactions which allow for purification of water streams.

Vanadosilicate AM-6 is a microporous zeolite-type crystalline material that is of particular interest due to its photocatalytic activity in the visible light range which has been attributed to the well-defined monoatomic …V-O-V-O-V… chains.[3,4] It has been previously synthesized using various methods[5-8] since it was discovered over two decades ago. AM-6 was first synthesized using ETS-10 seeds.[4] However, this synthesis approach was problematic because it hindered the ability to alter crystal characteristics without affecting product purity (i.e., Ti content from use of ETS-10 seeds). The first unseeded AM-6 was synthesized using tetramethylammonium cations (TMA$^+$) as a structure-directing agent.[3] However, the TMA$^+$ cations blocked the silica channels within the AM-6, thus hindering the crystal's ability for advanced photocatalytic applications, such as shape-selective photocatalysis. This led to the need for a synthesis method for AM-6 that did not require ETS-10 seeds or structure-directing agents such as TMA$^+$ ions. The synthesis of pure AM-6 without the use of seeds or pore-blocking structure-directing agents was achieved by using F$^-$ anions in the synthesis mixture.[6,9] However, the effects of crystallization parameters such as temperature, Si content, and water content have not been previously explored. Thus, here we report the investigation of crystallization parameters on the synthesis of TMA$^+$-free AM-6 crystals.

Experimental

Synthesis

Vanadosilicate AM-6 crystals were synthesized hydrothermally under static conditions at 503 K using mixtures of $1.44Na_2O : 0.20K_2O : ySiO_2 : 0.10V_2O_5 : zH_2O : 0.35F$; where y = 1.1-2.2, and z = 35-250 were explored. The following chemicals were used without any further purification: sodium chloride (NaCl, Sigma Aldrich), potassium chloride (KCl, Sigma Aldrich), sodium fluoride (NaF, 99+%, Fisher Scientifics), sodium hydroxide (NaOH, 98 %, Sigma Aldrich), N-Brand sodium silicate (28.59 % SiO_2, 8.88 % Na_2O, PQ Corporation), and vanadyl (IV) sulfate hydrate ($VOSO_4 \cdot 5H_2O$, Sigma Aldrich).

A typical synthesis mixture with y = 2.2, and z = 35 required 1.065 g NaCl, 0.725 g KCl, 0.365 g NaF, and 0.125 g NaOH for solution A. After dissolving these components in 3.75 g DI water, 12.665 g N-Brand was added and hand shaken until the solution appeared transparent. Solution B was prepared by dissolving 1.415 g of $VOSO_4 \cdot 5H_2O$ in 3.75 g DI water. Solution A was added to solution B resulting in a gel, which was hand shaken for 15 min. After measuring the pH, the gel was transferred to 10 mL Teflon-lined stainless steel autoclaves and placed in an oven for hydrothermal synthesis. After predetermined times (2 days at 473 K for the synthesis described above), the autoclaves were removed from the oven and quench cooled. The products were washed and filtered with 1 L of DI water, and dried in air at 343 K.

Characterization

X-ray powder diffraction (XRD) patterns were collected on a Philips PW1729 X-ray Powder Diffractometer with a Cu Kα source (30 kV, 35 mA) to determine product purity. A JEOL JSM-5510LV scanning electron microscope (SEM) was used to determine product purity, crystal morphology and size. An accelerating voltage of 3kV and working distance of 8-10 mm using secondary electron imaging mode were used. Diffuse reflectance UV-vis (DR-UV-vis) spectroscopy was performed using a Cary 5000 UV-vis-NIR spectrometer equipped with a Praying Mantis accessory. Powder Spectralon™ standard was used

as the reference. The measurements were taken in ambient air in the appropriate wavelength range with a bandwidth of 1.0 nm.

Results and Discussion

It is well known that synthesis parameters such as Si content, H_2O content, pH, and crystallization temperature affect the development, size and purity of zeolite-type products.[3,8,10] Thus, effects of Na_2O, SiO_2, and H_2O contents as well as pH on the synthesis of AM-6 were investigated. Individual parameters were varied while holding all other parameters constant in order to investigate the effect of each parameter fully on the crystallization and growth of the AM-6 products.

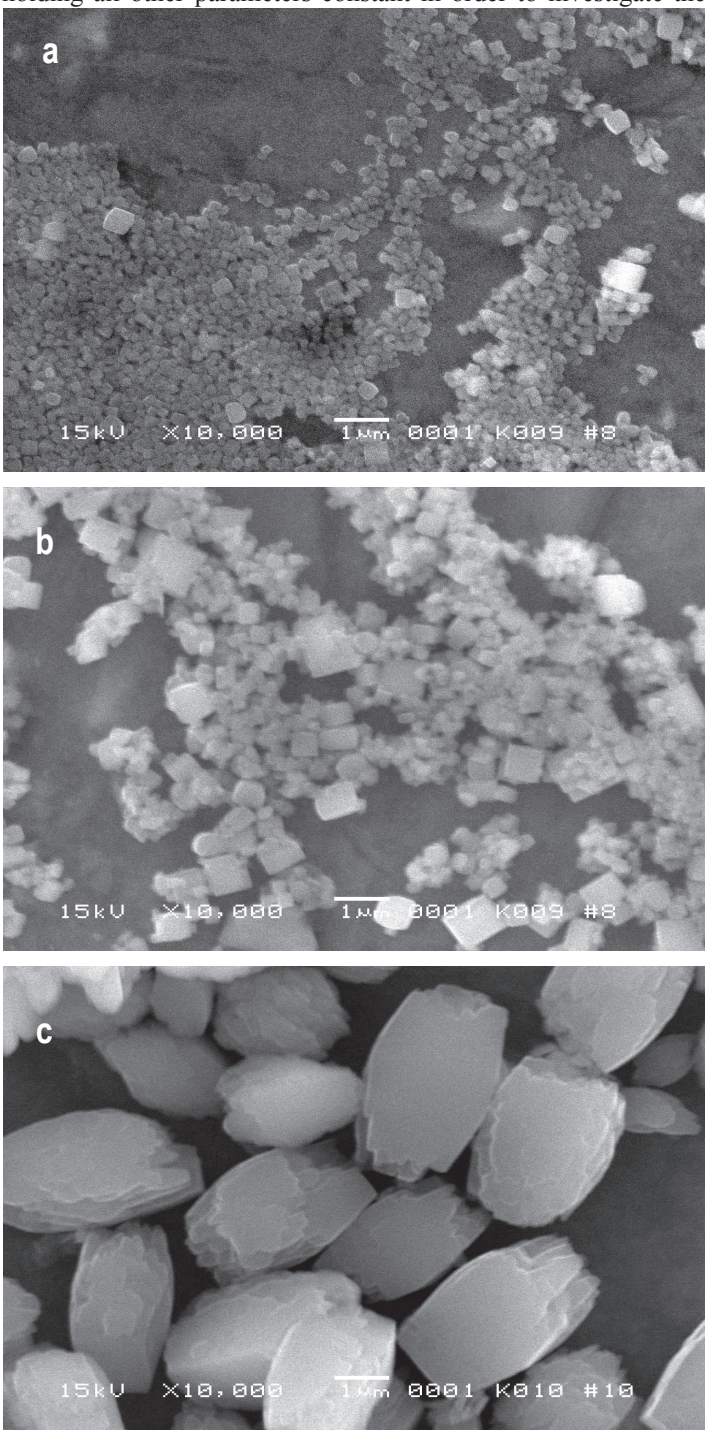


Figure 1. SEM images of AM-6 products synthesized at 503 K for 3 days from mixtures with molar compositions $1.44Na_2O : 0.19K_2O : ySiO_2 : 0.11V_2O_5 : 195H_2O : 0.34F$: (a) y = 2.2, pH = 10.93; (b) y = 1.65, pH = 10.67; (c) y = 1.1, pH = 10.20.

The effect of the Si content was investigated by varying the SiO_2 content in the synthesis mixtures molar composition from y = 1.1 to 2.2. At 503 K, these synthesis mixtures resulted in AM-6 products with varying degrees of size and purity. The decrease in y from 2.2 to 1.1 resulted in an increase in the average particle size from 0.15 μm to 3.5 μm (Figure 1). The larger average particle size suggests lower nucleation rates for AM-6 with decreasing Si content, and thus lower supersaturation levels. This is consistent with prior findings.[5] Products synthesized at 503 K all exhibited quartz impurity as shown by XRD (Figure 2). However, the presence of quartz appeared to be less in products synthesized with lower Si content (Figure 2). This was evident by the relative intensities of the peaks at ~ 25 °2θ and ~ 26.8 °2θ, corresponding AM-6 and quartz, respectively. Since, smaller crystals are generally more desirable for photocatalysis due to larger surface area,[12] it was necessary to find a way to reduce the quartz impurities for products obtained with y = 2.2 (Figure 1a) while maintaining a small crystal size. Additionally, it was found that the natural pH of these synthesis gels ranged from 10.20 to 10.93. Thus, it was critical to investigate the effect of pH on product purity using synthesis mixtures with y = 2.2.

The pH of the synthesis gel is known to play a crucial role in zeolite formation due to the mineralizing role of the OH^- anion with respect to the polymerization of the silicate species in the gel. In order to investigate the effect of pH on the formation of AM-6 products, the pH values of the synthesis gels were modified between ~ 10.2 and ~ 10.9 using 12 M HCl solution for syntheses with molar composition $1.44Na_2O : 0.20K_2O : 2.2SiO_2 : 0.09V_2O_5 : 195H_2O : 0.35F$. At pH = 10.22, XRD showed an increase in the quartz peaks (Figure 3b) compared to the standard pH of 10.93 (Figure 3a). These observations disagree with what is known about the role of OH^- anions in zeolite synthesis. Thus, it is speculated that the amount of water was drastically increased when the pH of the system was modified to 10.22 since ~ 43 drops of 12 M HCl were used. There was no effect of pH on the size of the crystals formed as observed through SEM analysis (not shown here).

The effect of water content on the formation of AM-6 was investigated for the system with molar composition $1.44Na_2O$:

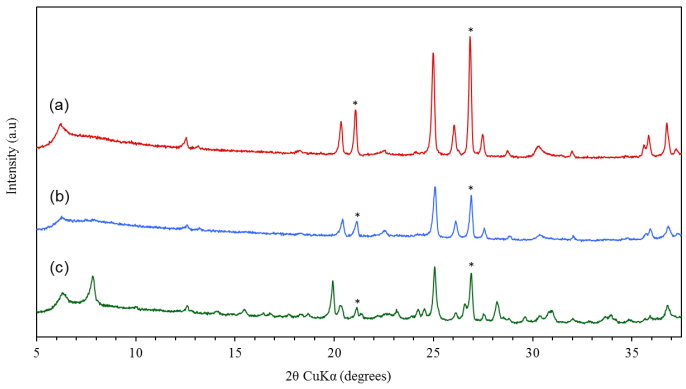


Figure 2. XRD patterns of AM-6 products synthesized at 503 K from mixtures with molar compositions $1.44Na_2O : 0.19K_2O : ySiO_2 : 0.11V_2O_5 : 195H_2O : 0.34F$: (a) y = 2.2; (b) y = 1.65; (c) y = 1.1. * indicates quartz phase.

$0.20K_2O : 2.2SiO_2 : 0.09V_2O_5 : zH_2O : 0.35F$, where z was varied from 195 to 250, at 503 K for 3 days. The XRD patterns of the synthesized products showed an increase in the presence of quartz as observed through the intense quartz peaks with increasing water content (Figure 4). The increase in water content also resulted in a slight increase in crystal size as observed from SEM analysis (Figure 5). This is likely attributed to the suppression of the two-dimensional nucleation rate of AM-6 and a decrease in the supersaturation levels.[3,11] Thus, further lowering of water content should lead to smaller crystals with improved overall product purity.

Crystallization temperature is another means to control growth rate and thus potentially improve product purity. Thus, synthesis using molar composition of $1.44N_2O : 0.20K_2O : 2.2SiO_2 : 0.10V_2O_5 : 35H_2O : 0.34F$ was carried out at lower crystallization temperature (i.e., 473 K) and significantly lower water content in an effort to synthesize highly pure AM-6 products with submicron size distribution. The pH of the resulting synthesis gel was measured to be ~ 11.0; which is within the ideal pH range (~10.8 to ~11.0) for AM-6.[5] XRD patterns of products synthesized at 473 K (Figure 6a) showed highly pure AM-6 product. These results were consistent with the SEM analysis (Figure 6b) showing no quartz impurity, and crystals of 100-200 nm in size. Therefore, it appears that lower water content and lower crystallization temperature suppressed the nucleation of quartz impurities and promoted the two-dimensional nucleation and growth of AM-6 crystals.

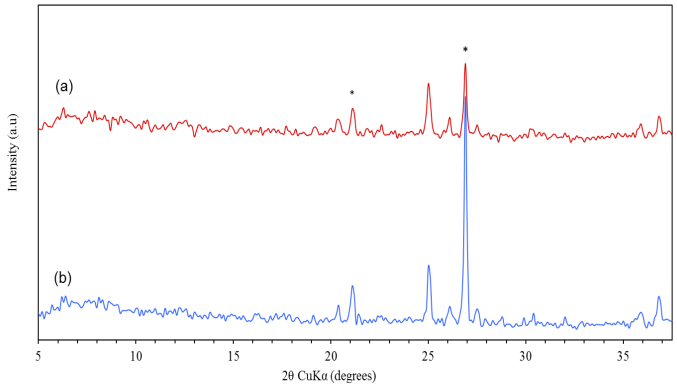


Figure 3. XRD patterns of AM-6 products synthesized at 503 K from mixtures with molar compositions $1.44Na_2O : 0.19K_2O : 2.2SiO_2 : 0.11V_2O_5 : 195H_2O : 0.34F$ with different initial pH values: (a) pH = 10.93; (b) pH = 10.22. * indicates quartz phase.

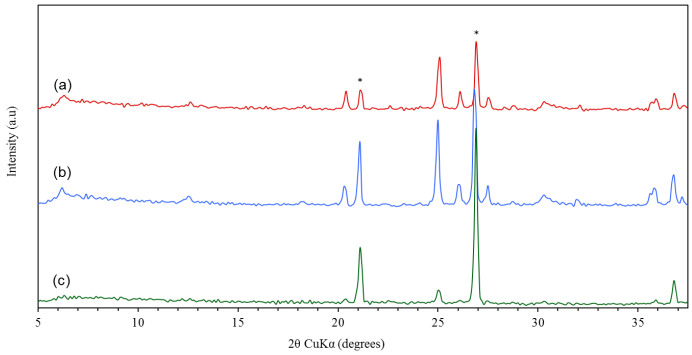


Figure 4. XRD patterns of AM-6 products synthesized at 503 K from mixtures with molar compositions $1.44Na_2O : 0.19K_2O : 2.2SiO_2 : 0.11V_2O_5 : zH_2O : 0.34F$: (a) z = 195; (b) z = 220; (c) z = 250. * indicates quartz phase.

Diffuse reflectance UV-Vis spectroscopy of the pure vanadosilicate AM-6 product (Figure 7) showed the typical broad absorption in the 200-350 nm region attributed to the O(2p) → V(3d) charge-transfer transition.[13,14] In addition to these UV-region features, two absorption features in the visible light region were also observed. The feature between 400 nm and 500 nm has been attributed to the $O^{2-} \rightarrow V^{5+}$ charge-transfer in distorted octahedral V^{5+};[14] whereas the feature centered around 595 nm has been attributed to metal-to-metal transitions of distorted octahedral V^{4+}.[15,16] These results suggest two different oxidation states for

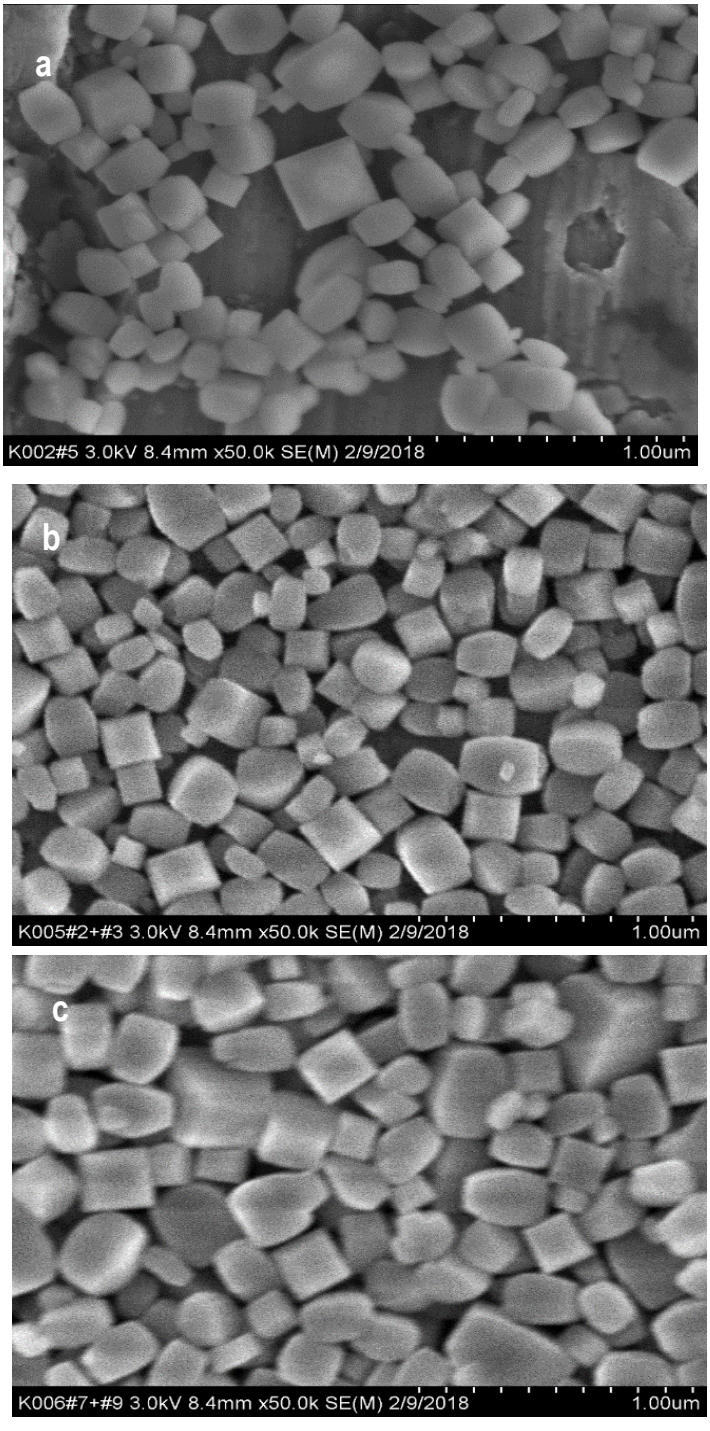


Figure 5. SEM images of AM-6 products synthesized at 503 K from mixtures with molar compositions $1.44Na_2O : 0.19K_2O : 2.2SiO_2 : 0.11V_2O5 : zH_2O : 0.34F$: (a) z = 195; (b) z = 220, (c) z = 250.

vanadium in AM-6 synthesized in the absence of seeds and TMA^+ cations.

Conclusions

Effect of synthesis parameters on the crystallization of TMA^+-free vanadosilicate AM-6 products were explored. Highly pure, submicron-sized AM-6 crystals were obtained using molar compositions with low water content and low crystallization temperature. It was found that an ideal pH of ~ 10.8-11.0 was necessary for crystallization of highly pure products. Increase in water content resulted in an increase in crystal size and quartz impurities. Low Si content resulted large in AM-6 crystals compared to high Si content. Thus, this study shows the narrow range in which TMA^+-free AM-6 can be synthesized for potential use in photocatalytic applications.

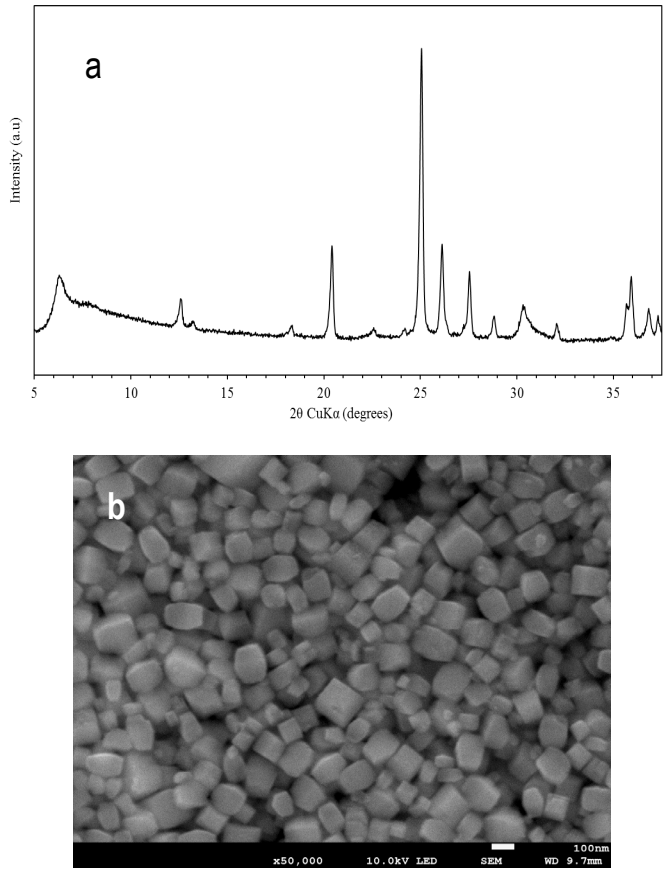


Figure 6. (a) XRD patterns and (b) SEM images of AM-6 products synthesized at 473 K for 2 days from mixtures with molar composition $1.44Na_2O : 0.19K_2O : 2.2SiO_2 : 0.11V_2O_5 : 35H_2O : 0.34F$.

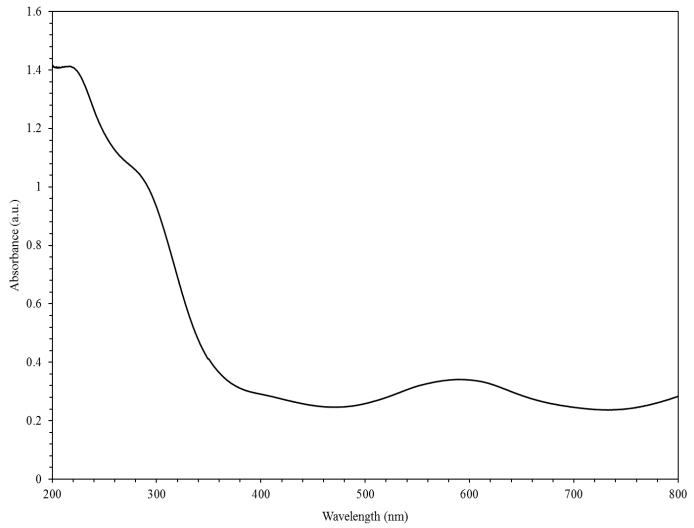


Figure 7. Diffuse reflectance UV-vis spectra AM-6 products synthesized at 473 K for 2 days from mixtures with molar composition $1.44Na_2O : 0.19K_2O : 2.2SiO_2 : 0.11V_2O_5 : 35H_2O : 0.34F$.

Acknowledgements

The authors thank Simmons University Student Research Fund and the Summer Undergraduate Research Program at Simmons (SURPASs) for funding this work. The authors also thank Vicente Franzin for machining the autoclaves used in this synthesis.

References

1.https://thewaterproject.org/water-scarcity/water_stats.

2. Mills, A.; Hunte, S.L. *J. Photochem. Photobiol. A: Chemistry*, **1997**, 108, 1-35.

3. Ismail, M.N.; Warzywoda, J.; Tekin, R.; Sacco, A. Jr. J. *Photochem. Photobiol. A: Chemistry*, **2018**, 353, 206-214.

4. Kuzyaka, D.; Galioglu, S.; Altin, I.; Sökmen, M.; Akata, B. *J. Photochem. Photobiol. A: Chemistry*, **2018**, 366, 127-135.

5. Ismail, M.N.; Fraiman, N.D.; Callahan, D.M.; Gursoy, G.; Viveiros, E.; Ozkanat, O.; Ji. Z.; Willey, R.J.; Warzywoda, J.; Sacco, A. Jr. *Micropor. Mesopor. Mater.*, **2009**, 120, 454-459.

6. Rocha, J.; Brandao, P.; Lin, Z.; Anderson, M.W.; Alfredsson, V.; Terasaki, O. *Angew. Chem. Int. Ed.*, **1997**, 36, 100-102.

7. Datta, S.J.; Yoon, K.B. *Angew. Chem. Int. Ed.,* **2010**, 49, 4971-4975.

8. Mani, F.; Wu, L.; Kuznicki, S.M. *Micropor. Mesopor. Mater.*, **2013**, 177, 91-96.

9. Tekin, R.; Warzywoda, J.; Sacco, A. Jr. *Micropor. Mesopor. Mater*., **2017**, 251, 94-104.

10. Lv, L.; Su, F.; Zhao, X.S. *Micropor. Mesopor. Mater.* **2004**, 76, 113-122.

11. Ji, Z.; Warzywoda, J.; Sacco, A. Jr. *Micropor. Mesopor. Mater.,* **2008**, 109, 1-11.

12. Dodd, A.C.; McKinley, A.J.; Saunders, M.; Tsuzuki, T. J. *Nanopart. Res.*, **2006**, 8, 43-51.

13. Shough, A.M.; Lobo, R.F.; Doren, D.J. *Phys. Chem. Chem. Phys*., **2007**, 9, 5096-5104.

14. Nash, M. J.; Rykov, S.; Lobo, R.F.; Doren, D.J.; Wachs, I. *J. Phys. Chem. C*, **2007**, 111, 7029-7037.

15. Catana, G.; Rao, R.R.; Weckhuysen, B.M.; Van Der Voort, P.; Vansant, E.; Schoonheydt, R.A. *J. Phys. Chem. B*, **1998**, 102, 8005-8012.

16. Morey, M.; Davidson, A.; Eckert, H.; Stucky, G. *Chem. Mater*., **1996**, 8, 486-492.