Supplementary information for

Solvent free synthesis of nanocrystalline hexaaluminate-type mixed oxides with high specific surface area for CO oxidation reaction

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Example of synthesis, case of $BaAl_{12}O_{19}$.

Barium hexaaluminate was prepared by activated reactive synthesis. Simple oxides powders were used as starting materials. The starting materials with stoichiometric ratios were blended in a laboratory mixer for 2 h prior to calcination at 1500°C for 5 h under an air atmosphere using a heating rate of 10 °C min^{-1}. Once the synthesis of hexaaluminate structure was confirmed by XRD analysis, the synthesized sample in powder form were charged in a 50 ml tungsten carbide (WC) crucible containing 3 WC balls of 11 mm in diameter. Crucible is closed under air and fixed in a laboratory SPEX grinder. Grinding is performed at an agitation speed of 1100 cycles per minute for times varying between 30 min and 300 min. This step was evidenced to result in a significant crystal size decrease. In order to enhance the specific surface area, 60 g of milled powder was subjected to a second step of mechanical milling at lower energy in a conventional laboratory attritor containing 4.5 mm balls. This step is performed under the following conditions: powder to ball mass ratio of 60/1200; time of LEBM = 15 min; rotation speed of 250 rpm.

Characterization techniques

Phase identification and crystallite size measurement by X-ray diffraction: patterns were collected on a SIEMENS D5000 using Cu Kα radiation (λ = 1.54184 nm) as X-ray source. Scanning was performed between 10° and 80° and the diffractograms were recorded using 2 s of acquisition for each step of 0.04°. Phase identification was obtained by comparison with JCPDS database files.

Particles sizes (D_{cryst}) were evaluated by means of the Scherrer equation $D = K\lambda/\beta\cos(\theta)$, after Warren's correction for instrumental broadening. K is a constant and λ is the wavelength of the X-ray used. β is the effective line width of the X-ray reflection, calculated by the formula $\beta^2 = B^2 - b^2$, where B is the FWHM and b is the instrumental broadening determined by the FWHM of the X-ray reflection of quartz at $2\theta \approx 27$°C

Specific surface area: Measurements were obtained from N_2 adsorption-desorption experiments. A known mass of sample was first out gassed at 300 °C at least for five hours. Isotherms were obtained on a Micromeritics TRISTAR instrument. The specific surface area, S_{BET}, was calculated from the linear part of the BET plot.

SEM: SEM micrographs were obtained on a JEOL JSM-840 with an acceleration voltage of 15 kV. The samples were first dispersed on an aluminum stub and coated with an Au/Pd film before analysis.

TEM: Morphological evolution was also observed by TEM. Micrographs were collected on a JEOL 2100 instrument (operated at 200 kV with a LaB6 source and equipped with a Gatan UltraScan camera).

CO oxidation measurement: Catalytic properties of substituted hexaaluminates were investigated using the CO oxidation reaction. 75 mg of catalyst powder was placed in U-shaped quartz reactor and pre-treated for 2 h under a 20 vol.% O_2 in N_2 gas mixture with a flow rate of 100 ml min^{-1} at 400 °C. Thereafter, the catalyst was purged with N_2 for 10 min before starting the reaction. The test was performed under a mixture of gas composed of 5 vol.% CO – 20 vol.% O_2 in N_2, at a total gas feed of 60 ml min^{-1}. The temperature was then decreased by steps. Reactants and reaction products were quantified at the target temperature using a gas chromatograph once the conversion rate was stabilized (about 30 min). Conversions presented are average values of three successive conversion measurements obtained after stabilization.

Hexaaluminate characterization results

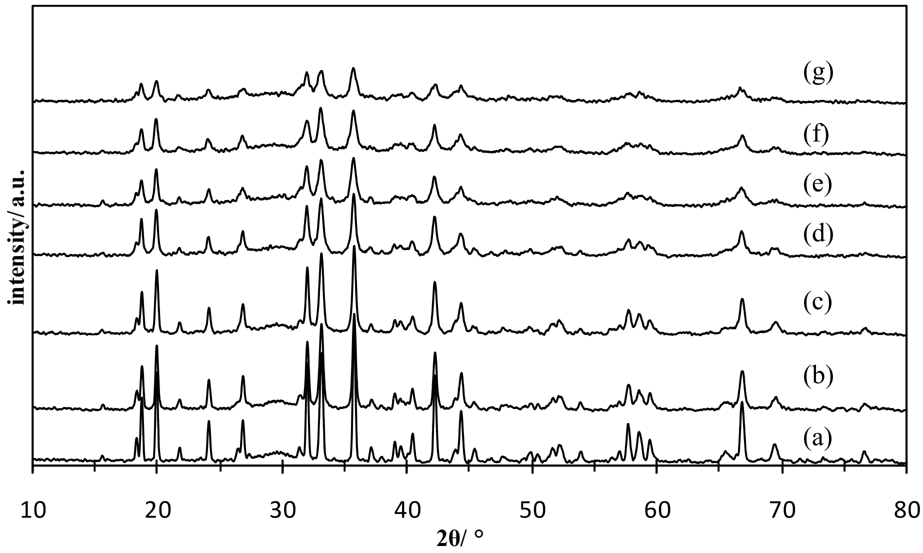

Figure S1 Evolution of the XRD patterns with time of high energy ball milling (HEBM). Case of $BaAl_{12}0_{19}$: (a) 0 min; (b) 30 min (c) 60 min; (d) 120 min; (e) 180 min; (f) 240 min; (g) 300 min.

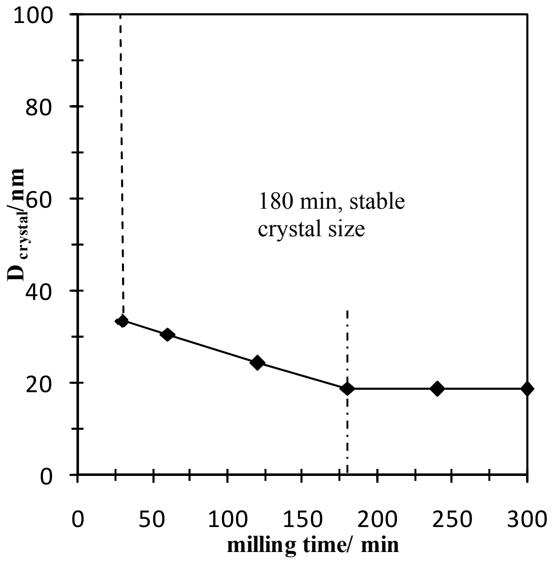

Figure S2 Evolution of BHa crystallite size with the time of high energy ball milling (HEBM).

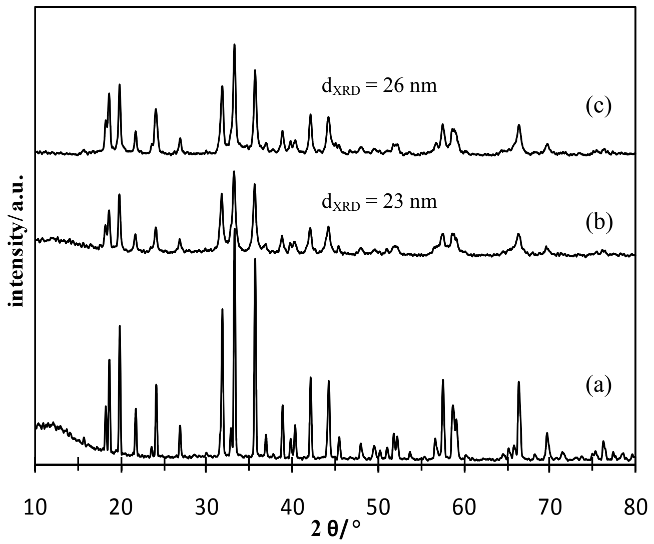

Figure S3 XRD patterns of $BaCo_1Al_{11}O_{19}$ at each step of synthesis: (a) sample SSR; (b) sample HEBM (180 min); (c) sample after LEBM.

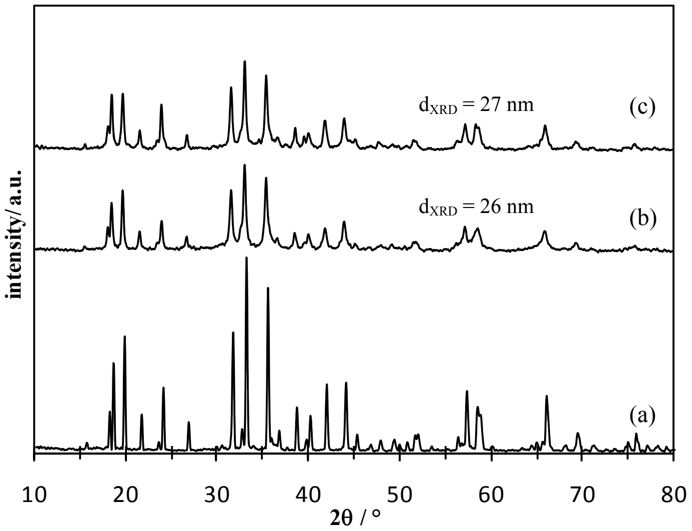

Figure S4 XRD patterns of $BaMnPd_{0.07}Al_{10.93}O_{19}$ phase at each step of synthesis: (a) sample SSR; (b) sample HEBM; (c) sample after LEBM.

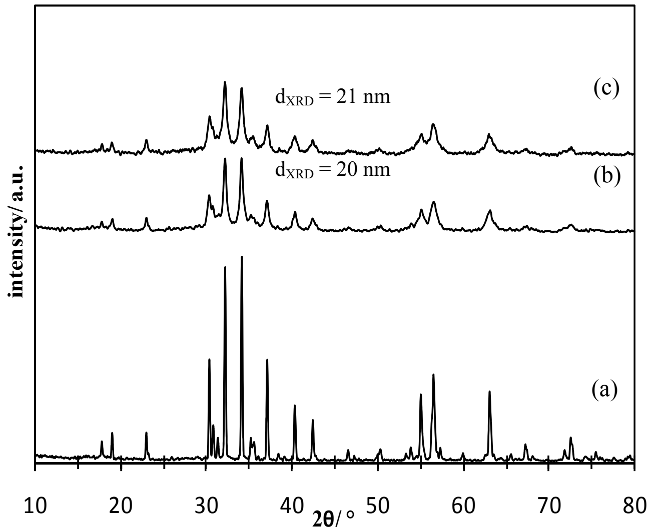

Figure S5 XRD patterns at each step of hexaferrite phase synthesis: (a) sample SSR; (b) sample HEBM (180 min); (c) sample after LEBM.

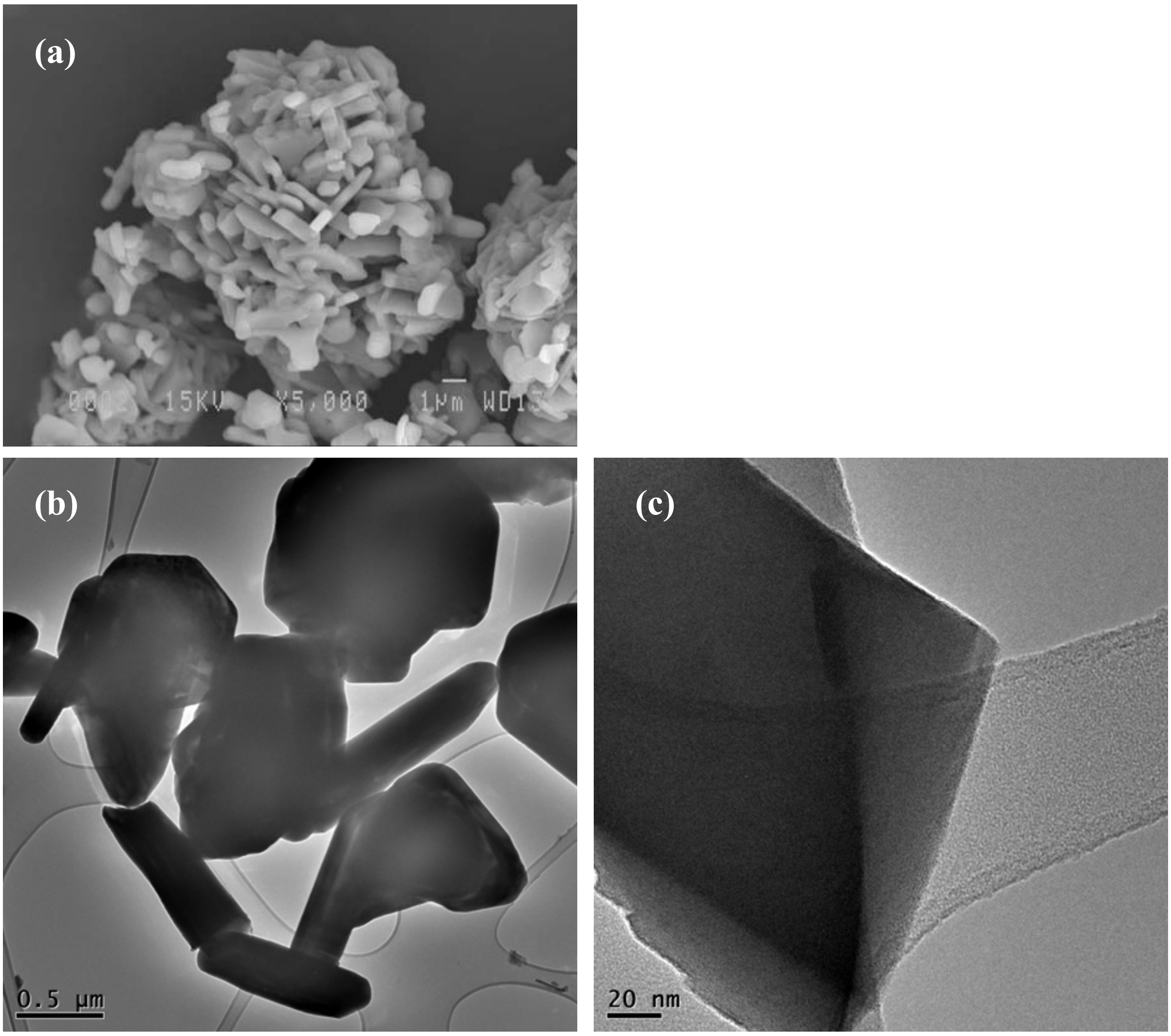

Figure S6. SEM (a) and TEM (b, c) images of the $BaAl_{12}O_{19}$ SSR material.

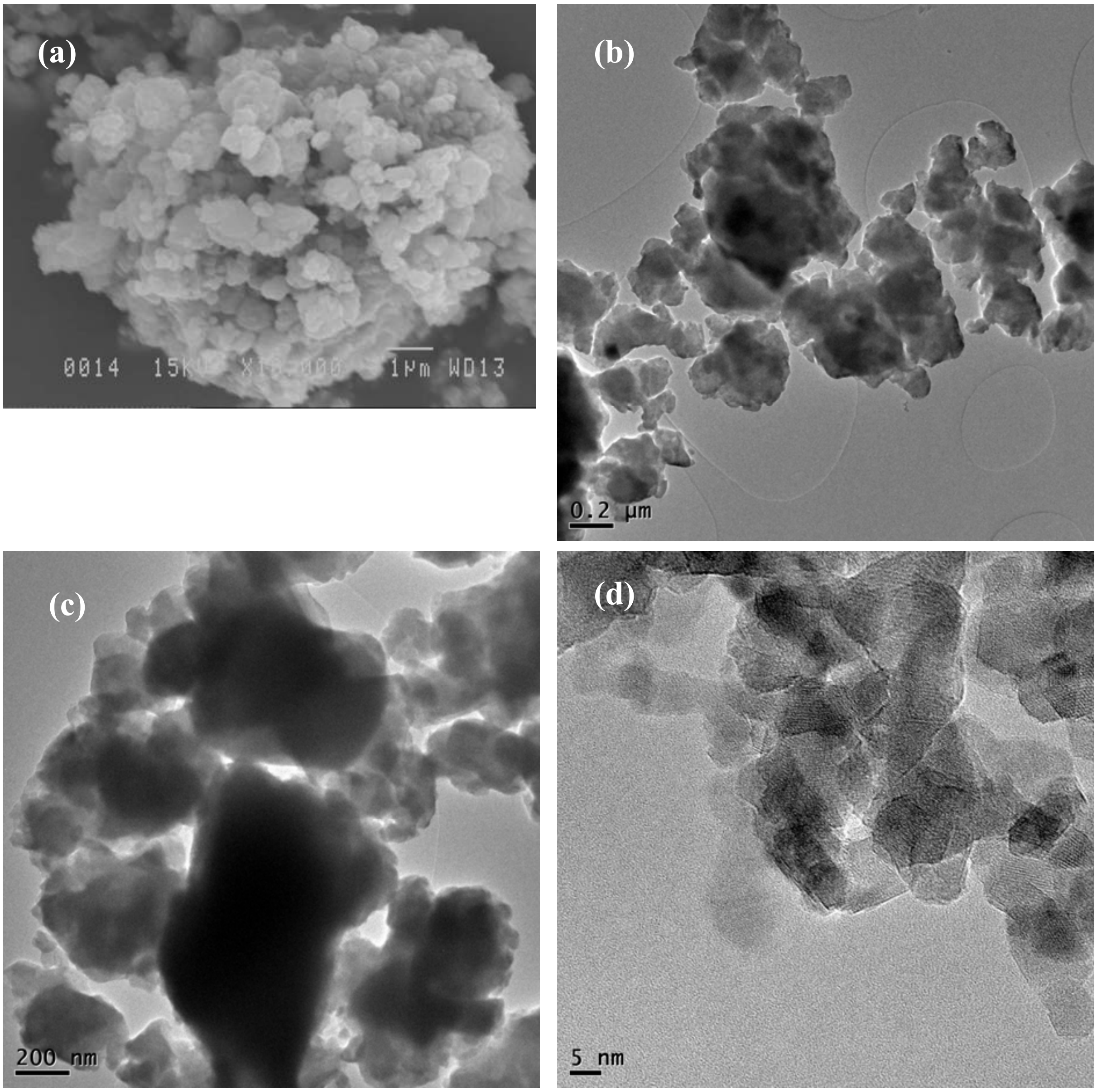

Figure S7. SEM (a) and TEM (b, c,d) images of the $BaAl_{12}O_{19}$ HEBM material.

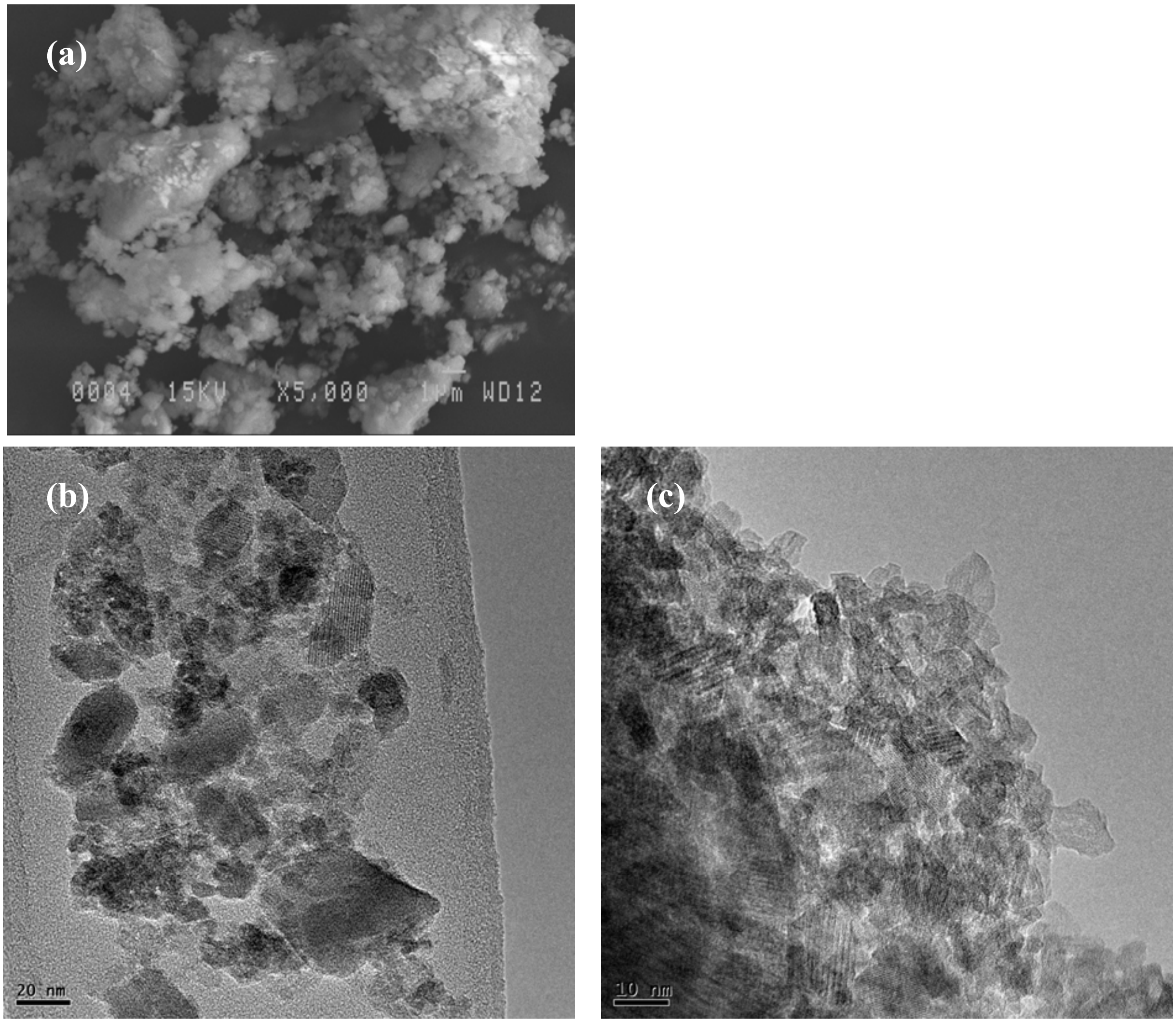

Figure S8. SEM (a) and TEM (b, c) images of the $BaAl_{12}O_{19}$ LEBM final material.