

Ultrasound-Assisted Design of Metal Nanocomposites

Ekaterina V. Skorb, Helmuth Möhwald, Torsten Irrgang, Andreas Fery, Daria V. Andreeva

Experimental

Materials: Aluminum powder (<100 μm , >99,5%, Roth), magnesium powder (325 mesh, 99,8%, Alfa Aesar), 1:1 aluminum – nickel alloy powder (Fluka), zinc (dust, <50 μm , 98%, Aldrich) gold (powder, 99,99%, Fluka), platinum (powder, 99,99%, Aldrich), silver (powder, 99,9%, Aldrich), palladium – aluminum alloy (powder, 1 % Pd, Alfa Aesar), copper – palladium – aluminum alloy (powder, 0,3 % Cu, 1 % Pd, Alfa Aesar) were used as received. The water was purified before use in a three stage Milipore Milli-Q Plus 185 purification system and had a resistivity higher than 18.2 M Ωcm .

Ultrasonication (US): 40 ml of 10 wt% suspension of metals in purified water were sonicated in a thermostated flow cell (FC100L1-1S) (at 65°C temperature) with the VIP1000hd (Hielscher, Germany) operated at 20 kHz with a maximal output power of 1000 W ultrasonic horn BS2d22 (head area of 3.8 cm²) and equipped with a booster B2-1.2. The maximum intensity was calculated to 57 W/cm² at a mechanical amplitude 81 μm .

Catalytic reactions: The hydrogenation of ketones was studied as described in Ref. (Sharma, G.; Mei, Y.; Lu, Y.; Ballauff, M.; Irrgang, T.; Proch, S.; Kempe, R. *J Catalysis* 2007, 246, 10). The hydrogenation experiments were carried out using parr instrument stainless steel autoclaves N-MT5 300 mL equipped with heating mantles and temperature controller. GC analyses were carried out on an Agilent 6890 N Network GC System using a Lipodex E column (25 m x 0.25 mm; Machery & Nagel). In a glass vial 0.05 g of the catalyst were weigh in and suspended in 1 mL water. Additionally acetophenone (300 μL , 0.31 g, 2.57 mmol) were transferred via a sealed Fortuna-Pipette. The filled vial was put into the autoclave. Subsequently the autoclave was purged three times with H₂. The reduction was taken out at room temperature under vigorous stirring by using a continuous pressure of 70 bar H₂. The experiment was stopped after 24 hours by releasing of the hydrogen gas. The reaction mixture was worked up by the addition of dodecane (584 μL , 0.44 g, 2.57 mmol) as internal standard and 2.5 mL diethyl ether. The product was extracted from the organic layer. The catalytic reactions were all carried out twice and several runs were analysed.

Characterization. ²⁷Al solid state MAS NMR: NMR spectra were recorded at ambient temperature with a Bruker CMX-300 instrument operating at 300.15 MHz (FU Berlin) at a rotation frequency of 4 kHz, typical pulse delay of 10 s. The external reference for chemical shift calibration was 0.1M Al(NO₃)₃.

Microscopy studies: Scanning electron microscopy (SEM) measurements were conducted with a Gemini Leo 1550 instrument at an operation voltage of 3 keV. Transmission electron microscopy (TEM) images were obtained on a Zeiss EM 912 Omega transmission electron microscope operating at 300 kV. The samples were ultramicrotomed (Leica EM FC6) and placed onto the copper grids coated with carbon film.

X-ray diffraction (XRD): X-ray diffraction of the samples was studied on a Bruker AXS – D8 ADVANCE X-ray diffractometer and on a Nanostar Bruker AXS diffractometer.

BET analysis: The specific surface areas of the samples were determined by a Micromeritics ASAP 2000 surface area analyzer. All samples were outgassed under vacuum at 120°C for 8 hours before N₂ adsorption. BJH evaluation was used for determine the pore diameter.

Modification of noble metals by ultrasound

The SEM images (Figure S1) of the noble metals show that ultrasound irradiation didn't change the metal surface.

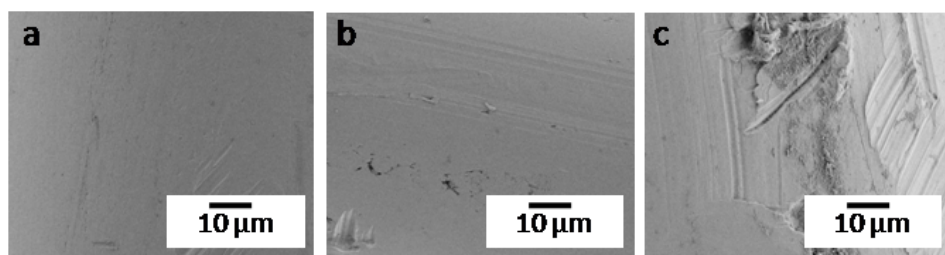


Figure S1. SEM images of the surfaces of the noble metals after sonication at 57 W/cm² for 60 min: silver (a), gold (b) and platinum (c).

Effect of sonication on Mg particles

The study of influence of the high intensity ultrasound onto magnesium particles has the same character with modification of aluminum. XRD patterns (Fig. S2a) evidence that sonication results in the formation together with Mg porous structure the formation of magnesium hydroxide phase (Brucide, syn) which appearances after irradiation and its peak increases in time of ultrasound influence.

Adsorption desorption isotherms of nitrogen for magnesium after 20 min of ultrasound exposure is shown in Fig. 4b. The obtained isotherm characterizes as Type IV general isotherms and the hysteresis loop is related to the capillary condensation in mesopores. The isotherm in this case is very similar to the isotherms which were obtained for the case of

porous Al. Simultaneously after the same time of ultrasound treatment magnesium formed more porous structure: the surface areas for Mg and Al are 68.7 m²/g and 53.9 m²/g, correspondly. Together with higher surface area magnesium sample has larger pores: average pore sizes are ~ 14 nm in the case of magnesium and ~ 4 nm in the case of aluminium. This fact could attributes first of all to higher chemical reactivity of magnesium in comparison with aluminum together with lower melting point of magnesium.

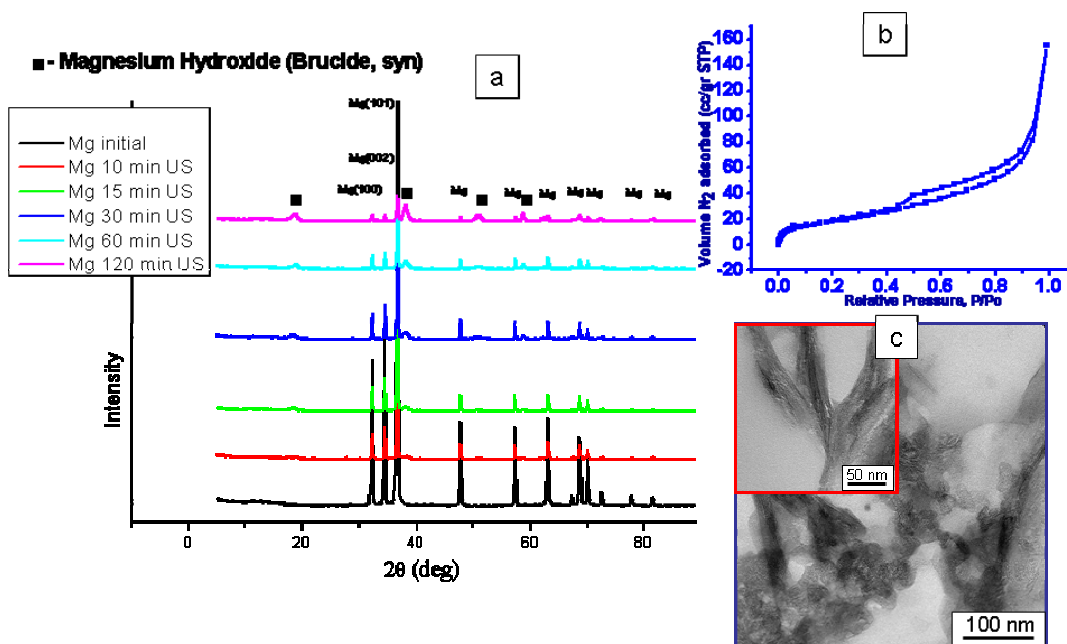


Figure S2. XRD patterns of Mg particles (a); BET isotherm (b) and TEM images (c) for magnesium particles after 20 min of 20 kHz, 57 W/cm² ultrasound exposure in aqueous solution.

Effect of sonication on crystalline structure of Al particles

Highly ordered aluminum crystals can be observed in the electron diffraction images (Figure S2b) after ultrasound treatment of the Al particles in water.

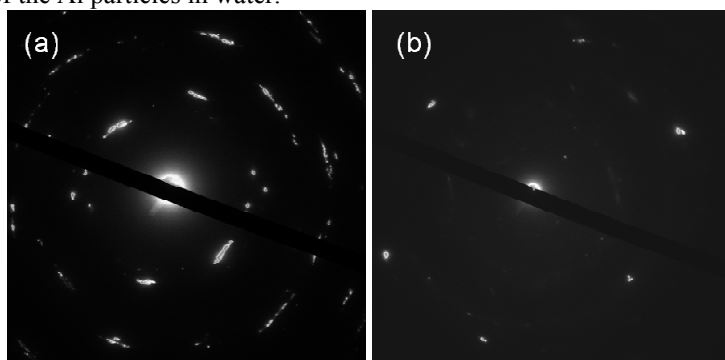


Figure S3. Electron diffraction images of the initial Al particles (a) and after 60-min-modification by ultrasound (b).

Effect of sonication time on Al particle porosity

The isotherms (Figure S4) show that the volume of N₂ adsorbed and desorbed per unit mass of the sample increases and the decreases with the increase of the duration of ultrasonic treatment. The isotherms obtained seem to fall between Type II and Type IV general isotherms, as classified by BDDT (Branauer, Deming, Deming, and Teller) theory. At the relative pressure values of around 0.08, especially in the case of long time ultrasound treatment, there is an inflection point, which indicates the completion of monolayer coverage and the starting point of multilayer N₂ adsorption. Between the relative pressure values of 0.08 and 0.45, all the isotherms are almost linear indicating the presence of micropores along with the macropores. After the relative pressure value of 0.45, the value of adsorbed N₂ starts to increase sharply. This is due to the continuous progression from multilayer adsorption to capillary condensation, in which the smaller pores become completely filled with liquid nitrogen. This occurs because the saturation vapor pressure in a small pore is reduced, according to the Kelvin equation, by the effect of surface tension.

At the early stages of ultrasound treatment, the sample contains mesopores in which capillary condensation occurs when the relative pressure reaches a value corresponding to the radius of the pore by the Kelvin equation. At the longer ultrasound influence, microporous structures are produced and at low relative pressures larger amounts of micropores are filled by N₂. Thus, at the beginning moment the formation of mesopores takes place, simultaneously, we observed the formation both of

micropores and mesopores after long term ultrasonic treatment. The specific surface area is increasing with treatment time and reaches maximum ($80 \text{ m}^2/\text{g}$) after 60 min of sonication. Further continuing of sonication leads to decrease of porosity of the particles. These results are in agreement with the SEM images showing surface smothering of the 2 hr treated samples.

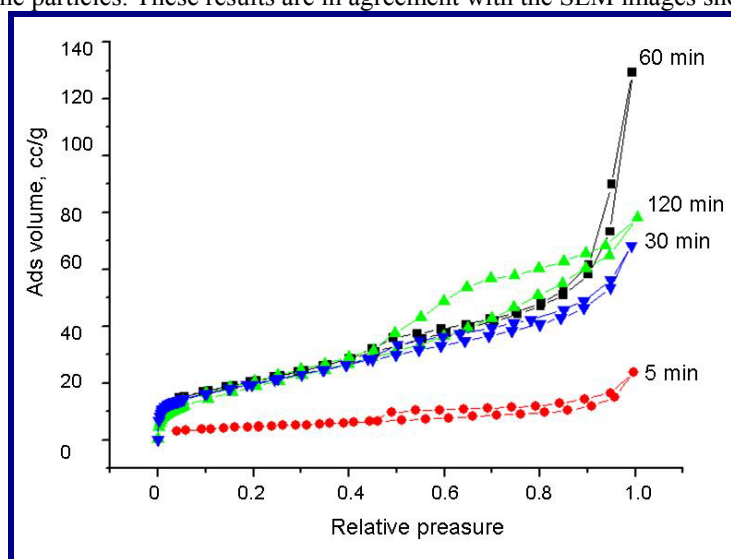


Figure S4. The BET isotherms of N_2 adsorbed and desorbed per unit mass for Al particle with different duration of ultrasonic exposure (20 kHz , $57 \text{ W}/\text{cm}^2$).

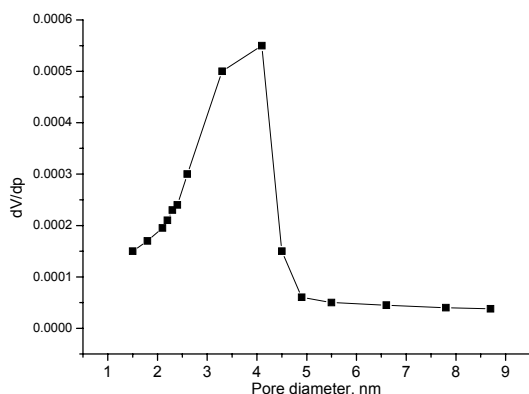


Figure S5. Pore size distribution of Al particles sonicated at $57 \text{ W}/\text{cm}^2$ for 60 min.

Modification of Zn particles

The SEM images (Fig. S6) of the Zn show that ultrasonic treatment leads to its immediate transformation into ZnO, in particular during the first stage of modification we form “hedgehog” like structure which is Zn metal core and ZnO hollow rods attached to the Zn core. Quantity of these hollow ZnO particles increases 15 min from the beginning of sonication and after that begin to decrease. There are no porous particles were detected in 60 and 90 min sonicated samples. In 90 min practically all initial Zn particles are converted to not porous ZnO.

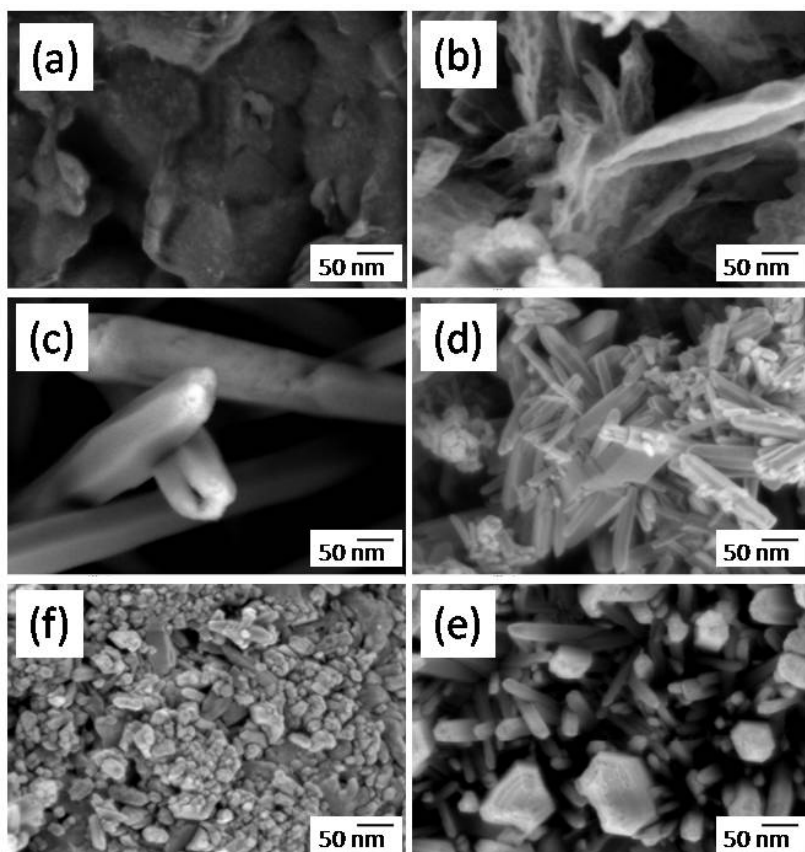


Figure S6. SEM images of initial Zn particles (a) and the particles sonicated at 57 W/cm² for 1 min (b), 3 min (c), 5 min (d), 50 min (f) and 90 min (e).

Catalytic runs

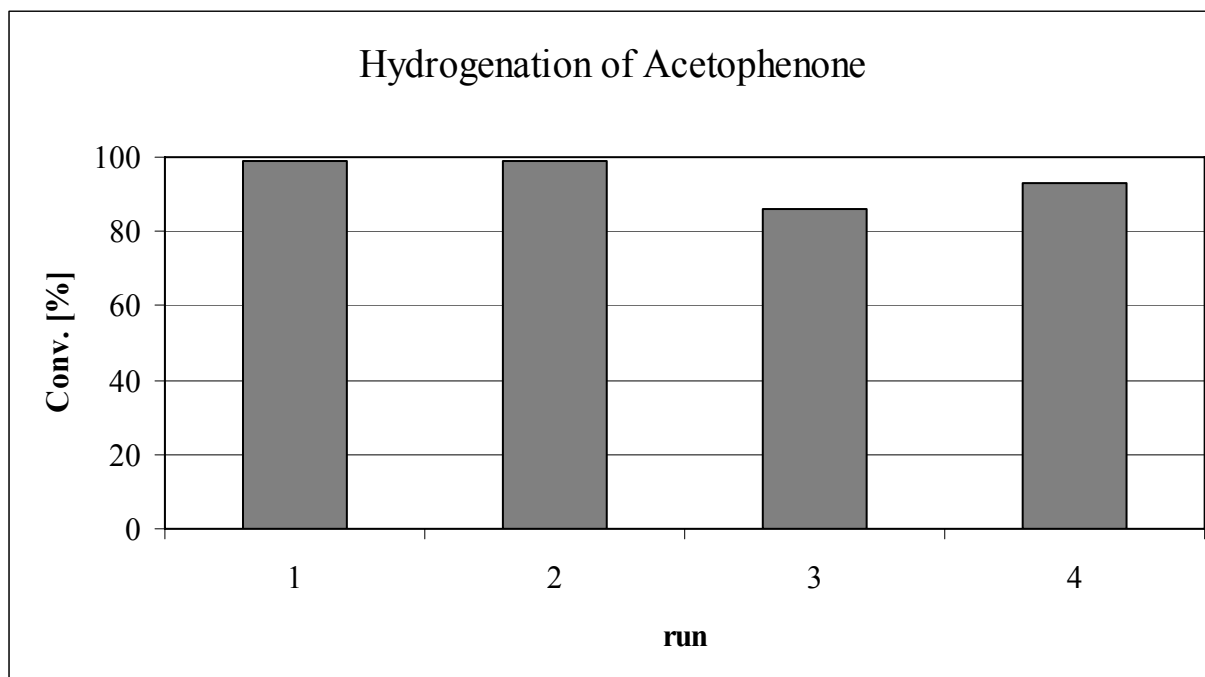


Figure S7. Stability and re-use of the Al/Ni mesoporous particles prepared by sonication at 57W/cm² for 60 min (hydrogenation of acetophenone). The same catalyst was used for 4 runs. After each run products were extracted by ether (3 times with 3 mL) and fresh substrate was added.