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Dawsonite Production with Caterpillar Microreactor

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Co-precipitation is one of the most frequently applied methods in preparing precursors of catalysts and support materials with good dispersion of the components, carried out most of the time in a batch mode. The paper presents co-precipitation of NH_4-dawsonite catalyst within the channel of an IMM-Caterpillar microreactor. Aluminium nitrate nonahydrate and ammonium carbonate were used as reagents for precipitating the catalyst within a microreactor set-up proposed by our group. Correlation between reagents flow rate and concentration by changing their values enables the production time to be better controlled and to give certain information about the catalyst properties. Ammonium dawsonite have been characterized by X-Ray Diffraction Technique (XRD) and Thermogravimetric Analysis (TGA) in order to determine the cristalinity and purity of the product and then scanning electron microscopy (SEM) was used for visualizing the morphology. Particle size was measured by J-Image program.

1. Introduction

As coprecipitation methods are not easy to control and reproduce, and impregnation techniques cannot always be made to yield the desired active-phase distribution, as van Santen et al. (2000) and Schütz et al. (1997) specified it is worthwhile to consider alternative methods. One of these methods is In-Line Dispersion-Precipitation (ILDP) applied at microscale. Santiago et al. (2006) characterized alumina as the most common catalyst support in the chemical and petrochemical industries, as well as for automotive emission control. γ-Al2O3 is produced by decomposition of hydrated alumina, which are synthesized by precipitation of aluminium ions with OH^- and typically lead to surface areas in the range of 200–300 m^2 g^{-1}. Ammonium aluminum carbonate hydroxide, named also Dawosnite, (AACH, with formula $NH_4Al(OH)_2CO_3$) is a unique precursor for alumina with enhanced properties compared to those derived from the conventional Bayer process. Preparation of AACH is typically practiced by *batch* precipitation of aqueous solutions of aluminum salts (NH4, $Al(SO4)_2$, $AlCl_3$, or $Al(NO_3)_3$) or $Al(OH)_3$ suspensions with aqueous solutions of ammonium (bi)carbonate. Dawsonite compounds have been applied as an ingredient in antacids, a stabilizer in polymers, a dry extinguisher in fuel leak fires, and an additive in synthetic fertilizers (Stoica and Pérez-Ramírez, 2007). Santiago et al.(2006) synthesized NH4-dawsonite by using In-Line-Dispersion-Precipitation Method (ILDP), based on miniaturization of the

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precipitation chamber, controlled resistance time and highly effective stirring. Fletcher et al. (2002) proved that the miniaturization of chemical reactors offers many fundamental and practical advantages which are constantly searching for controllable, large surface-to-volume ratio, increased heat and mass transfer coefficient, information rich, high throughput and environmentally friendly methods of producing products with a high degree of selectivity. Regarding the advantages that miniaturization of the systems gives in developing of industry, the work is focused in producing ammonium dawsonite (AACH) using a Caterpillar microreactor. As Hessel et al. (2004) published CPMM1200/8 microreactor uses split-recombine approach performing multiple splitting and recombination of liquid compartment. The miniaturization of the system is going further till micro scale.

2. Experimental section

2.1 Chemical and reagents

The reagents used for precipitation of MH_4-dawsonite were aluminum nitrate nonahydrated ($Al(NO_3)_3x9H_2O$) purchased from Chem-Lab NV. and ammonium carbonate ($(NH_4)_2CO_3$) from Fluka and J.T.Baker. Milli-Q water was used for aqueous phases in microfluidic system.

2.2 Methodology and equipment

Miniaturization of the process, at micro scale, was following the same procedure as ILDP (constant pH), but it had to take into account the optimization of the parameters and the particularity that the precipitation process will take place in a laminar regime. A possible set-up is presented further (Figure 1a). The acid and base solutions are continuously fed with peristaltic pumps into Caterpillar microreactor with an effective volume of 78 μl and a microchannel width about 0.47mm. (Figure 1b). As it is shown in Figure 1b,c the microreactor presents a very tiny zig-zag channel which is giving the split-recombine approach and a laminar regime of mixing. The two peristaltic pumps are fixed at different flow rates and are connected to both inlets of the reactor. The flow rates are adjusted in such a way that both solution to reach the entrances of the microreactor at the same time. NH4-dawsonite was first prepared by microsystem using aqueous solutions of 1.1M $Al(NO_3)_3x9H_2O$) and 2M $(NH_4)_2CO_3$ continuously fed at 333K (60^0C) to the precipitation channel. Syntheses were carried out at constant pH = 7-9 into a laminar regime at the atmosphere pressure. For comparative purposes dawsonite synthesis was held further at different value of flow rates and concentrations of acid and base solution. The resulting products were aged at 333 K ($60\ ^0$C) for 3 h, followed by filtration, washing and drying at 333K ($60\ ^0$C) for more than 12 h.

2.3 Characterization of Dawsonite

The metal content of the dawsonite product was investigated by X-Ray Diffraction Technique (XRD) and Thermogravimetric Analysis (TGA) which showed that the only crystalline phase appeared for hydrated dawsonite ($NH_4Al(OH)_2CO_3 \cdot xH_2O$). The morphological properties of NH_4-dawsonite were characterized by scanning electron microscopy (SEM) using a Joel JSM-6400 scanning microscope series.

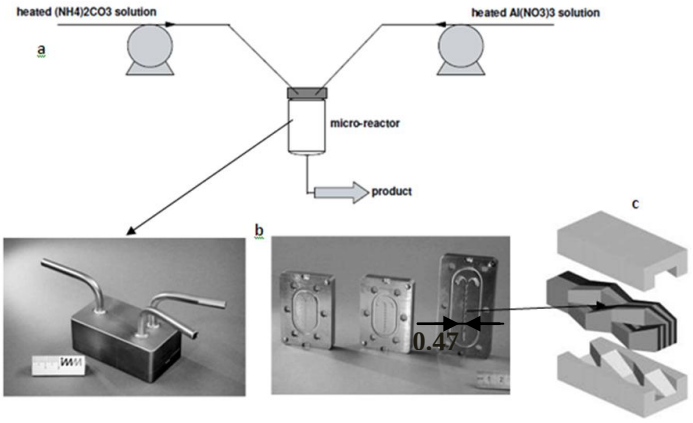

Figure 1: a,b,c. Microsystem set-up photo: peristaltic pumps, heaters and the microreactor; b. CPMM1200/8 microreactor

3. Results and discussion

The metal content analysis was necessary for assuring that crystalline dawsonite was obtained at different parameters (increasing/decreasing specific parameters as flow rate (ml/min) and/or concentration (M). Resulting crystalline dawsonite are shown in Table1. The experimental section was following two important issues: one referring to the optimization of process parameters by playing with aqueous solutions concentrations and/or flow rates and the second one was taking into account the aggregation phenomena and crystal growth during and post process. Particle size of the precipitate was determined. First, the concentration of 1.1 M for aluminum based solution, respectively 2 M for carbonate based solution were kept fixed and their flow rates were increased (4-12 mL/min for ($Al(NO_3)_3x9H_2O$)), 16-48mL/min for ($(NH_4)_2CO_3$)). A white precipitate was obtained during an interval of some seconds till 1 minute. Second step in process optimization was the decreasing the concentrations (till 0.12 M ($Al(NO_3)_3x9H_2O$)/1.09 M ($(NH_4)_2CO_3$)), in order to evaluate entire microsystem performance. By using lower concentrations of aqueous solutions less quantity of moles were introduced in the system, the aggregation phenomenon was reduced, and the time of production was increased (e.g. 1080 seconds, See Table 1). A primary system optimization was achieved, which represents a step forward in development of solids microtechnology production. The metal content in NH_4-dawsonite was determined by X-Ray Diffraction technique (XRD) and matches the pure NH_4-dawsonite reference pattern - see Figure 4. As shown in the XRD spectra above the dried precipitate typically exhibited the NH_4-dawsonite ($NH_4Al(OH)_2CO_3$), as the only crystalline phase and no traces of amorphous phase were found (Figure 2).

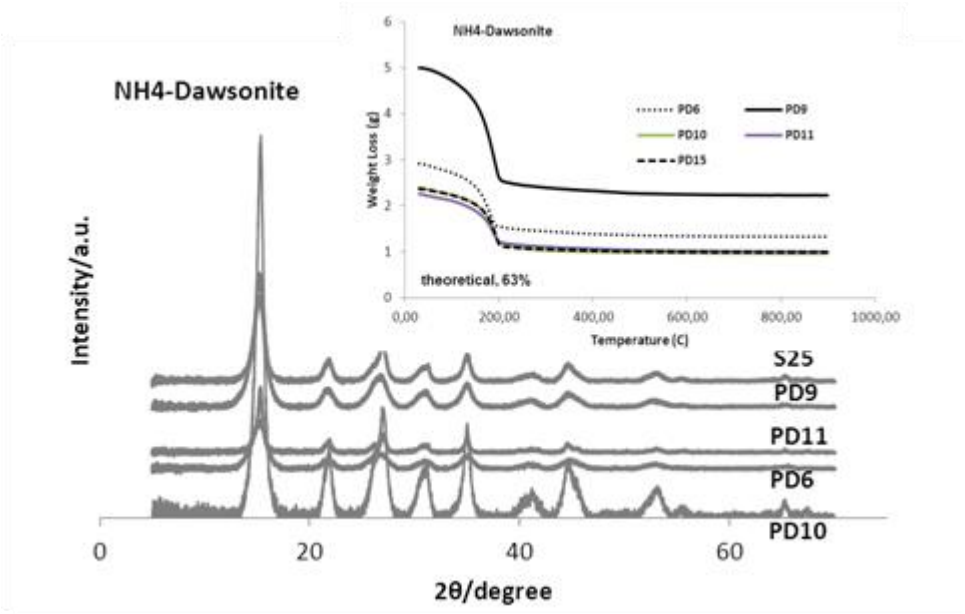

Figure 2:. X-ray diffraction spectra of NH_4-Dawsonite at different process parameters. Inset: Thermogravimetric analyses – thermal decomposition profile in synthetic air.

Thermogravimetric analysis (TGA) confirms the purity of the product (Figure 2). The thermal process of ammonium dawsonite in synthetic air shows a one-step weight loss for all samples analyzed in the range 30-200 ^{0}C (Figure 2) which is assigned to the thermal decomposition. The total weight loss of each sample involved was in the range 53-58 %. This indicates that product obtained has a high purity between 90-95 %. SEM analysis (Figure 3) of NH_4-dawsonite confirms the presence of big particles (aggregates) (Table. 1) which explains the limited production interval of this catalyst due to clogging. Regarding the high degree of porosity and ultra-fine particle size (≤10 nm) of the product obtained by Javier Perez-Ramirez et al. using ILDP method, the powder produced, by applying microreactor technology, presents big particles (aggregates) with an average of size of μm and a very irregular surface (Figure 3 a, b, c). An interesting correlation can be made between aqueous solutions flow rate, concentration and particle size of the product. Decreasing the concentration of both solutions at fixed flow rate the average particle (aggregate) size of the precipitate obtained is decreasing also (Table 1). SEM analysis is confirming these observations (Figure 3 d, e, f). As micrographs show the morphological properties of the product obtained in these specific conditions, presents the average size measured for aggregates and not for individual particles.

Table1: Experimental parameters used, time of production and average particles size of dawsonite powder

Al $(NO_3)_3x9H_2O$ flow rate (ml/min)	*$(NH_4)_2CO_3$ flow rate (ml/min)*	*Al (NO3)3x9H2O concentration (M)*	*(NH4)2CO3 concentration (M)*	*Production Time (s)*	*Average particles size (µm)*
4	16	1.1	2	60	-
4	20	1.1	2	100	193
6	20	1.1	2	55	111.04
10	20	1.1	2	40	-
12	48	1.1	2	50	-
4	20	0.55	1	90	97.05
6	20	0.55	1	101	132.3
10	20	0.55	1	56	-
12	48	0.55	1	58	-
4	20	0.5	0.91	90	50.72
20	20	0.22	2	154	896.7
40	40	0.22	2	55	932.75
60	60	0.22	2	59	-
80	80	0.22	2	24	-
20	20	0.12	1.09	1080	-

The aggregation is probably formed because the slurry obtained by precipitation is stirred for 3 h at 60^0C. The residence time of the precipitation process which differs for each experiment varying from 0.1 to 0.2 s is a great advantage in term of reaction speed and in controlling the particles formation comparing with the conventional process.

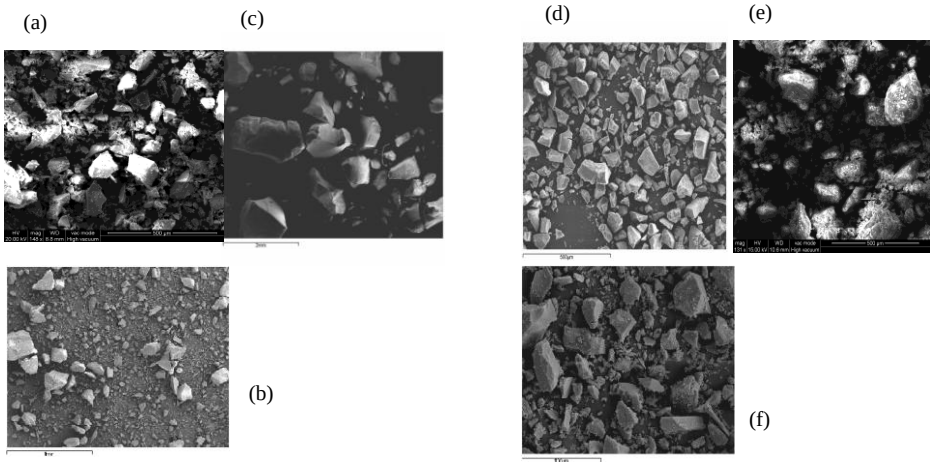

Figure 3: SEM micrographs for (a) 111,04 μm – Sample 2; (b) 132,3 μm – Sample 4; (c) 896,7 μm – Sample 6; (d) 193μm- Sample 1; (e) 97.05μm – Sample 3; (f) 50.718 μm – Sample5.

For this reason further experimental work is needed in order to understand better the correlation between physical and chemical factors that could influence the kinetics of the precipitation process. Following the objective of this paper new experimental conditions are needed and a new set-up was developed. Future work will be based on producing NH_4-dawsonite by using the same microreactor but operating the process under pressure.

4. Conclusions

Ammonium dawsonite was successfully prepared within the channel of IMM Caterpillar microreactor by precipitation reaction. The limited production time interval was increased by adjusting the flow rate and the concentration of the acidic and base solutions, reaching 18 minutes. Using XRD and TGA techniques the metal content, crystalline phase and purity of the product were illustrated. SEM analysis characterized the morphology of the aggregates obtained by showing the shape and size, but in the same time opened new questions that have to be solved. In general terms, microreactor technology can be applied to synthesize ammonium based catalysts but more research is needed in order to demonstrate the real advantages of this micro scale approach. This paper shows the first steps in understanding the precipitation process at micro scale and further work will consist in characterizing the product properties obtained within microreactor compared with conventional one.

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