Exploiting Shape Effects of La$_2$O$_3$ Nanocatalysts for Oxidative Coupling of Methane Reaction

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Experimental:

**Synthesis of La$_2$O$_3$ nanorods:** 5 mL 25% NH$_3$•H$_2$O was added to 250 mL 0.1M La(NO$_3$)$_3$ solution with vigorously stirring at about 800 rpm for more than one hour to get the formation of a white slurry. The white precipitate was obtained through centrifugation, and washed with nanopure water and ethanol for two times. Then a 250 mL sealed glass beaker loaded with the above white precipitate suspended in 125 mL nanopure water was laid in an oven with 105°C. After 24 hours, the precipitate was separated by centrifugation, washed with ethanol several times, followed by drying at 80°C in air overnight. The as-prepared powders were calcined with a muffle at 690°C for 2 h.

**Synthesis of La$_2$O$_3$ nanoparticles:** 25 mL 0.66 mol/L citric acid was slowly added into 25 mL 0.2 mol/L La(NO$_3$)$_3$ solution with vigorous stirring for 15 minutes. The mixture was placed in a constant-temperature bath at 70°C with continuously for 6 h. Then the stirring was stopped, and the solution was heated at 110°C for 24 h in a digital-type temperature-controlled oven. The oven was cool down to room
temperature naturally, and the obtained yellow powders were calcined with a muffle at 750°C for 2 h.

**OCM reaction test:** The catalytic activities for oxidative coupling of methane were evaluated at atmospheric pressure in a fixed-bed quartz tubular reactor. All the catalysts used for the OCM reaction were pelletized, crushed, and sieved to 40-80 mesh. 0.2 g catalyst and 0.8 g quartz sands as a diluent were placed in the reactor. Before the reaction, the catalyst in the reactor was heated to the reaction temperature (400°C) with 40 min at O2 flow. The reactant gases CH4 and O2 went through the reactor at a rate of 120 mL/min with n(CH4): n(O2) = 3 and the gas hour space velocity (GHSV) was fixed in 36000 mL/(g·h). The OCM reaction temperature was controlled from 400°C to 800°C. The composition of the gas exiting the reactor was monitored by two gas chromatographies with thermal conductivity detector (GC-TCD). One gas chromatography with carrier gas of H2 was used to analyze O2, CO, CH4, CO2, C2H4, and C2H6, and the other gas chromatography with carrier gas of Ar was used to analyze H2, O2, CO, CH4, and CO2. A cold trap was placed at the outlet of the reactor to separate water from the reaction products. Generally, the carbon mass balance can be achieved up to 98%.

**Characterization:** Powder XRD measurements were performed with a Rigaku D/Max-RB X-ray diffractometer with Cu Kα radiation. TEM images were recorded with JEOL JEM-2100 Electron Microscope (JEOL). The Brunauer–Emmett–Teller (BET) surface areas were determined by nitrogen adsorption-desorption isotherm measurements at 77 K (ASAP 2010). The catalytic products were analyzed by a gas chromatograph (Agilent Technologies: 6890N). Programmed Desorption (TPD) was performed with a flow of 40 mL/min O2-He and a heating rate of 10 K/min to 800°C. XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hv=1253.6 eV) or Al Kα radiation (hv=1486.6 eV).
Supporting Figures

Figure S1. (a) TEM image of La$_2$O$_3$ nanoparticles. (b) HRTEM image of a nanoparticle. Note that the 0.27 nm apart of the lattice fringes is corresponding to the (200) planes of La(OH)$_3$, which may be result from the water adsorption of La$_2$O$_3$ in air.
Figure S2. CH$_4$ conversion over quartz sand without La$_2$O$_3$ catalyst.
**Figure S3.** Catalytic results of OCM over La$_2$O$_3$ bulk.
Figure S4. Variation of coupling selectivity as a function of reaction temperature on (a) La$_2$O$_3$ nanorods, (b) La$_2$O$_3$ nanoparticles and (c) La$_2$O$_3$ bulk, respectively.
Figure S5. The side and the top views of the slab model of La$_2$O$_3$ (110) (a) and (101) (b). The 3-fold coordinated and 4-fold coordinated oxygen atoms in the top layer are labeled O$_3$, O$_4$ and colored magenta and chocolate, respectively; the one in the bulk are red, La atoms in the top layer are blue; the one in the bulk are cyan (One has five oxygen coordinations (La$_5$), and another has four O$_4$ oxygen coordinations (La$_4$).