Ceria Facet-Dependent Oxidative Coupling of Methane towards C_2 Products

(Jiye Fang, SUNY Binghamton)

(09/01/2017-08/31/2018)

1. Major Achievements of Research

In the first award year, our research mainly focused on the work package 1 (WP1, that is, the development of shape-controlled CeO_2 nanocatalyst synthesis) as well as partial work packages 2 (WP2) and 3 (WP3), OCM performance investigation and catalyst characterization (refer to the original proposal). This part summarizes the progress of synthesis, preliminary performance and catalyst characterization.

1a. CeO_2 synthesis development of {100}-nanocubes and {111}-nano-octahedra nanocatalysts (WP1)

CeO_2 Nanocubes: We have successfully prepared {100} crystalline facet-dominated CeO_2 nanocubes using a modified two-phase method.[1] We use triethanolamine (TEA, Alfa Asear) to provide an alkaline environment and use oleic acid (OA, 90%, Sigma-Aldrich) as a capping ligand to stabilize the {100} facets of CeO_2 nanocatalysts. In brief, 7.5 mL of $Ce(NO_3)_3$ (Alfa Asear) aqueous solution (16.7 mM) was added into a 20 mL Teflon-lined stainless-steel autoclave. 7.5 mL of toluene, 0.75 mL of OA and 75 µL of TBA were then added into the autoclave, respectively. The sealed autoclave was kept in a preheated oven at 180 ^oC for 24 h. The brownish turbid upper layer was collected after the autoclave was cooled to RT and sufficient ethanol was added. The products (**Fig. 1a**) were harvest by centrifugation, washed using a mixture of hexane and ethanol (1:2) and ethanol (200 proof) in sequence, and dried in a vacuum oven. We further ***improved the synthesis approach*** by replacing OA with stearic acid (SA), receiving cubic CeO_2 nanocatalysts with a relatively narrow size distribution (**Fig. 1b**).

CeO_2 Nano-octahedra: In this synthesis, PO_4^{3-} plays a key role in stabilizing the {111} facet of CeO_2 while CeO_2 nanocatalysts are yielded in an alkaline environment through a hydrolysis reaction.[2] In a typical preparation, 5.0 mg of tri-potassium phosphate was dissolved in 30 mL of deionized water and 214.5 mg $Ce(NO_3)_3 \bullet 6H_2O$ was dissolved in 2.5 mL of deionized water, respectively. Both solutions were mixed and transferred into a 20 mL Teflon-lined stainless-steel autoclave, and kept in a preheated oven at 180 ^oC for 12 h. The resultant white turbid suspension was isolated by adding a sufficient amount of ethanol alcohol and washed with a mixture of deionized water and ethanol (1:1) several times. The octahedral CeO_2 nanocatalysts (**Fig. 1c**) were collected by centrifugation and dried in a vacuum oven.

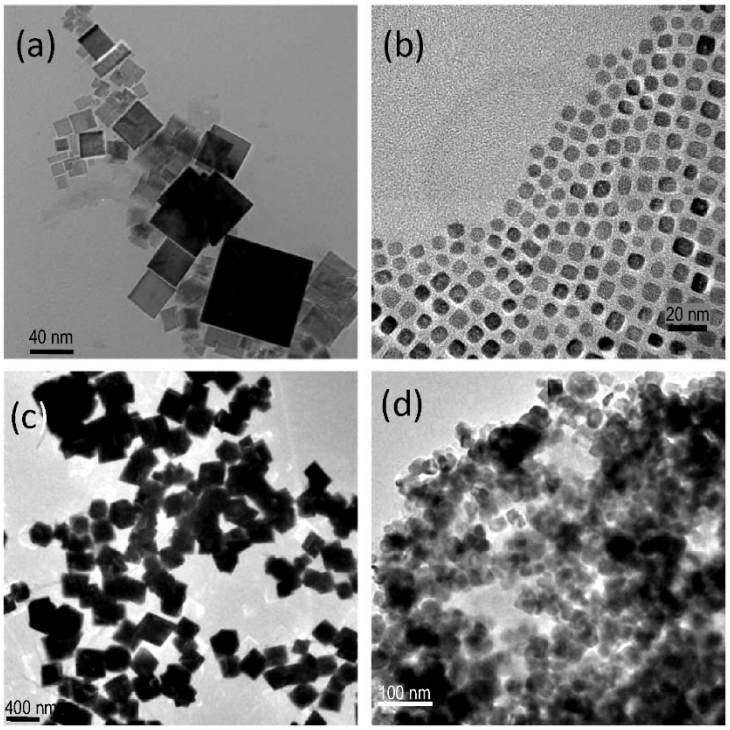

Fig. 1. TEM images of CeO_2. (a), OA-nanocubes; (b), SA-nano-cubes; (c), nano-octahedra; and (d), irregular nanoparticles.

CeO_2 irregular nanoparticles: For comparison, irregular CeO_2 nanoparticles were also synthesized using an established method.[3] Typically, 1.086 g of $Ce(NO_3)_3 \bullet 6H_2O$ was dissolved in 10.0 mL of deionized water in the presence of 1.3 mL of triethanolamine that acts as a base. The mixture was transferred into a 20.0 mL Teflon-lined stainless-steel autoclave and sealed tightly. The reaction was carried out at 180 ^oC for 24 h in an oven. After cooling to room temperature, the solids were collected by centrifugation, washed three times using deionized water, and calcined at 450 ^oC for 2 h in the air (**Fig. 1d**).

1b. Characterization of the CeO_2 nanocatalysts (WP3)

Fig. 1a shows a TEM image of the as-synthesized CeO_2 nanocatalysts in cubic shape. The particle size distribution is broad although most {100} facets of the particles are well-preserved. When the synthesis approach was modified with SA, we received uniform CeO_2 nanoparticles (Fig. 1b) with an average size of ~10 nm. Fig. 1c presents projective images of CeO_2 nano-octahedra with an average size of ~200 nm and narrow size distribution. The TEM image of the irregular CeO_2 sample (Fig. 1d) indicates a partial agglomeration. The corresponding synchrotron XRD patterns (1D and 2D) of all the reported CeO_2 samples were recorded at CHESS (Cornell University) and presented in Fig. 2. Their lattice parameters were also determined by Pawley fitting.

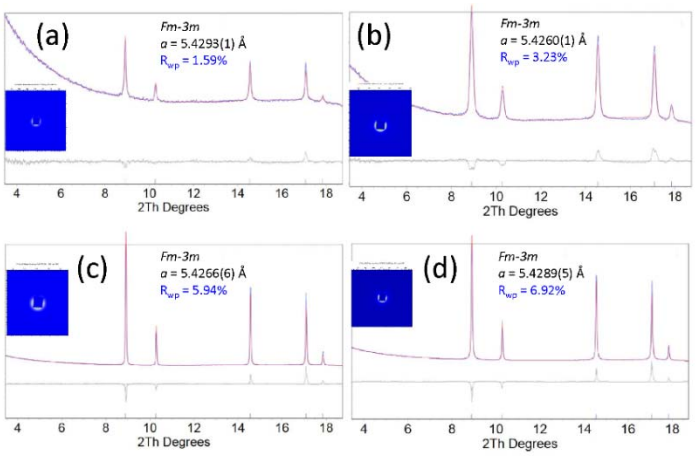

Fig. 2. Synchrotron XRD patterns of CeO_2 and their unit cell parameters extracted from Pawley fitting. (a), OA-nanocubes; (b), SA-nanocubes; (c), nano-octahedra; and (d), irregular nanoparticles. Insets are 2D diffraction patterns.

1c. Partial investigation of facet-dependent OCM performance the CeO_2 nanocatalysts (WP2)

The OCM performance test was conducted at the University of Kansas through collaboration. 40 mg of catalysts were loaded for each experiment and the gas flow rates are CH_4 (pure): 10mL/min; O_2 (pure): 2.5 mL/min; N_2 (pure): 12.5 mL/min. Three testing temperatures (750 °C, 800 °C, and 850 °C) were chosen. At this moment, only the cubic samples have been completed, whereas the study on the rest is still in progress. Fig. 3 shows the partial evaluation results.

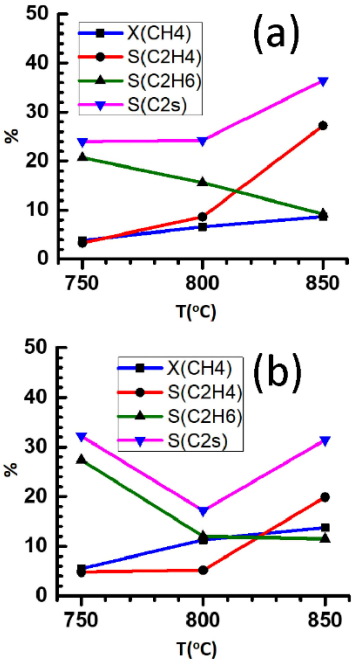

Fig. 3. OCM performance of CeO_2. (a), OA-nanocubes; and (b), SA-nano-cubes.

2. Impact of PI's Career and Students and Further Research Tasks

Impact: The PI received *two* Federal major grants from NSF (DMR) and DOE (EFRC) using this fund as seed money; one graduate student received "Supplementary Stipend Award" from Chemistry Alumni Community, Binghamton University (BU) in the summer of 2018.

Future work: (WP1): (1) To tune the OA/SA ratio for improving the quality of cubic CeO_2; (2) To improve the approach for reducing the size of octahedral CeO_2; (3) to increase the active sites by surface doping noble metal atoms for enhancing the conversion yield. (WP2) To complete the OCM evaluation including the 1st batch measurement (Fig. 3) and to finalize the OCM instrument setup at the PI's institution. (WP3) to conduct in-depth surface modification of the catalysts and analysis.

3. Publication

Shaojie Jiang, Yiliang Luan, Jiye Fang, et al., "Phase Transitions of Formamidinium Lead Iodide Perovskite under Pressure", *J. Am. Chem. Soc.* accepted, (2018). <Note: this publication is not exactly from this research project. However, the author/c-authors from BU were partially supported by this grant.>

4. References

1). Yang, S.; Gao, L., *J. Am. Chem. Soc.* 2006, *128* (29), 9330-9331.
2). Chen, Y.; Chen, Y.; Qiu, C.; Chen, C.; Wang, Z., *Mater. Lett.* 2015, *141*, 31-34.
3). Fu, C.; Li, R.; Tang, Q.; Li, C.; Yin, S.; Sato, T., *Res. Chem. Intermediates* 2011, *37* (2), 319-327.