Response to Comment on “High-surface-area corundum by mechanochemically induced phase transformation of boehmite”

Amol P. Amrute1*, Zbigniew Łodziana2, Hannah Schreyer1, Claudia Weidenthaler1, Ferdi Schüth1*

1Department of Heterogeneous Catalysis, Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim an der Ruhr, Germany. 2INP, Polish Academy of Sciences, PL-31-342 Kraków, Poland.

*Corresponding author. Email: amrute@kofo.mpg.de (A.P.A.); schueth@kofo.mpg.de (F.S.)

Li et al. commented that our report claims that methods reported thus far cannot enable the production of high-purity corundum with surface areas greater than 100 m² g⁻¹, and that our obtained material could be porous aggregates rather than nanoparticles. We disagree with both of these suggestions.

High-surface-area corundum (α-Al₂O₃) with nanometer-sized particles is a highly desirable material from both industrial and academic viewpoints (1, 2). However, the synthesis of high-purity α-Al₂O₃ in nanoparticulate form is not so straightforward because of the high activation barrier for its formation from transition aluminas. Previously studied methods reporting the production of high-surface-area corundum suffer from the requirements of harsh conditions either in the pre-synthesis step (2–4) (i.e., to obtain an appropriate precursor, such as diaspore, which can be converted to corundum at lower temperature) or in the post-synthesis step to remove the seed materials, matrix, or contamination (e.g., iron or iron oxide) in which corundum is formed. When micrometer-sized preformed corundum is milled, it is also severely contaminated with milling media and jar material. Our approach reported in (1) presents a simple procedure, enabling easy access to high-surface-area α-Al₂O₃, from which impurities, if any, can easily be removed, or can be avoided altogether, if milling proceeds in corundum milling equipment. Our report in (1) (i) describes ball milling of boehmite (γ-AlOOH) at room temperature to produce nano-corundum, and (ii) sheds light on the microstructural changes, and on the chemistry and thermodynamic aspects, involved in the transformation of γ-AlOOH to α-Al₂O₃.

We do not agree with the points raised by Li et al. (5) concerning our paper (1), although we should have included citations to their recent papers on the synthesis of α-Al₂O₃ nanoparticles (NPs) as prior art (6–8). The omission was unintentional and has been corrected. Their work did not appear in our searches, likely owing to the different scope of our study. Also, the conversion of transition aluminas by phase transformation, or of preformed large-crystal conventional α-Al₂O₃ by top-down ball-milling approaches, had been described somewhat more extensively before (9–12).

Regarding the first point raised by Li et al., we have not made any strong claim that there is no method available to produce α-Al₂O₃ with high surface area (>100 m² g⁻¹). Instead, we have pointed out the difficulties of achieving high-surface-area α-Al₂O₃. In fact, we have included an example of the diaspore route, which allows the production of corundum at mild calcination temperatures and thus enables the preservation of high surface area. This route has long been known to produce α-Al₂O₃ with surface areas exceeding 150 m² g⁻¹ (2). However, the production of precursor diaspore is a difficult process (3, 4), which makes this route technically unattractive.

Regarding the second point raised by Li et al. on the size of ball milling–derived corundum NPs, we have additional evidence, in addition to transmission electron microscopy (TEM), that supports the particle sizes we have reported. The TEM images may suffer from the sample preparation, deposition on the sample holder, or both (13, 14). As we had mentioned, our sample preparation includes a sprinkling of dry sample specimens on the TEM grid. We chose this approach because we wanted to analyze the sample directly after milling or after mild calcination of the ball-milled sample. Such sample preparation could lead to the deposition of an excessive amount in a less dispersed manner. Therefore, what appears in the TEM images as agglomerates are the overlapped particles; they are certainly not aggregates of ~200 nm.

To substantiate this, we have repeated our TEM analysis by varying the sample preparation. In this case, we used...
ethanol as a solvent to disperse the sample and ultrasonicated it for ~20 min, then placed a drop (2 μl) on the TEM grid and allowed it to dry under ambient conditions. Such sample preparation is also routinely used for microscopy analysis. The obtained images visualize well-separated NPs in the range of 3 to 30 nm (Fig. 1). The NPs might be separated even more if we were to reduce the concentration of the sample in ethanol during the sample preparation and selectively take a sample from the solution phase during ultrasonication. However, this procedure might not lead to a realistic picture, as a much smaller fraction of the sample will be visualized. We emphasize that we analyzed the materials directly after ball milling (or after mild calcination of the ball-milled sample) and did not process it further by methods such as fractional coagulation, which discards larger NPs and selectively collects the smaller ones from the acid solution phase (6, 7).

In addition to TEM, dynamic light scattering (DLS) analysis shows hydrodynamic diameter after 3-hour milling of ~26 nm [see figure 2B of (1), blue curve, data point for 180-min milled sample]. Therefore, if one excludes the contribution of the charged layer in this value, our particle diameter will fall in the range we observed from TEM images. DLS is a bulk method, providing a more comprehensive picture of particle size. Moreover, size analysis from x-ray diffraction (XRD) also provides an average domain size of ~18 nm [table 1 of (1)]. Thus, we are convinced that our sample is mostly composed of corundum NPs of ~15 nm (average particle diameter), in agreement with the value for surface area.

Regarding porosity, it is highly unlikely that we have intraparticle pores or channels. If such voids were formed, they would collapse under the high compression force applied in the high-intensity ball-milling process. There is also no indication of pores or channels from the different analytical methods. Still, we cannot exclude any contribution from surface roughness to the observed surface area values. Some surface roughness could indeed be seen in the TEM images shown in (1). We hope that this explanation further clarifies that our sample is mostly composed of small NPs that give the high surface area. Note that particle sizes obtained from TEM analysis, sorption, DLS, and XRD reflection broadening agree quite well, which supports the statement made above.

We want to emphasize that the simplicity of our process provides greater prospects for scalability. In fact, we have already achieved success in scaling up to several hundred grams in a mill type called Smoloyer. Because Smoloyer is available with milling jar sizes ranging from 1 to 900 liters, it provides good perspectives for further scale-up. In contrast, scale-up of the process reported by Li and colleagues (6) might not be straightforward or cost-effective, considering their starting materials, milling time, and harsh post-synthesis separation process.

REFERENCES


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**Fig. 1. TEM image of corundum NPs derived by ball milling of boehmite.** TEM analysis was performed on a Hitachi HF-2000 microscope with a cold field-emission cathode at a maximum acceleration voltage of 200 kV. Samples were prepared by suspending the specimen in ethanol, followed by ultrasonication for 20 min, placing a drop of sample suspended in ethanol on the TEM grid, and allowing it to dry under ambient conditions.
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