Supporting Information

Catalytic transfer hydrogenation of furfural using mechanically activated MgO as catalyst

Antonio Manuel Pérez-Merchán,[a] Benjamín Torres-Olea,[a] Marcella Scala,[b,c] Nikolaos Dimitratos,[b,c] Irene Malpartida,[d] Cristina García-Sancho,[a] Josefa M. Mérida-Robles,[a] Pedro Maireles-Torres,[a] Ramón Moreno-Tost,[a] Juan Antonio Cecilia*[a]

a Departamento de Química Inorgánica, Cristalografía y Mineralogía, Universidad de Málaga, Facultad de Ciencias, Campus de Teatinos. 29071 Málaga (Spain)
b Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale Risorgimento 4, 40136 Bologna, (Italy)
c Center for Chemical Catalysis - C3, Alma Mater Studiorum Università di Bologna, Viale Risorgimento 4, 40136 Bologna, (Italy)
d Deasyl S.A., Plan-les-Ouates, Geneva, 1228, Switzerland

Physico-chemical characterization

Powder X-ray diffraction patterns were obtained using an X-Pert Pro-automated diffractometer, which is composed of a Ge (111) primary monochromator with Cu Kα1 radiation and a X'Celerator detector with a step size of 0.017˚. The analysis was carried out between 2θ = 10–70˚, with an equivalent counting time of 712 s per step.

Transmission electron microscopy (TEM) images were obtained by using a FEI Talos F200x high-resolution transmission electron microscope (Thermo Fisher Scientific) to study the morphology and dispersion of the active phase. Moreover, elemental microanalysis was carried out with an EDX Super-X system with four X-ray detectors and a X-FEG beam, which allows for 3D chemical characterization with compositional mapping.

Particle size measurements were performed on a Malvern Panalytical Zetasizer Nano ZS using ethanol as dispersant in disposable polystyrene cuvettes. Samples were sonicated for 120 seconds prior to measurement.

Attenuated Total Reflection (ATR) was performed in a Bruker Vertex 70 FT-IR spectrophotometer, which displays an accessory of the golden gate single reflection diamond ATR system. The samples were recorded without prior preparation. A standard spectral resolution of 4 cm^{-1} in the spectral range of 4000–500 cm^{-1} was used for spectrum acquisition, as well as 64 accumulations per sample.

Textural parameters were obtained from N_2 adsorption-desorption at -196 ˚C by using an automated ASAP 2420 Micromeritics equipment. Firstly, samples were outgassed at 150 ˚C for 12 h at 10^{-4} mbar. The Brunauer–Emmet–Teller (BET) method was utilized to determine the specific surface areas, the pore volume was calculated at P/P0 = 0.98, the pore size distribution was obtained using a DFT method. The average pore size was determined by applying the Barrett-Joyner-Halenda (BJH) method to the desorption branch.

The basicity of the samples was determined by thermo-programmed desorption of CO_2 (CO_2-TPD). The desorption was measured between 80 and 450 ˚C, using an AutoChem 2920 apparatus equipped with a TCD detector.

In order to study the surface composition of the catalysts, they were analyzed by X-ray photoelectron spectroscopy (XPS). The analyses were performed in a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg Kα radiation (300 W, 15 kV, 1253.6 eV) with a multichannel detector. Spectra were recorded using the constant pass energy mode at 29.35 eV with a 720 μm diameter analysis area. The maximum peak of adventitious carbon was used as the reference for the different peaks (C 1 s at a binding energy of 284.8 eV). Moreover, a PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. The peaks were deconvoluted by using the least squares method, Gaussian–Lorentzian (90% G and 10% L) curves to determine the binding energy (BE) values of the different element core levels more accurately, and a Shirley-type background line.

FTIR analysis coupled with isopropanol adsorption were carried out in a Tensor 27 (Bruker) with a Michelson interferometer coupled to a DTGS infrared detector and a He-Ne laser as internal reference. The measurements were obtained with a spectral resolution of 4 cm^{-1} from 4000 to 400 cm^{-1} and 64 accumulations in transmission mode. Prior analysis, the samples were calcinated at 450 ºC at 5 $ºC \cdot min^{-1}$ for 2 h, before cooling down to 200 ºC. The MgO was then compacted into pellets of weight close to 0.05 g. These pellets were loaded into a greaseless vacuum cell with CaF_2 windows. The sample was then evacuated at 300 ºC for 1.5 h to remove any surface impurities. After this, the system was filled with 200 torr of isopropanol for 15 min before outgassing at 35, 100, 200 and 300 ºC, sequentially, for 15 min each. After each outgassing step, the sample was submitted to FTIR.

2-propanol adsorption studies were carried out in a Surface Characterization 3FLEX model, from Micromeritics Instrument Corporation. Firstly, samples were outgassed at 100 ˚C for 20 h, and then 2-propanol adsorption was performed at 25 ºC.

Calibration of the reactive and potential products was performed with commercial chemicals supplied by Merck Co., with known purities and densities. For calibration, known amounts of reagents and/or products were weighed and dissolved in 2-propanol, using the same amount of o-xylene, used as an internal standard, in all cases. These solutions were transferred to 25 mL volumetric flasks and injected twice into the gas chromatograph to obtain each calibration point. The regression line was obtained considering the ratio of reagent or product area/standard area was represented on the y-axis and the amount of reagent or product injected on the x-axis. In all cases, an R value greater than 0.99 was obtained. To quantify the conversion and yields values, the reaction liquid was microfiltered and injected directly into the gas chromatograph. From the calibration slope and the ratio of reagent or product areas/standard area determined by the gas chromatograph, the amount of the potential products and reagents were obtained. Quantification was carried out considering the initial mole and the mole of reagents and products obtained. In all cases, a material balance was made where the unquantified moles of reagents or products were considered as undetected products.

Supplementary Figures

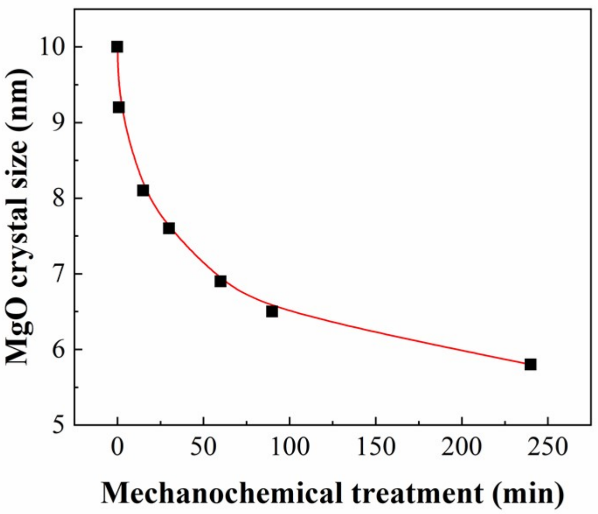


Figure S1. Correlation between the time of mechanochemical treatment and the MgO crystal size.

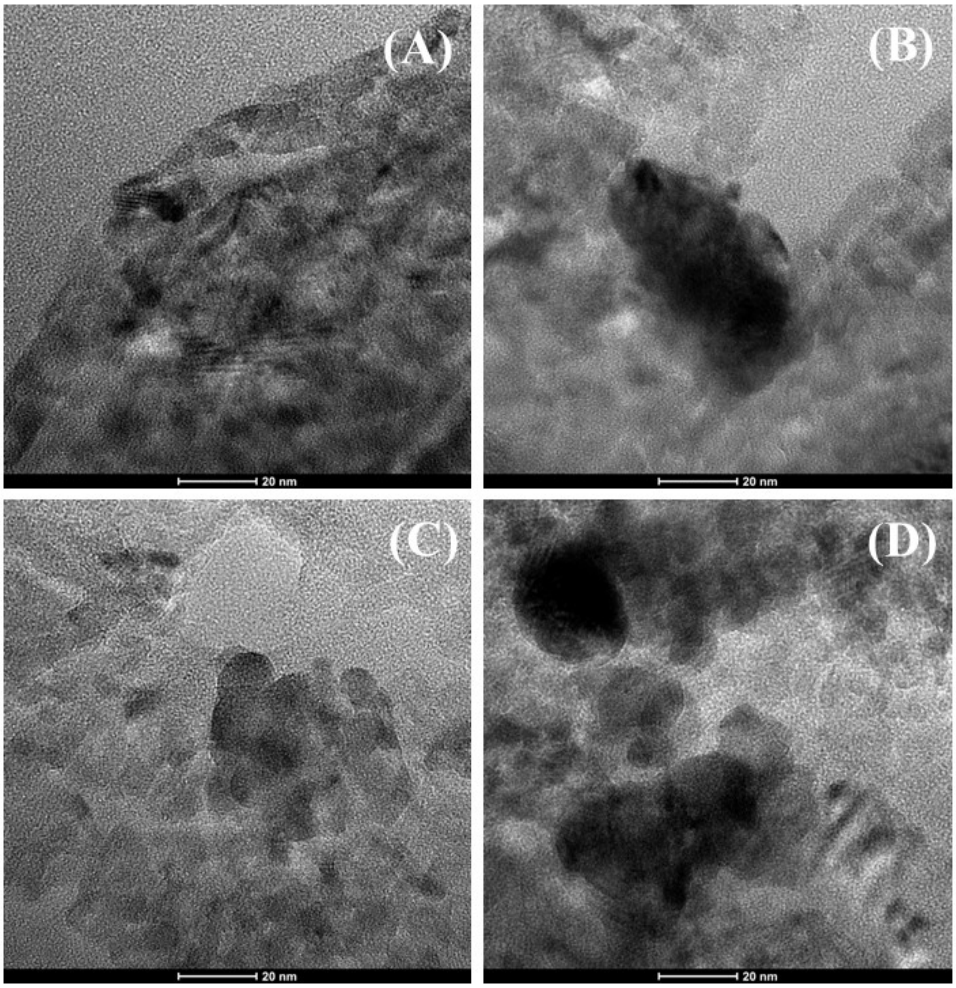


Figure S2. TEM micrographs of MgO_untreated (A), MgO_15m (B), MgO_60m (C) and MgO_240m (D) catalysts. (Magnification: 20 nm).

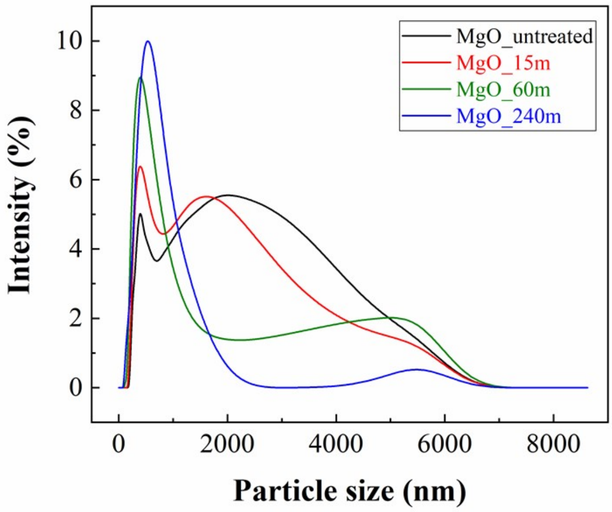


Figure S3. Particle size distribution for MgO_untreated, MgO_15m, MgO_60m and MgO_240m catalysts.

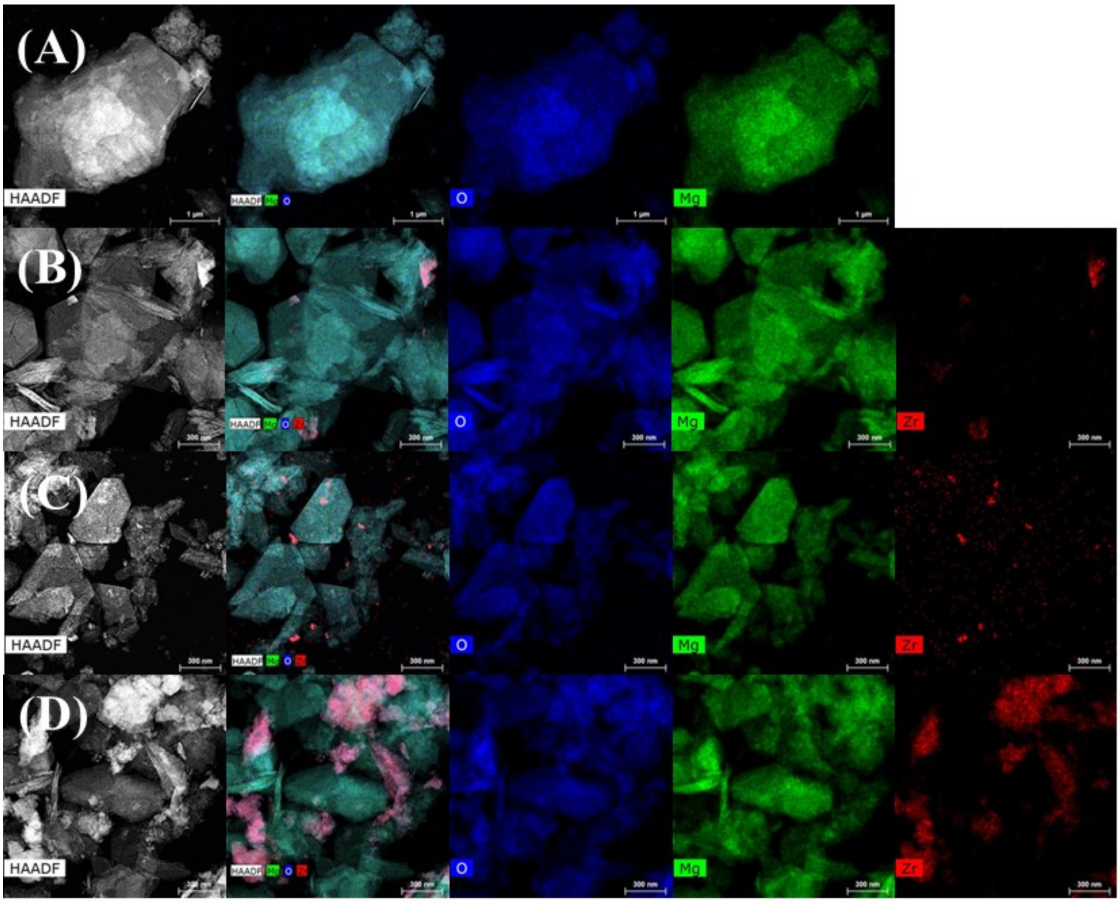
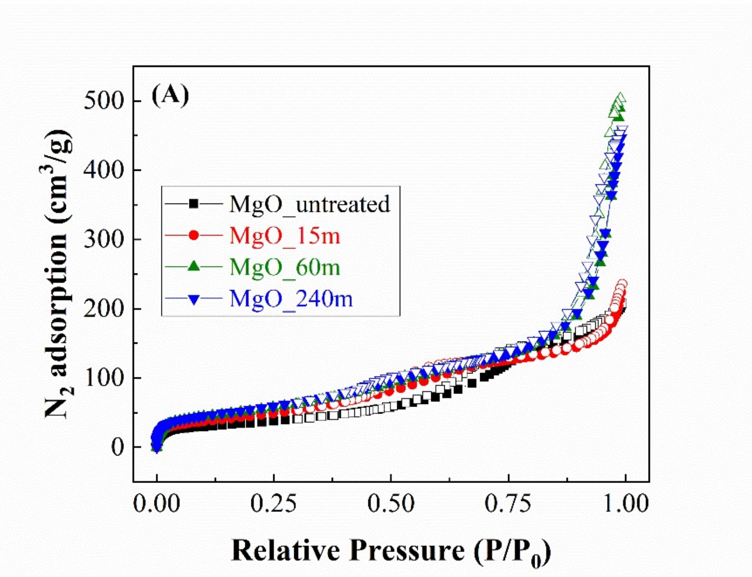


Figure S4. EDX images of MgO_untreated (A), MgO_15m (B), MgO_60m (C) and MgO_240m (D) catalysts



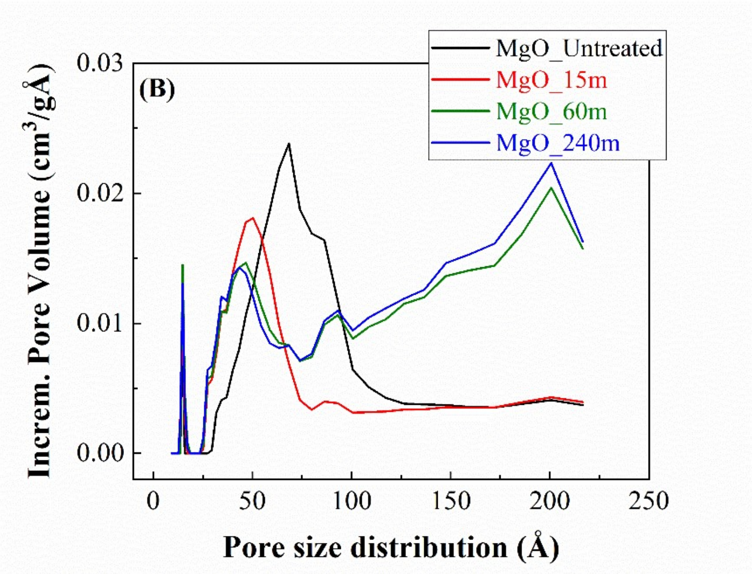


Figure S5. N_2 adsorption-desorption isotherms at -196 ºC (A) and pore size distribution (B) of MgO_untreated, MgO_15m, MgO_60m and MgO_240m catalysts.

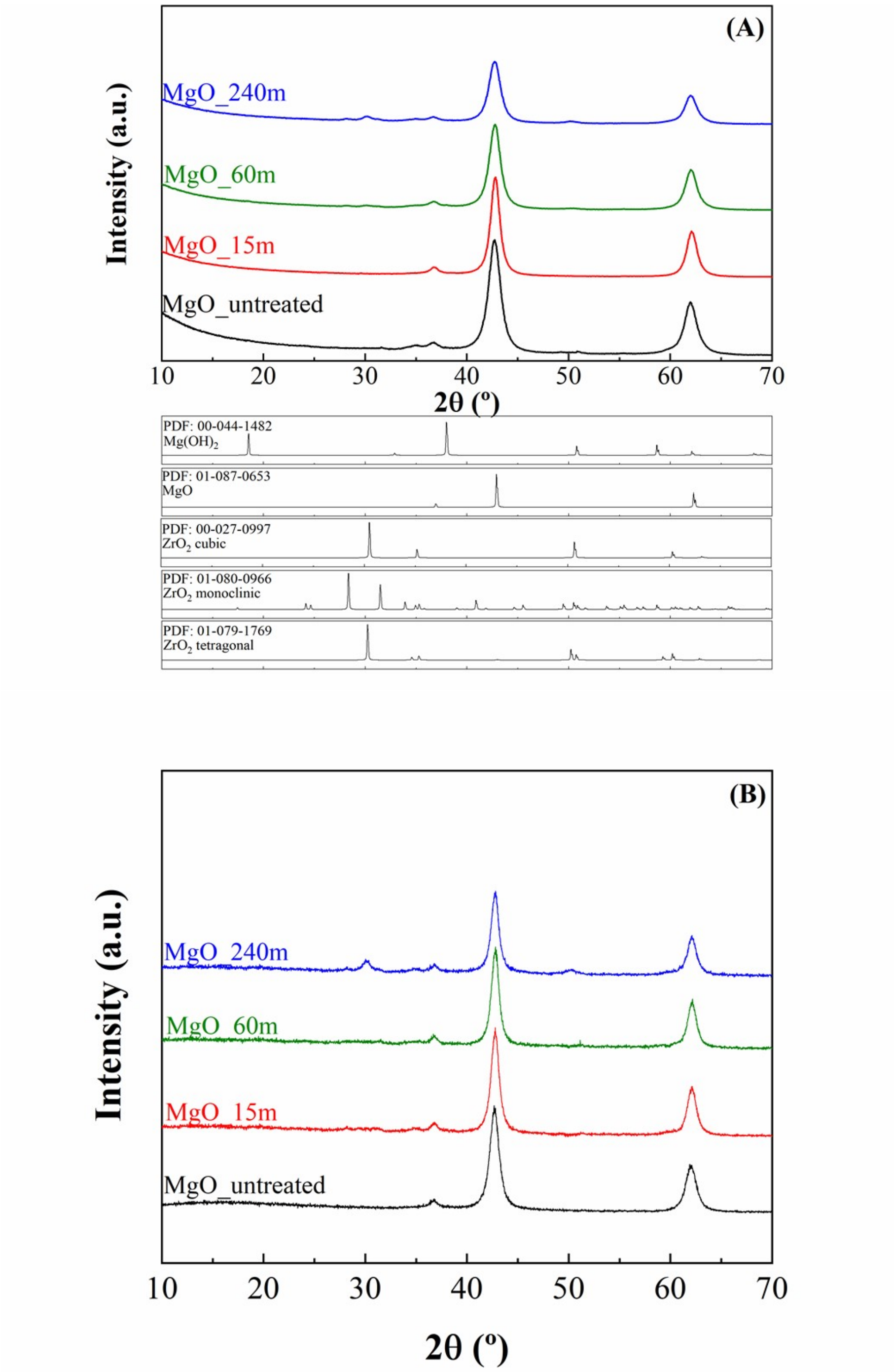


Figure S6. X-ray diffraction patterns of MgO_untreated, MgO_15m, MgO_60m and MgO_240m catalysts before (A) and after the CO_2-TPD until 450 ºC (B).