Effect of Kneading Conditions on the Textural Properties of Heterogeneous Catalyst Supports

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Highlights

- Kneading operating conditions and boehmite paste composition were studied.
- Mechanical effect of kneading is captured by the accumulated deformation.
- Paste composition (pH) significantly affects pore volume and specific surface area.
- An empirical control parameter was defined to collapse all data onto master curves.

1. Introduction

Controlling the mechanical and textural properties of heterogeneous catalyst supports is key to the design and manufacturing of innovative and efficient catalytic materials. In particular, the microstructure of the support strongly affects mass transport within the porous medium and mechanical resistance [1]. Industrially, the manufacturing of γ-alumina supports from boehmite paste by a kneading – extrusion process allows to modify the mechanical and textural properties of the final solid support by changing the operatory conditions of each unit operation [2,3]. The present experimental study focuses on kneading and aims at quantifying the effects of this manufacturing step on the properties of the boehmite paste.

2. Methods

The present experimental study focuses on boehmite pastes prepared using Pural SB3 (Sasol) powder. This boehmite powder typically consists of micrometer-sized grains, ranging from 1 to 100 µm. Boehmite powder has a BET specific surface area of 260 m^2/g and a mesoporous volume of 0.38 ml/g, as determined by nitrogen sorption. In addition, mercury intrusion porosimetry showed a macroporous volume of about 0.19 ml/g.

Dense boehmite pastes (40 wt% boehmite) are prepared into an 80cc laboratory pilot kneader (Pastograph, Brabender) equipped with two contra-rotating cam blades with a velocity ratio of 2/3. The pilot kneader is also equipped with an HBM force sensor for torque measurement and a Pt100 sensor to monitor the temperature. The operating conditions investigated are the mixing duration – from 3 minutes to 4 hours –, the blade rotation speed – from 10 to 100 rpm – and the paste composition – pH from 5 to 9. After kneading, the textural characteristics of dried (20 hours at 80°C followed by 6 hours at 110°C) boehmite pastes are determined by nitrogen adsorption analysis and mercury intrusion porosimetry.

3. Results and discussion

The primary goal of this experimental investigation is to assess how the textural properties of boehmite paste in both its peptized and neutralized state are affected by kneading speed, duration, and paste composition. First, the influence of the kneading speed and duration was studied on neutralized pastes (pH = 6.2) by varying the mixing speed from 50 to 100 rpm, while the total mixing duration varies from 80 min to 158 min. The temporal evolution of torque Γ and temperature T recorded during the kneading process is illustrated in Figure 1a. During the peptization phase, the torque Γ initially experiences a rapid increase, followed by a plateau value associated with the kneading of a stable granular paste. When neutralization occurs, the torque sharply increases due to the agglomeration of boehmite aggregates, followed by an exponential decay associated with paste homogenization. While this temporal evolution of both Γ and T is significantly impacted by both the mixing speed and duration, the torque curves at various operating conditions collapse onto a single curve when plotted against the total accumulated deformation γ, calculated as the product of the kneading speed and duration (Figure 1b). The influence of the paste composition was studied by modifying the pH of ammonia solution added during the neutralization phase between 11.3 and 11.9, resulting in pastes with a pH varying from 5.2 to 8.7. This has a significant effect on the torque evolution and on the textural properties of the dried pastes (Figure 2). Finally, an empirical control parameter was defined to collapse all data onto master curves.

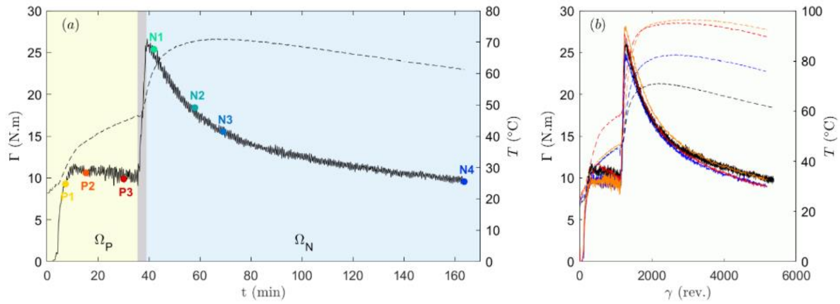

Figure 1. (a) Time-evolution of torque Γ (continuous line) and temperature T (dashed line) as measured in-situ in the kneader during a typical kneading experiment performed on a 40% neutralized paste (peptization – neutralization) (b) Torque Γ and temperature T evolution vs. accumulated deformation γ (line colors refer to various pairs of rotation speeds)

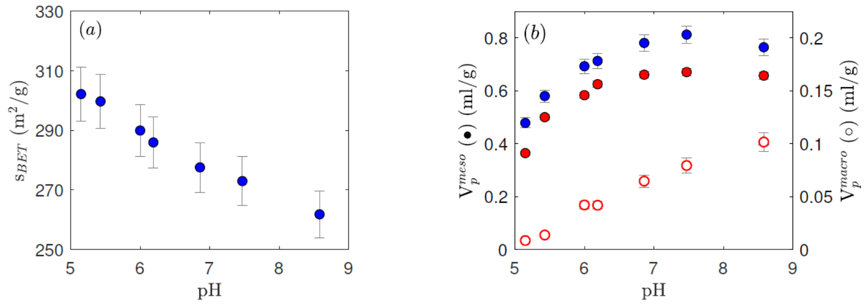

Figure 2. (a) Specific surface area of dried pastes vs. pH of soft pastes; (b) Mesoporous (full symbols) and macroporous (empty symbols) volumes of dried pastes vs. pH of soft pastes (nitrogen sorption (blue) – mercury porosimetry (red)).

4. Conclusions

The influence of both kneading operating conditions (speed and duration) and paste composition on in-situ measurements (torque and temperature) in the pilot kneader and on textural properties of the pastes were studied. The mechanical effect of kneading is captured by the accumulated deformation, while the paste pH stands out as a significant factor regarding paste composition. Comparatively, the paste pH has more effect on textural properties (e.g., increase in pore volume from 0.48 to 0.78 ml/g with an increase in pH from 5.2 to 6.9) than the accumulated deformation (e.g., increase in pore volume from 0.62 to 0.71 ml/g with an increase of two-hour duration of basic kneading). Both mechanical and physicochemical effects on the textural properties of γ-alumina supports were captured using a single empirical parameter. Although this parameter remains purely phenomenological, it underscores the coupling of two independent control parameters –mechanical and chemical– adjustable to tune textural properties by modifying the kneading operating conditions. In industrial applications, this descriptor can be used as a guide to define the operating conditions required to achieve targeted properties for the catalyst support. Future work will to explore the applicability of this descriptor for other pastes or synthesis protocols.

References

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Keywords
Kneading ; Boehmite pastes ; Gamma-alumina supports ; Textural properties.