

Chapter 2

Experimental Materials and Methods

2.1 Preparation of Catalyst

2.1.1 Main Chemical Reagent

The experimental work in this PhD study is based on the use of several characterization techniques. These techniques are briefly described in the following chapters. The focus is set on the reasons for selecting the various techniques for this study, accompanied by a general description of each technique. A detailed description of the different measurement parameters and equipments can be found in the experimental section of the articles that compose this PhD work. The chemical reagent materials used in this study are outlined in Table 2.1. All of the chemicals (A.R. in purity) were purchased from Tianjin Guangfu Fine Chemical Research Institute and used without further purification.

2.1.2 Main Equipments

The main equipments and gases for reaction experiments used in this research are summarized in Table 2.2.

2.1.3 Preparation of 1D Single-Crystalline LSCO Nanowires

The LSCO catalysts were prepared by means of the DHR strategy with metal nitrates as the precursor. In a typical preparation process, 0.01 mol of lanthanum (III) nitrate hexahydrate, strontium nitrate, and cobalt nitrate was first dissolved in 25.0 ml of deionized (DI) water under magnetic stirring. After being well mixed,

Table 2.1 Chemicals and gases used in the experiments

Item	Chemical reagent	Molecular formula
1	Deionized (DI) water	H ₂ O
2	Lanthanum(III) nitrate hexahydrate	La(NO ₃) ₃ ·6H ₂ O
3	Strontium nitrate	Sr(NO ₃) ₂
4	Manganese(II) nitrate	Mn(NO ₃) ₂ (50 wt% aqueous solution)
5	Citric acid	C ₆ H ₈ O ₇
6	Dextrose	C ₆ H ₁₂ O ₆
7	L-Lysine	HO ₂ CCH(NH ₂)(CH ₂) ₄ NH ₂
8	Nitric acid	HNO ₃ (38 wt%) solution
9	Potassium peroxydisulfate	K ₂ S ₂ O ₈
10	Methyl methacrylate	CH ₂ =C(CH ₃)COOCH ₃
11	Pluronic P-123	HO(CH ₂ CH ₂ O) ₂₀ (CH ₂ CH(CH ₃)O) ₇₀ (CH ₂ CH ₂ O) ₂₀ H
12	L-Lysine	HO ₂ CCH(NH ₂)(CH ₂) ₄ NH ₂
13	PEG400	C _{2n} H _{4n+2} O _{n+1} , n = 8.2–9.1
14	Methanol	CH ₃ OH
15	Ethylene glycol	C ₂ H ₆ O ₂
16	DMOTEG	Dimethoxytetraethylene glycol
17	Aqueous solution	HAgCl ₄ aqueous solution
18	Sodium borohydride	NaBH ₄

Table 2.2 Apparatus used in the experiments

Item	Equipments
1	Magnetic stirring
2	pH value
3	Teflon-lined stainless steel autoclave
4	Buchner funnel
5	Furnace
6	Oven
7	GC-Agilent 7890A
8	Porapak-Q/molecular sieve 5A
9	RT-QPlot divinylbenzene PLOT
10	Fixed-bed quartz tubular microreactor (6 mm)
11	CH ₄ /He (4.95 %)
12	N ₂ (99.999 %)
13	O ₂ (99.999 %)
14	SO ₂ /He (5000 ppm)
15	He (99.999 %)
16	Air

Table 2.3 Preparation parameters of the as-prepared $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ catalysts

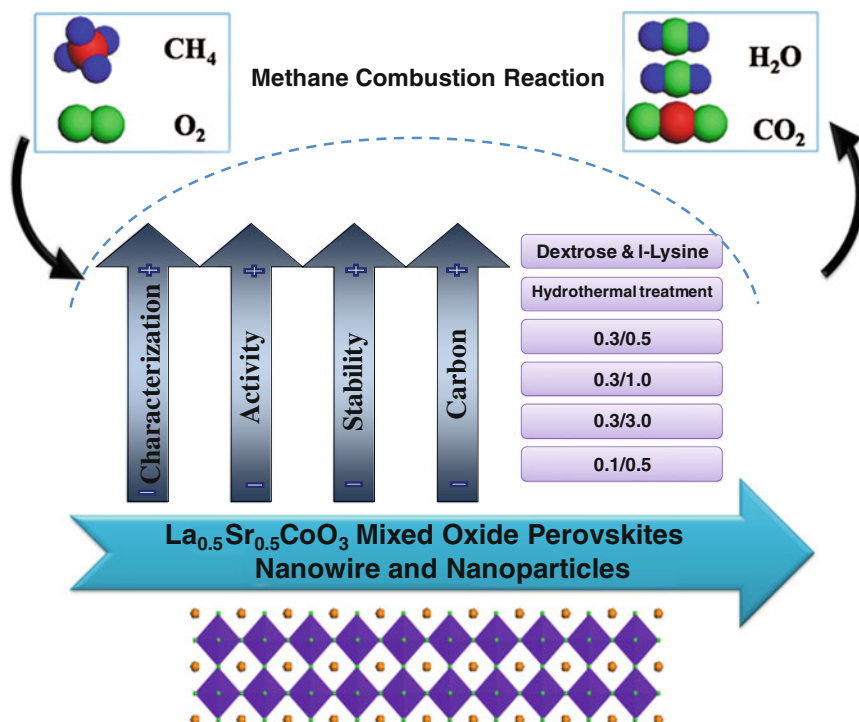
Catalyst code	Preparation method	Solution	Calcination condition
LSCO-0	Hydrothermal 170 °C, 30 h	0.1 mol/l Dex + 0.5 g L-Lysine	300 °C, N_2 (20 ml/min), 2 h → 800 °C, air (50 ml/min), 4 h
LSCO-1	Hydrothermal 170 °C, 30 h	0.3 mol/l Dex + 0.5 g L-Lysine	300 °C, N_2 (20 ml/min), 2 h → 800 °C, air (50 ml/min), 4 h
LSCO-2	Hydrothermal 170 °C, 30 h	0.3 mol/l Dex + 1.0 g L-Lysine	300 °C, N_2 (20 ml/min), 2 h → 800 °C, air (50 ml/min), 4 h
LSCO-3	Hydrothermal 170 °C, 30 h	0.3 mol/l Dex + 3.0 g L-Lysine	300 °C, N_2 (20 ml/min), 2 h → 800 °C, air (50 ml/min), 4 h
LSCO-4	Sol-gel	Deionized (DI) water	800 °C, air (50 ml/min), 4 h

specific amounts of $\text{C}_6\text{H}_8\text{O}_7$ (total metal/citric acid molar ratio = 1/1), dextrose, and L-Lysine were in order added to the above mixed solution. Then, the nitric acid (38 wt%) solution was added dropwise to adjust the pH value (ca. 5). After being diluted to a total volume of 40.0 ml, the mixture was then transferred into a 50-ml Teflon autoclave.

Then start hydrothermal treatment which placed in an oven at 170 °C for 1800 min. As shown in Table 2.3, the catalysts fabricated at different dextrose/L-Lysine volumetric ratio 0.1/0.5, 0.3/0.5, 0.3/1.0, and 0.3/3.0 were denoted as LSCO-0, LSCO-1, LSCO-2, and LSCO-3, respectively. When the autoclave was cooled RT, the obtained precursor was first dried at 120 °C overnight and then well ground. As a final point, the obtained black powders were calcined in a N_2 flow of 20 ml/min at a rate of 1 °C/min from RT to 300 °C. Maintained at this temperature for 120 min, and further to 800 °C and kept at this temperature for 240 min in an airflow of 50 ml/min. For comparison, we also prepared a polycrystalline $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ catalyst (calcined at 800 °C for 240 min) by means of sol-gel method [1] which was denoted as LSCO-4 (as shown in Scheme 2.1).

2.1.4 Synthesis of Monodisperse PMMA Microspheres

Monodisperse (PMMA) microspheres with an average diameter of ca. 291 nm (Figs. 2.1 and 2.2) were synthesized adopting the procedures described in the literature [2–4]. 0.40 g (3.00 mmol) of potassium peroxydisulfate ($\text{K}_2\text{S}_2\text{O}_8$) and 1500 ml of deionized water were mixed under stirring at 400 rpm, heated at 70 °C, and degassed with flowing N_2 in a separable four-necked 2000-ml round-bottom flask. After equilibrating to 70 °C, 115 ml of methyl methacrylate was poured into the flask, and the resulting suspension was stirred at 70 °C for 60 min. The PMMA colloidal crystal template was prepared with 120 ml of the colloidal suspension (ca. 10.0 g) in a 25-ml centrifugation tube for 75 min (Fig. 2.1).



Scheme 2.1 Schematic illustration of 1D single-crystalline LSCO nanowire application

When the DI water was evaporated in water bath at 80 °C, the obtained wet dense material was first dried at RT for two days and then well ground. During the polymerization, several factors (such as monomer, temperature, initiators, and the stirring rate) could influence the PMMA microspheres' sizes.

2.1.5 Preparation of Three-Dimensionally Ordered Macroporous LSMO

A series of 3DOM LSMO catalysts with mesoporous walls were synthesized by the DMOTEG-assisted PMMA-templating strategy with nitrates of lanthanum(III) nitrate hexahydrate, strontium nitrate, and cobalt nitrate as metal precursors as well as present or absence of L-lysine, PEG400, Pluronic P-123, EG, methanol (MeOH), and DMOTEG [5–10]. The typical synthesis procedures are as follows:

- (i) 1.00, 3.00, or 5.00 ml of DMOTEG, 5.00 ml of PEG400, 7.79 g of lanthanum(III) nitrate hexahydrate, 2.53 g of strontium nitrate, and 6.97 ml of manganese nitrate (50 wt% aqueous solution) were dissolved in 9.00 ml of DI

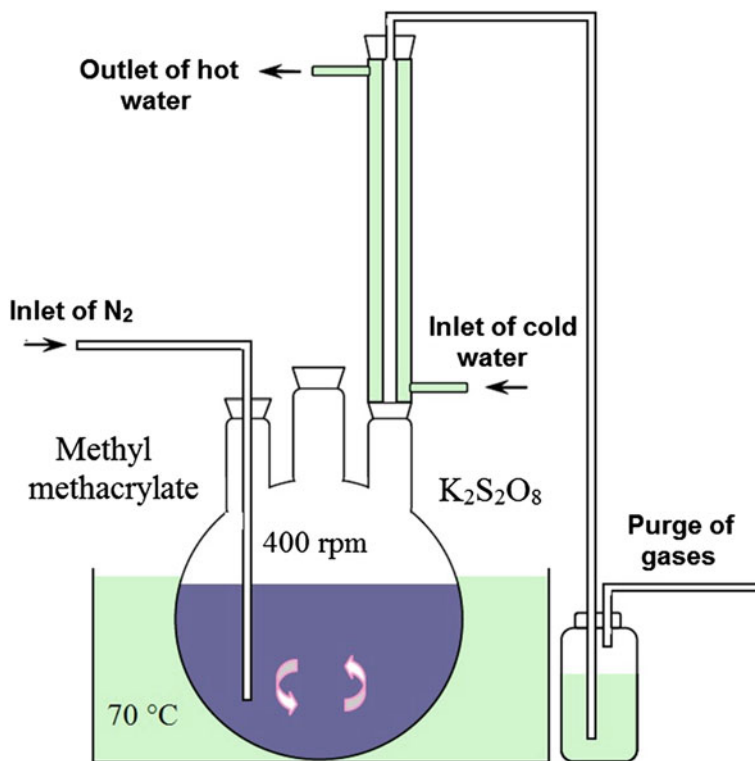


Fig. 2.1 The schematic equipment used for the synthesis of monodisperse PMMA microbeads

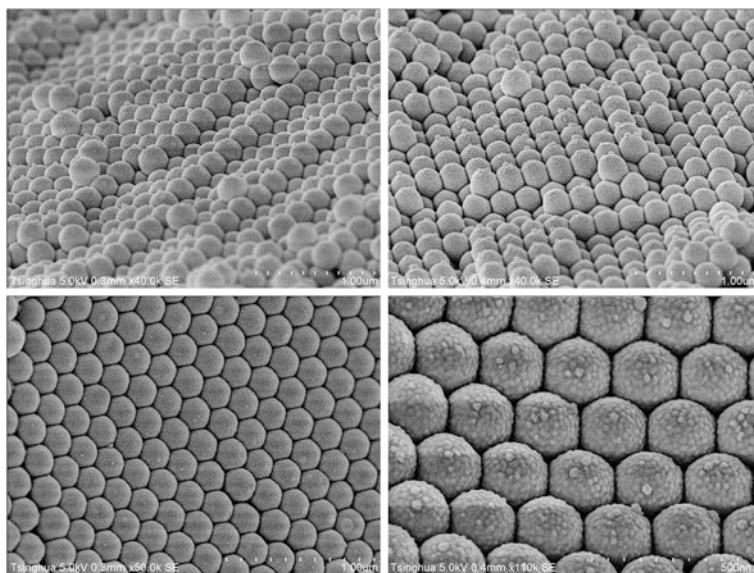
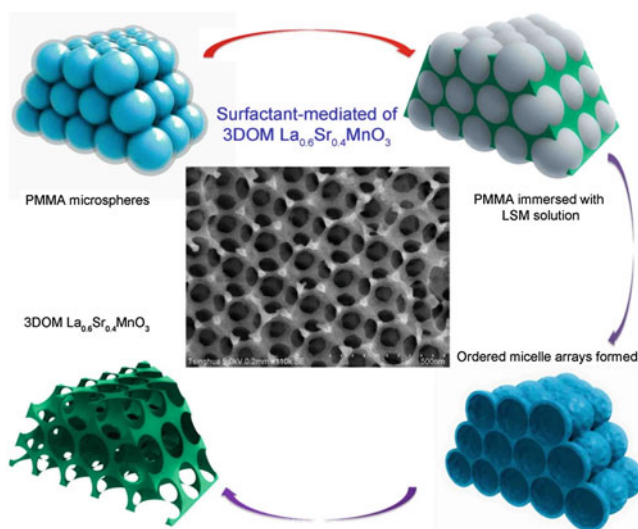


Fig. 2.2 As-prepared monodisperse (PMMA) microspheres

at room temperature under stirring for 240 min to obtain a clear solution. After obtaining a homogeneous precursor solution, ca. 2.00 g of highly ordered PMMA colloidal crystal microspheres was added and flooded with the above mixed solution. Then, excessive liquid was filtered via a Buchner funnel vacuum (0.07 MPa), after dried at room temperature for overnight. The 3DOM materials were reached by calcination according to the two procedures: (a) burned in a nitrogen gas of 50 ml/min at a ramp of 1 °C/min from room temperature to 300 °C. Then held at 300 °C for 180 min; and (b) after being chilled to 30 °C in the same atmosphere and purged in an airflow of 50 ml/min. Then, solid was burned at a ramp of 1 °C/min from room temperature to 300 °C and then held at 300 °C for 60 min. Finally, at the same ramp from 300 to 800 °C and maintained at 800 °C for 240 min (Scheme 2.2).

The obtained samples were, respectively, denoted as LSMO-DP1, LSMO-DP3, and LSMO-DP5. In order to be able to examine the study on calcination temperature on the pore structure, the LSMO-DP3 sample calcined at 850 and 900 °C, thus reaching the LSMO-DP3-850 and LSMO-DP3-900 samples, respectively.

- (ii) 1.00 g of L-lysine was dissolved in a nitric acid (38 wt%) solution (5 mol/l), and the pH value of this solution was set to ca. 6 in order to avoid the formation of metal hydroxide precipitates in the following steps. 3.00 ml of PEG400, 0.79 g of lanthanum(III) nitrate hexahydrate, 2.53 g of strontium nitrate, and 6.97 ml of manganese nitrate (50 wt% aqueous solution) were dissolved in 9.00 ml of DI water under stirring (Fig. 2.3). Then, the L-lysine-containing solution was mixed with the metal nitrate-containing transparent solution under stirring for 60 min to get a uniform precursor solution. After dissolution, 2.00 g of highly



Scheme 2.2 Schematic illustration of the preparation of 3DOM catalyst

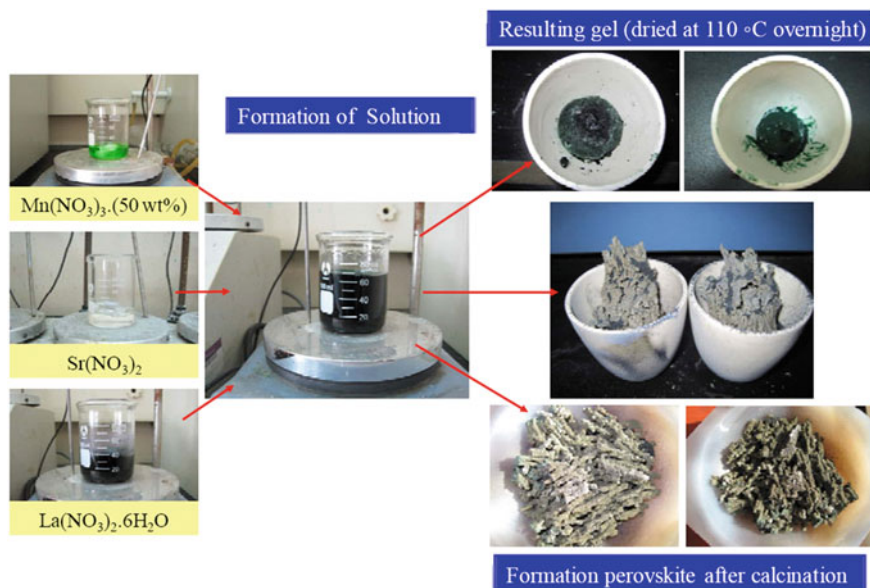


Fig. 2.3 Illustrate the procedure of preparation 3DOM catalyst

ordered PMMA colloidal crystal microspheres was added. The subsequent procedures were the same as those described in (i). The obtained catalysts were denoted as LSMO-LP1, in which the “LP” represents the use of “L-lysine” and “PEG400” as surfactant.

- (iii) 5.00 ml of EG, 3.00 ml of MeOH, 1.20 g of Pluronic P-123 ($MW_{\text{aver.}} = 5800 \text{ g/mol}$), 7.79 g of lanthanum(III) nitrate hexahydrate, 2.53 g of strontium nitrate, and 6.97 ml of manganese nitrate (50 wt% aqueous solution) were dissolved in 9.00 ml of deionized water under stirring. After dissolution, 2.00 g of PMMA colloidal crystal microspheres was added. The subsequent processes were the same as those described in (ii). The obtained samples were denoted as LSMO-PE1 (Table 2.4).

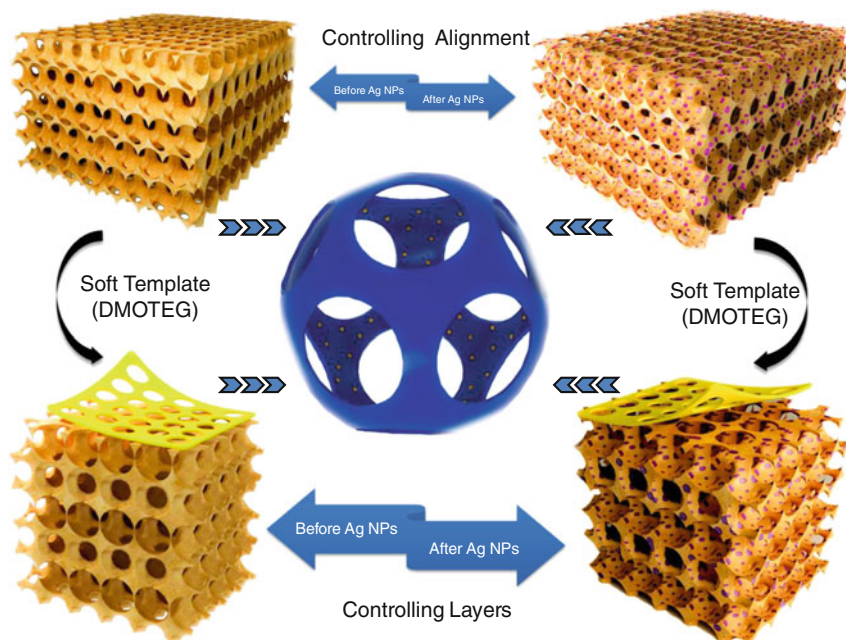
2.1.6 Preparation of ywt% Ag/3DOM LSMO Series

The $\text{La}_{0.4}\text{Sr}_{0.6}\text{MnO}_3$ -supported silver (yAg/3DOM $\text{La}_{0.4}\text{Sr}_{0.6}\text{MnO}_3$) catalysts were prepared via a DMOTEG-assisted reduction method. During the homogeneous catalysis of methane combustion by Ag NPs supported on 3DOM $\text{La}_{0.4}\text{Sr}_{0.6}\text{MnO}_3$, we observed that DMOTEG was used as a multifunctional reagent for the formation of Ag NPs. It was found that the DMOTEG-mediated route not only produced size-controlled Ag NPs, but also stabilized them against conglomeration without the need

Table 2.4 Preparation parameters of the 3DOM LSMO and 1D LSMO samples

Catalyst code	Surfactant	Soaking time (h)	Calcination condition
1D LSMO	–	–	850 °C 4 h (in air)
LSMO-DP1	1.0 ml DMOTEG + 5.0 ml PEG400 + 9.0 ml H ₂ O	4	300 °C 3 h (N ₂) → 300 °C 1 h (air) → 800 °C 4 h (air)
LSMO-DP3	3.0 ml DMOTEG + 5.0 ml PEG400 + 9.0 ml H ₂ O	4	300 °C 3 h (N ₂) → 300 °C 1 h (air) → 800 °C 4 h (air)
LSMO-DP5	5.0 ml DMOTEG + 5.0 ml PEG400 + 9.0 ml H ₂ O	4	300 °C 3 h (N ₂) → 300 °C 1 h (air) → 800 °C 4 h (air)
LSMO-LP1	1.0 g L-lysine + 1.4 ml HNO ₃ + 3.0 ml PEG400 + 9.0 ml H ₂ O	3	300 °C 3 h (N ₂) → 300 °C 1 h (air) → 800 °C 4 h (air)
LSMO-PE1	1.2 g P123 + 5.0 ml EG + 3.0 ml MeOH + 9.0 ml H ₂ O	3	300 °C 3 h (in N ₂) → 300 °C 1 h (air) → 800 °C 4 h (air)
LSMO-DP3-850	1.0 ml DMOTEG + 5.0 ml PEG400 + 9.0 ml H ₂ O	4	300 °C 3 h (in N ₂) → 300 °C 1 h (air) → 850 °C 4 h (air)
LSMO-DP3-900	1.0 ml DMOTEG + 5.0 ml PEG400 + 9.0 ml H ₂ O	4	300 °C 3 h (in N ₂) → 300 °C 1 h (air) → 900 °C 4 h (air)

for additional stabilizers. Thus, we present a facile DMOTEG-mediated synthesis of Ag NPs in the absence of any extra reducing or capping agent. The typical preparation procedure is as follows: A desired amount of PEG (MW = 400 g/mol) and DMOTEG (MW = 222.28 g/mol) was added to a 100 mg/L HAgCl₄ aqueous solution (Ag/DMOTEG mass ratio = 1.5:1) at RT under vigorous bubbling for 10 min. After rapid injection of an aqueous solution of 0.1 mol/l NaBH₄ (Ag/NaBH₄ molar ratio = 1:5), one could obtain a dark brown solution (so-called silver sol). A desired amount of the La_{0.4}Sr_{0.6}MnO₃-supported silver was then added to the silver sol (theoretical Ag loading = 2, 4, or 6 wt%), and the obtained suspension was subjected to sonication (60 kHz) for 30 s. A gas-bubble-assisted stirring operation with three bubble outlets in solution was used to further agitate the system, and the suspension was vigorously bubbled with N₂ for 8 h. The solid was collected by filtration, followed by washing with 2.0 L of deionized water. After obtaining a uniform precursor solution, ca. 3.00 g of highly ordered PMMA colloidal crystal microspheres was added and soaked with the above mixed solution. After the PMMA microspheres were thoroughly wet, the excessive liquid was filtered via a Buchner funnel connected to vacuum (0.07 MPa). After being dried at room temperature for 24 h, the 3DOM materials were thermally treated in a tubular furnace according to the two steps: (a) heating in a N₂ flow of 50 ml/min at a ramp of 1 °C/min from RT to 300 °C and keeping it at this temperature for 3 h; and (b) after being cooled to 30 °C in the same atmosphere and purged in an airflow of 50 ml/min, the solid was heated at a ramp of 1 °C/min from RT to 300 °C and kept at this temperature for 1 h, finally same ramp 300–800 °C and maintained at 800 °C for 4 h (Scheme 2.3).



Scheme 2.3 Schematic illustration of loading Ag NPs on 3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ catalysts

The obtained samples were, respectively, denoted as $\gamma\text{Ag}/3\text{DOM La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$. The results of inductively coupled plasma atomic emission spectroscopy (ICP-AES) investigation reveal that the real Ag loading (γ) was 1.58, 3.63, and 5.71 wt%, respectively (Table 5.1). For comparison purposes, we also prepared 1D $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ sample. The 1D $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ sample was prepared using the citric acid-complexing method described elsewhere [11–14]. The obtained solid precursor was first calcined in air at a ramp of 1 °C/min in a muffle furnace from RT to 300 °C and kept at this temperature for 1 h and then from 300 to 800 °C at the same ramp and maintained at 800 °C for 4 h (Table 2.5).

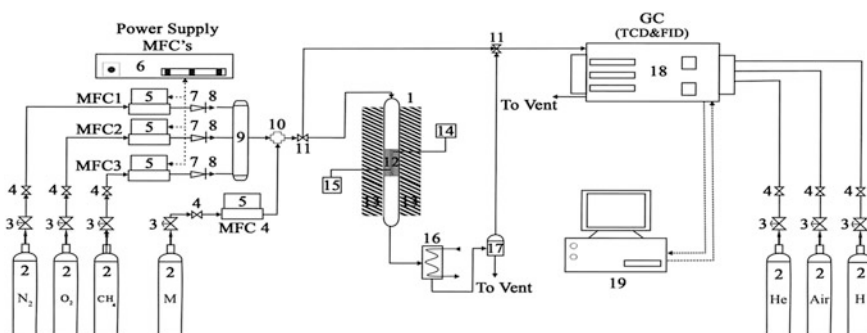
2.2 Catalytic Activity Measurement

2.2.1 Gas Flow Measurement

Catalytic performance assessment was carried out in a fixed-bed quartz tubular microreactor (i.d. = 6.0 mm), as shown in Fig. 2.4. To minimize the effect of hot spots, the sample (20 mg, 40–60 mesh) was diluted with 0.25 g quartz sands (40–60 mesh). The volumetric composition of the reactant mixture was 2 % CH_4 + 20 % O_2 + 78 % N_2 (balance), and the total flow was 41.6 ml/min, thus giving a gas hourly space velocity (GHSV) of ca. 30,000 ml/(g h).

Table 2.5 Preparation conditions of the 1D $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$, 3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$, and $\gamma\text{Ag}/3\text{DOM } \text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ samples

Catalyst	Method	Hard template/soft template	Calcination condition
1D $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	Citric acid	—/—	850 °C, air (50 ml/min), 4 h
3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	PMMA templating	PMMA/ (DMOTEG-PEG400)	300 °C, N_2 (50 ml/min), 3 h $\rightarrow$ 300 °C, air (50 ml/min), 1 h $\rightarrow$ 800 °C, air (50 ml/min), 4 h
1.58 wt% Ag/3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	In situ PMMA templating	PMMA/ (DMOTEG-PEG400)	300 °C, N_2 (50 ml/min), 3 h $\rightarrow$ 300 °C, air (50 ml/min), 1 h $\rightarrow$ 800 °C, air (50 ml/min), 4 h
3.63 wt% Ag/3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	In situ PMMA templating	PMMA/ (DMOTEG-PEG400)	300 °C, N_2 (50 ml/min), 3 h $\rightarrow$ 300 °C, air (50 ml/min), 1 h $\rightarrow$ 800 °C, air (50 ml/min), 4 h
5.71 wt% Ag/3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	In situ PMMA templating	PMMA/ (DMOTEG-PEG400)	300 °C, N_2 (50 ml/min), 3 h $\rightarrow$ 300 °C, air (50 ml/min), 1 h $\rightarrow$ 800 °C, air (50 ml/min), 4 h

**Fig. 2.4** Schematic diagram of the experimental setup: 1 fixed-bed reactor, 2 gas cylinder, 3 regulator, 4 on-off valve, 5 mass-flow controller, 6 power supply MFC's, 7 check valve, 8 needle valve, 9 mixture, 10 cross-flow section, 11 three- and four-way valves, 12 catalyst bed, 13 electrical oven, 14 temperature controller, 15 temperature indicator, 16 condenser, 17 liquid trap, 18 gas chromatograph, 19 computer, and M gas mixture

2.2.2 Gas Chromatography

The concentrations of the reactants and products were online-monitored by a GC (Agilent 7890A) equipped with FID and TCD detectors. Using the columns of Porapak-Q/molecular sieve 5A (2 m in length) and RT-QPlot divinylbenzene PLOT (30 m in length). The catalytic performance of the samples was evaluated using the

temperatures (T_{10} , T_{50} , and T_{90}) required for methane conversions of 10, 50, and 90 %, respectively. CH_4 conversion was given by $(c_{\text{inlet}} - c_{\text{outlet}})/c_{\text{inlet}} \times 100 \%$, where the c_{inlet} and c_{outlet} were the CH_4 concentrations of inlet and outlet feed stream, respectively.

2.3 Further Characterization for Catalyst Tests

All of the catalysts were characterized by means of techniques, such as N_2 adsorption–desorption (Brunauer–Emmett–Teller, BET), X-ray diffraction (XRD), inductively coupled plasma atomic emission spectroscopy (ICP-AES), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), H_2 temperature-programmed reduction (H_2 -TPR), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), selected-area electron diffraction (SAED), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FT-IR). The detailed procedures are described in the following sections.

2.3.1 X-Ray Diffraction (XRD) Pattern

The X-ray diffraction (XRD) experiments were carried out on a Philips PW 1800 diffractometer by means of $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) at 40 kV and 30 mA to conclude the crystalline phases and to analyze the lattice parameters. Scattering intensities were planned over a pointed range of $8^\circ < 2\theta < 90^\circ$ for all of the samples with a step size (2θ) of 0.03° and a count time of 2 s per step. The diffraction patterns were indexed by JCPDS (Joint Committee on Powder Diffraction Standards) files.

2.3.2 Scanning Electron Microscopy (SEM)

The morphologies of the as-prepared samples were considered by scanning electron microscopy (SEM) using a Philips XL30 microscope in use at an accelerating voltage of 30 kV, with a work distance (WD) between 10 and 13 mm and magnification values in the range $100\text{--}100,000\times$. SEM was used in the backscattered electron detector (BSED). The secondary electron detector (SED) modes show the morphologies of the surface structures.

2.3.3 Energy-Dispersive Spectroscopy (EDS)

For the determination of the chemical composition of the crystalline phases, energy-dispersive spectroscopy (EDS) was used to conclude the EDS spectra by means of

an EDS DX-4 analysis system. A very thin Au deposit was used to get better the conductivity of the sample such as PMMA.

2.3.4 Transmission Electron Microscopy (TEM) and Selected-Area Electron Diffraction (SAED)

Transmission electron microscopic (TEM) images as well as the selected-area electron diffraction (SAED) patterns of the typical catalysts were verified using a JEOL JEM-2010 apparatus.

2.3.5 BET Surface Area and N₂ Adsorption–Desorption

The surface areas and pore size distributions were planned using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. The N₂ adsorption–desorption isotherms, surface areas, and pore parameters of the samples were determined via N₂ adsorption at –196 °C on a Micromeritics ASAP 2020 adsorption analyzer. Before measurement, the samples were degassed at 250 °C for 3 h.

2.3.6 Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

For the ICP-AES analyses, the freshly prepared 20 mg samples were introduced into a 60-ml Teflon-made digestion vessel (Savillex, USA). The sample mixed with a solution mixture containing 4 ml (37 % HCl 3 ml + 70 % HNO₃ 1 ml), 0.5 ml HF (50 %), and 0.5 ml HClO₄ (70 %). The vessel digested at 150 °C with a pressure of 80 psi until a yellowish liquid solution observed. After cooling the vessel to RT, 1 % HCl was added to make sample measurements using OPTIMA 3300 DV model (PerkinElmer, USA).

2.3.7 H₂ Temperature-Programmed Reduction (H₂-TPR)

Hydrogen temperature-programmed reduction (H₂-TPR) studies were conducted with an Autochem II 2920 (Micromeritics) apparatus equipped with a TCD detector. The experiments were conducted on the samples (approximately 50 mg). The samples were firstly flushed with He at a flow rate of 40 ml/min as the heat was increased

at a ramp rate of 10 °C/min to 200 °C and held at this temperature for 30 min to remove H₂O. Then, the reducing gas (5.1 % H₂ in Ar) was introduced at a flow rate of 40 ml/min with a ramp rate of 10 °C/min from RT to 750 °C. The difference in H₂ concentration of the effluent was monitored online by the chemical adsorption analyzer. The reduction peak was calibrated against that of complete reduction of a known standard of powdered CuO (Aldrich, 99.995 %).

2.3.8 Temperature-Programmed Reduction of Methane (CH₄ TPR-MS)

Temperature-programmed reduction of methane (CH₄-TPR) was carried out in a continuous-flow quartz microreactor. The sample (100 mg), held in the quartz tube, was degassed in a Helium flow (30 ml/min) at 600 °C for 1 h, and then, the temperature was allowed to decrease to room temperature. The TPR test was conducted in a 20 ml/min mixture of CH₄/He (5 % CH₄) at a ramp rate of 10 °C/min from room temperature to 1000 °C and maintained at this temperature for 100 min. Gases evolved from the microreactor were analyzed with a Pfeiffer Omnistar quadrupole mass spectrometer.

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