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Research paper

Al–Mn-silicate nanobubbles phase as an intermediate in zeolite formation

Amal Bejar [a], Semy Ben Chaabene [a], Maguy Jaber [b], Jean-François Lambert [c], Latifa Bergaoui [a,d,*]

[a] Laboratory of Materials Chemistry and Catalysis, Faculty of Sciences of Tunis, El Manar University, Tunis, Tunisia
[b] Laboratoire d'Archéologie Moléculaire et Structurale, Sorbonne Universités UPMC Univ Paris 06 and CNRS UMR8220, Case courrier 225, 4 Place Jussieu, 75252 Paris CEDEX 05, France
[c] Laboratoire de Réactivité de Surface, Sorbonne Universités UPMC Univ Paris 06 and CNRS UMR 7197, Case courrier 178, 3 Rue Galilée, Ivry-sur-Seine, 94200 Paris, France
[d] Department of Biological and Chemical Engineering, National Institute of Applied Sciences and Technology, Carthage University, Tunis, Tunisia

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ABSTRACT

Manganese (II) carbonate, silicic acid and aluminum nitrate were treated hydrothermally at different temperatures (120–210°C) and for different durations (6–72 h) in an aqueous basic medium. Different compositions of starting mixtures were used. The synthetized materials were characterized by powder X-ray diffraction, FTIR-spectroscopy, N_2 adsorption analysis, Transmission Electron Microscopy (TEM), energy dispersive X-ray analysis (EDX), thermal analysis (TG-DTG), Temperature-programmed reduction (TPR), X-fluorescence, X-ray photoelectron spectroscopy (XPS), electronic paramagnetic resonance (EPR) and ^{29}Si and ^{27}Al MAS-NMR spectroscopy. The formation of kaolinite, smectite-like and Mn-containing lamellar phases was observed, but only in minor amounts contrary to previous studies. The majority phase was an original Al–Mn silicate with nanobubble-like morphology, a high surface area and mesoporosity, containing both Mn(IV) in lattice positions and Mn^{2+} as exchangeable cations. This amorphous Al–Mn-silicate nanobubbles phase seems to be an intermediate in a zeolite formation. Indeed, the increase of the reaction temperature, the reaction time or the reagent concentrations promoted the crystallization of a zeolite of the analcime type by transformation of the Al–Mn-silicate nanobubbles.

1. Introduction

Clay minerals have always been of great interest due to their attractive properties especially their high specific surface area and natural abundance. For these reasons, clays have been widely used to catalyze different reactions (Adams and McCabe, 2006; Patel et al., 2008; Pawar et al., 2009). Much work has been carried out to synthesize smectites, chlorites, or kaolinites in hydrothermal conditions (Jaber et al., 2013). The major advantage of synthetic materials over natural is that it can be produced in high purity. Synthetic clay minerals may also offer improved specific properties (textural and structural properties) as compared to natural ones (Di et al., 2010); in addition, they provide the possibility to fine-tune the chemical composition of the clay network, introducing elements that are not present in great amounts in most natural clays. Thus, in the last few years, transition metal (Cu, Co, Zn and Mn)-rich clay minerals have attracted much interest to establish new specific catalytic applications (Di et al., 2010; Sivaiah et al., 2011). In addition, synthetic clays may offer many advantages: controlled composition, high active sites dispersion and better reproducibility of the properties. Recently, some researchers have been trying to improve the physicochemical properties of kaolinite by incorporating transition metals into its framework. Very few data exist on the synthesis of Mn-containing kaolinite. Komarneni's group has reported that it is possible to prepare Mn-kaolinite under hydrothermal conditions using as starting materials silicic acid, aluminum nitrate and Mn carbonate mixed with aqueous solutions of NaOH or KOH (Choi et al., 2009; Seliem et al., 2010). The synthesis was performed at 100–200°C for 24–96 h. The best result was found using the composition $3.83K_2O{:}0.08Al_2O_3{:}0.30MnO{:}0.43SiO_2{:}1380H_2O$. Based on XANES spectroscopy, these authors have reported that manganese is octahedrally coordinated and its oxidation state is (+III). Thus, they deduced that both Al and Mn lie in the octahedral sites. When attempting to reproduce these published syntheses using NaOH in smaller batches, the main reaction product was a zeolite of the analcime type, which is interesting in its own respect: the synthesis of analcime was reported in previous papers (Bejar et al., 2014; Bejar et al., 2015). When kaolinite is synthesized from amorphous aluminosilicate in alkaline solutions at temperatures between 175 and 230°C, unlike the Na^+ ions, the K^+ ions prevented the formation of zeolite (De Kimpe, 1976; De Kimpe and Rivard, 1981). The same phenomenon seems to take place even when manganese is present in the reactive media.

In this study, different experimental parameters (reaction temperature, reaction time and reactants concentrations) were modified with the aim to pinpoint the effect of each parameter on the formation of the final zeolite product and of the intermediate phases. A sample free

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* Corresponding author at: INSAT, Centre Urbain Nord, BP 676-1080 Tunis Cedex, Tunisia.

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of analcime was characterized by different techniques to identify intermediates and to elucidate the formation mechanisms.

2. Experimental

2.1. Hydrothermal synthesis

The synthesis procedure is based on the protocol proposed by Choi and al. (Choi et al., 2009). The starting materials were a mixture in aqueous solution of NaOH (Acros, purity: pure pellets), silicic acid (Sigma Aldrich, purity: 99.9%), manganese (II) carbonate (Sigma Aldrich, purity: 99.9%) and aluminum nitrate nonahydrate (Acros, purity: 99.9%). All chemicals were mixed in distilled water (final volume of dispersion: 15 mL) in Teflon-lined stainless steel Parr reactors (25 mL capacity). The reactors were heated in the 120–210°C temperature range for 6 to 72 h. After this hydrothermal treatment, the vessels were cooled to room temperature. The solids and solutions were separated by centrifugation. The synthesized solids were washed several times with distilled water and dried overnight at 60°C. Table 1 lists the masses of starting chemicals and the hydrothermal conditions used for different preparations and the table S1 (supporting information) lists the molar composition of starting chemicals. Used parameter settings were inspired from the work of Choi and al. (Choi et al., 2009): reaction time 48 h, reaction temperature 175°C, 50.62 mg silicic acid, 73.58 mg $Al(NO_3)_3$ $9H_2O$, 41.84 mg $MnCO_3$, 60 mg NaOH which corresponds to a $0.649SiO_2$:$0.098Al_2O_3$:0.363MnO:$0.750Na_2O$:$833H_2O$ molar composition. Several series of syntheses were carried out, labeled from A to F. In each series a single reaction parameter was systematically varied while keeping the others constant. Parameter values are listed in Table 1. Series A to F respectively correspond to the effect of NaOH concentration, temperature, duration, global precursors concentration, Mn / (Mn + Al) molar ratio and Si / (Mn + Al) molar ratio.

2.2. Characterization of the solids

XRD was used systematically to follow the crystallinity of the hydrothermally prepared solids. The diffractometer was a Siemens D-500 X-ray diffractometer using the CuKα radiation; the diffractograms were recorded in the 5–70° 2θ range with a scanning step of 2° min^{-1}. The FT-IR spectra were recorded using a Nicolet IR200 spectrometer (Thermo Scientific) on KBr pellets. XPS analyses were performed using an X-ray photoelectron spectrometer (SPECS, Germany) equipped with a monochromatized aluminum X-ray source. Nitrogen physisorption measurements were performed on a Micromeritics ASAP 2020M. Specific surface areas were determined by the BET method while the average pore diameter was determined using the BJH method applied to the adsorption branch. The morphologies of the solids were observed using transmission electron microscopy (TEM-JEOL100CX) equipped with an energy dispersive X-ray spectroscopy (EDAX). The thermal behavior was studied by TG/DTA under dry air flow using a LABSYS evo Setaram Instrument. Samples were heated starting from room temperature up to 150°C with a heating rate of 2°C min^{-1}, then the temperature was kept constant at 150°C for 70 min to ensure the removal of strongly physisorbed water and finally samples were heated up to 500°C with a heating rate of

2°C min^{-1}. Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) spectra were recorded on a Bruker 300 WB spectrometer ($B_0 = 7.1$ T) operating at 78.2 MHz (Larmor frequency for ^{27}Al) and 59.6 MHz (Larmor frequency for ^{29}Si), with a spinning frequency of 8 kHz, using respectively pure liquid TMS and a solution of $AlCl_3 \cdot 6H_2O$ as chemical shift references. H_2-TPR of the samples was carried out using a Micrometrics Autochem adsorption instrument. The sample was first pretreated under He at 300°C for 1 h and then reduced in 10% H_2/Ar flow (50 cm^3 min^{-1}) with a temperature ramp of 10°C min^{-1} up to 550°C. The elementary composition was evaluated by X-fluorescence using a Spectro XEPOS Ametek instrument. EPR spectra were recorded at −196°C on a JEOL FA-300 series EPR spectrometer at $\nu \approx 9.3$ GHz (X band) using a 100 kHz field modulation and a 2.5 G standard modulation width. The average oxidation state of manganese was estimated by titration. The method consists in dissolving 10 mg of the solid in a solution containing NaI (4 mol L^{-1}) and NaOH (8 mol L^{-1}), heating the solution to about 40°C and adding 2 mL of concentrated H_2SO_4. The manganese oxidizes the iodide ions to iodine, which is titrated by sodium thiosulfate (0.25 mol L^{-1}). In order to investigate the swelling behavior of named LS sample, the hexadecyltrimethyl-ammonium bromide (CTAB) was used. 1 g of LS sample was

Table 1
Experimental conditions of different prepared materials. For all experiments, 15 mL of water was used in a Teflon vessel volume of 25 mL (the LS sample is in bold).

Series	Time (h)	Temperature (°C)	m silicic acid (mg)	m $Al(NO_3)_3 9H_2O$ (mg)	m $MnCO_3$ (mg)	m NaOH (mg)	(Si + Al + Mn + Na) / H_2O molar ratio (×10^3)	Mn / (Mn + Al) molar ratio
A	48	175	25.31	36.79	20.92	15	1.18	0.65
						30	1.63	
						92.5	3.50	
						185.00	6.28	
B	**48**	140	**50.62**	**73.58**	**41.84**	**60**	**3.25**	**0.65**
		160						
		175						
		210						
C	6	**175**	**50.62**	**73.58**	**41.84**	**60**	**3.25**	**0.65**
	28							
	38							
	48							
	72							
D	**48**	**175**	25.31	36.79	20.92	30	1.63	**0.65**
			50.62	**73.58**	**41.84**	**60**	**3.25**	
			101.24	147.16	83.68	120	6.50	
			202.8	294.32	167.36	240	13.01	
E	**48**	**175**	**50.62**	200	0	**60**	3.22	0
				131.25	21.5		3.22	0.35
				73.58	**41.84**		**3.25**	**0.65**
				29.75	50		3.20	0.85
				0	61.25		3.22	1
F	**48**	**175**	0	**73.85**	**41.82**	**60**	2.47	**0.65**
			50.62				**3.25**	
			101.24				4.03	
G	48	175	0	0	41.82	60	2.24	1