Data set relating to “Selective conversion of 5-hydroxymethylfurfural to cyclopentanone derivatives over Cu-Al2O3 and Co-Al2O3 catalysts in water”.

Sample name in paper File reference

Ni-Al2O3 Re Ni-Al

Cu-Al2O3 Re Cu-Al

Co-Al2O3 Re Co-Al

Zn-Al2O3 Re Zn-Al

Mg-Al2O3 Re Mg-Al

**Catalyst preparation**

Catalyst precursors were prepared by co-precipitation using the urea-based method developed by Constantino *et al*. [25] Firstly, a calculated mass of urea (Sigma) was weighed into glass vials (27 ml) and combined with distilled water using a Chemspeed Accelerator SLT synthesis platform. Then, a mixture of 1.5 M aqueous solutions of AlCl3·6H2O (Fluka; ≥ 99%) and the corresponding metal precursors were dispensed into those vials using an Eppendorf epMotion 5075PC pipetting robot. The precursors used as Ni, Cu, Co, Mg, and Zn sources were: NiCl2·6H2O (Aldrich; ≥ 99.9%), Cu(NO3)2·3H2O (Fluka), CoCl2·6H2O (Fluka), MgCl2·6H2O (Sigma-Aldrich; ≥ 99%) and ZnCl2 (Aldrich; ≥ 99.99%), respectively. The volumes of the solutions and the mass of urea were selected to set the following molar ratios; nAl/(nMe+nAl) = 0.45 and nurea/(nMe+nAl) = 3.3. The vials were heated to 95 °C (1.5 °C min-1) and stirred under reflux. After aging for 65 h, the solutions were cooled to room temperature and filtered. In order to remove residual Cl, the precipitated materials were left in suspension with NH4HCO3 (Alfa Caesar) for 5 h. Subsequently, the samples were filtered, washed with distilled water and dried at 2 °C min-1 to 120 °C for 5 h in static air. Finally, the synthesised materials were calcined under air (75 cm3 min-1) at 500 °C for 5 h (heating ramp 5 °C min-1) and reduced under H2 (100 cm3 min-1) at 500 °C (700 °C in case of Co containing sample) for 5 h (heating ramp 5 °C min-1). The catalysts were then passivated at room temperature for 3 h under a flow of 1% v/v O2/N2 (100 cm3 min-1).

**Catalyst characterization**

The synthesised catalysts were characterised by X-Ray diffraction on a Panalytical X’Pert Pro diffractometer with Co Kα1 radiation (λ = 1.7890 Å). Samples were scanned at 0.023° s-1 over the range 10° < 2θ < 80° for phase identification using reference standards. The mean metal crystallite size was calculated using the Scherrer equation. Metal content of the catalysts was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) after digestion in acid (25 mg of sample in 10 ml HCl 37 %) and dilution with water (1:10 v/v). Textural properties were measured using nitrogen adsorption–desorption isotherms at 77 K with a Micromeritics TRISTAR II instrument. Prior to the measurement, the samples were outgassed at 120 °C under vacuum for 20 h. Specific surface area was calculated using the BET equation in the range 0.05 < P/P0 < 0.2, whereas pore volume and pore size distribution were determined by the BJH method.

Temperature programmed reduction (TPR) was measured using a Quantachrome ChemBET 3000 unit; *ca.* 50 mg of sample were loaded into a quartz cell and heated up to 750 °C at 5 °C min-1 under a flow of 5% v/v H2/N2 (100 cm3 min-1). The acid and base features of the catalysts were determined in a Micrometrics 2920 equipment by temperature programmed desorption (TPD) of ammonia and carbon dioxide, respectively. Previously, the samples were outgassed under a stream of He (20 cm3 min−1) heating at 5 °C min−1 up to 550 °C. For NH3-TPD curves, the samples were cooled to 180 °C and saturated under an ammonia stream (5% v/v NH3/He; 20 cm3 min−1) for 30 min. Subsequently, the physically adsorbed ammonia was removed by flowing helium (20 cm3 min−1) for 30 min. Thereafter, the chemically adsorbed ammonia was desorbed by heating to 550 °C with a rate of 10 °C min−1 in flowing He (20 cm3 min−1). The CO2-TPD experiment was initiated by cooling the sample to 50 °C followed by saturation with a flow of 5% v/v CO2/He (20 cm3 min-1) for 30 min. Afterward, the physisorbed carbon dioxide was removed by flowing He (20 cm3 min-1) for 30 min. Finally, the chemically adsorbed CO2 was desorbed by heating the sample to 650 °C (heating rate of 10 °C min-1) in flowing He (20 cm3 min-1). The variation of ammonia and carbon dioxide concentration in the effluent helium stream was recorded continuously using a thermal conductivity detector (TCD).

IR spectra were collected in ATR mode using a FT-IR Perkin-Elmer Spectrum 100 spectrometer (4 cm-1 resolution, 16 scans). Thermogravimetric analysis (TGA) were carried out on a Q600 TA Instruments; *ca*. 10 mg of sample were loaded into an alumina microcrucible and heated to 800 °C at 10 °C min-1 in flowing N2 at 100 cm3 min-1. Elemental analysis (C and H content) of the used catalysts were carried out on a Thermo EA1112 Flash CHNS Analyser. SEM images were taken using a Hitachi S-4800 Field-Emission Scanning Electron Microscope. Prior to recording the SEM micrographs, the samples were sputter-coated with Au to reduce charging effects. TEM images were obtained with a JEOL 2100 transmission electron microscope. EDX mapping was performed with a windowless EDAX EDX detector using the microscope in STEM mode. Previous to the observation, the samples were dispersed in acetone, stirred in an ultrasonic bath and deposited on a carbon-coated Cu grid.

**Catalytic experiments and product analysis**

The performance of the catalysts was studied in a high pressure 100 ml batch stirred reactor (Parr Instrument Co.) equipped with a Parr 4848 acquisition interface. A glass liner was loaded with 45 ml of an aqueous solution of HMF (0.04 M) and 0.02 - 0.06 g of catalyst, and placed into the stainless steel reactor. The reactor was then sealed, flushed with N2 and heated to the required reaction temperature (140 - 180 °C). Once the desired temperature was reached, the vessel was pressurized to 20 - 50 bar of H2 and the stirring speed was increased to 600 rpm. After the reaction, the product identification and quantification was carried out by GC-MS (Agilent 6890N GC with a 5973 MSD detector) and GC (Agilent 7890A GC with a FID detector), respectively. Both instruments were equipped with a DB-WAXetr capillary column (60 m, 0.25 mm i.d., 0.25 μm). Standard reference compounds like HMF (Sigma; > 99 %), furan-2,5-diyldimethanol (FDM; Manchester Organics), THFDM (Ambinter) and HCPL (Ambinter) were used for identification and calibration measurements. Identification of 1-hydroxyhexane-2,5-dione (HHD), 4-hydroxy-4-hydroxymethyl-2-cyclopentenone (HHCPN) and HCPN was carried out via a combination of GC-MS and NMR spectroscopy using a Bruker AVANCE III HD spectrometer. Details concerning conversion, yield and selectivity calculations are given elsewhere [22].