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A novel synthetic route to obtain RUB-15 phase by pseudo solid-state conversion

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ABSTRACT

The conventional method of zeolite synthesis consists of the hydrothermal treatment of a mixture of a silica source, structure-directing agent, water, and/or organic solvent. In this study, a simple physical mixture of a layered silicate (protonated magadiite) and solid tetramethylammonium pentahydrate (TMAOH.5H_2O) was treated in a Teflon-lined autoclave at 150 °C–170 °C for different periods of time. The protonated magadiite was completely transformed to RUB-15 after three days at 170 °C, the shortest time ever reported for this type of zeolite. By increasing the reaction time to five days, a different phase than RUB-15 was obtained and identified as PLS material. The conversion of the protonated magadiite depended on the amounts of water and TMAOH.5H_2O used. The addition of several drops of water to the mixture enhanced the formation of the PLS-1 phase within three days, and no RUB-15 was detected. These phases contain TMA cations in different environments, as supported by thermogravimetric analysis and ^{13}C solid state NMR. This method minimizes the use of water and the production of waste, in addition to reducing the reaction time compared to the conventional method.

1. Introduction

Hydrous layered silicates (HLS) have attracted much attention due to their diverse industrial uses in the production of catalysts, paints, ion exchangers, and other products [1–3]. The interlayer space of HLS can also be broadly modified to accommodate a number of organic and inorganic guests, keeping in some cases the crystallinity of the silicate framework. Layer silicates (kanemite, magadiite, octosilicate, etc.) are synthesized by the hydrothermal treatment of an aqueous gel of mixed SiO_2 sources and alkali metal hydroxides [4]. On the other hand, zeolitic layer silicates were synthesized using an organic structure directing agent (SDA), the same as used in zeolites. For instance, β-HLS and RUB-15 are prepared with tetramethylammonium (TMA), which is used as an SDA of sodalite (SOD) zeolite, and therefore they have a topology like SOD zeolite [5,6]. Layered zeolite precursors have attracted considerable attention due to their ability to transform to microporous materials via topotactic condensation by the removal of the organic spacers and the condensation of silanol groups [7,8]. However, it is also possible to modify this process. Precursor of ferrierite (PREFER) and related materials can be delaminated and re-assembled in a number of ways to give a series of high surface area derivatives with catalytically active sites accessible to bulky reactants, such as ITQ-2, ITQ-6, and ITQ-36 [9,10].

The use of layered silicates as starting materials for zeolite synthesis has attracted interest due to their intercalation and adsorption properties [11–13]. Na-kanemite was transformed to a HLS (helical layered silicate) phase when it was hydrothermally treated in a mixture of dioxane, tetramethylammonium hydroxide (TMAOH) solution and water at temperatures above 130 °C [14]. However, the same phase was also obtained without the presence of dioxane and water solution using a solid-state transformation (SST) technique in the presence of solid TMAOH.5H_2O as the directing agent, sealed in a glass tube, with shorter reaction times and at lower temperatures [15]. When another type of layered silicate, such as Na-magadiite, was reacted with TMAOH solution and water, a PLS-1 phase was achieved at 150 °C after three days [16]. The reaction with solid TMAOH.5H_2O at 150 °C in an autoclave has led to an unknown silica phase with good thermal stability up to 700 °C [17].

Here, we report the first exploration of the use of protonated magadiite (H-mag, where the Na cations were exchanged with

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protons in HCl solution) as a starting precursor and its conversion using solid $TMAOH.5H_2O$. The optimal conditions for the pseudo-solid-state conversion of H-mag were investigated. This method allowed us to obtain the RUB-15 phase without the use of water or organic solvents, even with a short reaction time of three days. When a few drops (200 μl) of water were added to a mixture of H-mag and $TMAOH.5H_2O$, the H-mag was converted to a different phase than RUB-15, identified as PLS-1. The obtained materials were fully characterized by multiple techniques. Our data indicates that the RUB-15 phase can be used as an intermediate phase to prepare PLS-1 material, and it is not stable at 500 °C against conversion to PLS-1.

2. Experimental

2.1. Materials

All of the chemicals were purchased from Sigma and were of analytical grade.

2.1.1. Preparation of Na-magadiite

Na-magadiite (Na-mag) was prepared by the reaction of NaOH and SiO_2 under hydrothermal conditions [18]. Solid NaOH (4.8 g) was dissolved in water (105 mL), and 16 g of Na-silicate was added. The gel was stirred for 1 h and was allowed to digest without stirring at 150 °C for 72 h in a Teflon-lined stainless autoclave placed in a static oven. The prepared Na-magadiite was filtrated, washed with deionized water several times, and air-dried at room temperature.

2.1.2. Preparation of H-magadiite

The protonic form of the prepared Na-magadiite (H-mag) was prepared by suspending 2 g of Na-magadiite in 100 mL of HCl solution (0.1 M) and stirring for 2 h at room temperature [18]. The solid was separated by filtration, washed several times with deionized water, and then dried in air at 40 °C. The yield of the product was 70%.

2.2. Conversion of H-magadiite

2.2.1. RUB-15 phase

In a typical conversion, 2.3 g $TMAOH.5H_2O$ was mixed with 1 g of dried H-mag, corresponding to a TMA/SiO_2 molar ratio of 1.25, in an agate mortar and was placed in a Teflon-lined autoclave at 170 °C for 72 h in a static oven. After the reaction, the autoclave was cooled to room temperature and the solid was collected by filtration, washed with water to eliminate the excess un-reacted $TMAOH.5H_2O$ and air-dried at 40 °C.

2.2.2. PLS-1 phase

1 g of dried H-mag was mixed with 2.3 g of $TMAOH.5H_2O$ and 0.5 mL of deionized water, corresponding to a $TMA/SiO_2/H_2O$ molar ratio of 1/1.25/4.40, in an agate mortar. The mixture was placed in a Teflon-lined autoclave at 170 °C for 72 h in a static oven. After the reaction, the autoclave was cooled to room temperature and the solid was collected by filtration, washed with water to eliminate the excess un-reacted $TMAOH.5H_2O$, and then air-dried at 40 °C.

The conversion parameters (temperature, reaction time, amounts of $TMAOH.5H_2O$ and water) were varied separately to study their effects on the H-mag conversion, and their values are presented in Table 1.

The calcination of the RUB-15 and PLS-1 products was conducted in air at 500 °C for 10 h at a heating rate of 3 °C/min. The samples were identified as RUB-15 (500) and PLS-1 (500), respectively.

Table 1
Chemical composition (molar ratios) of the reaction mixture in Teflon-lined autoclaves at different conditions.

Samples	TMA	SiO_2	H_2O	Temp.	Duration	Phases
Sample1	1	1.25	–	150	1 day	TMA-mag
Sample2	1	1.25	–	150	2 days	TMA-mag & RUB-15
Sample3	1	1.25	–	150	5 days	RUB-15
Sample4	1	1.25	–	150	7 days	RUB-15
Sample5	1	1.25	–	170	1 day	TMA-mag
Sample6	1	1.25	–	170	3 days	RUB-15
Sample7	1	1.25	–	170	5 days	Amorphous SiO_2
Sample8	1	1.25	0.087	150	5 days	RUB-15 & PLS-1
Sample9	1	1.25	2.20	150	5 days	PLS-1 + RUB-15
Sample10	1	1.25	4.40	150	5 days	PLS-1
Sample11	1	1.25	22.01	150	5 days	TMA-mag
Sample12	1	0.27	–	150	5 days	H-mag & TMA-mag
Sample13	1	0.81	–	150	5 days	PLS-1
Sample14	1	1.25	–	150	5 days	RUB-15
Sample15	1	2.72	–	150	5 days	Amorphous SiO_2

Temp. corresponds to temperature (°C). TMA-mag corresponds to intercalated magadiite with TMA cations.

2.3. Characterization

The products were characterized with different techniques. Powder X-ray diffraction (XRD) patterns were collected with a Bruker D8 Advance diffractometer equipped with Ni-filtered Cu-Kα radiation. Thermogravimetric analysis (TGA) was performed on a TA Instruments SDT2960 with an air flow of 100 mL min^{-1} and heating from 25 to 800 °C at a rate of 5 °C min^{-1}. ^{29}Si MAS (magic-angle spinning) NMR spectra were recorded on a Bruker ASX-400 spectrometer operating at a ^{29}Si NMR frequency of 78 MHz using a standard 4 mm probe and an 8.0 kHz sample rotation rate. In total, 30 scans were performed, with a recycle delay of 600 s. The ^{29}Si chemical shift is reported with respect to tetramethylsilane (TMS). ^{1}H–^{13}C cross-polarisation solid-state NMR (^{1}H–^{13}C CP/MAS) was conducted with a Bruker Advance DSX400 spectrometer operating at 400.16 MHz for ^{1}H and 100.56 MHz for ^{13}C with a MAS triple resonance probe head using 4-mm diameter zirconia rotors. The spinning rate was 4.0 kHz, the ^{1}H $\pi/2$ pulse length was 4.40 μs, and the pulse delay was 10.0 s ^{13}C chemical shifts are quoted in ppm with respect to TMS. ^{1}H MAS NMR spectra were acquired at a frequency of 400 Hz, using a pulse width of 10 μs and a pulse spacing of 5 s. The ^{1}H chemical shift is reported with respect to tetramethylsilane (TMS). The specific surface area (SSA) and total pore volume (TPV) of the examined samples were measured by nitrogen sorption using a Quantachrome Autosorb 6 instrument. Prior to analysis, the samples were degassed under vacuum at 120 °C overnight. The SSA values were estimated from the BET equation, and the TPV was calculated from the adsorbed amount at a relative pressure of $p/p_o = 0.95$. The micropore volume was deduced from the *t-plot* equation. The change of morphology in the products were examined by scanning electron microscopy (SEM) using a JEOL model JSM-6700F.

3. Results and discussion

3.1. XRD data

When a mixture of H-mag-$TMAOH.5H_2O$ was reacted at 130 °C for five days, no conversion occurred, and magadiite with intercalated TMA cations (TMA-mag) was obtained with a basal spacing of 1.91 nm. Fig. 1 presents the powder XRD patterns of H-mag treated with solid $TMAOH.5H_2O$ at 150 °C for different periods of time in closed Teflon-lined autoclaves. The powder XRD pattern of H-mag has a basal spacing of 1.21 nm, with broad reflections due to