Ceria Facet-Dependent Oxidative Coupling of Methane towards C_2 Products

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1. Major Achievements of Research

In the second award year, the major achievements consist of (1) further improvement of shape-controlled catalyst syntheses [the work package 1 (WP1), that is, the development of shape-controlled CeO_2 nanocatalyst synthesis - refer to the original proposal], completion of methane oxidative coupling generation and evaluation system [the work package 2 (WP2), investigation of oxidative coupling of methane (OCM) performance over facet-defined CeO_2], as well as the characterization of specimens yielded via the new preparation approaches [the work package 3 (WP3), characterization of CeO_2 nanocatalysts]. Our progress in this project during the second award year is summarized as follows.

1a. Novel approach development of {100}-nanocubic and {111}-nano-octahedral CeO_2 nanocatalysts (WP1)

CeO_2 Nanocubes: We have previously prepared {100} crystalline facet-dominated CeO_2 nanocubes. However, the quality of these nanocubes in terms of their size distribution is expected to improve as indicated in the last report. We have been dedicated to updating the synthesis recipe by optimizing the use of capping ligands, and successively received CeO_2 nanocubes with well-defined {100} facets and much better size- and morphology-distributions (**Fig. 1a** and inset). In the ***improved*** method, capping ligand triethanolamine (TEA) was replaced with tertbutylamine (TBA, >98%, from TCI) and a brief synthesis is described as follows: 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 oleic acid (OA, 90%, Sigma-Aldrich) 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 upper layer was collected after the autoclave was cooled to room temperature and sufficient ethanol was added. The products were harvested by centrifugation, washed using a mixture of hexane and ethanol (1:2) and ethanol (200 proof) in sequence for several cycles, and dried in a vacuum oven.

CeO_2 Nano-octahedra:

It was previously determined that PO_4^{3-} plays a key role in stabilizing the {111} facet of CeO_2 in an alkaline solution. We recently discovered that trioctylphosphine oxide (TOPO) can also retain the CeO_2 {111} facets in a high-temperature organic solution. Here are our improved synthesis recipe and procedure: 7.5 mL of toluene, 75 µL of TBA and 835 mg of TOPO (Sigma-Aldrich) were added into a 20 mL Teflon-lined stainless-steel autoclave that containing 7.5 mL of $Ce(NO_3)_3$ solution (16.7 mM). The sealed autoclave was transferred to a preheated oven at 180 ^oC and kept for 24 h. After cooling down, the brown and turbid upper layer was isolated using a separatory funnel and precipitated using a sufficient amount of ethanol alcohol. The resultant nano-octahedra were re-dispersed in hexane and further washed using a mixture of oleic acid - hexane - ethanol (1:99:200 by vol.) for several cycles, and dried in a vacuum oven (**Fig. 1b** and inset).

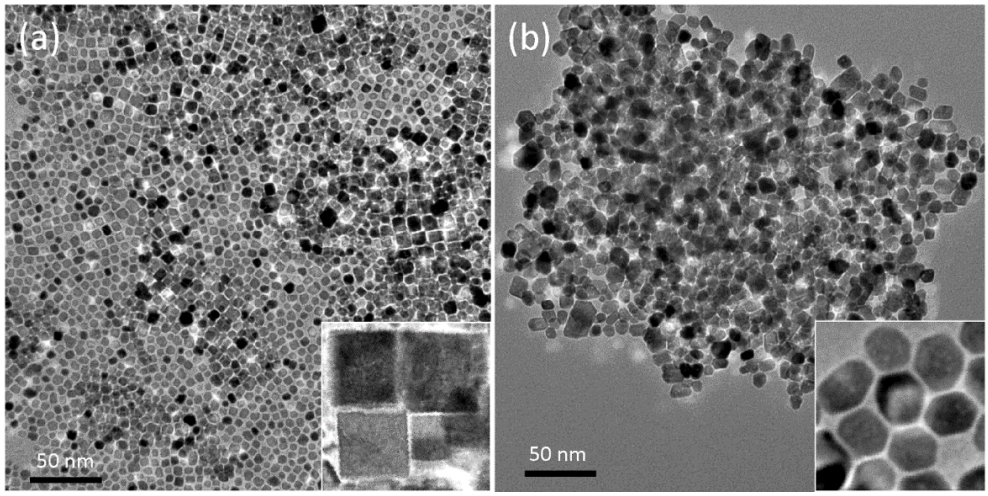

Fig. 1. TEM images of improved CeO_2. (a), nanocubes; (b), nano-octahedrons

CeO_2 irregular nanoparticles: For comparison, irregular CeO_2 nanoparticles were also synthesized using the same method reported previously (TEM image not shown).

1b. Characterization of the CeO_2 nanocatalysts (WP3)

Fig. 2 shows powder XRD patterns of two-type improved CeO_2 nanocatalysts together with its irregular counterpart. For comparison, the relative intensities of the diffraction peaks from the standard card (81-0792) were labeled on the bottom as well. By indexing these patterns, it is confirmed that all the three samples possess a cubic phase with S.G. of *Fm-3m* (225). It can be identified that the peak (200) is enhanced very much in the pattern of nanocubes, whereas peak (111) shows a great enhancement in that of nano-octahedra. This is due to a perfectly flat alignment of the nanocrystals on the surface of the substrate with (100) and (111) texture, respectively.

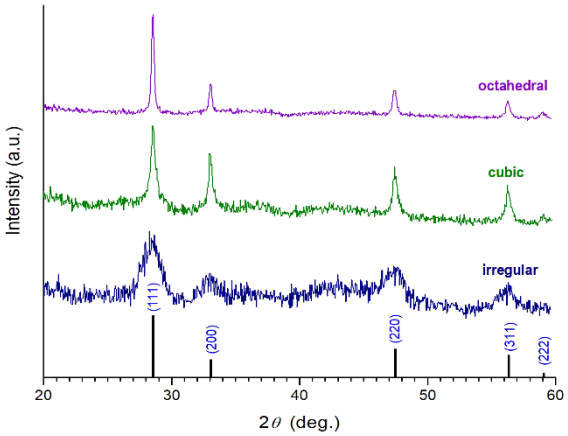

Fig.2. Powder XRD patterns of CeO_2 nanocubes, nano-octahedra, and irregular nanoparticles.

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

The OCM performance testing system has completely set up, including gas flow-control system, pyrolysis heating system and product determination system (GC equipped with TCD and FID detectors) as shown in Fig. 3. As an initial experiment conducted in this system, three abovementioned samples were tested under the following conditions, respectively: catalyst weight: 30 mg, gas flow rates - CH_4 (10% in Ar): 20 mL/min; O_2 (pure): 1.0 mL/min; Ar (pure): 10.0 mL/min. Reaction temperature: 800 °C. Preliminary results indicate that {111}-terminated CeO_2 nano-octahedra show an exceptionally high CH_4 conversion percentage among the three samples. Further testing under various conditions is in progress. Due to the delay of the equipment delivery, this project has been approved for a no-cost extension for one more year, in order to successfully complete WP2 and WP3.

Fig. 3. The setup of complete methane oxidative coupling system.

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

Impact: The PI received ***two*** major federal grants from NSF (DMR) and DOE (EFRC) using this fund as the seed money; ***two*** graduate students from Chemistry and MSE (Materials Sceince & Engineering) who were supported by this fund received "Graduate Student Award for Excellence in Research" (2018-9), which is the highest level of graduate student research award at this University.

Future work: (WP1): To manipulate the surface of these facet-controlled nanocatalysts with active site centers in atomic scale. (WP2) To conduct and complete the OCM evaluation systematically. (WP3) To determine and image the catalyst surface modification after a certain period of the OCM reaction.

3. Publications in the 2nd Year

"Size-Controlled Synthesis of CuNi Nano-Octahedra and Their Catalytic Performance towards 4-Nitrophenyl Reduction Reaction", Can Li, Yiliang Luan, Bo Zhao, Amar Kumbhar and Jiye Fang, *MRS. Adv.*, 4 (5-6) 263-269, (2019). http://dx.doi.org/10.1557/adv.2019.47

"The Effects of Dynamic Transformation on the Formation of Pt-M (M = Ni, Fe) Nanocrystals", Yiliang Luan, Can Li, Bo Zhao, Amar Kumbhar, Jun Zhang and Jiye Fang, *MRS. Adv.*, 4 (24) 1377 - 1382 (2019). https://doi.org/10.1557/adv.2018.656