Supporting Information

La_2O_3 catalysts with diversely spatial dimensionality for oxidative coupling of methane to produce ethylene and ethane

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Experimental:

Synthesis of La_2O_3 nanoparticles: 3.5 g $C_7H_5O_4N$ was added in a 50 mL solvent mixed with 80% alcohol and 20% deionized water. Then 5 mL 0.5 M $La(NO_3)_3$ was dropped into the above solution, and stirred for about 1 hour. After that, the mixture was putted to the 100 mL autoclave and then kept at 120°C for 24 hours. After the claves cooled to room temperature, the product was separated and washed by centrifugation by alcohol and deionized water. Finally the product was dried at 80°C and calcined at 680°C for 3 hours.

Synthesis of La_2O_3 nanorods: 4.33 g $La(NO_3)_3.6H_2O$ and 2.22 g PVP(10000) were added to 200 mL deionized water, and stirred for about 2 hours. Then the ammonia was added to the solution slowly and the solution became white. The gel sample was transferred to 100 mL autoclave and heated at 150°C for 24 hours. The product was separated and washed by deionized water after the autoclaves cooled down. Finally the product was dried at 80°C in a drying cabinet and calcined for 3 hours at 680°C at furnace.

Synthesis of La_2O_3 nanosheets: 1.625 g La $(NO_3)_3.6H_2O$ and 6 mL PEG400 were added in 50 mL deionized water, and stirred for 3h at 40°C. After that, the solution

was transferred to 100 mL autoclave and heated at 150^{o}C for 24 hours. The product was washed with deionized water. Finally the product was dried at 80^{o}C in a drying cabinet and calcined for 2 hours at 680^{o}C at furnace.

Synthesis of La_2O_3 nanoflowers: 10 g $La(NO_3)_3.6H_2O$, 2 mL water and 2 mL acetic acid were mixed into 60 mL glycol, then and stirred them for about 3 hours until dissolved. The solution was transferred into 100 mL autoclave and heated at 180^{o}C for 3 hours. After the autoclaves cooled down, the product was separated and washed for 5 times in alcohol. The product was dried at 80^{o}C and calcined for 2 hours at 680^{o}C.

OCM catalytic test

The oxidative coupling of methane (OCM) activity was evaluated in fixed bed quartz tubular reactor in at atmospheric pressure. 0.2 g 40-60 mesh La_2O_3 catalyst and 0.8 g silica sand were mixed together and then putted in quartz tubular. The catalyst was pretreated in N_2 atmosphere with 30 mL/min flow rate at 800^{o}C for 2 hours. When the feed temperature droped to 400^{o}C, the reactant gas was went into fixed bed reactor in the rate of 240 mL/min which consist of 75% methane and 25% oxygen. A cold trap was placed at the outlet of the quartz tube to separate any condensed water vapor from the reaction products. And the products were detected online by a micro gas chromatograph (3000 Micro GC; Inficon) equipped with two thermal conductivity detectors (TCD), one Molecular sieve 5A and one Plot U columns.

Characterization

SEM characterization was detected by ZEISS Supra 55. Powder XRD measurements were carried out with a Rigaku D/Max-RB X-ray diffractometer with Cu Kα radiation. TEM characterization was performed with JEOL JEM-2100 Electron Microscope (JEOL). The Brunauer−Emmett−Teller (BET) surface areas were recorded by nitrogen adsorption-desorption isotherm measurements at 77 K (ASAP 2010). X-ray photoelectron spectra (XPS) were detected on a Thermo Fisher Scientific K-Alpha X-ray photoelectron spectrometer. CO_2 temperature-programmed desorption measurements were examined on Micromeritics AutoChem II 2920 instrument connected to a MKS cirrus mass spectrum and our CO_2-TPD data was from mass

signal of molecular weight 44. The catalyst power (150 mg) was heated a He flow from 60 to 800^{o}C with a heating rate of 10^{o}C /min and then keep for 60 min at 800^{o}C, and cooled down to 60^{o}C. The CO_2 was injected at 60^{o}C for 60 min. after that He was injected and flow for 60 min, finally the temperature was raised to 880^{o}C with a rate of 10^{o}C/min ,the CO_2 desorption was detected by mass spectrograph.

Supporting Figures

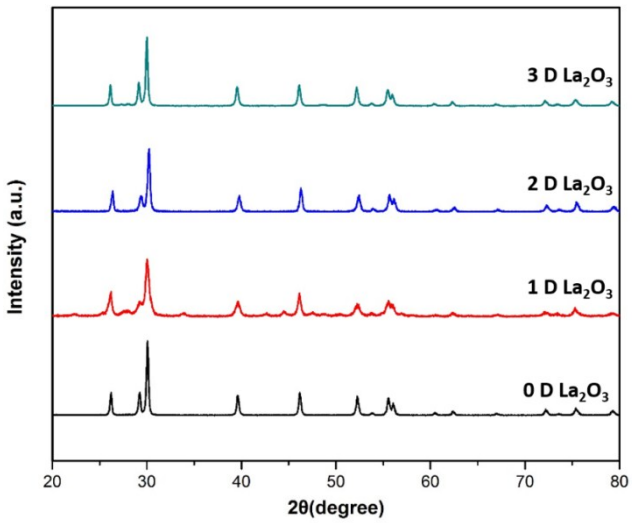


Fig.S1 XRD patterns of La_2O_3 catalysts.

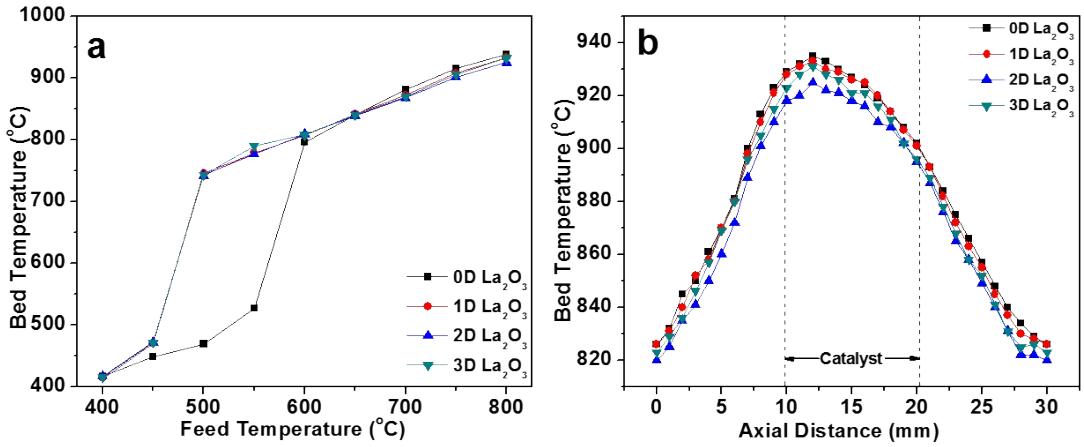


Fig.S2 (a) Feed and bed temperatures for OCM reaction over La_2O_3 catalysts. (b) Spatial temperature distribution in silica tube for OCM reaction over La_2O_3 catalysts.

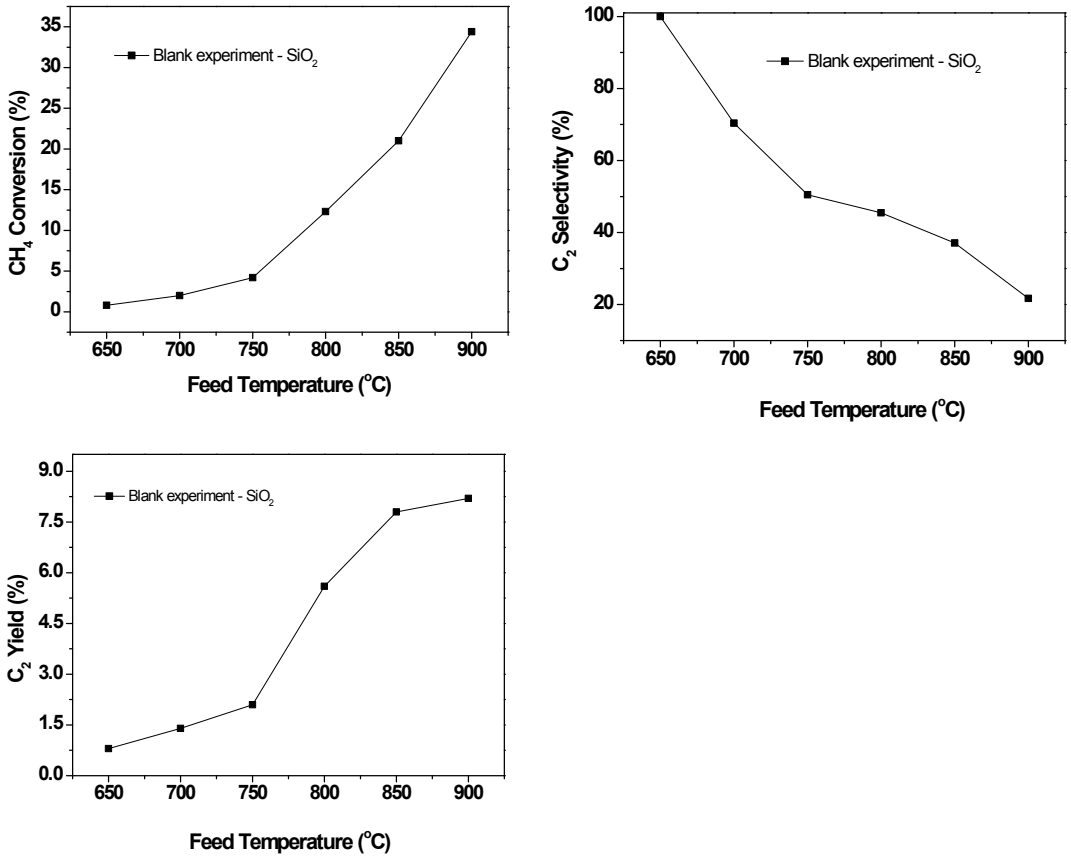
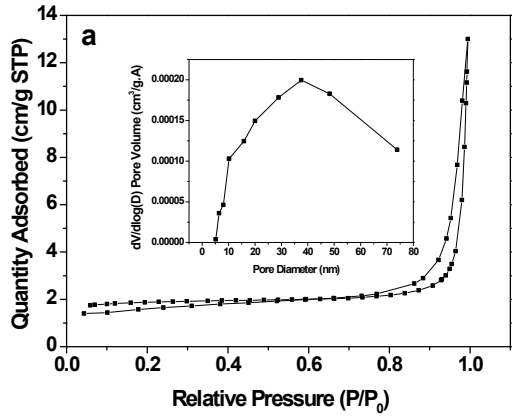
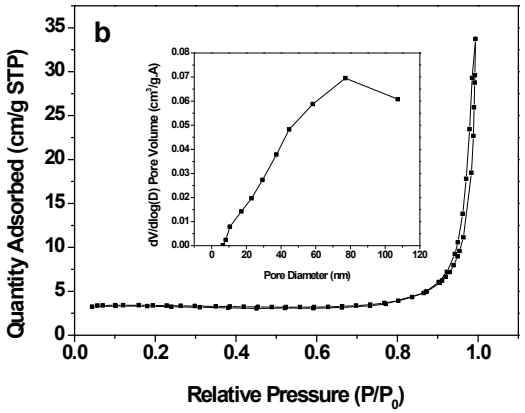
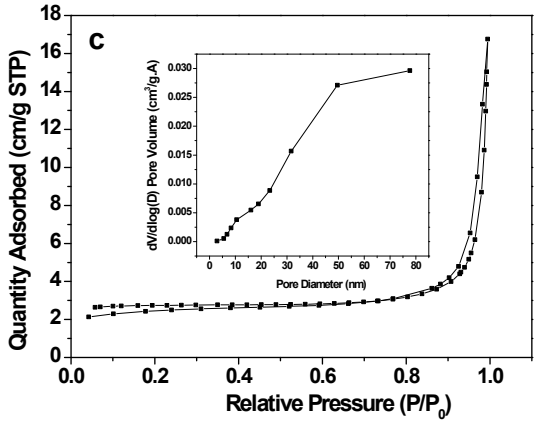


Fig.S3 The catalytic results of only silica sand for OCM reaction.


a
Quantity Adsorbed (cm/g STP)
Relative Pressure (P/P0)
dV/dlog(D) Pore Volume (cm3/g.A)
Pore Diameter (nm)


b
Quantity Adsorbed (cm/g STP)
Relative Pressure (P/P0)
dV/dlog(D) Pore Volume (cm3/g.A)
Pore Diameter (nm)


c
Quantity Adsorbed (cm/g STP)
Relative Pressure (P/P0)
dV/dlog(D) Pore Volume (cm3/g.A)
Pore Diameter (nm)

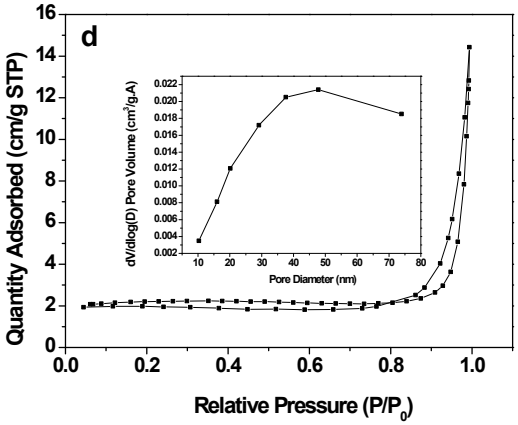


Fig. S4 The N_2 adsorption-desorption isotherms of La_2O_3 catalysts after catalytic reaction: (a) nanoparticles, (b) nanords, (c) nanosheets, and (d) nanoflowers. Insets are corresponding pore-size distributions.

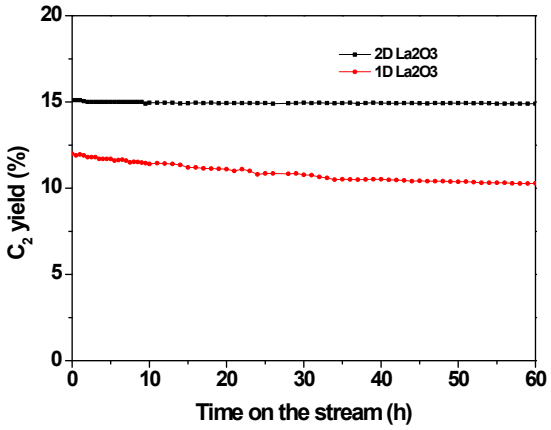


Fig. S5 The stability of 2D La_2O_3 and 1D La_2O_3 catalysts for OCM reaction at 550°C.