TEMPLATED SYNTHESIS OF POROUS HEA-BASED MATERIALS

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High entropy alloys (HEAs) are multi-principal element solid solutions composed of five or more randomly mixed metals in nearly equimolar concentrations. They are attractive materials for energy and catalysis applications, due to the enhanced thermal and chemical stability combined with tuneable surface properties.[1] High temperature followed by rapid quenching are typically required to produce homogeneous, stable high entropy alloys.[2,3] These techniques demand high energy input and often require post-synthesis treatments in order to obtain HEA with enhanced specific surface area for catalytic applications.[4] In this contribution we present a low-temperature, scalable and sustainable approach for the synthesis of HEA-based porous materials for catalytic applications.[5]

A templated aerosol approach, inspired to the sol-gel synthesis of porous oxides has been applied for the fabrication of HEA-based porous materials. The process consists on spray-drying an aqueous suspension containing the metal salts ($PtCl_4$, $PdCl_2$, $IrCl_3$, $RhCl_3$ and $RuCl_3$) in nearly equimolar concentrations, mixed with polymer latex particles, using a B-290 mini spray-dryer whose nozzle is heated at 150ºC. This generates an aerosol of droplets containing the dissolved metal salts and latex particles. Water evaporation induces latex particles self-assembly (EISA), yielding spherical super-structures of latex particles embedded in a matrix of metal salt (see figure 1). In this first step, homogeneous and random precursors mixing, required for the formation of a HEA, is achieved. Thermal annealing under inert atmosphere produces porous particles with a single fcc crystalline structure. The advantage of this approach is that the size of the pores can be tuned by choosing the size of the latex template particles. In this work, we produced both mesoporous particles and hierarchical macro- and mesoporous particles, with specific surface area of 150 m^2/g and 103 m^2/g respectively. These values are the highest obtained so far in the field of HEAs. STEM-EDX revealed that these porous structures are actually built of tiny nanocrystals (about 4-5 nm) with a fcc crystalline structure. Time of flight secondary ion mass spectroscopy confirmed the intimate and random alloying of the five elements at the *atomic scale* within the nanocrystals.

Besides the tunability of the pore size, the aerosol process is interesting because metal reduction and alloying occur at relatively low temperatures, simultaneously to the generation of pores. The reduction mechanism was further investigated with in situ thermogravimetry, coupled with GC-mass and FTIR. The evolution of HCl is observed in a narrow temperature range between 300ºC and 350ºC. Methyl methacrylate monomer is evolved at the same time, and detected up to 400 ºC. The evolution of HCl indicates that metal reduction probably occurs between 300ºC and 350ºC. This hypothesis is confirmed by XRD and XPS characterization, showing that the pristine particles are only partially reduced at 300ºC while full reduction is obtained at 350ºC. Reference non templated particles, obtained with the same aerosol method, could be reduced under inert atmosphere only at 450ºC. This study indicates that probably the polymer latex beads reduce the metal chloride upon radical depolymerization. This kind of carboreduction mechanism has already been observed for mono- and bi-metallic templated particles.[6]

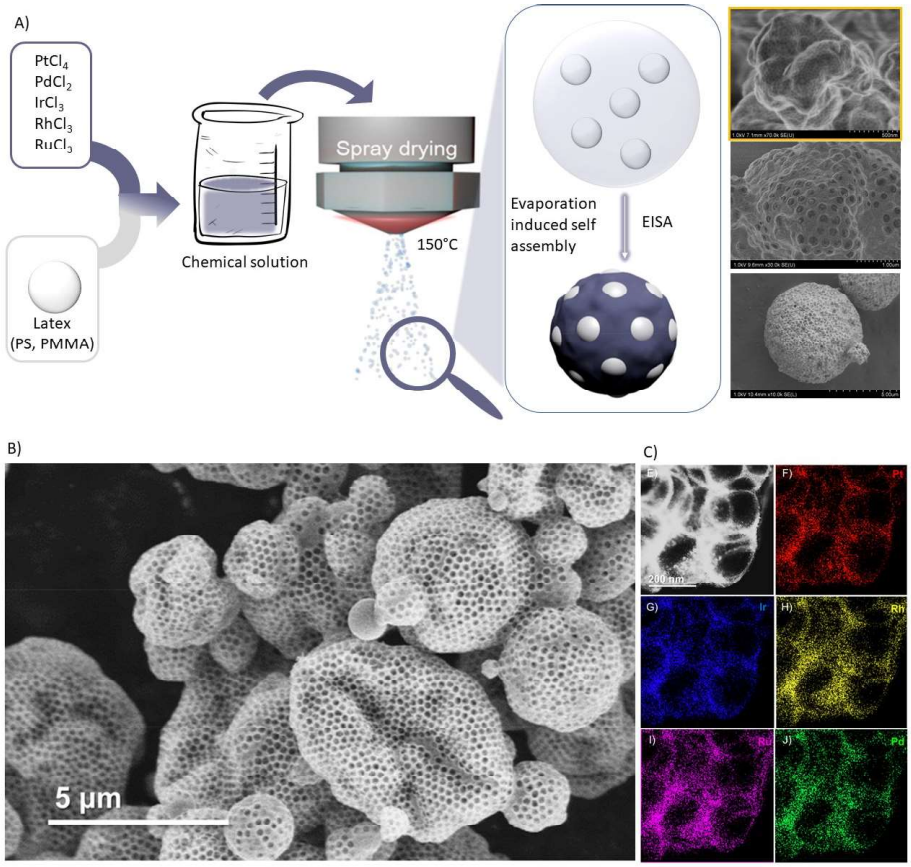

Figure 1: Synthesis protocol (A), SEM (B) and STEM-EDX characterization (C) of porous HEA-based materials

The catalytic activity of the porous HEA-based materials has been tested towards the CO oxidation reaction. Both the hierarchically porous and mesoporous HEA-based materials showed enhanced activity compared to non-porous references, with T50 of 97ºC and 113ºC respectively. These values are comparable to state-of-the-art benchmark catalysts, and are halved with respect to the activity of non-porous reference particles with the same composition. The increased activity can be attributed to the enhanced specific surface area, as well as a better alloying within the templated particles. Stability, besides activity, is another crucial property for thermal catalysis. We used *in situ* scanning transmission electron microscopy, coupled with EDX, to monitor the stability of the porous structure and the eventual occurrence of phase separation. The porous structures are stable up to 800ºC, and de-alloying does not occur across the whole range of temperature investigated (up to 900ºC). From this analysis it can be concluded that metal alloying considerable enhances structural stability, and that the Pt-group metals probably form a stable, homogeneous solid solution up to 900ºC. In conclusion, the spray-drying is a versatile, green and scalable technique for the production of free-standing, porous HEA-based catalysts.

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