Electronic Supplementary Information

Intercalation of Nanostructured CeO_2 in $MgAl_2O_4$ Spinel Illustrates the Critical Interaction of Metal Oxide and Oxides

Xinping Duan[1], Zhaojun Wen[1], Yuxin Zhao[1], Junfu Zhou[1], Huihuang Fang[1], Yanning Cao[2], Lilong Jiang[2]*, Linmin Ye[1], Youzhu Yuan[1]*

1. State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols-Ethers-Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, PR China.
2. National Engineering Research Center of Chemical Fertilizer Catalyst, Fuzhou University, Fuzhou 350002, Fujian, PR China.

* Corresponding author:

1. E-mail: yzyuan@xmu.edu.cn; Fax: +86-592-2183047; Tel: +86-592-2181659.

2. E-mail: llj@fzu.edu.cn; Tel: +86-591-83731234.

Experimental

Catalyst preparation

Magnesium aluminate spinel (MgAl) supports were prepared by hydrolysis of aluminium isopropoxide with magnesium nitrate hexahydrate in ethanol according the reported method with minor modification.[17] Stoichiometric quantities of aluminium isopropoxide (98+%, Alfa Aesar) (0.05 mol) and magnesium nitrate hexahydrate (98%, Alfa Aesar) (0.025 mol) were mixed in 150 ml denatured ethanol. The mixture was sealed and then put on a heating plate with strong magnetic stirring. After stirring for 12 h, the plate was heated to 150 °C and held there for 12 h. Then, the ethanol was evaporated and the resultant gel was dried at 100 °C overnight. Finally, the dried powders were calcined in ambient air at 800 °C for 12 h with a heating rate of 5 °C min^{-1}, resulting in the formation of MgAl support with pure spinel crystal phase. Ceria intercalated MgAl spinel (xCe-MgAl, x referred as the varied CeO_2 loading) support was prepared by the hydrothermal synthesis method similar to the above described. In detail, stoichiometric quantities of aluminium isopropoxide and magnesium nitrate hexahydrate and cerium nitrate hexahydrate were mixed in 150 ml ethanol. The mixture was stirred at room temperature for 12 h, and then it was transferred to a Teflon-lined stainless steel autoclave at 150 °C for 12 h. The resultant gel was dried at 100 ºC overnight. Finally, the dried powders were calcined in ambient air at 800 ºC for 12 h with a heating rate of 5 °C min^{-1}. For comparison, ceria supported MgAl (CeO_2 content, 10 wt%) was also prepared with impregnation method. Supported Ag catalysts with 10 wt% loading were prepared by incipient wetness impregnation of MgAl or Ce-MgAl using aqueous solutions of $AgNO_3$ at room temperature for 24 h. Impregnated samples were dried at 100 °C overnight and calcined at 350 °C for 4 h to manufacture the final catalysts, which is denoted as Ag/MgAl or Ag/Ce-MgAl.

Catalyst characterization

The X-ray diffraction (XRD) patterns of the catalyst samples were obtained by using a PANalytical X'pert Pro diffractometer with Cu-K_α radiation ($\lambda = 0.15418$ nm) at a scanning angle (2θ) ranging from 10° to 90°. The tube voltage was 40 kV, and the current was 30 mA. Each XRD pattern was identified by matching the results with reference patterns included in the JCPDS database. The N_2 adsorption–desorption isotherms of catalysts were measured at 77 K by using a Micromeritics TriStar II 3020 porosimetry analyzer. The samples were degassed at 573 K for 3 h prior to measurements. Specific surface area (S_{BET}) was calculated using the Brunauer–Emmett–Teller (BET) method, in which the isotherm data in a relative pressure (P/P_0) range of 0.05 to 0.30 were adopted. Total pore volume (V_{pore}) was derived from the absorbed N_2 volume at a relative pressure of approximately 0.99. X-ray photoelectron spectroscopy (XPS) was conducted using a JPS-9010MC photoelectron spectrometer equipped with an Al–Kα X-ray radiation source (hν = 1486.6 eV). Before measurements were performed, each sample was pressed into a thin disk and pretreated in an atmosphere of 5% H_2–95% N_2 at 693 K for 3 h. The pretreated samples were also carefully collected in a nitrogen atmosphere before XPS measurements were carried out. The binding energy (BE) was calibrated using C 1*s* peak at 284.6 eV as a reference with an uncertainty of ± 0.2 eV. The actual contents of Ag and Ce elements were determined by X-ray fluorescence (XRF) spectroscopy. Catalyst powders were compressed into a self-supporting wafer prior to analysis. The UV-vis absorption spectra of the catalysts were obtained for the dry-pressed disk samples on a UV–vis–NIR Cary 5000 spectrophotometer with DRA-CA-30I diffuse reflectance accessory using $BaSO_4$ as standard reflectance sample. Electron paramagnetic resonance (EPR) measurements were performed at -196^{o}C on a Bruker EMX-10/12 spectroscope operating in the X-band. The cavity operating at a frequency of ~9.6 GHz, and the magnetic field was modulated at 100 kHz. The g values were determined from precise frequency and magnetic field values. Ranman spectra were collected using Renishaw inVia equipment. A He-Ne laser source was used and the wavelength is 532 nm. Transmission electron microscopy (TEM) images were performed on a Tecnai F20 electron microscope operated at an acceleration voltage of 300 kV. Samples for TEM measurements were ultrasonically dispersed in ethanol. Drops of suspensions were deposited on a copper grid coated with carbon. H_2-temperature-programmed reduction (TPR) profiles were measured in a fix bed continuous flow reactor with a reduction mixture of 5% H_2/Ar at a flow rate of 30 mL/min and heating rate of 10 K/min. The amount of H_2 consumption was measured using a thermal conductivity detector (TCD). O_2-temperature-programmed desorption (O_2-TPD) measurements were carried out on a Micromeritics AutoChem 2920 II instrument. One hundred milligrams of sample was typically used for an analysis. Before each test, the samples were pretreated at 300 °C in Ar flow for 1 h and then cooled down to 30 °C. O_2 adsorption were carried out by exposing the samples to a flow of 10% O_2/Ar at 30 °C. After that removing O_2 in gas phase by Ar purge, the O_2-TPD (by monitoring $m/e = 32$) were recorded out in Ar flow at a ramping rate of 10 °C $\min^{-1}$ up to 1000 °C.

Catalytic tests

The catalytic carbon oxidation activity of the catalysts was evaluated by TG/DTA (HCT-2, HENVEN) technique using Printex-U soot (Degussa) as the model reactant.[24, 57] The effluent gas was analyzed by an on-line gas chromatograph equipped with two packed columns (Molecular sieve 5A and Porapak Q) and thermal conductivity detector (TCD). Typically, the soot was mixed with the catalyst in a weight ratio of 1:10 using a spatula for 5 min to obtain a loose contact. Then, the mixture samples were heated in 50 ml $\min^{-1}$ flow of air at a rate of 10 °C $\min^{-1}$ to 800 °C. By comparing the characteristic temperatures of the TG curves, the catalytic activity of the catalysts was evaluated. The temperature at which combustion occurs at the maximum rate (T_m) was taken for comparison of catalyst activities. We used the temperature for the maximum intensity of the exothermic DTA peak (T_{max}) as a parameter to compare the soot combustion activity of different catalyst. T_m was the peak temperature at which the maximum C_{CO2}value was obtained during the TPO procedure. In all TPO experiments, the reaction was not finished until the soot was completely burnt off.

The oxygen storage/release capacity of MgAl and Ce containing MgAl (Ce-MgAl or Ce/MgAl) mixtures to O_2 was also evaluated in repeatedly reduction/oxidation cycling mode, weight variation were measured by TG/DTA (HCT-2, HENVEN) technique. In detail, during the reduction or oxidation treatment, the MgAl or Ce-MgAl supports was placed in a stream of He at a constant temperature of 150–300 °C, where the flow was changed to 30% O_2/He at 700 °C for 30 min, the exchanged flow thereafter was altered to 5% H_2/He for at 700 °C for 30 min. The above oxidation/reduction process were repeatedly performed for several times. The total weight varation during the oxidation/reduction treatment was monitored by using TG/DTA technique.

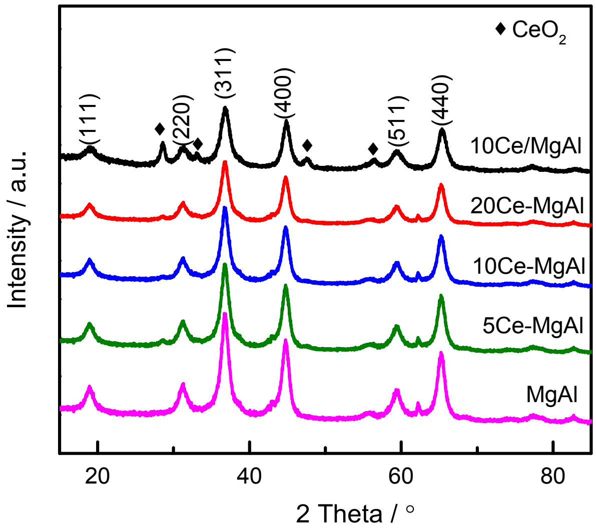

Fig. S1 XRD patterns of various Ce-involved and -free MgAl samples.

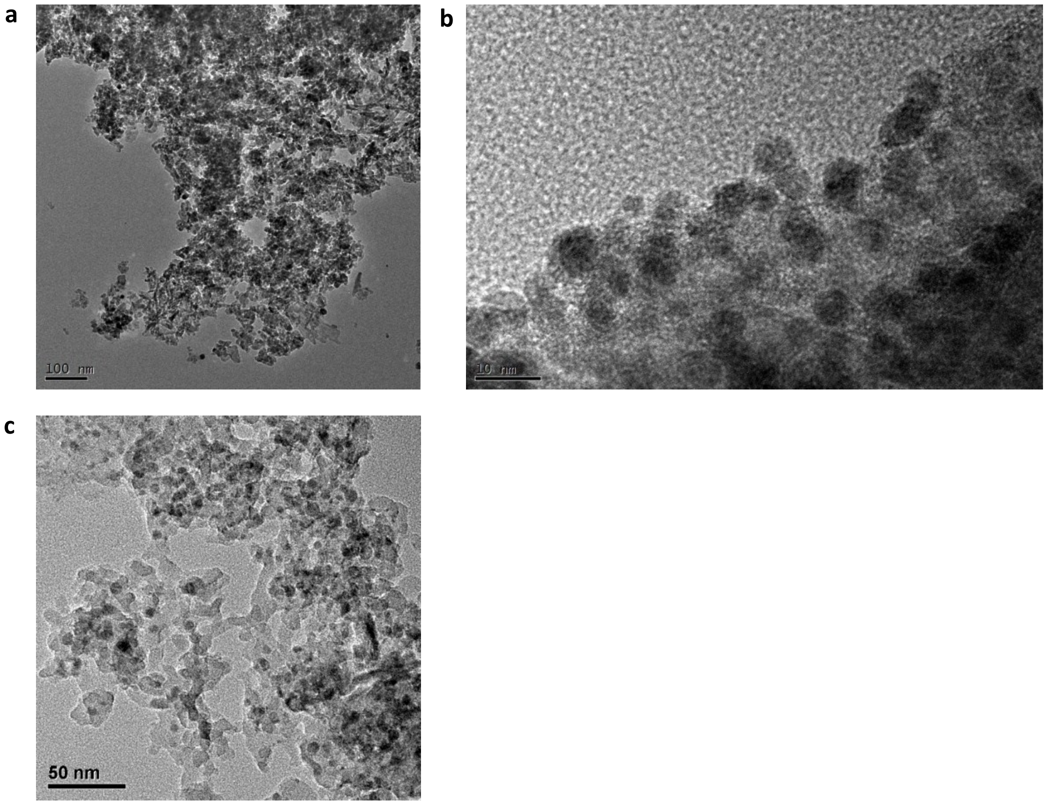

Fig. S2 (a) and (b) TEM and HRTEM images of nanostructured CeO$_2$-intercalated MgAl sample, respectively. (c) TEM image of Ce/MgAl catalyst, prepared by impregnation method.

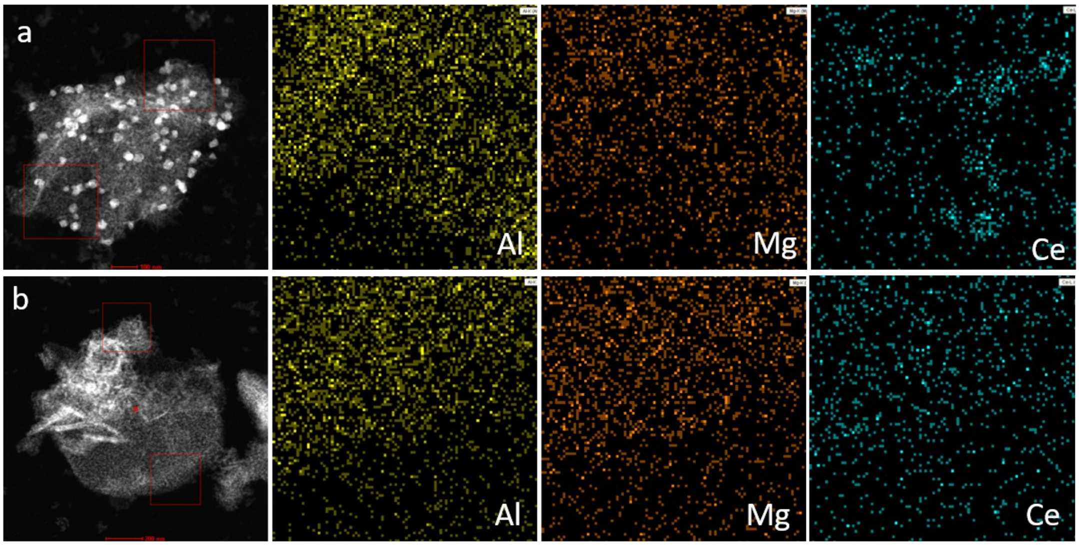

Fig. S3 STEM-EDX mapping of an as-prepared Ce-MgAl (a) and Ce/MgAl prepared using impregnation method (b). The corresponding phase separations of Al, Mg, and Ce were illustrated, respectively.

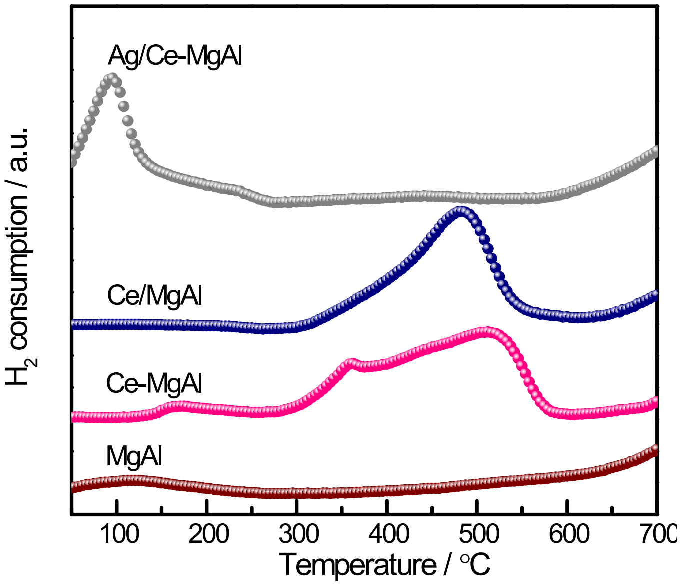

Fig. S4 The H_2-TPR profiles of MgAl, Ce-MgAl, Ce/MgAl, and Ag/Ce-MgAl.

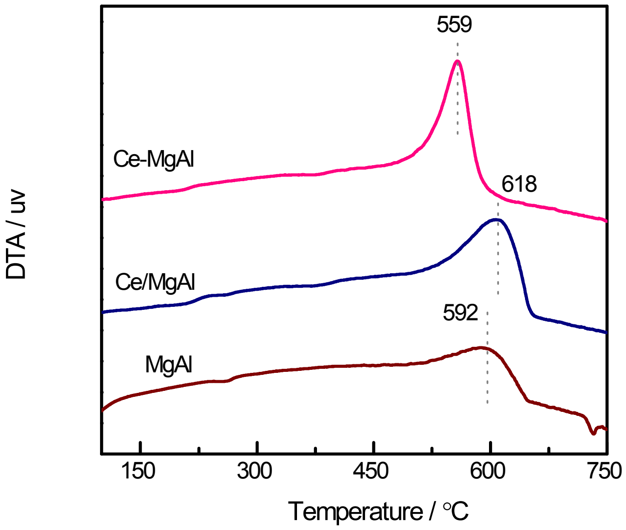

Fig. S5 TDA (differential thermal analysis) curves of the decomposition of CeO_2-free and -intercalated MgAl samples under He flow.

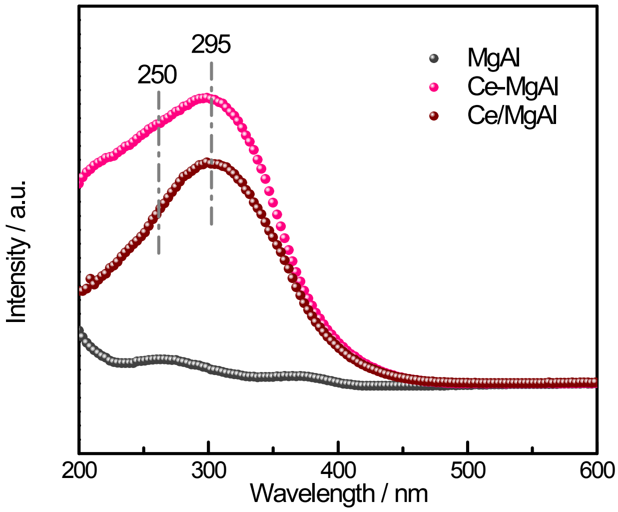

Fig. S**6** UV-vis spectra of the as-synthesized CeO_2-intercalated, -supported, and -free MgAl samples.

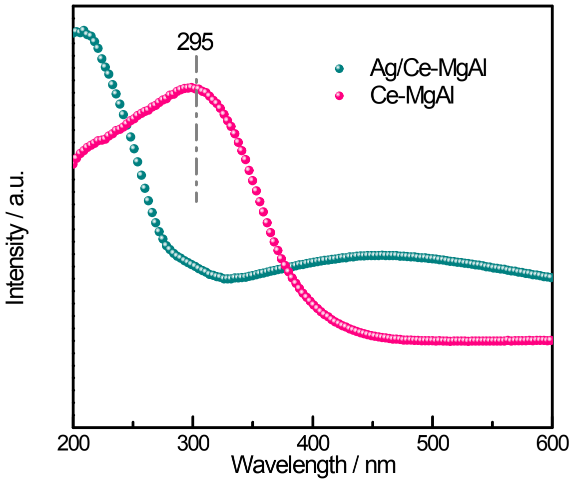

Fig. S7 UV-vis spectra of the as-synthesized Ce-MgAl and Ag/Ce-MgAl catalysts.