Thermally Stable Doped Ceria as a Single-Atom Catalyst Support

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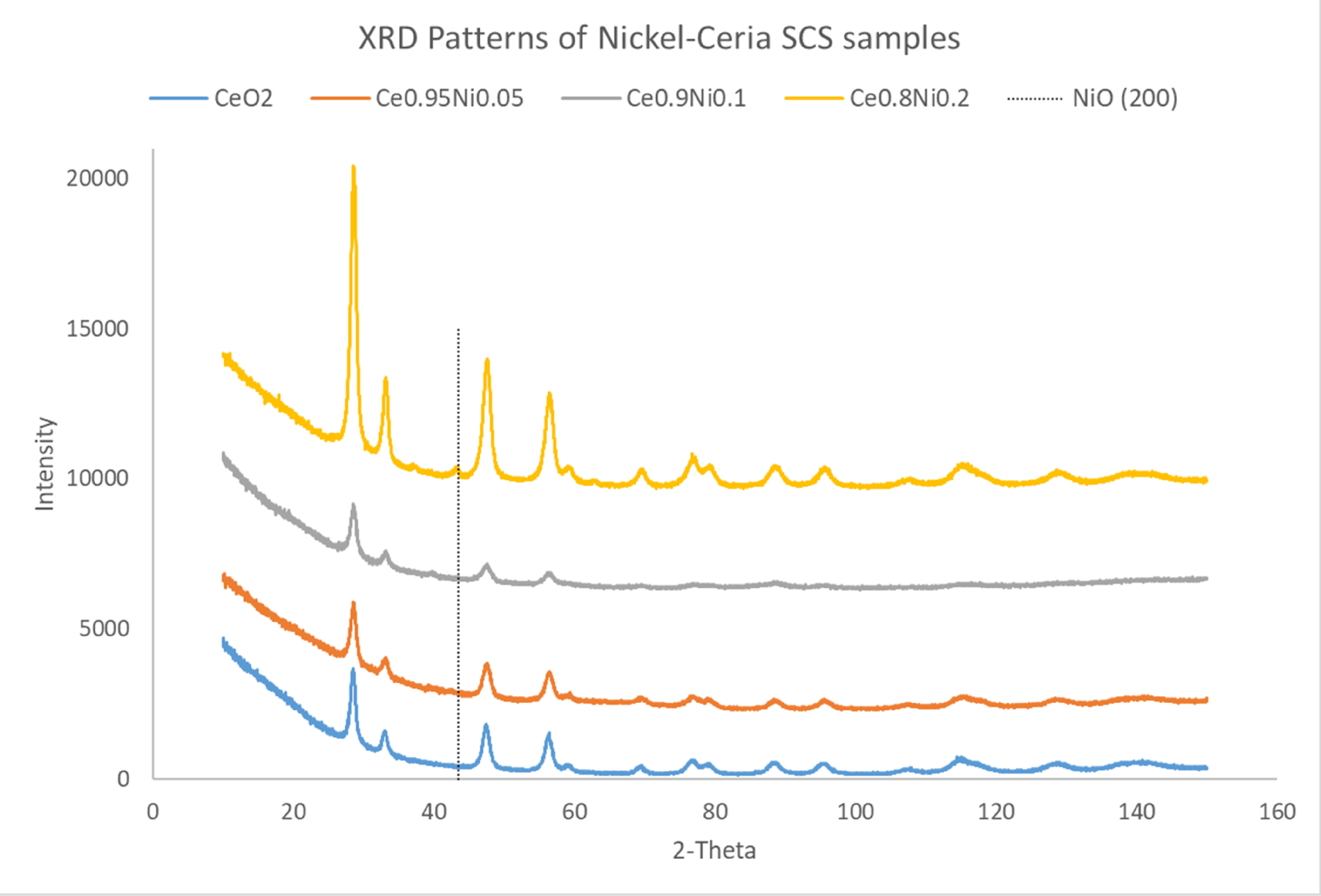
Problem

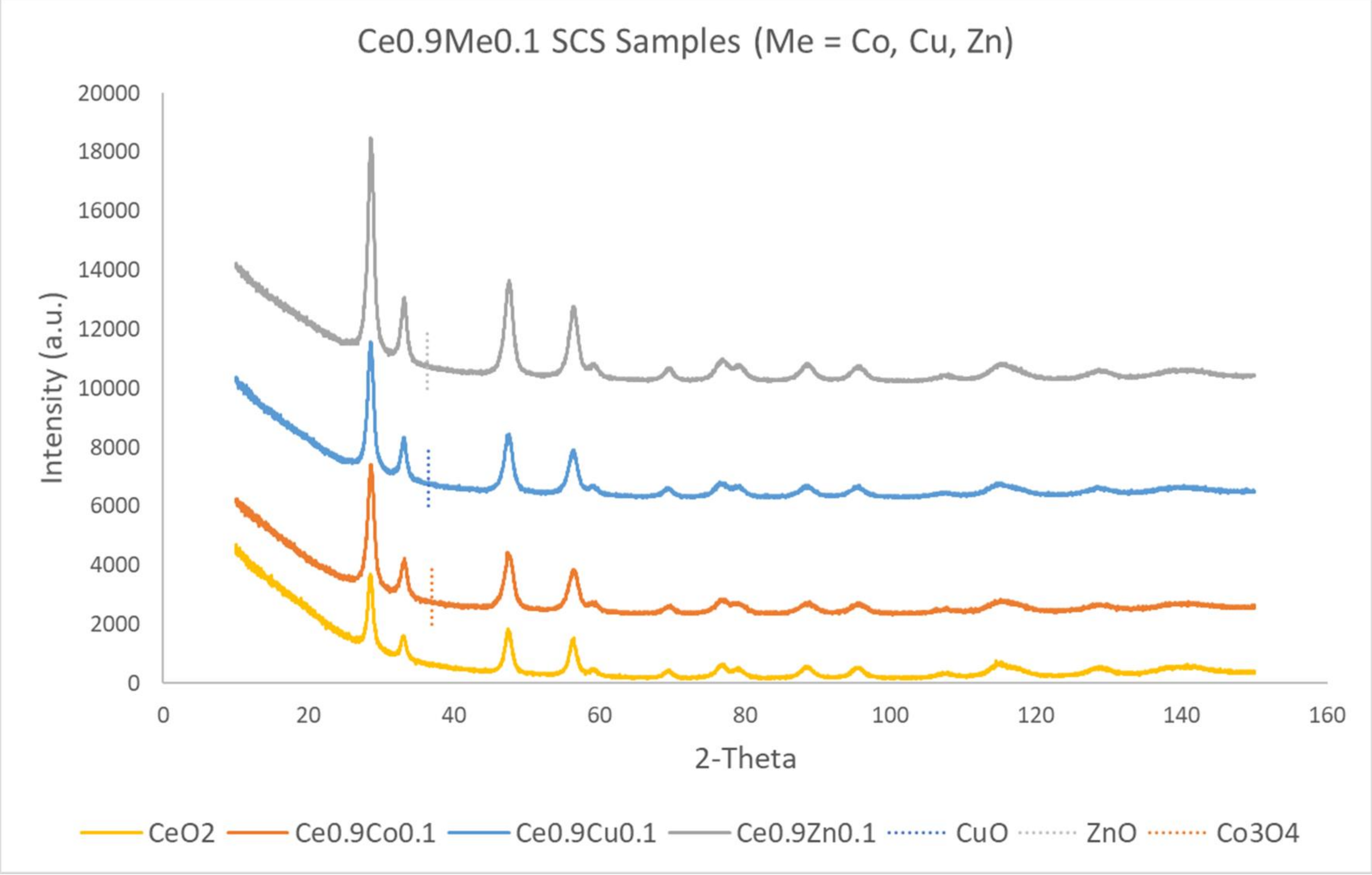
Single atom catalysts represent a maximum in efficient use of precious catalytic metals. Ceria has proven effective at trapping single platinum atoms. However, catalyst performance and stability deteriorate at high temperatures. Because of this it is important to design supports that can both lead to high activity and thermal stability. Dopants have been used to stabilize oxide supports and to enhance catalytic behavior. That's why we proposed to study the role of dopants on ceria thermal stability.

Methods

We chose nickel, copper, cobalt, and zinc as dopant elements. The first synthesis method that was explored was Solution Combustion Synthesis (SCS), which was aimed at creating homogeneous dopant distributions. The method of SCS involves dissolving metal nitrate precursors and urea (as a fuel source) in 30mL DI water, and heating while stirring until almost all water has evaporated and a gel is left. Next the gel is put into a furnace preheated to 400˚C for about an hour at which point it combusts. Then it is broken up and calcined at 400˚C. The second method used was Wet Impregnation (WI), which created a surface-rich dopant distribution. The method of WI involves depositing an aqueous solution containing a transition metal precursor onto the premade ceria, drying the sample overnight, then calacining it in a box furnace at 500˚C. The SCS method was used to make several doped ceria samples. Select samples were aged in air at 800˚C. Samples were characterized by X-Ray Diffraction (XRD), BET Analysis, and by Scanning Electron Microscope (SEM). XRD was used to determine whether any secondary dopant phases were fromed in addition to the ceria phase. BET analysis was used to measure surface area of the samples. SEM and were used to determine the composition of doped ceria samples, and to image sample morphology.

Results





The figure on the left, shows XRD patterns for nickel doped ceria made through SCS with different nickel loadings. The vertical line marks the location of the most prominent NiO peak, which appears in the Ce0.8Ni0.2 sample. This peak is absent in the other samples, indicating that the nickel is all incorporated in the ceria phase at those loadings. The Ce0.9Me0.1 loading was thus chosen as the composition for other doped ceria samples. The figure on the right shows an absence of dopant oxide phases, indicating that SCS creates homogeneously doped ceria with these additional dopants.

Dopant	Loading	SSA Calcined (m^2/g)	SSA Aged 800 (m^2/g)
Ceria	NA	59.8	3.0
Nickel	$Ce_{0.9}Ni_{0.1}$	48.5	4.5
Copper	$Ce_{0.9}Cu_{0.1}$	28.4	1.3
Cobalt	$Ce_{0.9}Co_{0.1}$	43.5	3.7

Sample	SSA Calcined (m^2/g)	SSA Aged 800 (m^2/g)
7 wt% Ni	88.0	32.0
6.5 wt% Cu	100.3	37.6

The table on the left shows BET surface area data for SCS doped cerias calcined at 400°C and after aging at 800°C. The results show that homogeneously doped ceria is not thermally stable. On the other hand, the table on the right shows ceria with dopants deposited on the surface. BET data for these samples indicates that ceria with a high surface concentration of dopant atoms can retain a higher surface area after aging at 800°C.

Conclusion / Future Work

The results show that method of dopant atom incorporation and dopant loading influence the homogeneity of the ceria structure. While homogeneous dopant distributions may be achieved, these do not thermally stabilize ceria. However, ceria may be stabilized through surface deposition of transition metals.