A novel synthesis of Zeolite W using organometallic precursors

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Abstract

Zeolite W has been synthesized using organometallic silicon and aluminum precursors in two hydrothermal systems: organocation containing and organocation-free. The reaction using the organocation yielded a fully crystalline, relatively uniform crystal size product, with no organic molecules occluded in the pores. In contrast, the product obtained from an identical reaction, except for the absence of the organocation, contained amorphous as well as crystalline material and the crystalline phase showed a large diversity of both crystal size and morphology. The use of organometallic precursors, either with or without an organocation, allows for the crystallization of the MER framework at much lower OH/SiO_2 and (K + Na – Al)/Si ratios than is typical of inorganic systems. The reaction products were characterized by XRD, SEM, EDS, and thermal analyses.

Keywords: Zeolite-W; Merlinoite; MER framework; Synthesis; Organocation template.

1. Introduction

Crystal product morphology in the inorganic Na_2O-K_2O-Al_2O_3-SiO_2-H_2O system has been found to be a function of the precursor ratios, precursor form, and synthesis temperature [1-5]. The phase relationships in this system have been explored to the extent that it is possible to predict the product morphology *a priori* for a given set of reagents and reaction conditions [1-3]. The reason for this is

largely that the form and relative concentrations of the precursors determine the system pH and hence the relative solubilities of the feedstock, which influences the product obtained [4]. Thus, in the wholly inorganic system the OH/SiO_2 ratio and the 'excess alkalinity' [3], (K + Na – Al)/Si, largely dictate the product obtained for a given temperature.

Bieniok, et al., [3] found that in order to crystallize MER the excess alkalinity had to be greater than 1.4 otherwise LTL zeolite was obtained (at OH/SiO_2 ~1.4). Quirin, et al., [4] were able to crystallize MER phase with the excess alkalinity as low as 0.8 and an OH/SiO_2 ratio of 0.87 by the addition of an organocation and using potassium exchanged Zeolite Y as the Al source in the reaction solution. Belhekar, et al., [5] were able to crystallize pure MER with an excess alkalinity near 0.6 by introduction of small amounts of Sr^{2+} cations, but at the elevated OH/SiO_2 ratio of 5.

In this paper we report the first synthesis of a pure form of Zeolite W, $1.2K_2O$-Al_2O_3-$8.5SiO_2$, using organometallic silicon and aluminum precursors. The reaction system had an excess alkalinity of 0.8 and an OH/SiO_2 ratio of 1.0. Zeolite W was obtained from two reaction solutions, one containing an organocation (1,6-diaminohexane) and the other organocation-free. The results of the subsequent characterization are used to evaluate the role of the organocation in this system.

2. Experimental

2.1 Synthesis

Two solutions, A and B were prepared. Solution A consisted of 13.1 g distilled water to which 0.296 g of potassium hydroxide (99.99% Aldrich) and 0.636 g of 1,6-diaminohexane (99.5+% Acros) were dissolved, respectively, with stirring. Solution B consisted of 0.098 g of aluminum tri-sec-butoxide (98+% Gelest) and 0.804 g of tetramethyl orthosilicate (99+% Aldrich) dissolved respectively in 1 g of 2-propanol (99.9% Fisher) with stirring. After preparing both solutions, solution A was added to solution B dropwise, with vigorous stirring. The dilute white suspension was placed into a 23 ml teflon lined steel autoclave and placed in a 165° C oven with mixing for 48 hours. The product was recovered by vacuum filtration, washed twice with de-ionized water, and allowed to dry at room temperature.

Synthesis of the sample without the organocation was identical except that no 1,6-diaminohexane was added to solution A. The ratio of precursors in the starting solutions are given in Table 1.

2.2 Characterization

Powder X-Ray diffraction (XRD) data were taken with Cu-Kα radiation on a Siemens D500 diffractometer. Elemental composition was determined via electron dispersive spectroscopy (EDS) using a JEOL T300 scanning electron microscope (SEM) and Iridium (IXRF Systems) software. SEM images were taken using the same system. Thermal analysis was performed using a TA Instruments SDT 2960 simultaneous Thermo Gravimetric Analyzer – Differental Thermal Analyzer (TGA-DTA).

3. Results

3.1 Zeolite Synthesized With Organocation

The recovered product is entirely crystalline and had a product yield of 8.5 percent based upon total possible conversion to the oxides K_2O, Al_2O_3, and SiO_2. The X-ray powder diffraction pattern is shown in Figure 1a, and d-spacing versus relative intensity data given in Table 2. This pattern deviates slightly from those given for natural merlinoite as well as from synthetic Zeolite W [1,2], however the XRD pattern matches very closely with that presented by Quirin, et al., [4] for Zeolite W synthesized in the presence of an organocation. The crystalline product shows two distinct morphologies (see Figure 2a & 2b). Rods very similar to those obtained by Quirin, et al., [4] as well as 'block' crystallites of a slightly smaller size. The blocks and rods appear similar except that the rods are elongated along one axis. The product is comprised of a network of slightly inter-grown crystals, consisting of roughly equivalent amounts of rods and blocks. Both morphologies occurr in large areas consisting of primarily either rods or blocks, and these areas are segregated by smaller regions containing roughly equivalent amounts of each.

The TGA data indicates that the zeolite contains 12.5 weight percent water, and the DTA data has the three distinct endothermic peaks associated with the loss of this water between 20 and 300 °C [3,5]. There are no TGA or DTA peaks between 300 and 800 °C. Elemental analysis was performed by EDS on ten separate areas. There are minor variations which were independent of

morphology, and the averaged results suggest the composition $1.2K_2O$-Al_2O_3-$8.5SiO_2$.

3.2 Zeolite Synthesized Without Organocation

The sample synthesized without the organocation has a product yield of 17.0 percent based upon total possible conversion to the oxides K_2O, Al_2O_3, and SiO_2. Although Zeolite W is the only crystal phase obtained, the powder diffraction pattern (Figure 1b), as well as SEM analysis (Figure 2c), indicate the presence of amorphous material.

SEM analysis also shows that the morphology of the crystalline phase is different than that obtained in the presence of the organocation (Figures 2c & 2d). The 'wheatsheaf' [4] morphology is prevalent here, though some rods and blocks are also present. The size range and relative amounts of the various crystalline morphologies varied considerably throughout the sample.

4. Discussion

Zeolite W typically has a water content of 15.5 to 15.7 weight percent and loses this water in two to three distinct stages between 50 and 300 °C [3,5]. Because the 12.5 weight percent loss in our sample also occurred in three stages we attribute it to the loss occluded water molecules. The lack of TGA-DTA data to indicate the occlusion of organocations indicates that these molecules are not acting as structure directing agents or framework charge balancing cations.

However, the organocation participates in the solution chemistry as is seen from comparison of the SEM and XRD analysis of the two samples.

The wide variation of crystal size in the non-organocation derived Zeolite-W may be explained by a series of nucleation and growth events. The subsequent changes in solution pH and precursor concentration between nucleation events (or precipitation in the case of the amorphous material) might explain the diverse morphology found in this sample. Yet, the slight difference in pH between the organocation containing and the organocation-free system, 12.45 versus 12.30, alone is insufficient to account for the morphological differences between the two systems. Therefor the morphological differences are due to the presence of the organocation. We speculate that the organocation isolates the $HSiO_3^-$ species in the reaction solution, delaying nucleation events and leading to the more uniform morphology and crystal size observed in the organocation containing system. Further studies to elucidate this phenomena are currently underway.

5. Conclusions

Pure MER phase zeolites may be synthesized outside of the phase regimes generally associated with purely inorganic systems via the use of organometallic precursors reactants. Addition of an organocation aids in the synthesis of uniform size and morphology crystals within this system, by moderating nucleation and growth episodes. The organocation can be selected such that it does not occlude in the zeolite pores.

Acknowledgements

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Figure Captions

Figure 1. X-ray powder diffraction patterns of Zeolite W synthesized (A) with organocation and (B) without organocation.

Figure 2. (a) and (b) SEM view of zeolite synthesized with organocation. (c) and (d) SEM view of zeolite synthesized without organocation.

Table 1

Initial conditions for precursor solutions

parameter	value
SiO_2/Al_2O_3	26.5
OH/SiO_2	1
H_2O/SiO_2	137
organocation/SiO_2 (sample with organocation only)	1
K/SiO_2	1
(K + Na – Al)/Si	0.8
pH (without organocation)	12.30
pH (with organocation)	12.45

Table 2

d-spacing and relative intensity for XRD pattern shown in Fig. 1a, Zeolite W synthesized with organocation

d	I/I_o
8.16	39
7.08	73
5.33	41
4.97	38
4.46	12
4.25	21
4.06	27
3.64	17
3.41	9
3.22	63
3.15	100
2.92	52
2.71	28
2.66	21
2.53	14
2.49	7
2.35	8
1.95	6
1.76	7
1.70	8
1.65	8

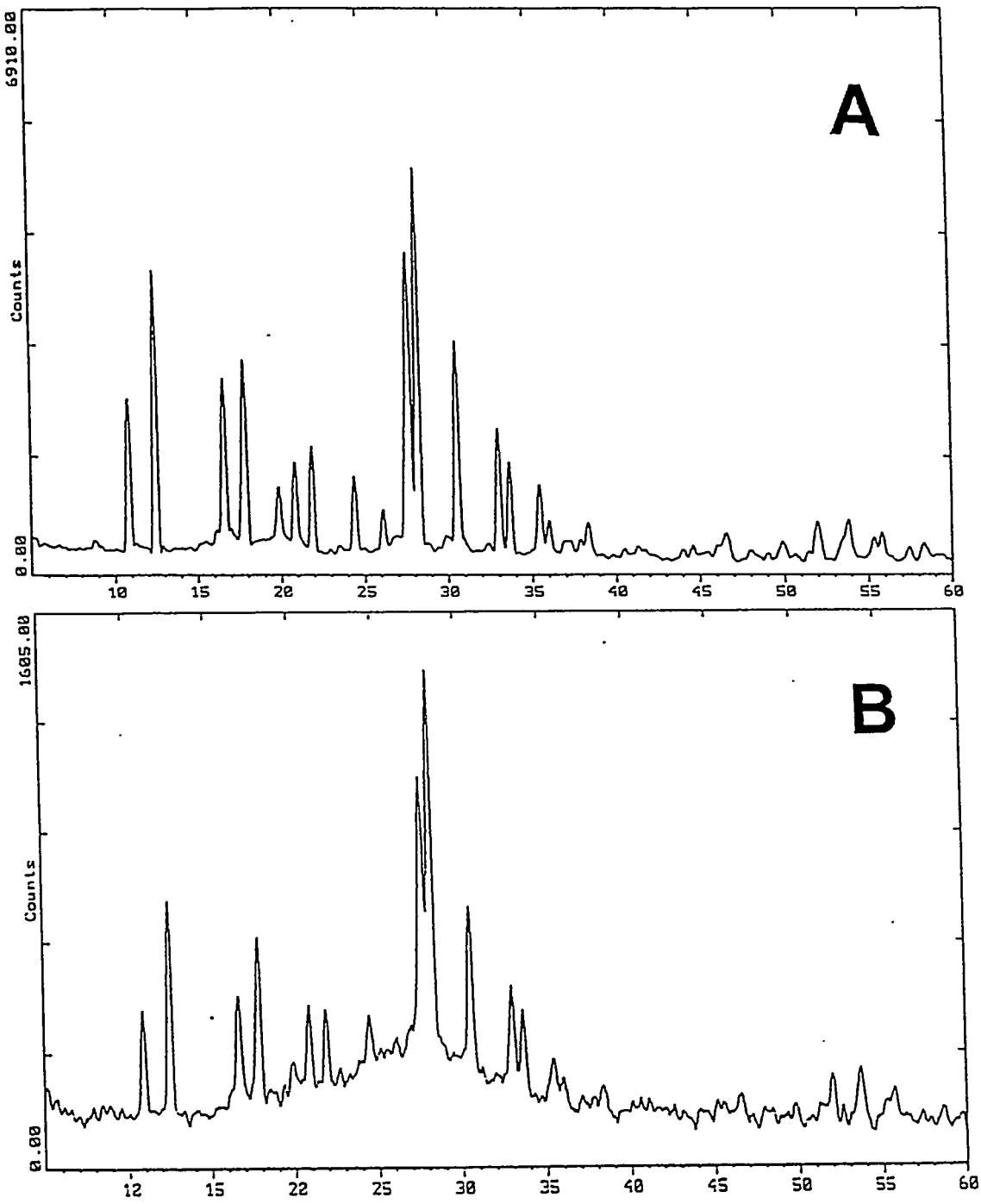
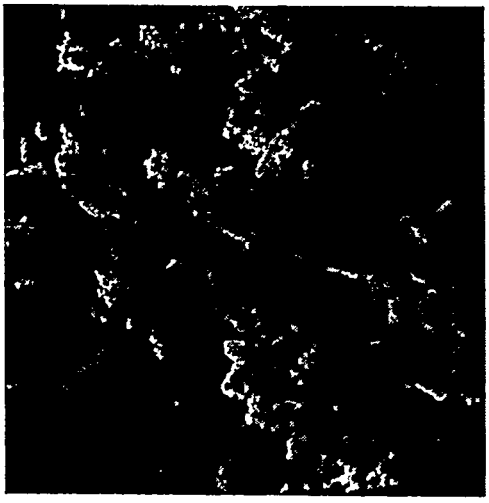


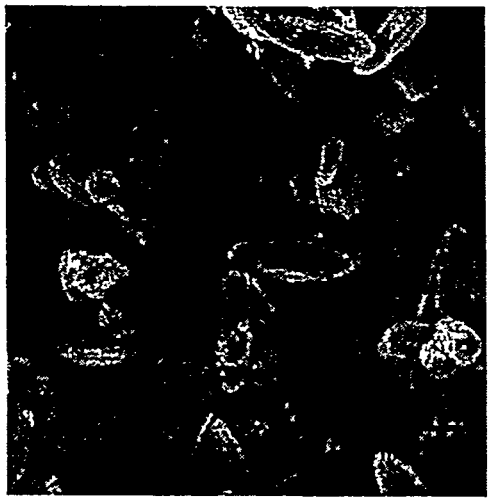
Fig. 1. X-ray powder diffraction patterns of Zeolite W synthesized (A) with organocation and (B) without organocation.

(a)

(b)



(c)



(d)

Fig 2. (a) and (b) SEM view of zeolite synthesized with organocation.
(c) and (d) SEM view of zeolite synthesized without organocation.