

Electronic Supplementary Information (ESI)

Mix and print: Fast optimization of mesoporous CuCeZrO_w for catalytic oxidation of n-hexane

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Ink formation

Different metal precursor inks of certain concentration are prepared in form of colloidal nanoparticle inks for the fabrication of MMOs libraries by IJP-A synthesis. The preparation procedure is a one-step, general synthesis of nanoparticles monodispersed in size for most common precursors. In a typical synthesis of colloidal nanoparticle ink, 20mmol metal species, 24 or 48 mmol of HCl or HNO_3 varied with respect to the type of metal source, 80mmol of HoAC and 3.2gF127 ($\text{EO}_{96}\text{PO}_{70}\text{EO}_{96}$, MW = 12000 g/mol) are dissolved in 60mL ethanol (or isopropanol) and stirred for 1 hour. For instance, in the preparation of CuCeZrO_w library, we need to formulate three kinds of metal precursor inks respectively. For “Cu ink”, 20mmol copper nitrate, 24mmol HCl, 80mmol of HoAC and 3.2gF127 are dissolved in 60mL ethanol. For “Ce ink”, 20mmol cerium (III) nitrate, 24mmol HCl, 80mmol of HoAC and 3.2gF127 are dissolved in 60mL ethanol. For “Zr ink”, 20mmol zirconium butoxide, 48mmol HCl, 80mmol of HoAC and 3.2gF127 are dissolved in 60mL ethanol. The parameters of nanoparticle size ($<3.2\text{nm}$), viscosity (5-10mPa·s) and surface tension (21-22dyn/cm) of the three metal precursor inks are matching for the strict fluid rheological property requirements of printing synthesis of MMOs by our modified Epson 4880C piezoelectric ink-jet printer.

Design of MMOs libraries

As for the design of MMOs libraries composition variation, we use bisection method to divide the selected parameter space into several groups with reasonable intervals. For $\text{M}_a\text{M}_b\text{M}_c\dots\text{M}_n\text{O}_w$ library with n element candidates with different molar ratios in (0, 1], first, we divide molar ratios parameter in (0, 1] into (0, 0.5] and (0.5, 1] for each candidate, thus form 2^n groups. Second, we select m composition points with reasonable interval for each element in each group, thus form m^n compositions mixed in each group, $2^n \cdot m^n$ compositions in each assay. In the subsequent screening, the groups with performance above a statistical threshold are selected as the candidates for the next iteration. The candidates are divided into 2^n subgroups and tested again.

C2FAST software

After design of MMOs libraries, composition variations design of each group are drafted in a

color image with corresponding CMYK (cyan, magenta, yellow, black) parameters by computer design program (e.g., Photoshop). The image is then converted to a C2FAST software. The software, developed by our lab, is used for data transfer between image and printer, which establish a one to one correspondence between the percent value of each color in an image and the printing volume of ink in relevant nozzle. What's more, it merges two CMKY images ($C1+M1+K1+Y1$ and $C2+M2+K2+Y2$) together to double the image parameter and therefore match with number of ink channels.

Modified ink-jet printer

A piezoelectric drop-on-demand (DOD) ink-jet printer (C2FAST-II) is used in IJP-A synthesis. The printer is modified based on a commercially available Epson printer (Stylus Photo 4880c). The modified printer has a holder for print head with 8 ink channels running on X direction and a platform of 400mm*500mm moving on Y,Z direction, thus forming a three-axis X-Y-Z table to print inks on various substrate, such as glass slides, filter paper, cloths and others. The print head is fitted with eight separate nozzles, each nozzle is fitted with a miniature electromagnetic valve that controls aspiration and dispensing and provides ink-jet printing from pressure provided by the stepper syringe. The nozzles can automatically visit a cleaning station for purging, external washing and air drying. In printing, appropriate inks filled in cartridges are input to ink channels through independent ink roads. The printer works in dispense mode by transferring specified volumes of several inks into a substrate to build a target MMOs mixture in various ratios. The amount of each ink printed is controlled through the CMYK (cyan, magenta, yellow and black) function. These inks were printed independently and allowed to mix on the substrate surface. As many as 8 different metal precursors' variation of composition could be precisely controlled via our modified piezoelectric ink-jet printer. A simple mixing of relative amounts of inks allows us to build libraries of recipes of multi-component mesoporous metal oxides with varying composition by the IJP-A system.



IJP-A synthesis

In printing operation, the prepared inks are transferred into the empty ink cartridges and full-filled the whole ink road. Distance between the substrate and print head is adjusted to 1-2 cm. Designed CMYK images are input to the C2FAST software on the PC and connected to the printer. The C2FAST software establishes a one to one correspondence between the percent value of each

color in an image and the printing volume of ink in relevant nozzle, thus control the composition variation of catalyst libraries. The repeated printing amount and printing resolution are settled to get the desired mounts of MMOs. After synthesizing, the printer head should be cleaned several times using non-aqueous solvents (such as ethanol and isopropanol) to avoid clogging and erosion. The printed membrane is evaporated at 40 °C with a relative humidity ~40%. After 12h, it is transformed into a 65°C oven and aged for an additional 24 hours. As-synthesized films are calcined at 450°C in air for 6 hours (ramp rate 2°C /min) to remove the block-copolymer surfactants. The oxides with different compositions and structures are collected for sequential physical characterizations and catalytic tests. Depending on the continuous high-precision compositional landscape provided by the IJP-A system, we have successfully high-throughput prepared MMOs libraries with desired composition variation.

Characterization

Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray (EDX) analyses were taken on a Hitachi S-4800 microscope with a field-emission electron gun operating at 25 KV. Transmission electron microscopy (TEM) images were taken on a TECNAI F-30 high-resolution transmission electron microscope operating at 300 kV. XRD patterns were recorded on a Bruker D8 diffractometer operated at 40 mA and 40 kV with Cu K α radiation with a step size of 0.02° and a scan rate of 2.5 s/step. Nitrogen adsorption-desorption analysis was carried out at 77 K on a Micromeritics ASAP 2020 adsorption analyzer. Before the adsorption analysis, the samples were outgassed under a vacuum at 200 °C in the port of the adsorption analyzer. Small-angle X-ray scattering (SAXS) patterns were recorded using a Xeuss SAXS/WAXS system with a rotating anode X-ray source.

Catalytic combustion of n-hexane

Catalyst activity for n-hexane combustion was determined using a fixed bed laboratory micro reactor. In order to avoid intra reactor gradients, the catalyst powder (50mg) was diluted in 0.5g of quartz sand. Mass flow controllers were used to prepare the reactant feed composed of 1000 ppm of n-hexane in air. A total flow rate of 200 ml/ min was used and catalysts were packed to a constant volume to give a gas hourly space velocity of 10,000 h⁻¹ for all tests. Analysis was performed using an on-line gas chromatograph with thermal conductivity and flame ionization detectors. Catalytic activity was measured at 350°C and temperatures were measured by a thermocouple placed within the catalyst bed. Once the reaction temperature was attained, the catalyst was allowed to stabilize for 20min before data were collected. Three consistent measurements were taken at reaction temperature. Conversion data were calculated by the difference between the inlet and outlet concentrations. Experimental errors on conversion were 100±2% and all carbon balances were in the range of 100±5%.

Characterization of IJP-A synthesized G3-8-8 catalysts library

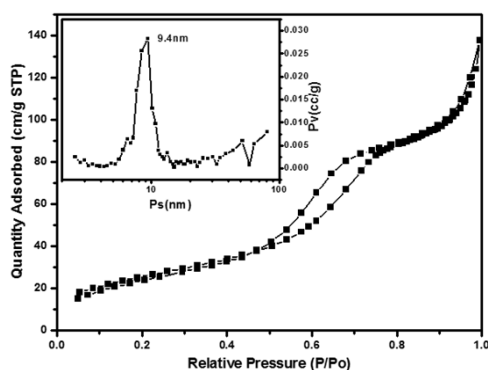


Figure S1: The nitrogen sorption isotherms and pore size distribution plots of G3-8-8 catalysts library.

The detailed mesoporous structure of G3-8-8 catalysts library are further investigated by nitrogen sorption isotherm shown in figure S1, which is a type IV nitrogen sorption isotherm with a broad, intermediate hysteresis loop between H1 and H2. The pore size of G3-8-8 catalysts library is calculated to be 9.4nm on the basis of a modified BdB model (close to SEM observation). The nitrogen adsorption results confirm that the material have high surface area of $93\text{m}^2\text{g}^{-1}$.

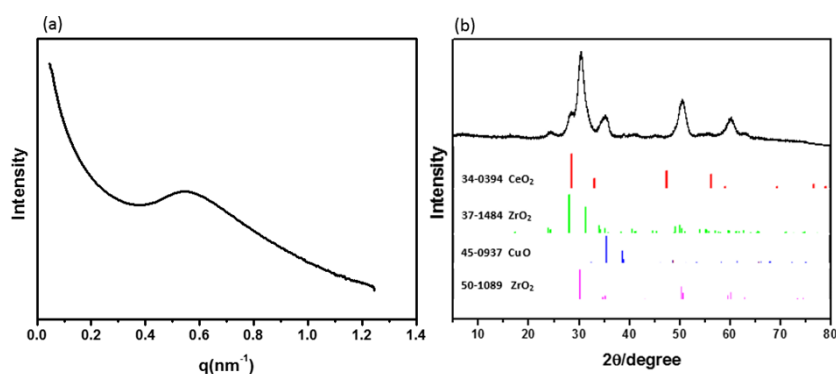


Figure S2: SAXS and XRD patterns of IJP-A synthesized G3-8-8 catalysts library.

The IJP-A synthesized G3-8-8 catalysts library shows excellent mesoporous structure, as confirmed by small-angle X-ray scattering (SAXS) (figure S2a) and transmission electron microscopy (TEM) analyses (Figure2). To further elaborate the mesostructure and local structure of inorganic walls, we used XRD (figure S2b) to characterize IJP-A synthesized G3-8-8 catalysts library. The pore-to-pore distance is around 11 nm as indicated by SAXS analysis. The inorganic walls of the mesochannels consisted of CuO, ZrO₂, CeO₂ nanocrystals (~ 7.3 nm) as indicated by wide-angle X-ray diffraction pattern.

Calculation of CAR and final composition

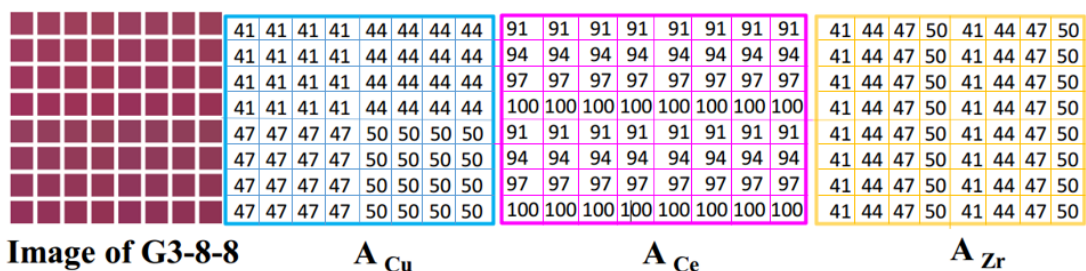


Figure S3: Designed image and A_{Cu} , A_{Ce} , A_{Zr} value of G-3-8-8 catalysts library.

As for the CAR calculation, take the G3-8-8 catalysts library for example. The designed image for G-3-8-8 is given in figure S3 which has established A_{Cu} , A_{Ce} , A_{Zr} by bisection method. There are 64 different formulations in the group, each group has special A_{Cu} , A_{Ce} , A_{Zr} values. A_{Cu} and A_{Zr} are diverse in 41,44,47,50, A_{Ce} are diverse in 91,94,97,100. The permutation and combination of A_{Cu} , A_{Ce} , A_{Zr} form 64 different formulations. For this group, according to the flowing definition,

$$CAR_{Cu/Zr} = \frac{A_{Cu1} + A_{Cu2} + \dots + A_{Cun}}{A_{Zr1} + A_{Zr2} + \dots + A_{Zrn}}$$

$$CAR_{Ce/Zr} = \frac{A_{Ce1} + A_{Ce2} + \dots + A_{Cen}}{A_{Zr1} + A_{Zr2} + \dots + A_{Zrn}}$$

We can calculate the value of $CAR_{Cu/Zr}$, $CAR_{Ce/Zr}$

$$CAR_{Cu/Zr} = \frac{41 \times 16 + 44 \times 16 + 47 \times 16 + 50 \times 16}{41 \times 16 + 44 \times 16 + 47 \times 16 + 50 \times 16} = 1$$

$$CAR_{Ce/Zr} = \frac{91 \times 16 + 94 \times 16 + 97 \times 16 + 100 \times 16}{41 \times 16 + 44 \times 16 + 47 \times 16 + 50 \times 16} = 2.1$$

As for the final composition in printed sample of G3-8-8, we can preliminary calculate from the working curve (figure 3). The calculated formulation of G3-8-8 is $Cu_{0.30}Ce_{0.24}Zr_{1.00}O_w$, which is very close to $Cu_{0.32}Ce_{0.28}Zr_{1.00}O_w$ as determined by EDX measurement, suggesting the excellent reproducibility of IJP-A synthesis.

Statistical threshold criterion

We calculate the threshold which is given by

$$\text{Threshold} = k_1\mu + k_2\sigma$$

μ is the mean value of the objective function, σ is the standard deviation of the objective function value, k_1 and k_2 are positive constants depending on the library. For simplification of our calculation, $k_1=1$ and $k_2=0.5$ are used.