

Continuous Synthesis of Porous Ammonium Dawsonite Within a New Microstructured System

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The present investigation deals with a new process for the preparation of nano-sized ammonium dawsonite ($\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$) with a substantially uniform size distribution and a substantially uniform pore size distribution. It is a continuous precipitation process in a microreactor under constant temperature, constant pH and under pressure. Aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) were used as aqueous solutions for precipitating the catalyst within a Caterpillar microreactor under-pressure system proposed by the authors. Uniform size distribution and nano-sized ammonium dawsonite particles production was controlled by choosing an optimal flow rate for both mother solutions and by increasing the system pressure step by step. Particles having a size between 6 nm and 16 nm assembled into higher/lower crystalline phase were found by using XRD (X-Ray Diffraction) and TEM (Transition Electron Microscopy) techniques. Product purity was characterized by TGA (Thermogravimetric) techniques by comparing the weight loss values with the ideal one, 63% weight loss as published in the literature for very pure ammonium dawsonite. The catalytic activity of the powder obtained was characterized by N_2 -adsorption at 77K and higher BET surface area values were found regarding the values obtained for ammonium dawsonite synthesized by conventional batch precipitation ($\sim 300\text{m}^2/\text{g}$). The limiting production time was increased using under-pressure system. This work is a continuation of previous paper Dubert et al. (2010) with the aim of optimizing the process parameters for a continuous precipitation of ammonium dawsonite within a microstructured system at high pressure.

1. Introduction

Molecular diffusion may be sufficient to mix ultrasmall volumes of fluid in the subpicoliter range reported Ou et al. (2007). However, in the absence of turbulent convection, mixing of larger volumes of fluids in microchannels at low Reynolds numbers is difficult, and often requires resourceful combinations of both convection and diffusion to reduce processing times, path lengths, and pressure drops within acceptable levels. In the same time Fletcher et al. (2002) reports that at low Reynolds number mixing is controlled by molecular diffusion, inducing the growth of vortices or flow patterns which stretch and fold fluid elements can bring the two fluids to be mixed

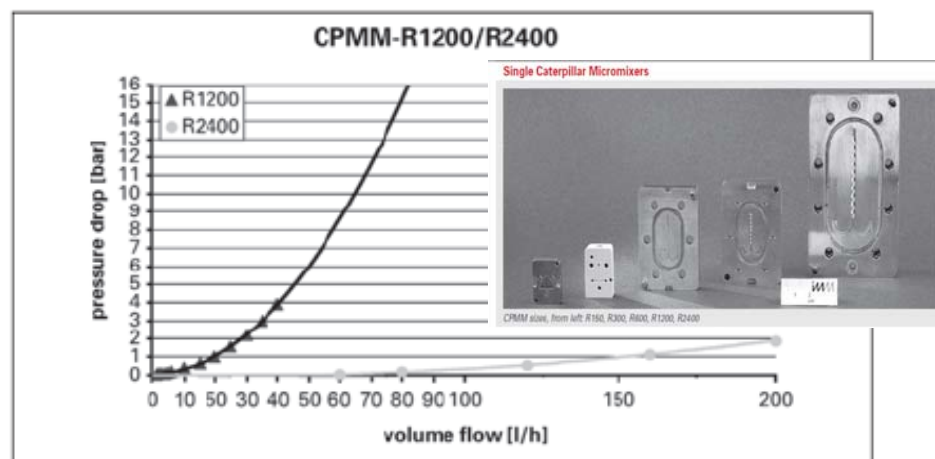


Figure 1: Pressure drop versus flow rate

closer together, thereby significantly reducing the time and the length of channel required to adequately mix the fluid components. The precipitation of ammonium dawsonite was held inside the same IMM Caterpillar micro-mixer with a split - recombine approach performing multiple splitting and recombination of liquid component, as reported in previous paper by Dubert et al. (2010). Studies regarding the pressure drop present inside the microchannel of the Caterpillar micro-mixer were studied and published by Institut für Mikrotechnik Mainz GmbH and showed an exponential dependency between the pressure drop and flow rates used (see Figure 1). Increasing the flow rate, pressure drop inside the zig-zag microchannel will increase proportionally. As the micro-mixer used for ammonium dawsonite (NH_4 -Dawsonite) production is CPM1200/8 (R1200 from Figure 1) and the paper presents the precipitation process running under pressure, information regarding the pressure drop inside the microchannel was important to be taken into account. Based on the information presented above and on practical advantages that microsystems are offering, also showed by Fletcher et al. (2002), a new precipitation set-up was proposed and developed by our group. The multiple usage of this catalyst: ingredient in antacids, stabilizer in polymer, dry extinguisher in fuel leak fire, additive in synthetic fertilizer and most important the production of very pure α -alumina by thermal decomposition increased during the last decades.

2. Experimental section

2.1 Chemicals and reagents

The reagents used for precipitation of NH_4 -dawsonite within a microsystem under-pressure were aluminum nitrate nonahydrated ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) purchased from Chem-Lab NV. and ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) from Fluka and J.T.Baker. Milli-Q water was used for aqueous phases in microfluidic system.

2.2 Methodology and equipment

The methodology applied was following the same procedure as described in previous paper published by Dubert et al. (2010), nevertheless the optimization of the parameters and the precipitation process will take place in a microsystem under pressures 1 bar. The proposed set-up, allows the system to work at the desired pressure values up to 16 bars.

Table 1: Process parameters used within the both systems studied

Sample code	Aqueous solutions concentration (M)		Aqueous solutions flow rate (mL/min)	
	Al(NO ₃) ₃ ·9H ₂ O	(NH ₄) ₂ CO ₃	Al(NO ₃) ₃ ·9H ₂ O	(NH ₄) ₂ CO ₃
S13	1.1	2	10	20
S18	0.55	1	12	48
S24	0.22	2	20	20
S44	0.12	1.09	20	20

The system pressure was adjusted by pressure dumper in such a way that the pressure drop inside the microreactor was minimized. The acid and base solutions were continuously fed by using metering pumps into the microreactor whereas the pressure inside the system was adjusted at 1 bar. Both metering pumps worked at high pressure (maximum 16 bars). The connection with the microreactor's inlets was made by one meter compact stainless steel coil for each inlet (see Figure 2 a), this allowed to have a better control of heat transfer from inside-outside or/and vice versa and in the same time to enhance the reaction time, respectively. NH₄-dawsonite was prepared by using different process parameters shown in Table 1. The new microsystem set-up was held under a fix pressure value, 1 bar, and the results were compared both with previous ones and with those listed in the literature.

2.3 Characterization of NH₄-Dawsonite

The metal content of the dawsonite product was investigated by X-Ray Diffraction Technique (XRD) for characterization of crystalline/amorphous phase that could appear for hydrated dawsonite (NH₄Al(OH)₂CO₃·xH₂O). Thermogravimetric analyses (TGA) was to determine the purity of these products.

The morphological properties, particle size distribution and particle size values of NH₄-dawsonite were characterized by TEM (Transition Electron Microscopy) using a JEOL 1011 model. The TEM images were processed by Image-J software. One of the most important characteristics of a catalyst is the porosity that leads to catalytic activity characterization. BET surface area value and micro and/or meso pores inside the product were analyzed by N₂-adsorption at 77 K using a Micrometrics ASAP 2000 device.

3. Results and discussion

The experimental procedure followed the pressure influence over the final product. Furthermore, the comparison among products obtained at 1 bar by using both systems gave us a better understanding regarding the precipitation process at microscale and also, about the optimal conditions that had to be applied in order to enhance the catalyst properties. Results shown in Table 2 confirm an increase of about 5 times in the time of production by running the precipitation process at 1 bar pressure and decreasing the concentration of both aqueous solutions. The crystalline phase was analyzed for all samples obtained, under specific process conditions. Almost all trials ran under pressure 1 bar showed lower crystallinity comparing with trials obtained by the system at atmospheric pressure. Traces of ammonium nitrate (NH₄NO₃) were found within trials experimented at high concentration of initial aqueous solutions.

Table 2: Experimental characterization of all trials including time of production.

Sample code	Time of production		* Process parameters	Analysis			
	System at atmospheric pressure	System at pressure 1bar		XRD	TGA ¹ (%)	TEM ¹ Particle size(nm)	BET ¹ surface area (m ² /g)
S1-S4	40	245	1.1-2M; 10- 20mL/min	LC**	69	13.35	83.8278
S5 group	58	260	0.55-1M; 12- 48mL/min	² HC	62	12.55	508.6357
S7 group	109	191	0.22-2M; 20- 20mL/min	LC (2 exp) A*** (1exp.)	56.2	6.105	516.8103
S8 group	558	371	0.12- 1.09M; 20- 20mL/min	A all	-	-	-

*(M) – initial aqueous solutions concentration; (ml/min) – flow rate used for each initial solution; ²HC – high crystalline; **LC – low crystalline; ***A – amorphous; 1 – average values

This could be explained by means of no reacted product or by the residence time inside the microreactor channel that was reduced under 0.2 seconds and could affect the precipitation reaction. The presence of amorphous phase within some trials confirmed the limiting interval of working parameters within the microchannel. The pressure influence over the purity was characterized by using TGA and the percentage of weight loss in each sample was calculated. Both TGA and TGA derivative curves showed higher purity for the products obtained within the microsystem under pressure comparing with the product obtained at atmospheric pressure (See Table 2). This could be explained by the presence of NH₄NO₃ traces inside the samples that decompose at different temperature during the thermal process. TGA derivative confirmed similar temperature transition for most of the samples and higher value (600⁰C) for those containing traces of NH₄NO₃. The highest purity value of the product obtained within the system under pressure 1 bar was obtained for S5 group as Table 2 showed.

These values presented confirmed higher product purity comparing with values obtained by using the microsystem at atmospheric pressure and ILDP milisystem presented by Stoica and Pérez-Ramírez (2007), (weight loss % = 50).

TEM evidences the presence of nanometer (nm) particles size (Figure 2 inset, a) in comparison with micro meter (µm) aggregates size obtained within the old system at atmospheric pressure (See Figure 2 inset, b). By applying pressure within the precipitation process we obtained a size distribution at the nanometers range of the particles (≤ 15 nm). Comparing with the results obtained in previous work and those published by Stoica and Pérez-Ramírez (2007), (~10nm), working at pressure 1 bar the results were similar and the particle size distribution was better controlled. The textural properties of the solid were determined by adsorption of nitrogen at 77 K (Figure 2).

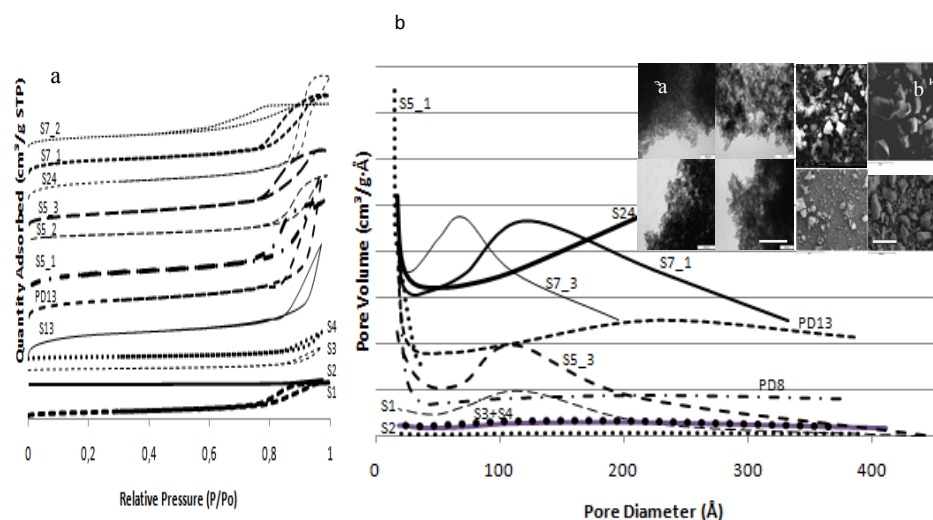


Figure 2: N_2 adsorption-desorption isotherms at 77 K of the NH_4 -Dawsonite samples obtained at 1 bar pressure. Inset: a. TEM micrographs of NH_4 -Dawsonite powder obtained within the microsystem under pressure 1 bar, new set-up; b. SEM micrographs of the same powder obtained within microsystem at atmospheric pressure, old set-up. The scale bar in the bottom micrograph applies to all the samples.

Following IUPAC recommendations from Sing et al.(1985) work, the N_2 isotherm of NH_4 -Dawsonite samples can be classified as a combination of type II and IV isotherms (with H1 hysteresis). The latter statement was substantiated by the narrow pore size distribution in the samples, which is centered differently for each group analyzed (Figure 2.b). BJH pore size distribution shows a similar narrow distribution of mesopores centered between 100\AA - 200\AA for all samples. The total pore volume (See Table 2) and specific surface area of NH_4 -Dawsonite are in a direct correlation. The presence of *micro* and *meso* pores in the samples had a very high influence in changing the BET surface, lowering/rising it. Comparing with the results presented by Stoica and Pérez-Ramírez (2007) the catalytic activity of the product obtained within the microsystem was similar and/or improved (S_{BET} – ILDP process was $773\text{ m}^2\text{ g}^{-1}$).

An overlook on the pore size distributions could give us precise information about all groups of samples obtained through microsystem working under pressure but further work is needed in order to demonstrate the advantages over conventional precipitation process and/or ILDP method used by Stoica and Pérez-Ramírez (2007).

4. Conclusions

The limited time interval of NH_4 -dawsonite production using the microsystem under pressure 1 bar was increased up to 5 times, comparing with the previous microsystem (at atmospheric pressure) but further investigation has to be done before its applicability in industry would be satisfied. The metal content determined by using XRD showed high crystalline phase for NH_4 -dawsonite obtained with a higher ratio between flow rate (12 mL/min – 48 mL/min), acidic solution ($(NH_4)_2CO_3$) being in excess. Some traces of ammonium nitrate were found during the analyses which were explained by means of

imperfect mixing inside the microchannel. The product purity was increased comparing with values obtained by using the microsystem at atmospheric pressure and ILDP milisystem. The latter materials are characterized by good catalytic activity of the product obtained by both type of microsystems, with a well-developed and uniform mesoporosity. The micrometer particle size of NH_4 -Dawsonite produced with the system at atmospheric pressure decreased till nanometer size applying pressure (between 7 nm-20 nm particle size). The results presented here sustain the fact that a microsystem under pressure is giving more benefits than a batch one or/and a miliscale but deeper analyses are needed, especially if the aim is to have a continuous production with a higher flexibility in the industry.

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