Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Tuning surface grafting density of CeO_2 nanocrystals with near- and supercritical solvent characteristics

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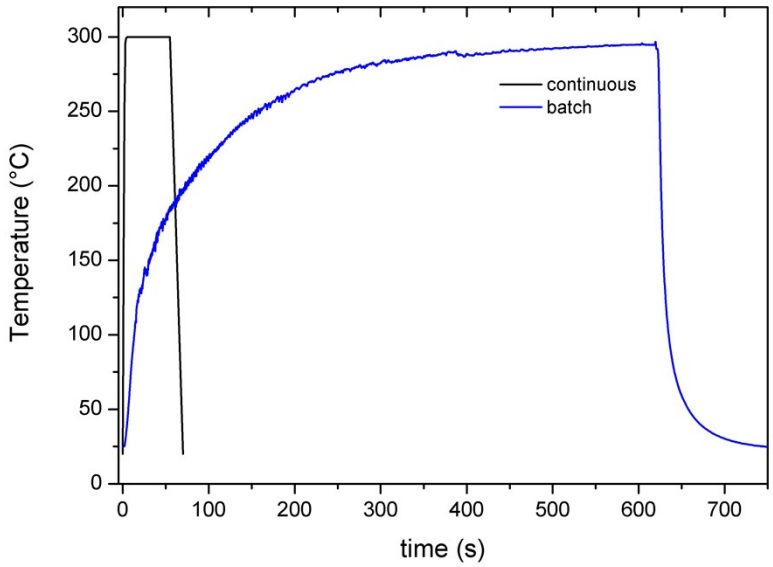

Figure S1 Temperature profiles during batch and continuous experiments

a)

	CONTINUOUS REACTOR			
Solvent	**Total WL (%)**	**Corrected WL(%)**	**Grafting density (molecules.nm^{-2})**	**Surface coverage (%)**
Methanol	*13.39*	*7.52*	*6.63*	*96.9*
Ethanol	*14.37*	*8.50*	*6.35*	*92.8*
Propanol	*12.11*	*6.28*	*4.11*	*60.1*
Butanol	-	-	-	-
Pentanol	*14.57*	*7.04*	*3.69*	*53.9*
Hexanol	-	-	-	-
Isopropanol	*9.56*	*6.09*	*5.58*	*81.6*

b)

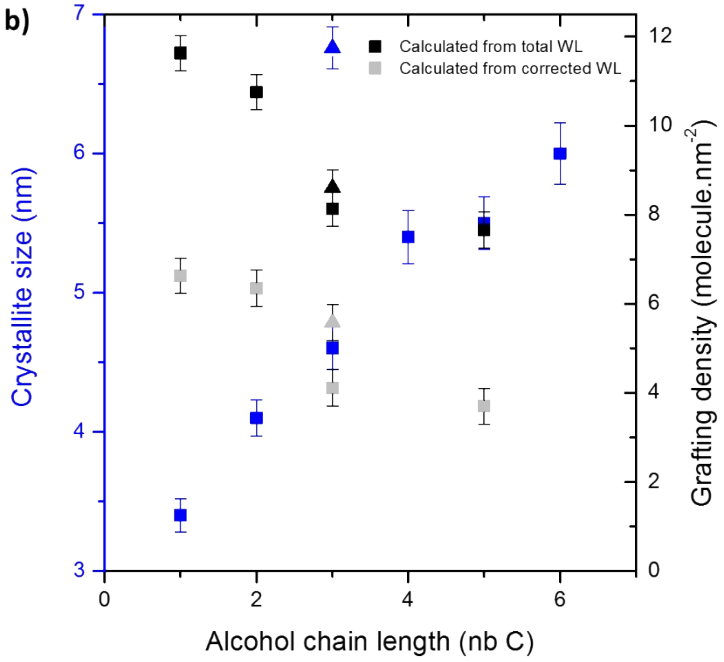

Figure S2 (a) Data on the grafting density and surface coverage for CeO_2 NCs synthesized in continuous, and (b) Crystallite size and grafting density of CeO_2 NCs synthesized in continuous mode. Primary alcohols are labelled with ■ and secondary alcohol is labelled with ▲

The detailed characterization of samples prepared using the continuous setup has been described in a previous paper.[31] It was demonstrated that the nature of the alcohol had a strong influence on the resulting crystallite size. A direct correlation between the crystallite size and primary alcohol chain length has been established.

A continuous decrease from 175 to 700 °C is observed by TGA, indicating a chemical bonding of the surface modifier to the nanoparticle surface. The corrected weight loss, from 100 to 800 °C, is attributed to the degradation of the organic surfactant (alcohol molecules) at the cerium oxide nanoparticle surface and will be used for the calculation shown in Figure 7.a. Surface coverage of CeO_2 NCs by alcohols calculated from the total weight losses (from 20 to 800 °C) are also displayed in Figure 7.b as an indication. The results obtained using these values are far above the maximum surface coverage considering the attachment of one alcohol molecule per surface cerium atom and therefore confirm the physical adsorption of water and/or CO_2.

A direct relationship between the surface coverage and the particle size can be observed for the material produced in continuous. It was concluded that the smaller the nanoparticles, the higher the surface coverage is, as seen in Figure

7.b. Due to the small steric hindrance of the methanol molecule, a high surface coverage of the cerium oxide is expected during the nanoparticle formation. Therefore, active surface states of nanoparticles are readily blocked and the nanoparticle growth is quenched. A lower surface coverage is anticipated for longer alcohol i.e. hexanol, due to higher steric hindrance induced by free rotation of the longer carbon chain. Active surface states are therefore more accessible to the precursor during the reaction and growth of CeO_2 nanoparticles is possible resulting in larger nanoparticles. The continuous increase of the nanoparticle size is consistent with the increase of the steric hindrance, with increasing alcohol chain length.