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Development of new alumina precipitation routes for catalysis applications

Robin Lafficher[*a,b], Mathieu Digne[a], Fabien Salvatori[a], Malika Boualleg[a], Didier Colson[b], François Puel[c]

[*]Corresponding author Tel: +33 4.37.70.21.15
Email: fabien.salvatori@ifpen.fr (Fabien Salvatori)

[a]IFP Energies Nouvelles
BP 3, F-69360 Solaize, France
[b]Univ Lyon, Universite Lyon 1, CNRS, UMR5007, LAGEP
43 bd du 11 Novembre 1918, F-69622 Lyon, France
[c]LGPM, Laboratoire de Génie des Procédés et Matériaux, CentraleSupélec, Université Paris-Saclay
Grande Voie des Vignes, 92295 Châtenay-Malabry, France

ABSTRACT

γ-Alumina is a widely used porous material for catalytic application. Possible routes for alumina improvement can be the use of alternative precursors as well as innovative precipitation technologies. In this study, we compare the influence of both precursor chemistry and mixing efficiency on γ-alumina properties. The conventionally used boehmite and the NH_4-dawsonite precursors were precipitated using three mixing technologies: a conventional stirred-tank reactor, a rotor-stator mixer and a sliding surface mixing device. It was observed that, in the study conditions, γ-alumina mean pore diameter and porous volume were particularly sensitive to both precursor and mixing technology, while specific surface area was rather precursor dependent. A wide porosity range can thus be covered at isospecific surface area, using several precursor/mixing technology systems.

Keywords
A1. Precipitation
A1. Micromixing
B1. Alumina
B1. Dawsonite

1. Introduction

Supported heterogeneous catalysts are widely used in refining and petrochemical processes. One way to better catalyst performances is to develop supports with enhanced properties. The properties of alumina-based catalyst supports are to a large extent fixed by the properties of the initial solid precursor, such as boehmite (AlOOH) [1]. Various synthesis routes are possible for alumina precursors: sol-gel process, using aluminium alkoxides [2], can lead to pure alumina with high thermal stability and surface area in the range of 200-500 $m^2.g^{-1}$ [3]; moreover, the use of various copolymers as structure-directing

agents can lead to ordered materials and enable good control of the porosity [4,5]. However, precipitation of aluminium salts in aqueous solution represents a cheaper way for alumina production at an industrial scale, even though these alumina generally exhibit surface areas lower than 300 $m^2.g^{-1}$ [6,7] and may have high impurities contents (200-3000 ppm Na_2O) [1,8]. In this context, possible routes for alumina improvement can lie in the use of alternative precursors as well as innovative precipitation technologies compared to the commonly used stirred tank reactor. Such a combination could lead to new textural properties.

Ammonium dawsonite ($NH_4Al(OH)_2CO_3$) can be an interesting alternative choice for preparation of γ-Al_2O_3 with high purity level and new textural properties [9]. Various methods can be used to synthesize this precursor [10], but the main one remains the precipitation in aqueous phase of aluminium salts ($Al(NO_3)_3$, $(NH_4)Al(SO_4)_2$, or $AlCl_3$) with precipitating agents such as $(NH_4)_2CO_3$ or NH_4HCO_3.

As precipitation of sparingly soluble materials, such as boehmite or NH_4-dawsonite, is generally associated with very fast reactions, the solid properties can be strongly influenced by mixing quality [11]. Therefore, the choice of the mixing technology is particularly important. The most commonly used reactor for precipitation is the stirred tank reactor in batch or semi-batch configuration. However, this technology suffers from two important drawbacks: the specific power dissipated by the stirrer is not homogeneously distributed in the whole reactor [12], and, due to discontinuous operation, precipitation conditions change throughout the process [9]. Using fast contacting mixers in continuous configuration could allow a better supersaturation control thanks to a more efficient mixing, while maintaining constant precipitation conditions throughout the process.

With this work, we present a comparative study of different γ-alumina properties, prepared by precipitation of boehmite or NH_4-dawsonite, using three mixing technologies: a stirred tank reactor (STR) operated in semi-batch, and two fast mixers operated continuously, a sliding surface mixing device (SSMD) and a rotor-stator mixer (RSM). This work complements previous studies on boehmite precipitation with SSMD technology [13] and NH_4-dawsonite precipitation with RSM technology [9].

2. Experimental set-up

Precipitated boehmite was synthesized at 60 °C from an aluminium sulphate solution (A) and a sodium aluminate solution (B) by simultaneous dosing of the reactants, with molar ratio $R_{B/A}$ = 4. Precipitated NH_4-dawsonite was synthesized at 60 °C from an aluminium nitrate solution (A') and a carbonate ammonium solution (B') by simultaneous dosing of the reactants, with molar ratio $R_{B'/A'}$ = 8.

The 3.5-L glass baffled STR used in this study is equipped with a three blade propeller TTP Mixel. The stirring speed was fixed so that the mean specific dissipated power $\bar{\varepsilon}$ = 0.2 $W.kg^{-1}$. The feed points were located in the discharge stream of the impeller, where the specific energy dissipation is the highest. Boehmite synthesis were set up at a constant pH of 9.7 and at final alumina concentration $[Al_2O_3]$ = 36 $g.L^{-1}$. Dawsonite synthesis were set up at pH between 7.5 and 8.5, and at final alumina concentration $[Al_2O_3]$ = 8 $g.L^{-1}$.

The SSMD (Fig. 1a) was designed based on the device presented by Rousseau et al [14]. It consists of a stainless steel cylindrical chamber in which is located a 120 mm large rotating disc. The gap h between the disc and the chamber flat bottom can be adjusted between 1 and 3 mm. Reactants were injected in the confined mixing zone under the disc through a central feed tube (A or A') and four lateral symmetrical feed tubes (B or B'), situated at equal distance r = 40 mm from the center. Boehmite synthesis were set up at pH between 9.1 and 9.9, and at final alumina concentration $[Al_2O_3]$ = 36 $g.L^{-1}$. Dawsonite synthesis were set up at pH 7.5 and 8.5, and at final alumina concentration $[Al_2O_3]$ = 10 $g.L^{-1}$.

The RSM (Fig. 1b) used in this study is a DK40 from CAT, equipped with a double feed system. The rotor radius is r_R = 16.5 mm and the gap between rotor and stator is e = 1 mm. Boehmite synthesis were set up at pH between 8.5 and 9.5, and at final alumina concentration $[Al_2O_3]$ = 12 $g.L^{-1}$. Dawsonite synthesis were set up at pH 7.5 and 8.0, and at final alumina concentration $[Al_2O_3]$ = 10 $g.L^{-1}$.

As flow rates in continuous mixers (SSMD, RSM) were much higher than that in STR, precipitation duration was shorter for a same final suspension volume. A precise pH control was therefore more complicated, which explains the slight differences observed depending on the mixer used. However, the

repeatability was tested for some operating conditions with the three mixers, and was satisfying according the precipitated solids properties.

Following the synthesis, suspensions were filtered, washed with water and dried at 120 °C for 14 h. The dried precursors (noted B/xxx and D/xxx, for boehmite and NH_4-dawsonite respectively, xxx corresponding to the mixer used: STR, SSMD or RSM) were then calcined at 500 °C for 4 h to obtain γ-Al_2O_3 final support (noted Al-B/xxx and Al-D/xxx, for boehmite derived and NH_4-dawsonite derived alumina, respectively, xxx corresponding to the mixer used)

Solids were characterized by X-ray diffraction (XRD) and thermogravimetric analysis (TGA) to determine their crystallinity and purity. Their textural properties (specific surface area S_{BET}, pore volume V_p and mean pore diameter D_p) were determined by using nitrogen adsorption analysis.

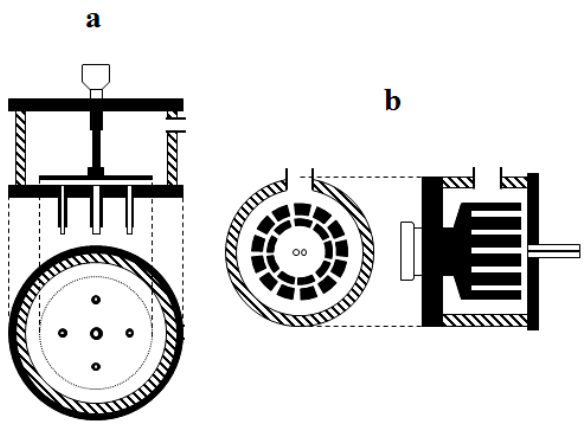

Fig. 1. Schematic representation of fast contacting mixers : (a) SSMD and (b) RSM

3. Results and discussion

3.1. Precipitation in stirred tank reactor

First, boehmite and NH_4-dawsonite have been precipitated in the STR in semi-batch mode. Both precursors and derived aluminas were characterized in order to be used as references for the rest of the study.

As confirmed by powder XRD analysis, precipitation of aluminium sulphate with sodium aluminate led to the obtention of boehmite (ICDD 21-1307) and precipitation of aluminium nitrate with ammonium carbonate led to the obtention of NH_4-dawsonite (ICDD 42-0250). Neither crystalline mixed boehmite and NH_4-dawsonite phases, nor other crystalline phases, were detected. Average crystallite sizes were determined using Scherrer's equation.

Physical properties of both precursors and their derived aluminas are summarized in Table 1. In the studied conditions, NH_4-dawsonite exhibited larger crystallites than boehmite. As a consequence, the precursors displayed quite different textural properties. Despite a similar pore volume, NH_4-dawsonite indeed exhibited a lower specific surface area but a mean pore diameter four times higher. It can be noted that mean pore diameters of both precursors were broadly consistent with their respective average crystallite sizes, even though boehmite seemed to present a more compact aggregation than NH_4-dawsonite. After calcination at 500 °C, a strong increase of porosity and specific surface area was noted in the case of dawsonite derived alumina: its pore volume reached 1.0 $cm^3.g^{-1}$, and its specific surface area outreached 420 $m^2.g^{-1}$, leading to a solid with superior textural properties compared to boehmite derived alumina. Interestingly, we noted that decreasing the NH_4-dawsonite reactants molar ratio from 8 to 3 led to an increase of the derived alumina porosity, with pore volume near 1.2 $cm^3.g^{-1}$, mean pore diameter in the range of 30 nm and specific surface area still higher than 400 $m^2.g^{-1}$.

However, it turns out that an important part of the dawsonite derived alumina specific surface area is due to microporosity. This can be explained by the thermal decomposition process of NH_4-dawsonite, in which H_2O, NH_3 and CO_2 are released in important quantities, leading to the formation of intracrystalline porosity [15]. Indeed, NH_4-dawsonite mass loss measured by TGA is in the range of

60%, which is close to the theoretical value of 63%. On the contrary, boehmite only lost 23% mass, corresponding to both dehydration of hydroxyl groups and physisorbed water.

Table 1. Physical properties of precursors and derived aluminas precipitated in the STR

Sample	L [a] (Å)	S_{BET} ($m^2.g^{-1}$)	S_{micro} [b] ($m^2.g^{-1}$)	V_p ($cm^3.g^{-1}$)	D_p (nm)
B/STR	47	286	0	0.70	3.9
D/STR	114	198	0	0.72	16.3
Al-B/STR	-	299	7	0.83	5.6
Al-D/STR	-	428	198	1.01	2.7 – 16.4

[a] Average crystallite size determined using Scherrer's equation. [b] Determined using t-plot method.

3.2. Fast-mixer influence

In SSMD case, the mixing influence on the solid properties was investigated with the following operating parameters: the disc rotational speed (N = 150-2000 rpm), the total reactants flow rate (Q = 150 – 2500 $ml.min^{-1}$) and the confined mixing zone height under the disc (h = 1-3 mm). Micromixing times were directly determined using Eq. (1), proposed by Rousseaux et al. [14] in case of a laminar flow in the confined mixing zone.

In RSM case, the mixing influence on the solids properties were investigated with the following operating parameter: the rotor rotational speed (N = 2500-7000 rpm). Micromixing times were determined using Eq. (2) [16], the specific power dissipated being estimated using Eq. (3) [17]. This correlation was adapted from rotor-stator in batch configuration and did not account for the potential flow rate influence. However, since studies on specific power dissipated by rotor-stator mixers are still very empirical, and so limited to the studied tool, there is no general correlation for in-line rotor-stator mixers [18].

The studied micromixing times range from 1 to 4 ms on the RSM, and from 10 to 180 ms on the SSMD. In comparison, STR micromixing time in the studied conditions, estimated with Eq. (2) and (4), is in the range of 15 ms. However, for a given micromixing time, continuous configuration still allows a better control of the supersaturation as the environment in which supersaturation occurs remains the same during the whole precipitation process.

$$t_m = \frac{1}{\sqrt{0.0090\left(\frac{rN}{h}\right)^2 + 0.065\left(\frac{Q}{r}\right)^2 \frac{1}{h^4}}} \quad (1)$$

$$t_m = 17{,}2\sqrt{\frac{\nu}{\varepsilon}} \quad (2)$$

$$\varepsilon = \frac{\nu\omega^2 r_R^2}{e^2} \quad (3)$$

$$\varepsilon = \Phi \cdot \bar{\varepsilon} = \Phi \frac{N_P\, N^3 {D_a}^5 \rho}{m} \quad (4)$$

The mixing influence on boehmite and NH_4-dawsonite crystallographic and textural properties was thus studied. As in the precipitation in STR, the precursor purity was first verified by XRD and TG

analysis. The mass losses measured during a thermal treatment of the precursors precipitated with fast contacting mixers were in the same range as that of the precursors precipitated in the STR.

It can be clearly noted on Fig. 2 that precipitation in a fast contacting mixer led to a decrease in the precursor respective crystallite size, from 15 to 40%, compared to precipitation in STR. Moreover, we can observe that the crystallite size is sensitive to the micromixing time, and increased with it, particularly in NH_4-dawsonite case. This is consistent with a better supersaturation control at smaller micromixing times: a higher supersaturation level is thus reached, leading to a more intense primary nucleation kinetic, and so to a crystallite size decrease.

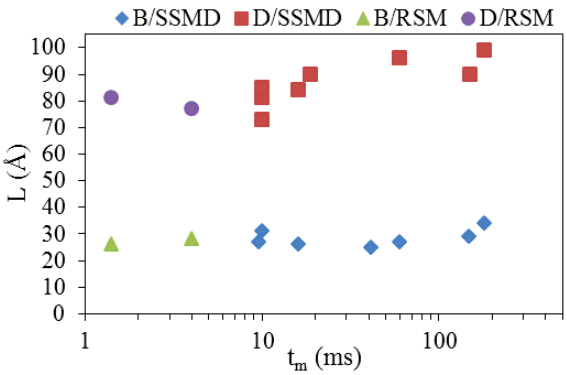

Fig. 2. Precursors crystallite size (L) evolution with micromixing time (t_m) for different fast contacting mixers

Fig. 3 presents the alumina textural properties evolution with micromixing time for both fast contacting mixers. In boehmite derived alumina case (products Al-B/SSMD and Al-B/RSM), micromixing time does not seem to have a major influence on the textural properties of the solids: both the specific surface area and the pore volume remained approximately constant, ranging from 250 to 300 $m^2.g^{-1}$ and from 0.3 to 0.4 $cm^3.g^{-1}$, respectively. Only the solid precipitated at micromixing time of 1 ms exhibited a higher specific surface area, near 350 $m^2.g^{-1}$. Furthermore, no effect of the fast contacting mixer type can be observed, as the textural properties obtained with the RSM are in the SSMD's continuity. On the contrary, dawsonite derived alumina (products Al-D/SSMD and Al-D/RSM) showed a biggest sensitivity to micromixing. If the specific surface variations between the precursors precipitated at various micromixing time (data not shown) finally disappeared after the calcination step, the pore volume remains particularly sensitive to this parameter. This lead to alumina exhibiting specific surface area higher than 400 $m^2.g^{-1}$ and tunable pore volume between 0.5 and 0.9 $cm^3.g^{-1}$. However, it is more difficult in that case to determine a potential influence of the fast contacting mixer in the same range of micromixing time, as the pore volume can vary from 0.5 to 0.7 $cm^3.g^{-1}$ for micromixing times between 1 and 10 ms.

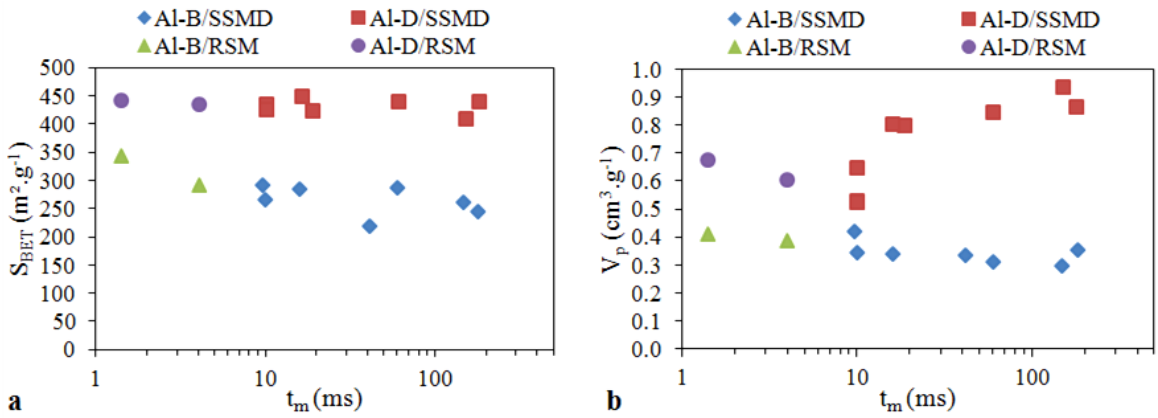

Fig. 3. (a) Specific surface area and (b) pore volume evolution with micromixing time of boehmite and NH_4-dawsonite derived alumina prepared with different fast contacting mixers

Overall, it can be noted that alumina prepared by precipitation in fast mixers exhibit a specific surface area relatively close to that of alumina prepared in STR (or a bit lower for some boehmite derived alumina), but a lower porosity.

In the case of boehmite derived alumina, this trend can be observed on the whole micromixing time range studied. Fig. 4 shows the N_2 adsorption-desorption isotherms and pore size distributions trend obtained with the three mixers. Alumina prepared with both fast mixers exhibited very close properties, but differed from the one prepared with the STR. Since the hysteresis loops are representative of the pore network shape, we can assume that crystallite arrangement depends on the use of semi-batch or continuous mixers, but not on the micromixing time.

In the case of dawsonite derived alumina, we can observe that at high micromixing times, the textural properties of alumina prepared with SSMD tend towards that of alumina prepared with STR. Comparison of N_2 adsorption-desorption isotherms and pore size distributions (Fig. 5) confirms the micromixing influence on these alumina porosity. Indeed, for micromixing times shorter than 15 ms, pore network shape and pore size distribution obtained with both fast contacting mixers were similar. However, alumina prepared in the SSMD at micromixing times higher than 15 ms exhibited intermediate properties between those obtained with the RSM and the STR. Thus, NH_4-dawsonite appears to be more sensitive than boehmite to micromixing time in the studied range. Those two trends could be explained by precipitation kinetics with very different intensities, depending on the precursor.

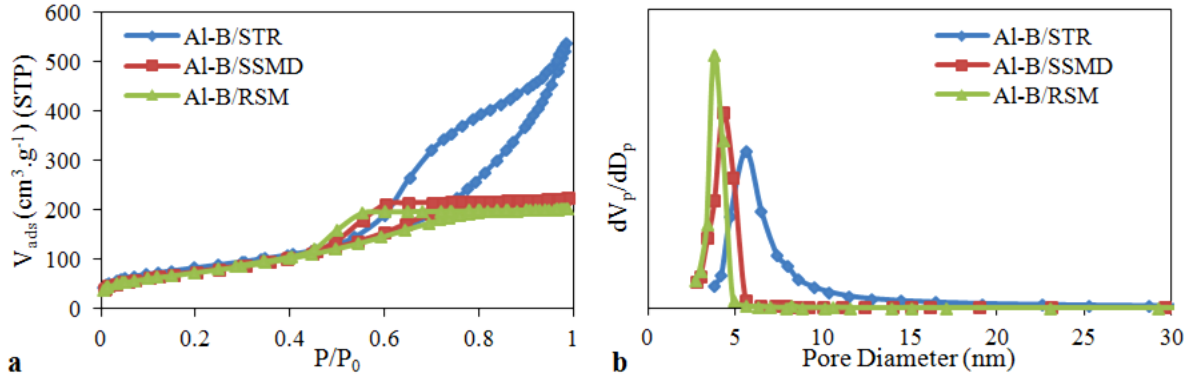

Fig. 4. (a) N_2 adsorption-desorption isotherm and (b) pore size distributions of boehmite derived alumina prepared with different mixing technologies

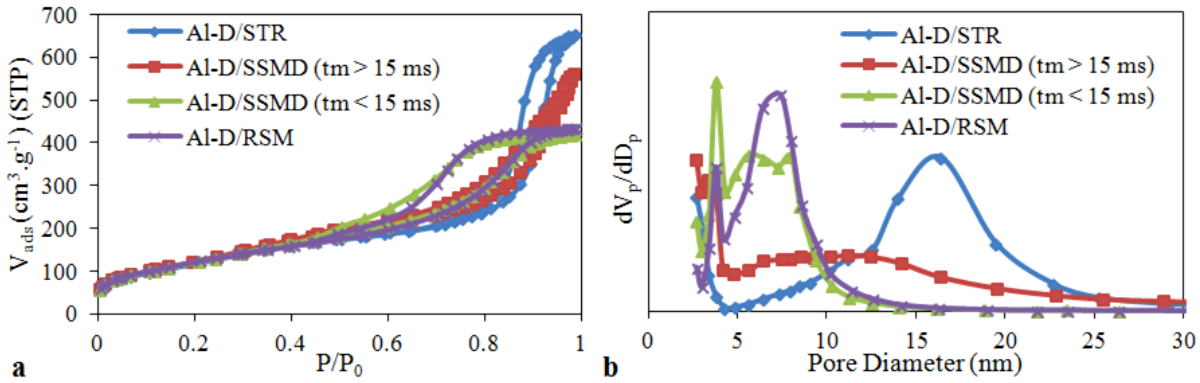

Fig. 5. (a) N_2 adsorption-desorption isotherm and (b) pore size distributions of NH_4-dawsonite derived alumina prepared with different mixing technologies

4. Conclusion

In this study, two alumina precursors, boehmite and NH_4-dawsonite, were precipitated in three different mixing technologies. The influence of micromixing time on the precursors and their respective alumina properties were evaluated.

It was observed that precipitation in a continuous fast mixer leads to a decrease of the solid porosity compared to the precipitation in a classical semi-batch STR.

However, in continuous mode, only NH_4-dawsonite turns out to be sensitive to micromixing time. It is thus possible to tune the pore volume between 0.5 and 0.9 $cm^3.g^{-1}$ on the derived alumina, but not the specific surface area, which always range between 400 and 450 $m^2.g^{-1}$ after the calcination step.

It is also interesting to note that for given micromixing conditions, boehmite and NH_4-dawsonite lead to alumina exhibiting very different textural properties. Overall, it can be observed that dawsonite derived alumina are more porous than boehmite derived alumina, with both larger mean pore diameter and larger pore size distribution. Dawsonite derived alumina also exhibit particularly high specific surface area, but part of it is due to microporosity created during the calcination step, because of their particular thermal decomposition process.

It is thus possible to get varied γ-alumina with specific porosity range using the appropriate precursor/mixing technology system (Fig. 6).

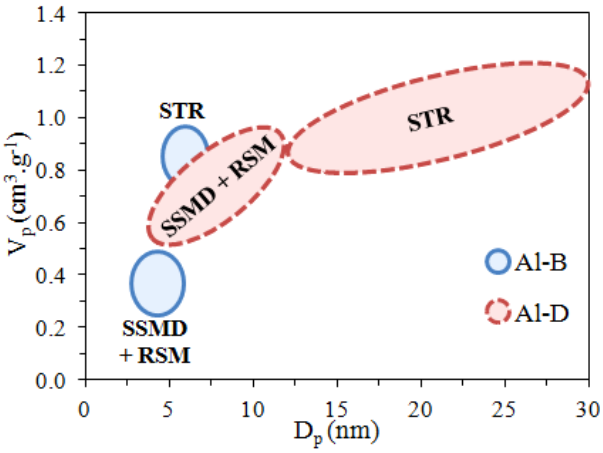

Fig. 6. γ-alumina porosity ranges covered by several precursor/mixing technology systems (STR: stirred tank reactor ; RSM: rotor-stator mixer ; SSMD: sliding surface mixing device)

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