Electronic supplementary information

Effect of Mg substitution on $LaTi_{1-x}Mg_xO_{3+\delta}$ catalysts for improving C2 selectivity of the oxidative coupling of methane

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1. Supplementary information on experimental

Synthesis of pure oxide catalysts

Pure oxide catalysts (La_2O_3, TiO_2 e MgO) were prepared by the polymerized complex method. 0.2 moles of each cation precursor (lanthanum nitrate, titanium isopropoxide or magnesium nitrate) were added to 4 moles of ethylene glycol and 1 mol of anhydrous citric acid under constant stirring. The solution was stirred for 30 min at ambient temperature and then heated at 120 °C until full polymerization. The polymer was calcined at 300 °C for 2 h, macerated and calcined at 800 °C for 4 h.

XPS analyses

The inelastic background of the La 3d, Ti 2p, Mg 2s, C 1s, and O 1s spectra was subtracted using Shirley's equation. The binding energy scale of the spectra was corrected using the C1s hydrocarbon group (284.8 eV). The atomic composition of the surface layer (<5 nm) was determined by the relative proportions of the areas of the spectra corrected by Scofield's atomic sensitivity factors, with an accuracy of ± 5%. The spectra were deconvolved using a Voigtian function, with Gaussian (70%) and Lorentzian (30%) combinations.

CO_2-TPD analyses

The catalysts samples (200 mg) were heated in Ar flow (50 $mL.min^{-1}$ and 10 $°C.min^{-1}$ heating rate) from 30 to 800 °C and then cooled to 30 °C. After this step, the samples were treated with CO_2 flow (30 $mL.min^{-1}$) for 1 h and Ar flow (20 $mL.min^{-1}$) for 30 min. Finally, the Ar flow was maintained for recording the CO_2-TPD results, and the samples were heated at 5°$C.min^{-1}$ from 30°C to 800°C and held at this temperature until the curve returned to the baseline.

DRIFTS analyses

The catalysts were heated in He flow (20 mL.min^{-1}) up to 500 °C and held for 30 min; they were then cooled to 50 °C and kept under CO_2 flow (20 mL.min^{-1}) for 30 min, followed by He flow (20 mL.min^{-1}) for 15 min. The spectra were collected after this step, and the processes were repeated for the chemisorption at 300 and 500 °C. The background spectra at each temperature were obtained before the CO_2-chemisorption. Data were treated by the Smooth and Kubelka Munk functions.

2. Supplementary information on results

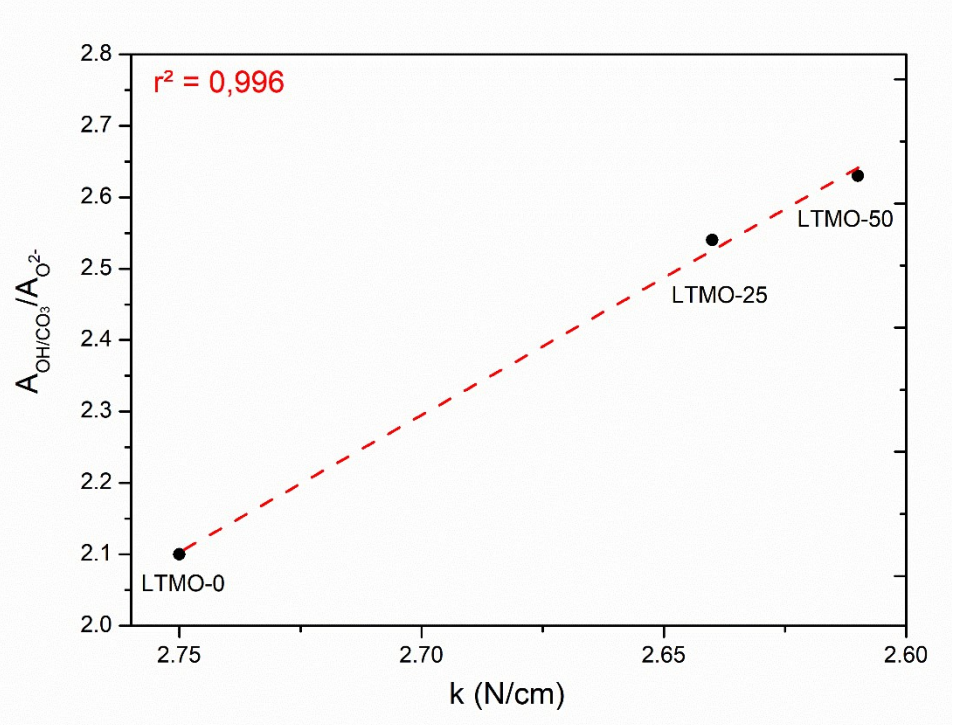

Figure S1. The ratio of hydroxyl/carbonate oxygen and lattice oxygen ($A_{OH/CO3}/A_{O2-}$) versus bond force constant. A linear fit was performed with $r^2 = 0.996$.

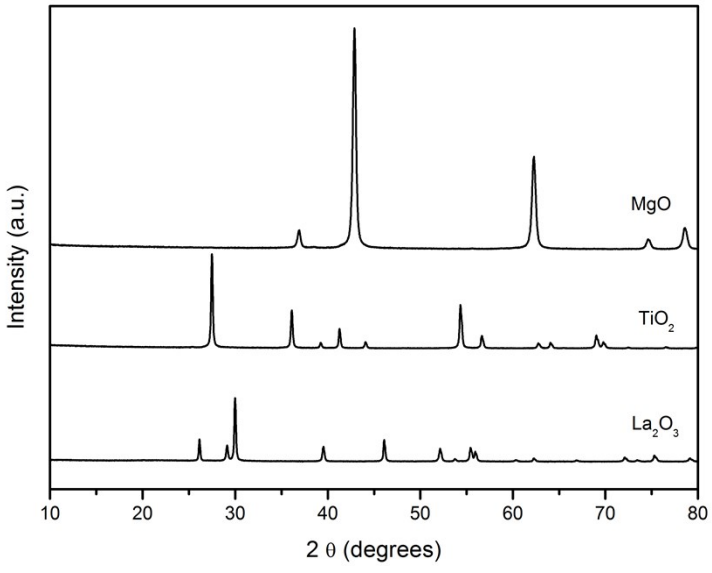

Figure S2. X-ray diffraction patterns of La_2O_3, TiO_2 and MgO catalysts.

The patterns for all pure oxide structures were verified by X-ray diffraction analysis (Fig. S1). Lanthanum oxide (PDF No. 05-0602) showed diffraction patterns corresponding to a hexagonal crystalline system and P-3m1space group. Titanium oxide (PDF No. 71-0650) was formed in a rutile crystalline structure (tetragonal, P42 / mnm), and magnesium oxide (PDF No. 45-0946) was formed in a periclase crystalline structure (cubic, Fm -3m).

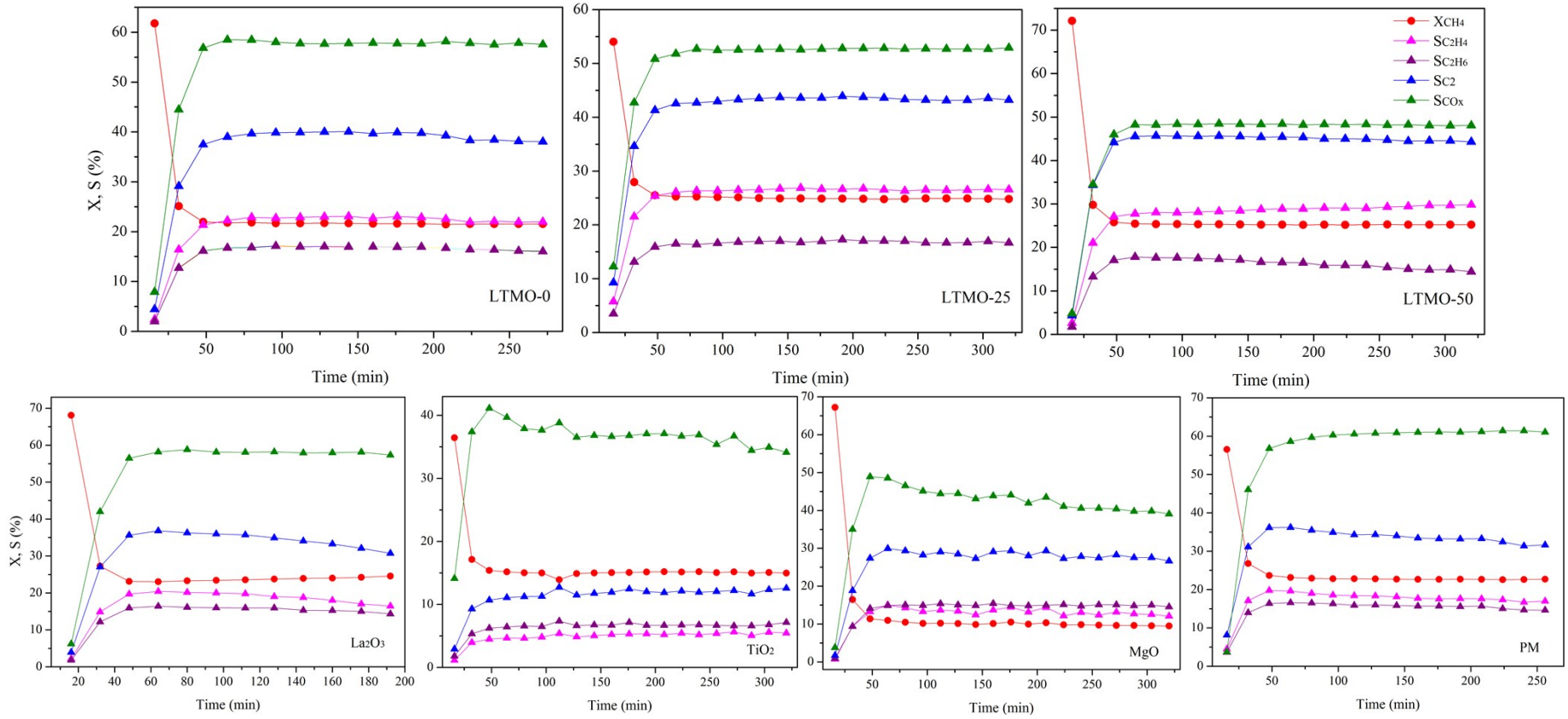

Figure S3. Methane conversion (X_{CH4}), CO_X selectivity (S_{COx}), C_2H_4 selectivity (S_{C2H4}), C_2H_6 selectivity (S_{C2H6}) and C2 selectivity (S_{C2}) over the OCM reaction time for LTMO-0, LTMO-25, LTMO-50, La_2O_3, TiO_2, MgO and PM. Reaction conditions: $CH_4/O_2 = 8$, W = 45000 $mLg_{cat}^{-1}.h^{-1}$ and T = 800 °C .

Table S1. Catalytic performance of LTMO-50 catalyst and other perovskite structures of OCM literature.

Catalysts	X_{CH4} (%)	S_{C2} (%)	C_2H_4/C_2H_6	GHSV (h^{-1})	T (°C)	CH_4/O_2	S_{BET} (m^2/g)	Productivity	
								$mmol_{C2}.g^{-1}.h^{-1}$	$mmol_{C2}.m^{-2}.h^{-1}$
LTMO-50	17.3	51.4	0.97	30,000[a]	800	8	5.0	68.2	13.6
$La_2Ti_2O_7$ [1]	18	32	0.5	18,000[a]	800	4	16.3	18.9	1.2
$LaAlO_3$ [2]	24	44	0.6	10,000	800	4	3.0	4.4[b]	1.5
$LaFeO_3$ [2]	18	19	1.4	10,000	800	4	3.0	1.5[b]	0.5
$LaNiO_3$ [2]	14	2	3	10,000	700	4	3.3	0.1[b]	0.03
$BaSrTiO_3$ [3]	47	29.5	-	6,000	800	2	4.4	17.0	3.9
$MgBaSrTiO_3$ [3]	46.5	43	-	6,000	800	2	0.9	29.5	32.7
$SrTiO_3$ [4]	15	62.6	2	151,200	850	4	1.5	115.3[b]	76.8
$SrTi_{0.9}Mg_{0.1}O_3$ [4]	24	64	1.3	151,200	850	4	3.2	188.6[b]	58.9

a. WHSV ($mL.g^{-1}.h^{-1}$)

b. catalyst mass was calculated from catalyst volume using the following densities: $LaAlO_3$ = 6.52 g/cm^3; $LaFeO_3$ = 6.40 g/cm^3; $LaNiO_3$ = 6.93 g/cm^3; $SrTiO_3$ = 4.81 g/cm^3.

3. References for supplementary material

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