Supporting Information

Metal Ions (Li, Mg, Zn, Ce) Doped into La_2O_3 Nanorod for Boosting Catalytic Oxidative Coupling of Methane

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Experimental details

Preparation of the catalysts.

The specific experimental process is as follows: accurately weigh four portions of 1.0000 g $La(NO_3)_3 \cdot 6H_2O$ and add 50 ml deionized water to dissolve them, and then take 1 g $Li(NO_3) \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Ce(NO_3)_2 \cdot 6H_2O$ and dissolve them in 10 ml deionized water respectively. Ensure complete dissolution. Take 2 ml of the metal-doped nitrate solution and add them to the $La(NO_3)_3 \cdot 6H_2O$ aqueous solution, stir for 5 min. Then to prepare a 10% NaOH aqueous solution. Add dropwise to the above mixed solution, adjust the pH to 11.5, produce a white precipitate, and keep stirring for 10 min. The solution was transferred to the hydrothermal reactor and heated at 160°C for 12 h. The product was filtered and washed three times with deionized water and three times with absolute ethanol. Then dry in an oven at 50°C for 12 h. Then the product was calcined at 800°C under air conditions for 4 h. A series of catalyst in the form of a nanorod is obtained. The process is shown in Figure S1.

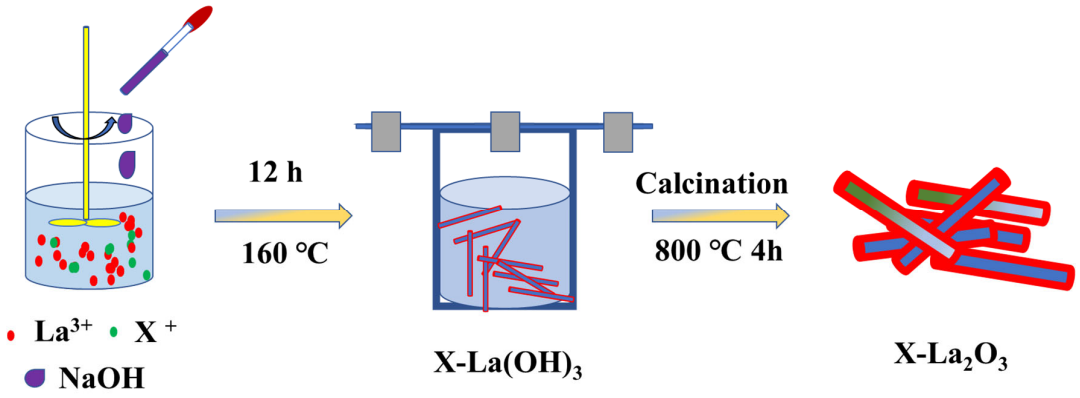

Figure S1. Schematic Process for the preparation of X-La_2O_3 catalysts.

Table S1. Reagents applied for preparation of catalysts.

Reagent	Manufacturer	Purity	Specification	Area
$La(NO_3)_3 \cdot 6H_2O$	innochem	99.90%	500 g	Beijing
NaOH	Xi long	AR	500g	Beijing
$Li(NO_3) \cdot 6H_2O$	An nai ji	99%	500g	Beijing
$Mg(NO_3)_2 \cdot 6H_2O$	innochem	99%	100g	Beijing
$Zn(NO_3)_2 \cdot 6H_2O$	Aladdin	AR,98%	500g	Beijing
Ethanol absolute	An nai ji	AR	5L	Beijing
$Ce(NO_3)_2 \cdot 6H_2O$	MACKLIN	AR 99.9%	100g	Beijing
Deionized water	Luo en	Deionized	2L	Beijing
Silica sand	Feng fan	AR	500g	Beijing

Catalyst activity evaluation

The OCM test was performed on a fixed-bed tubular quartz microreactor with an inner diameter of 6 mm and a length of 450 mm. The catalyst bed was placed between the quartz wool plugs in the reactor. The reaction temperature is accurately measured by a thermocouple placed in the middle of the catalyst bed. Under the total flow rate of CH_4:O_2:N_2=3:1:13 reaction gas (50 mL min^{-1}), treat the ground catalyst (100 mg) CH_4 for 1 h, heat up to 500°C, and heat from 500°C at a heating rate of 2 °C min^{-1} to 800°C. The product gas is cooled by a self-refrigeration trap to achieve the purpose of removing water vapor. Use an online gas chromatograph (GC9890B, Beijing) with a flame ionization detector (FID) to monitor the concentration of CH_4, C_2H_4, C_2H_6, C_3H_{10}, C_3H_8, CO and CO_2 outlet gas. Through a reasonable gas ratio and the flow rate of the reaction gas, a suitable reaction can be created for the reaction premise. All the above reaction conditions are obtained through a large number of literature studies and previous experimental verifications, and combined with the specific conditions of the laboratory, the most reasonable test conditions.

A kind of La_2O_3 nano-particle catalysts were synthesized successfully by calcination method in our previous work. The nano-particle La_2O_3 show the crystal facet of random distribution. Compared with nano-particle La_2O_3, nanorod La_2O_3 exhibits much better catalytic performance for OCM reaction. So, it is proposed that the {110} crystal facet is beneficial for OCM reaction. The SEM (Figure S2) and catalytic tests (Figure S12) results are shown in Supporting Information. In addition, the $La_2O_2CO_3$ catalysts reported by Xia and coauthors put forward a series of $La_2O_2CO_3$ catalysts with different crystal facets. Wu and coauthors reported a kind of Au supported La_2O_3@$La_2O_2CO_3$ catalysts and they think the {110} crystal facets are more energetic. Combined with references and experimental results, we suggest that the exposed {110} crystal facets of La_2O_3 nanorods play a crucial role for OCM reaction.

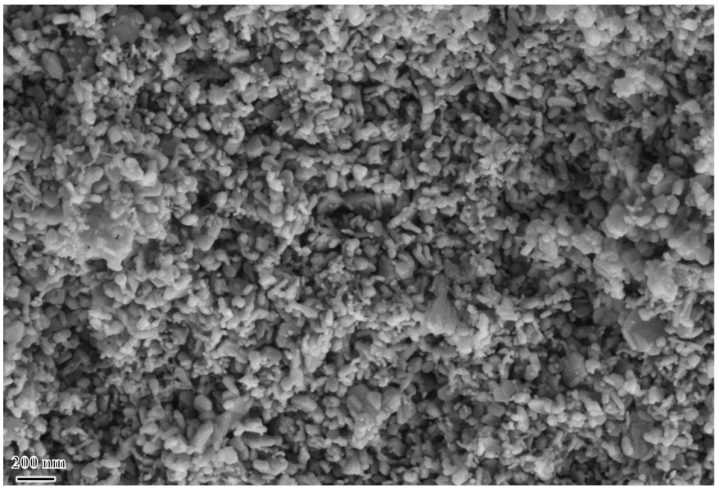

Figure S2. SEM images of pure La_2O_3 nanoparticles catalyst.

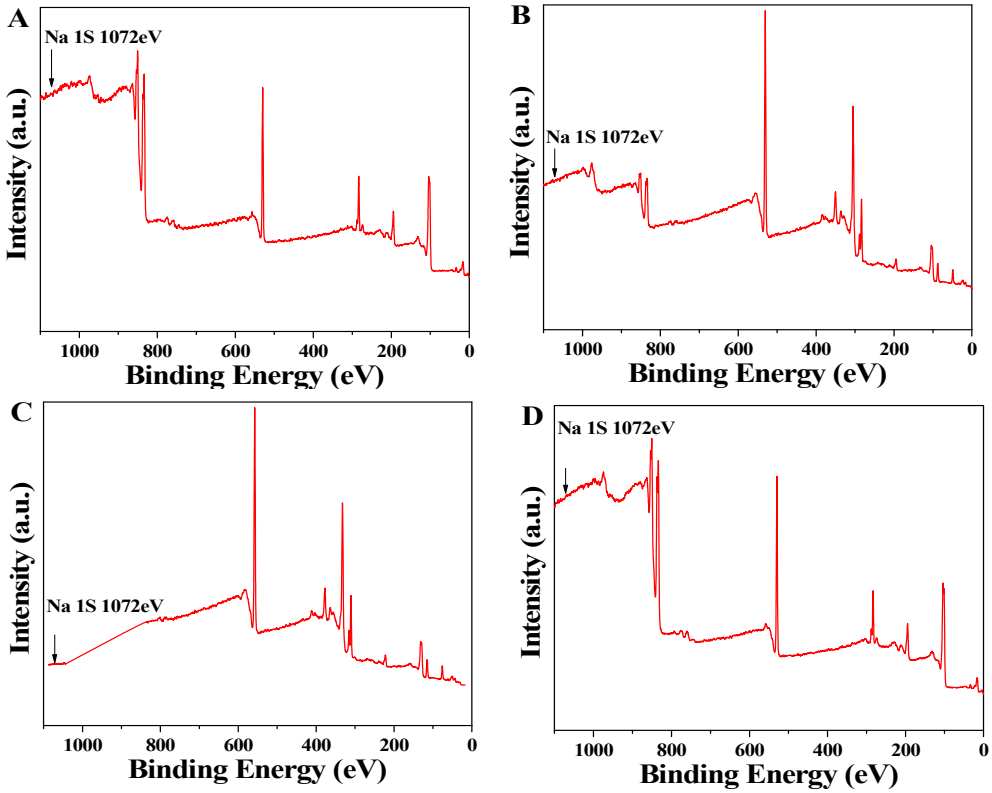

Figure S3. XPS survey spectrum (0-1100 eV) of X-La_2O_3 catalysts. (A) Li-La_2O_3; (B) Mg-La_2O_3; (C) Zn-La_2O_3; (D) Ce-La_2O_3.

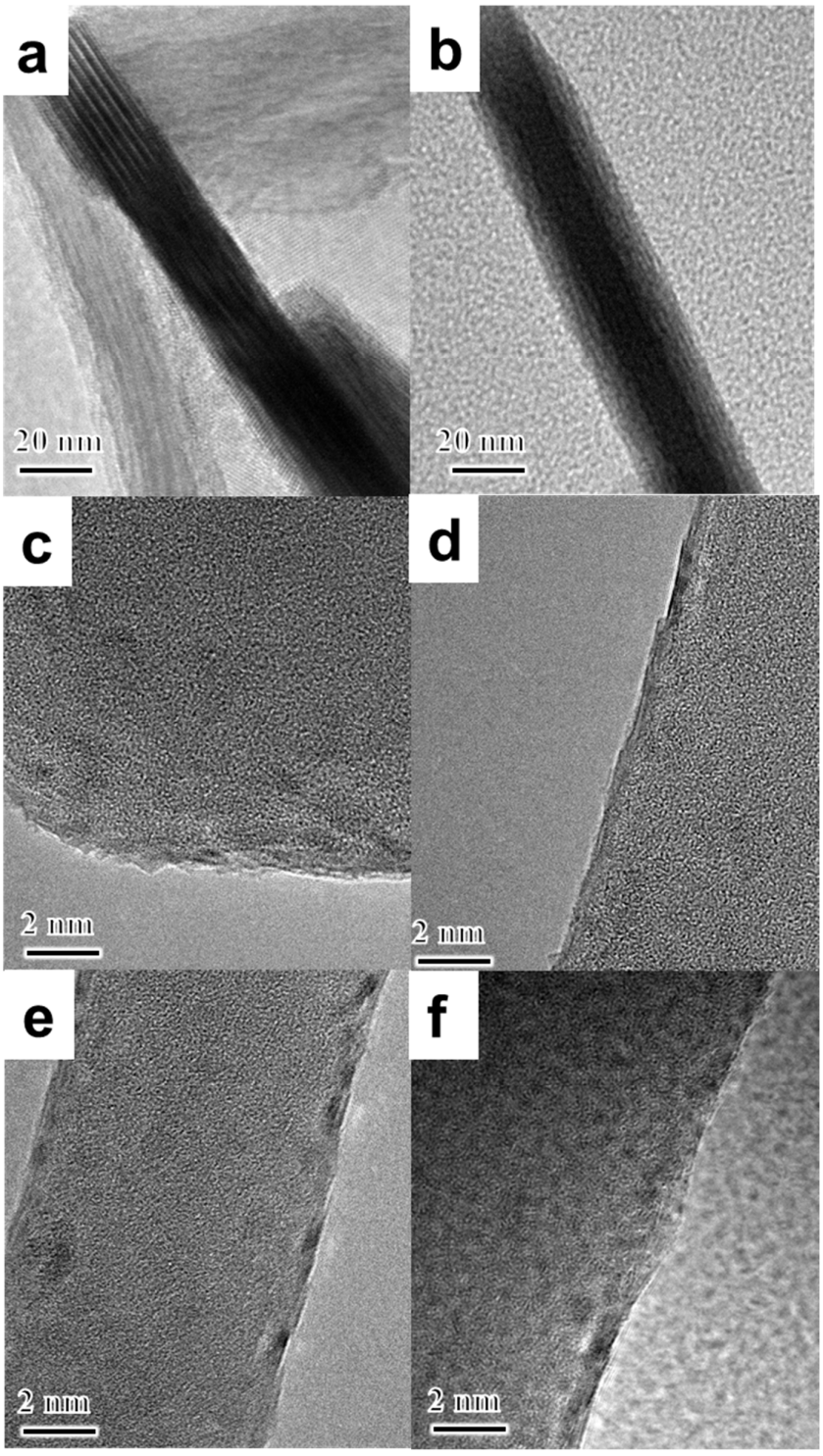

Figure S4. TEM Images of pure La_2O_3 (a, b), Li- La_2O_3 (c) Mg-La_2O_3 (d) catalyst.

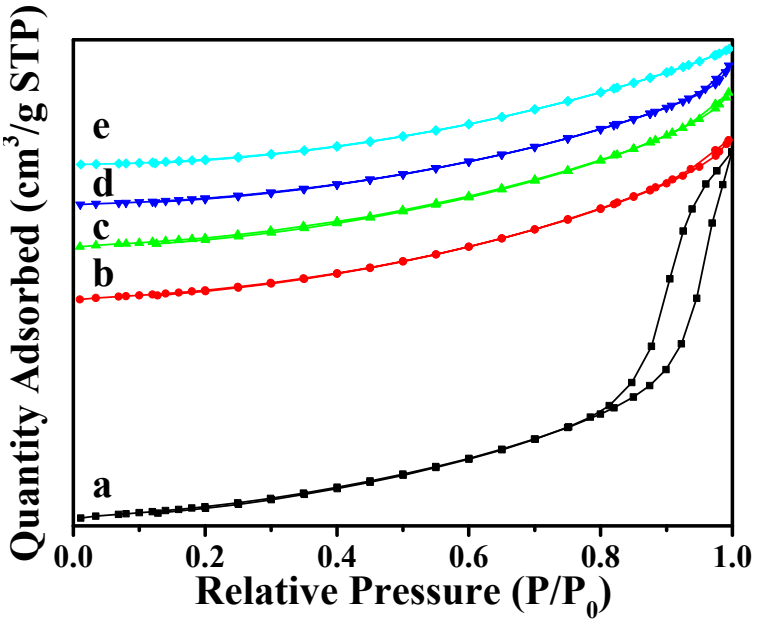

Figure S5. N_2 adsorption-desorption isotherms of the La_2O_3 and X-La_2O_3 catalysts. (a) La_2O_3; (b) Li-La_2O_3; (c) Mg-La_2O_3; (d) Zn-La_2O_3; (e) Ce-La_2O_3.

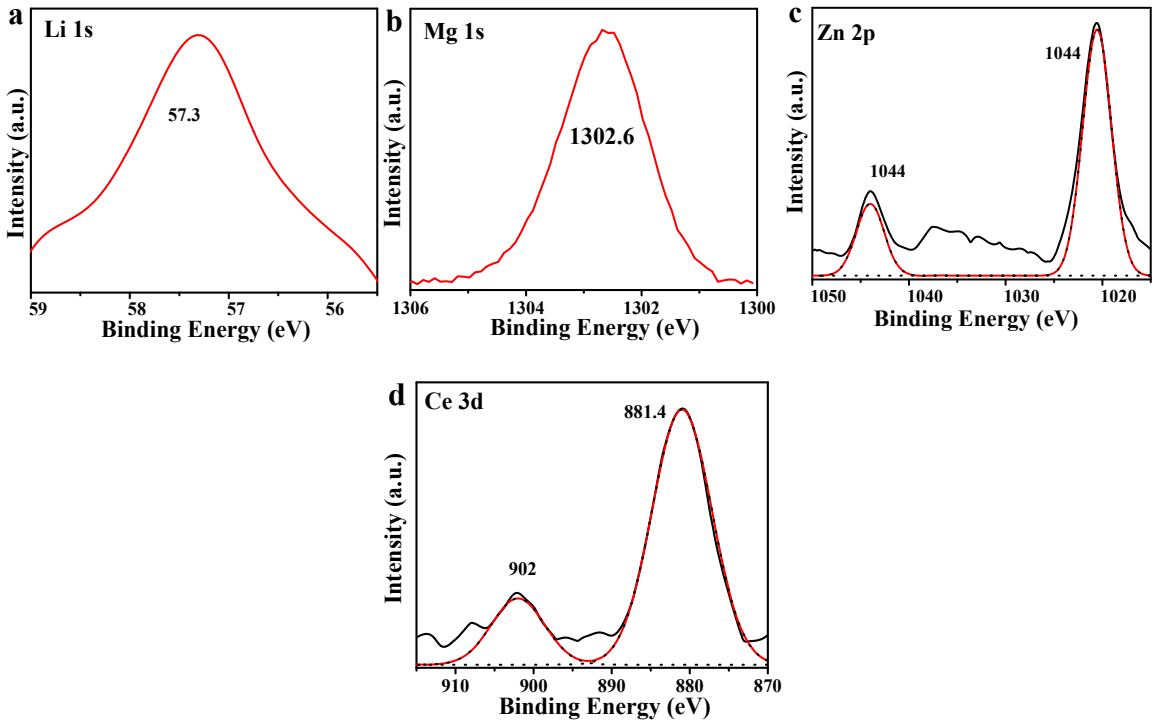

Figure S6. X-ray photoelectron spectra (XPS) of Li1s, Mg1s, Zn2p and Ce3d in X-La_2O_3 catalysts. (a) Li-La_2O_3; (b) Mg-La_2O_3; (c) Zn-La_2O_3; (d) Ce-La_2O_3.

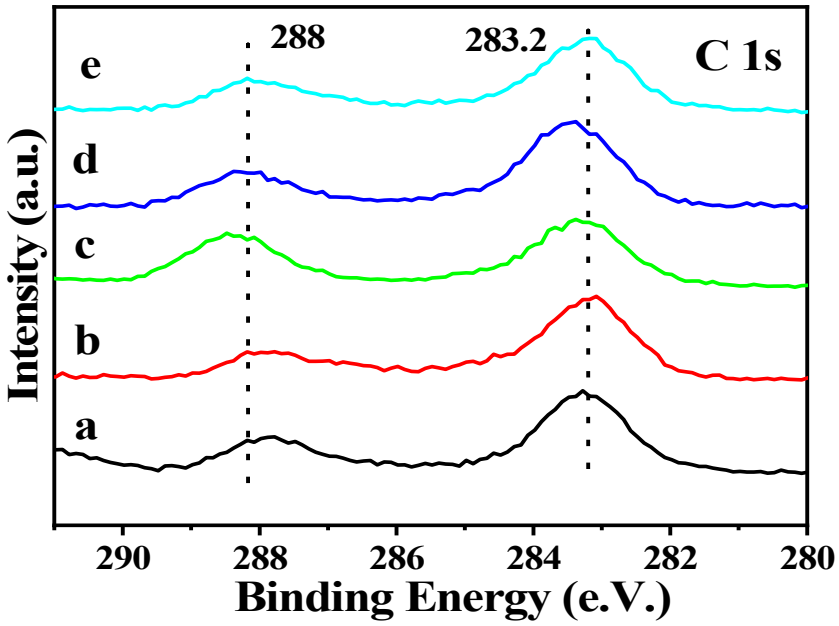

Figure S7. X-ray photoelectron spectra (XPS) of C1s over the La_2O_3 and X-La_2O_3 catalysts. (a) La_2O_3; (b) Li-La_2O_3; (c) Mg-La_2O_3; (d) Zn-La_2O_3; (e) Ce-La_2O_3.

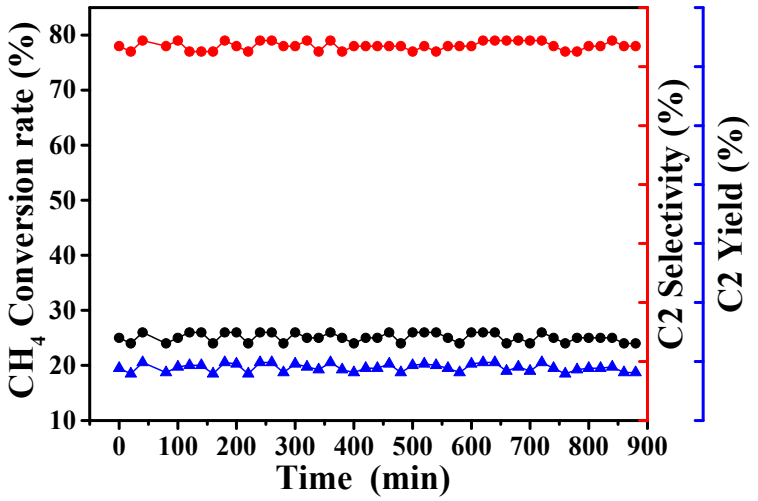

Figure S8. Stability test of the Mg-La_2O_3 catalysts for OCM.

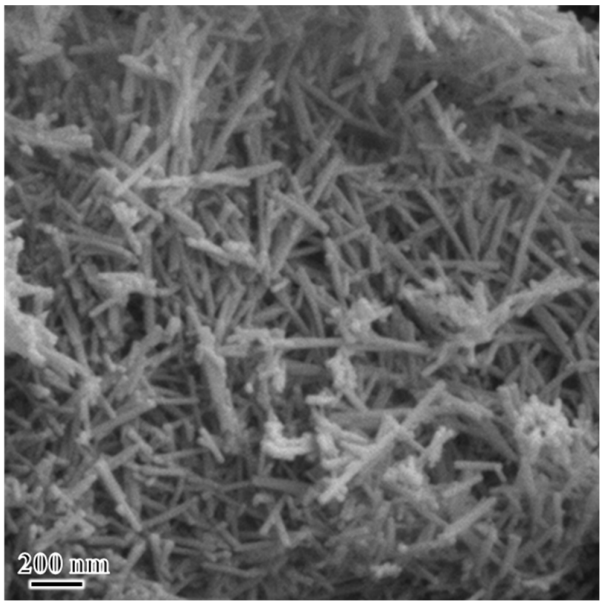

Figure S9. SEM images of Mg-La_2O_3 catalyst used for 15 h during OCM reaction.

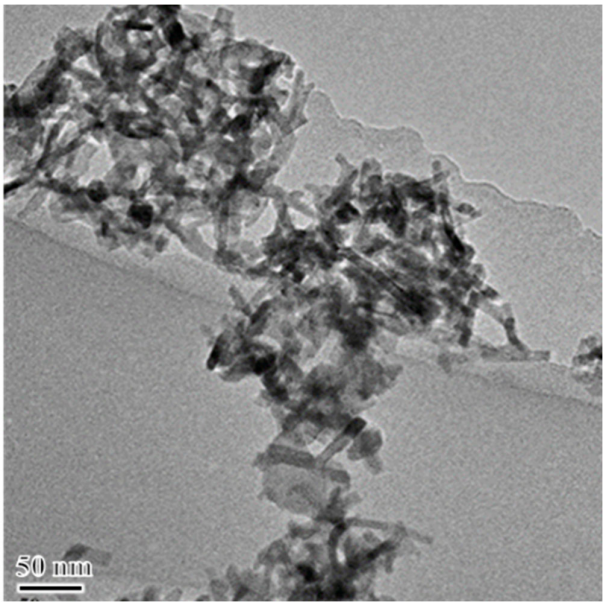

Figure S10. TEM Images of Mg-La_2O_3 catalyst used for 15 h during OCM reaction.

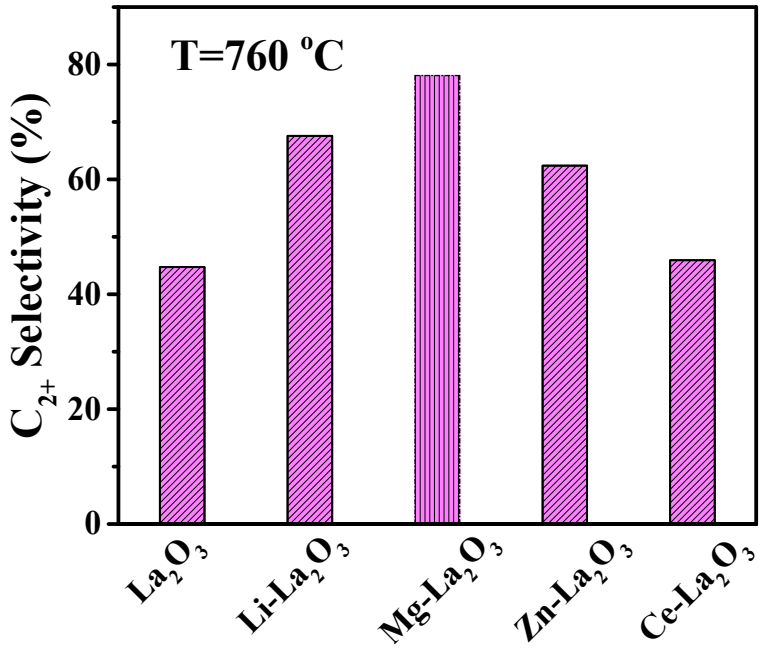

Figure S11. The selectivity of C2 products for OCM reaction over the La_2O_3 and X-La_2O_3 catalysts.

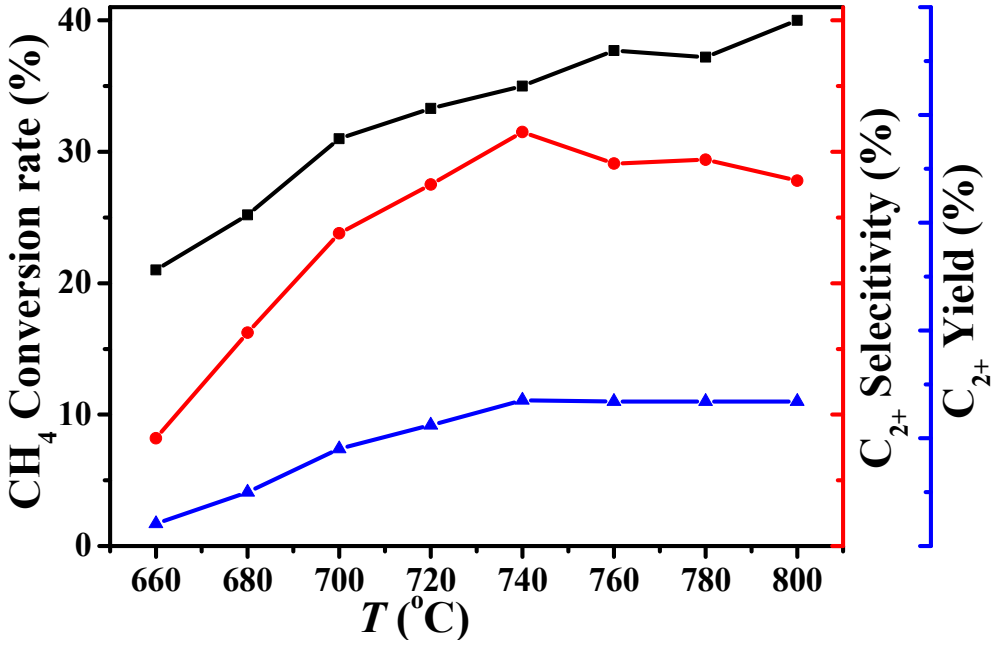

Figure S12. Catalyst performance of La_2O_3 nanoparticles catalyst.