Electronic Supplementary Information

Exploiting Shape Effects of La_2O_3Nanocatalysts for Oxidative Coupling of Methane Reaction

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Experimental:

Synthesis of La_2O_3 nanorods: 5 mL 25% $NH_3 \cdot H_2O$ 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^{o}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^{o}C for 2 h.

Synthesis of La_2O_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^{o}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^{o}C) with 40 min at O_2 flow. The reactant gases CH_4 and O_2 went through the reactor at a rate of 120 mL/min with *n* (CH_4): *n* (O_2) =3 and the gas hour space velocity (GHSV) was fixed in 36000 mL/(g·h). The OCM reaction temperature was controlled from 400^{o}C to 800^{o}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 H_2 was used to analyze O_2, CO, CH_4, CO_2, C_2H_4, and C_2H_6, and the other gas chromatography with carrier gas of Ar was used to analyze H_2, O_2, CO, CH_4, and CO_2. 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 O_2-He and a heating rate of 10 K/min to 800℃. XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hν=1253.6 eV) or Al Kα radiation (hν=1486.6 eV).

Supporting Figures

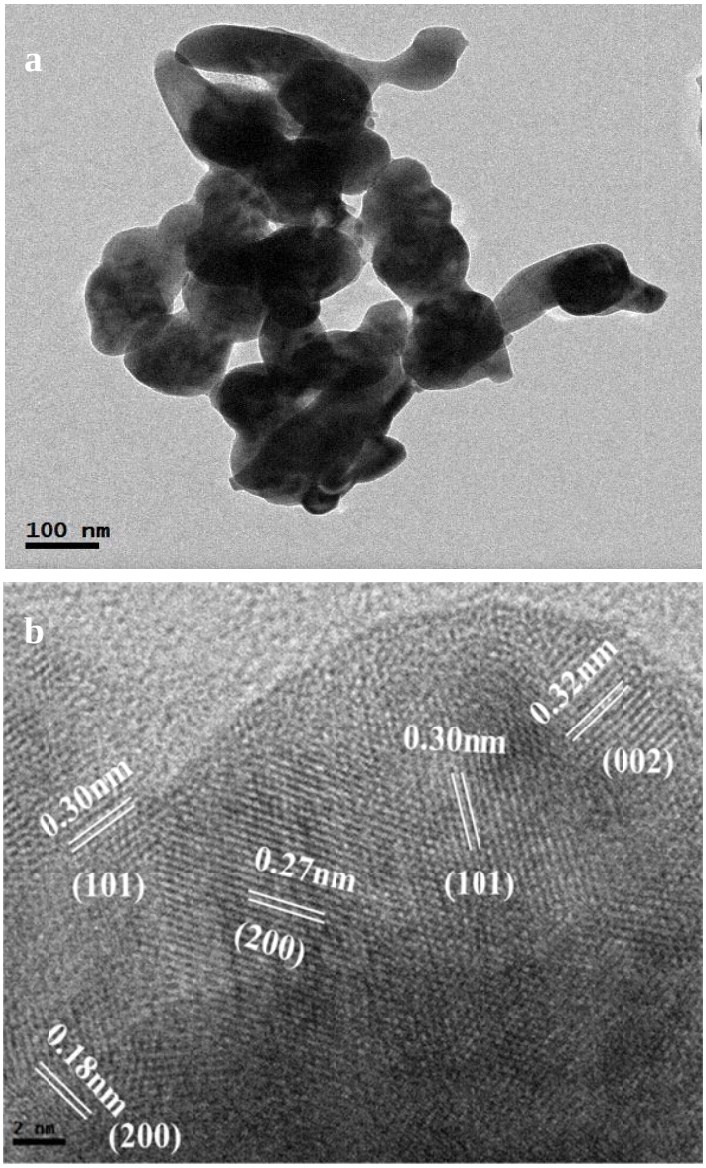

Figure S1. (a) TEM image of La_2O_3 nanoparticles. (b) HRTEM image of a nanoparticle. Note that the 0.27 nm apart of the lattice fringes is corresponding to the (200) planes of $La(OH)_3$, which may be result from the water adsorption of La_2O_3 in air.

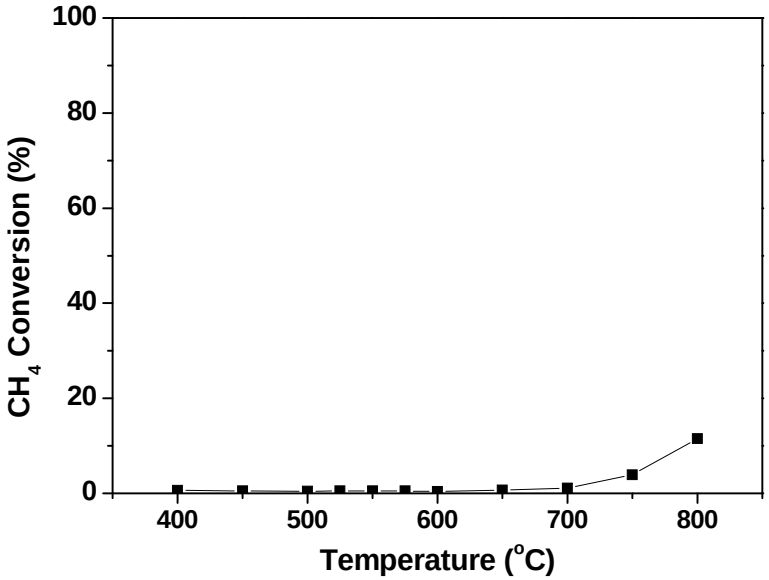

Figure S2. CH_4 conversion over quartz sand without La_2O_3 catalyst.

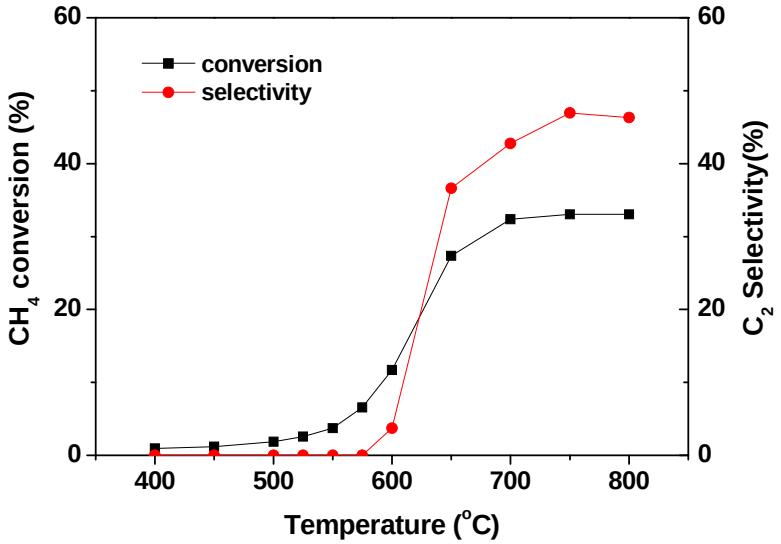

Figure S3. Catalytic results of OCM over La_2O_3 bulk.

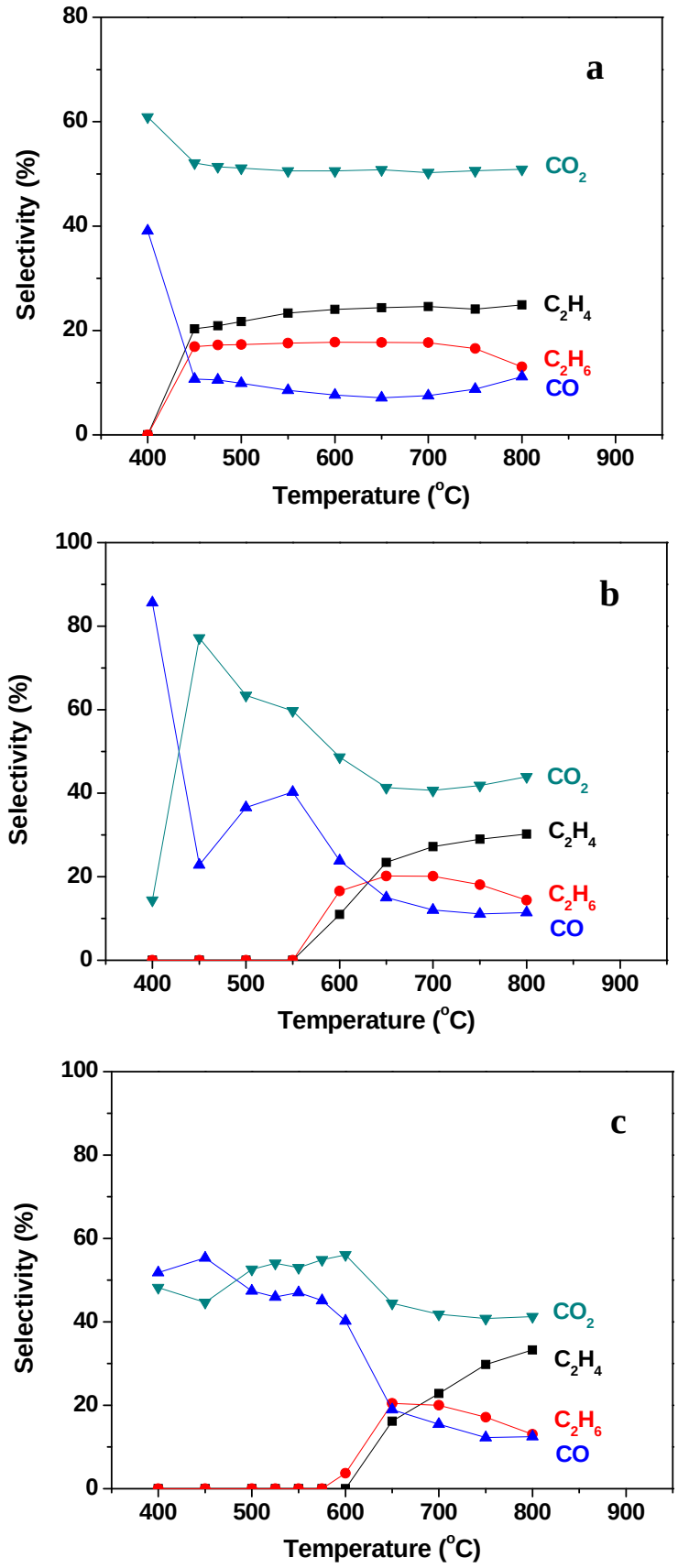

Figure S4. Variation of coupling selectivity as a function of reaction temperature on (a) La_2O_3nanorods, (b) La_2O_3 nanoparticles and (c) La_2O_3 bulk, respectively.

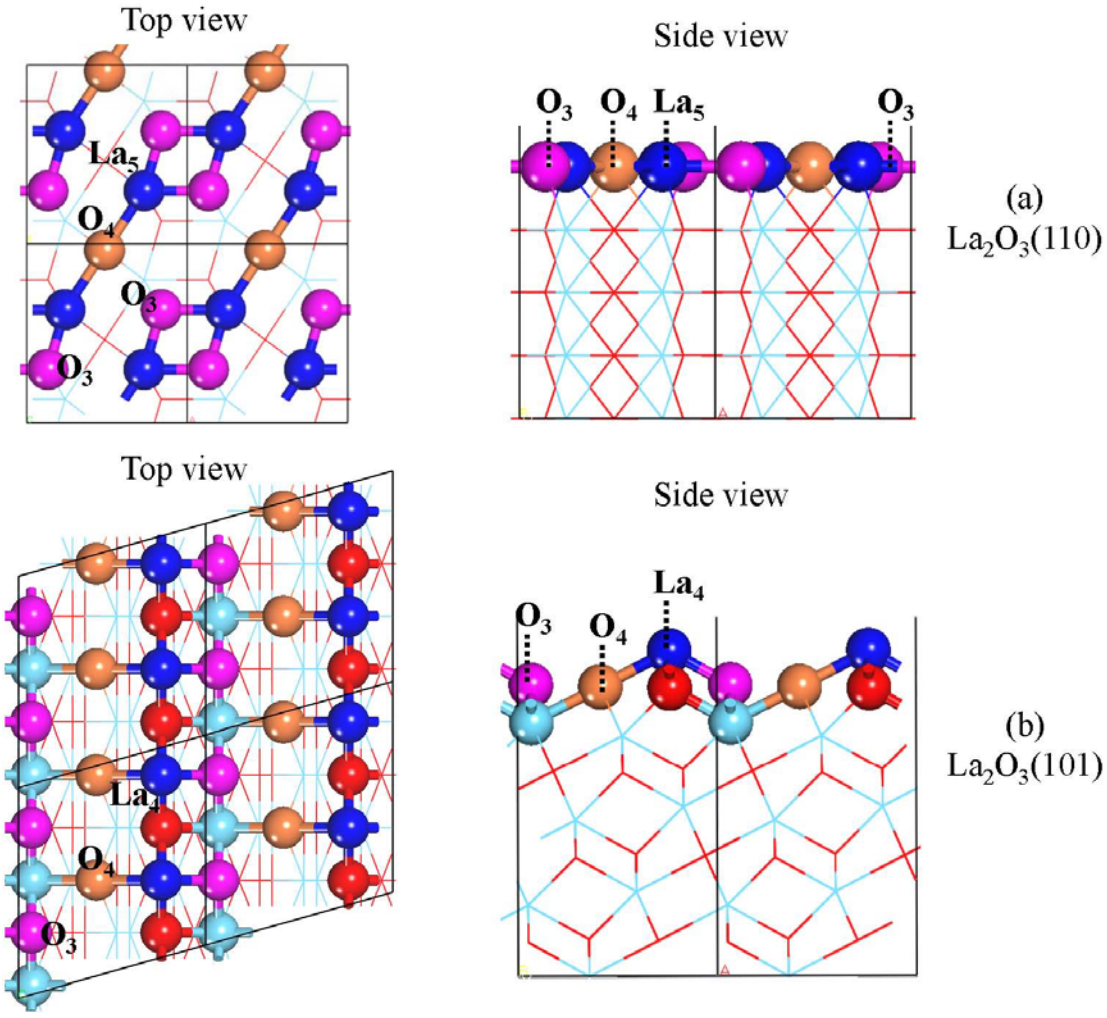

Figure S5. The side and the top views of the slab model of La_2O_3 (110) (a) and (101) (b). The 3-fold coordinated and 4-fold coordinated oxygen atoms in the top layer are labeled O_3, O_4 and colored magenta and chocolate, respectively; the one in the bulk are red, La atoms in the top layer are blue; the one in the bulk are cyan (One has five oxygen coordinations (La_5), and another has four O_4 oxygen coordinations (La_4).