Synthesis of Porous Composite Metal Oxides

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Contributor: Hongxia Lin , Yuxi Liu , Jiguang Deng , Lin Jing , Hongxing Dai

Porous transition-metal oxides with good intrinsic activities can be used to disperse and stabilize the active noble metal phases, thus promoting improvements in selectivity and activity of the supported noble metal catalysts and in the meanwhile reinforcing the optimized utilization of noble metals.

methane combustion porous catalyst preparation ordered porous metal oxides

1. Introduction

Methane is one of the cleanest fuel sources and can play an irreplaceable role in achieving carbon neutrality. As the main component of natural gas, incomplete CH_4 combustion causes resource waste and aggravates air pollution. Methane is inflammable and explosive when it is accumulated to a certain volume fraction, which causes serious property damage and casualties. The global warming potential of methane is at least 72 times higher than that of CO_2 over the last 20 years, which is related to the strong greenhouse effect.

Methane is the most stable hydrocarbon with a regular tetrahedral structure, which is difficult to activate and oxidize under mild conditions. Conventional combustion of natural gas requires a high temperature of above 1500 °C, which generates a large number of water vapor, sulfur dioxide, and insufficient combustion products (CO) as well as NO_x (formed via the reaction of N_2 and O_2 at high temperatures). In the 1970s, Pfefferle [1] proposed a heterogeneous catalytic gas-phase combustion process to realize effective combustion of hydrocarbons and low emissions of pollutants. Catalytic combustion remarkably decreases CH_4 oxidation temperatures, which can reduce or avoid the formation of NO_x and CO. The adsorption of NO on the active component (MnO_2) and support (TiO_2) was studied by the density functional theory calculations [2]. NO was adsorbed at the top sites of Mn Lewis site in the way of the O-down orientation. Although there was an electron transfer between NO and Mn, NO adsorption belonged to a weak physisorption. In the case of NO adsorption, the hybridization between Ti and NO could be found, corresponding to a strong chemisorption. Striking is the positive influence of the catalyst regeneration by introducing NO_x for methane conversion in the transient reactivation experiment [3]. The oxidation of NO and reduction of NO_2 on the catalyst surface during the methane conversion process could be able to reactivate the catalyst. Reactivation of a catalyst deactivated under the lean-burn conditions could be achieved by adding NO and/or NO_2. Öcal et al. [4] investigated the influence of high NO amount (2.3 vol%) on catalytic performance of the Pd/hexaaluminate catalyst. Increased activity was found in the presence of NO above 400 °C. The authors attributed such a behavior to the increased reoxidation of Pd during the CH_4 oxidation process or to the formation of the highly reactive O* species on the catalyst surface from the dissociation of NO_2.

CH_4 is weakly adsorbed on the catalyst surface, while H_2O and SO_2 display strong adsorption, which induces poisoning and deactivation of the catalyst. Design and preparation of a high-performance catalyst with good low-temperature activity, excellent thermal stability, high selectivity, and admirable H_2O and SO_2 resistance are crucial to achieve CH_4 elimination.

A thermo-catalytic methane decomposition reactor system is thoroughly discussed to achieve optimized heat management and better methane conversion. Raza et al. [5] proposed a methane decomposition reactor system configuration for industrial and commercial application, and gave the involved working principle, technical advantages, and limitation. A suitable catalyst used in a reactor system can decrease the activation energy and accelerate the reaction process; however, catalyst deactivation and huge energy consumption are still big challenges to be overcome.

The influencing factors of catalytic activity include the reactant diffusion from the gas phase to the catalyst surface, the adsorption and activation of reactants at the surface active sites, oxidation of reactants with oxygen species at the active sites to generate products, desorption of products from the active centers, and diffusion of products from the catalyst surface to the gas phase. Generating a porous structure is one of the most available strategies to develop the high-surface-area materials, so that the number of the active sites can be increased and the catalytic activity is, thus, improved significantly. The large surface areas of porous materials are beneficial for adsorption of the reactants as well as desorption and diffusion of the products, which reduces the mass transfer resistance of methane and O_2 in the reaction system and maximizes the contact capability of reactants with the surface active centers substantially. Lu and coworkers [6] prepared mesoporous $LaCoO_3$ via a nanocasting route using an ordered mesoporous cubic ($Ia3d$) vinyl silica as template. The ordered three-dimensional mesostructured $LaCoO_3$ displayed a high surface area of 96.7 m^2/g and showed a much lower light-off temperature of 335 °C. Further analysis demonstrated that the large surface area and well-ordered mesopore structure were associated with formation of the high-valence cobalt ions and abundant O_2^{2-}/O^- species. Hence, the mesostructured $LaCoO_3$ catalyst exhibited a superior activity for deep oxidation of methane.

There are two main typical catalysts for methane oxidation: (i) transition-metal oxides (single- and mixed-metal oxides) and (ii) supported noble metals. The essence of improved oxidation–reduction (redox) ability of metal oxides is to optimize the oxygen storage–release properties and oxygen transfer capability, and the role of metal oxides with a high oxygen storage capacity is prospected to allow the metal to keep sustainable work in cycle. Transition-metal oxides possess multiple oxidation states and flexibly realize the oxidation sand reduction processes between different cation valence states. The release of lattice oxygen and formation of oxygen vacancies in a redox cycle generate a large number of surface-adsorbed oxygen species, which are attributed to the adsorption and activation of reactants and O_2. Catalytic performance of transition-metal oxides is related to their physicochemical properties, such as surface areas, defects, redox ability, crystallinity, exposed crystal planes, and morphologies. Transition-metal oxides display poor thermal stability, whose phase transitions induced by treating with the fluctuating reaction conditions significantly affect their catalytic activities. Li and coworkers [7][8] prepared spinel-structured Co_3O_4 octahedra with a relatively strong (111) diffraction signal via a facile redox-precipitation route, which showed an inert catalytic activity for methane combustion. High-resolution transmission electron microscopic (HRTEM) studies indicated that irregular Co_3O_4 nanoparticles (NPs) with predominantly exposed other crystal facets presented a more consistent activity compared with the Co_3O_4 octahedra with exposed low Miller-index (111) facets that possess the lowest surface energy. The same group also fabricated manganese–cobalt oxides with various Co/Mn molar ratios to investigate the oxygen mobility that influenced methane oxidation rates below 320 °C [9]. The addition of manganese to the spinel-structured cobalt oxide multiplied the crystal defections which was contributed to an enlarged number of octahedrally-coordinated divalent cobalt ions. The −OH groups in the Mn-doped catalysts further demonstrated the dehydroxylation by the doping of Mn to produce an optimal catalyst for the combustion of methane. Similarly to the previous work, the same group pointed out that cobalt–chromium oxide with Co/Cr molar ratio = 1/2 showed excellent resistance to water vapor poisoning [10]. The investigation of excellent methane oxidation activity of the Co_1Cr_2 catalyst revealed that the higher valence Cr^{3+} and Cr^{6+} species and coordination number of cations significantly enhanced adsorption of the chemisorbed oxygen species.

Perovskite-type oxides are the most available catalysts which are calcined at above 850 °C, thus exhibiting the high-temperature thermal stability in CH_4 oxidation. Perovskite-type oxides remain prominent among the mixed-metal oxides with a general formula of ABO_3, in which the size of A cation is bigger than that of B cation, the A-site cations are rare-earth or alkaline-earth ions that coordinate with 12 oxygen anions, whereas the B-site cations are transition-metal ions which coordinate with six oxygen anions. The mixed-metal oxides, such as ABO_3, double perovskites (A_2BBO_6), perovskite-like oxides (A_2BO_4), and pyrochlore ($A_2B_2O_7$)), are one kind of complete oxidation catalytic material with abundant oxygen vacancies that can activate O_2 into various oxygen species, and the presence of at least two kinds of metal cations in various oxidation states achieves a facile redox cycle. Structural defects and lattice oxygen mobility that is in relation with the Mars–van Krevelen mechanism are also critical factors governing the catalytic activity. The surface-adsorbed oxygen at oxygen vacancies of the ABO_3 catalysts is involved in the combustion of methane at low temperatures, while surface or bulk lattice oxygen species play an important role at high temperatures. The catalytic activity of ABO_3 mainly depends on the B-site ion, while the A-site ion plays an important role in stabilizing the perovskite structure. Both A and B sites can be partially substituted by heterovalent ions to regulate distributions of the B-site cation oxidation states to promote redox property of the perovskite-structured materials. However, some poisons (e.g., SO_x, especially the progressive sulfidation of perovskite-type oxide structures) can cause a permanent loss in catalytic activity [11][12]. Hao and coworkers [13][14] investigated partial substitution of the composite metal oxide by a transition metal (Co) to achieve superior methane oxidation performance at moderate–high temperatures. The $La_2Co_xSn_{2-x}O_{7-\delta}$ catalysts with a pyrochlore structure were prepared via the coprecipitation route [13]. The authors found that the doping of Co ions to the pyrochlore lattice significantly influenced the thermal stability and redox property, and increased the reduction rates and oxygen vacancy amount for CH_4 oxidation. The diffusion reflectance infrared Fourier transform spectroscopic (DRIFTS) measurements indicated that the lower-energy Sn–O bond strength was weakened by Co doping to achieve easier lattice oxygen release and promoted formation of oxygen vacancies. The authors concluded that the good catalytic performance of $La_2Co_xSn_{2-x}O_{7-\delta}$ was associated with their high surface areas, rich oxygen vacancies generated due to Co doping, and improved redox ability. The same group also examined the effect of transition metal (Mn, Fe, Co, Ni, or Cu) doping on methane oxidation activity of $La_2Zr_2O_7$ [14]. DRIFTS spectra revealed that the introduction of a transition metal strongly influenced catalytic activity for CH_4 combustion, which was related to the Zr–O bond strength and pyrochlore phase formation temperature as well as the redox properties and crystallite sizes of the pyrochlores.

Methane is the most stable hydrocarbon and the breakdown of C–H bond is considered to be the rate-determining step for methane combustion. Noble metals possess special electron states of *d*-band, which is beneficial for the activation of the C–H bond to decrease the activation energy of methane dissociation for low-temperature oxidation. Therefore, noble metals catalysts are most widely investigated in catalytic methane combustion due to its lower light-off temperature and high resistance to carbon deposition and sulfur dioxide.

Supported noble metals are constructed to be the bifunctional catalysts which reinforce resistance of the noble metals to sintering and strengthen the cooperative effect between the metal and the substrate (i.e., the dual-site mechanism). Bifunctional catalysts exhibit enhanced thermal stability and excellent catalytic performance as well as inhibit side reactions. Small-sized noble metal NPs possess high surface energies with exceptional properties and favored reactants activation, thus showing good low-temperature activities. Cargnello et al. [15] developed a novel tactic to successfully stabilize the noble metal catalysts with ultrafine Pt dispersion without NPs agglomeration using the template and impregnation methods at high temperatures. The Pt NPs were first uniformly dispersed on the surface of the porous organic framework (POF) through a wet impregnation approach, and a new polymer solution was introduced to overlay Pt/POF samples. Then, an alumina precursor infiltrated into the channel of the polymer, and the removal of template after calcination at 600 °C realized the encapsulation of Pt NPs inside the porous alumina framework. The encapsulated Pt catalyst after sintering at 800 °C in the presence of oxygen and steam with a slight size change showed a difference of 3 °C in reaction temperature for propylene conversion compared with the fresh sample, while the conventional Pt catalyst displayed a loss of 78% Pt surface area (the average Pt size increased from 3.8 to 17.2 nm) with a conversion temperature being increased by 35 °C under the similar reaction conditions. These authors also prepared the Pd–Pt bimetallic catalysts to realize higher hydrothermal stability to inhibit PtO_2 consumption by inducing appropriate Pd. The encapsulated Pd–Pt bimetallic catalyst maintained a small size after treatment at 1100 °C in air and steam and did not show significant deactivation.

Another effective scheme is appreciated to enhance the catalytic performance of supported materials with less noble metal consumption by adding a small amount of a base metal to modify microstructure and redox property of the particles. Supported noble metal catalysts exhibit lower light-off temperatures and remarkable sulfur tolerance in methane combustion, while sintering under the thermal treatment conditions is well known to lead to initial small particle growth to be larger ones with irreversible catalyst deactivation. Hutchings and coworkers [16] carried out a number of valuable works on development and refinement of fabricating supported bimetallic NPs with controlled morphological properties, such as small sizes, metal oxidation states, and metal–support interaction. The introduction of a second metal was favorable for the adjustment of electronic and geometrical properties; thus, the bimetallic catalysts achieved notably enhanced catalytic activities with good stability and high selectivity. AuPd colloidal NPs with a high selectivity of 90–92% for methane transformation were synthesized via a surfactant-assisted route by using polyvinyl pyrrolidone (PVP) instead of polyvinyl alcohol (PVA) as stabilizer in the presence of O_2 and H_2O_2 [17]. The mechanism was revealed to be radical-based due to the presence of both •OH and $•CH_3$ radicals during the reaction process. Furthermore, O_2 instead of H_2O_2 was confirmed to be the oxidant by $^{18}O_2$ labeling. The primary CH_3OOH was produced by recombination of $•CH_3$ with the dissolved O_2; thus, promoted oxygen incorporation through generation of the $CH_3OO•$ radicals could be achieved by inducing O_2.

In summary, porous transition-metal oxides with good intrinsic activities can be used to disperse and stabilize the active noble metal phases, thus promoting improvements in selectivity and activity of the supported noble metal catalysts and in the meanwhile reinforcing the optimized utilization of noble metals. A three-dimensionally well-ordered porous structure facilitates adsorption and diffusion of the reactants and O_2 molecules, and the facile mass transfer, large surface area, increased active sites, and ultrahigh active noble metals dispersion are responsible for the excellent catalytic performance and good hydrothermal stability of porous transition-metal oxides-supported noble metals for CH_4 combustion. Dai and coworkers [18][19][20][21][22][23][24][25][26][27][28] systematically investigated multifunctional metal oxides with porous structures and generated a number of high-surface-area 3DOM-structured porous-oxides-supported noble metal materials (e.g., CoPd/3DOM CeO_2 [27], AuPd/meso-Co_3O_4 [28], meso-PdPt [29], and PdPt/3DOM $LaMnAl_{11}O_{19}$ [20]) using the surfactant-assisted PMMA- or KIT-6-templating methods in the last 15 years. The same group demonstrated that large surface area and well-developed pore architecture were the key factors for the high performance of the catalysts in methane combustion. The surfactants were anchored by the noble metals and removed after calcination; thus, noble metal NPs occupied partial adsorption sites of pore structures with high dispersion and smaller sizes. The modification of noble metal NPs and the reasonable specific support remarkably promoted the resistance to sintering, and the addition of a base metal to noble metal(s) improved the hydrothermal stability with a high utilization efficiency of noble metals.

In the past years, several reviews on catalytic methane combustion have been reported in the literature [30][31][32][33][34]. For example, Ciuparu et al. [30] reviewed the Pd-based catalysts for methane conversion and discussed the catalytic performance, redox mechanism and CH_4 activation at the PdO site. The kinetics of methane combustion and the sulfur-dioxide-poisoning behaviors, as well as the effect of metal NPs on catalytic performance of the noble metal catalysts, were reported [31]. Yang et al. summarized the outstanding methane oxidation activities of nanostructured perovskite oxides and proposed the novel catalysts design strategy via lattice oxygen activation, lattice oxygen mobility, and materials morphology engineering [32]. Bashan et al. reported the perovskite preparation methods and the substitution effects of the doped perovskites as well as the sulfur-dioxide-poisoning behaviors of the perovskite catalysts [33]. Nkinahamira et al. summarized the noble-metals- and transition-metal-based catalysts for methane activation and discussed physicochemical properties of the promoters, such as reduction/oxidation potential, acidity/basicity, reducibility, and oxygen storage capacity [34].

2. Synthesis of Porous Composite Metal Oxides

2.1. Preparation of Templates

The template synthesis method is an important route for nanocomposites fabrication using the nanostructural, shape-controlled, and low-cost solid or colloidal crystals as a template. The related materials are first deposited into the holes or on the surface of the template via the physical or chemical routes, and the template is then removed to obtain the nanomaterials with the standard template-specific morphologies and controlled porosity. The template route is the most frequently used strategy to design and construct multifunctional materials with specific properties and pore-structure morphologies to meet the actual applications. Various templates, such as activated carbon, silicas (SBA-15, KIT-6, and silica xerogel), and colloidal crystals [35], are employed to assist the preparation of ordered porous materials.

Most of the three-dimensionally ordered macroporous (3DOM) materials are synthesized by the colloidal-crystal-templating method. The colloidal crystal templates, such as polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(styrene-methyl methacrylate-acrylic acid), and SiO_2 colloidal microspheres, can be fabricated simply, accurately, and uniformly on a laboratory scale, and are the most commonly used for preparing well-constructed 3DOM materials [36]. The 3DOM materials were first successfully generated via a colloidal crystal template approach in the 1990s [37]. The as-obtained material displayed a three-dimensionally ordered arrangement of pore structures where the average pore sizes were all over 50 nm (up to a few microns), and avoided the shortcomings that molecular sieves and mesoporous materials with small pore structures did not allow macromolecules to enter the cavities. Usually, the colloidal microspheres used as the template are chemically stable and readily impregnated by the precursor solution. The pore diameter of a 3DOM material can be controlled by regulating the average particle size of colloidal microspheres. PS and PMMA microspheres are usually synthesized via the emulsion polymerization [38] or dispersion polymerization process [39], whereas SiO_2 colloidal microspheres are usually obtained using the classical Stöber method [40]. SiO_2 microspheres are resistant to high temperatures and a weaker pore shrinkage appears after the template removal, while it is limited for further application due to the fact that the silica template can only be left out by the highly corrosive HF solution or the hot strong alkali aqueous solution. In contrast, polymer microspheres can be easily removed through calcination or extraction with an organic solvent and are more commonly used in the colloidal crystal templating method. The formation of colloidal template always undergoes a self-assembly process of colloidal microspheres in suspension. Such a self-assembly process of polymer microspheres is the most crucial step for the fabrication of 3DOM materials, and the arrangement of colloidal crystal templates directly determines the final degree of pore order and porosity structure of 3DOM materials. In order to control the self-assembly process of monodisperse colloidal microspheres to be converted into three-dimensionally ordered colloidal templates, several methods have been investigated, such as centrifugation, sedimentation, and electrophoresis. Centrifugation is considered to be the best method due to its low cost and flexible operation as well as the obtained highly ordered assembly colloidal crystal template.

A typical emulsion polymerization route of the colloidal crystal template can be illustrated by the PMMA-templating fabrication. Such a method involves several steps: The uniform dispersion of the precursor (methyl methacrylate, MMA) in a N_2 atmosphere at a given temperature in a water bath under stirring, the introduction of an inducer ($K_2S_2O_8$), polymerization at above the glass transition temperature, centrifugation, washing for the removal of inorganic K^+ and SO_4^{2-} ions, and gravity evaporation. After drying overnight at room temperature (RT), the as-synthesized PMMA microspheres are ready for use as a template. Gravity evaporation is a key step to ensure the ordering of PMMA microspheres. The PMMA microspheres obtained by drying emulsion with a specific concentration can be employed as colloidal template. Colloidal particles can self-assemble into a highly ordered three-dimensionally compact stacking structure through emulsion polymerization. The polymerization is well controlled and the sizes of microspheres are uniformly adjusted by controlling the reaction temperature and duration time. Higher temperature and longer reaction time will give rise to an excessive polymerization, thus resulting in larger particle sizes and possible aggregation of polymer microspheres. The initiator influences the surface charge on the polymer microspheres, which governs the interaction with the precursor. After polymerization, the polymer microspheres must be cleaned many times with deionized water to protect the catalytic material from being polluted by the residual impurities using the microspheres as a template.

Mesoporous materials are mainly divided into silicon-based and nonsilicon-based samples. The synthesis mechanisms of mesoporous silica materials (such as liquid crystal template and synergistic effect mechanisms) and synthesis methods (such as hydrothermal and sol–gel methods) were studied. Nonsilicon mesoporous materials include mesoporous metal oxides/composites, mesoporous carbon, mesoporous metals, and mesoporous aluminum phosphate. The synthesis of nonsilicon mesoporous materials (especially mesoporous metal oxides) is more difficult than the silicon-based materials due to the diverse components, uncontrolled hydrolysis rates, and variable chemical valence states. The Pd/Al_2O_3 catalyst with adjustable and uniform pore sizes was prepared via the sol–gel route by adjusting the template (deoxycholic acid and polyvinyl pyrrolidone acid) amounts. The as-obtained Pd/Al_2O_3 catalyst with relatively large pore sizes (ca. 12 nm) exhibited an efficient and sustained catalytic methane combustion performance under a variety of operating conditions compared with the catalyst with small pore sizes (5–7 nm) [41]. Cobalt-doped ordered mesoporous alumina with intrinsic activity for methane combustion were synthesized using the sol–gel method with a P123 template. The as-obtained Pd–Co bimetallic catalyst exhibited a lower activation energy and a higher activity, which was attributed to the abundant active oxygen species for stabilizing the active PdO phase [42].

There are two kinds of templates for preparing mesoporous materials: soft template and hard template. The soft template method is to form the inorganic–organic composite mesoporous structure through the molecular self-assembly of inorganic precursors and soft template agents, and the soft template is then removed to obtain the corresponding mesoporous materials. Soft template is a kind of surfactant; biomacromolecules or supramolecule (PEO-PPO-PEO, PE10300) with special structures are assembled into an ordered arrangement in dissolved solution, which plays a structure-oriented role in the fabrication of mesoporous materials. Amorphous mesoporous metal oxides are formed by the soft template method at lower temperatures, at which insufficient thermal treatment is offered to form crystalline materials, but they can be converted to crystalline oxides by calcination.

Ryoo’s research group developed the technique of preparing ordered mesoporous materials via nanoreplication with ordered mesoporous silicon or carbon as hard template [43]. A typical synthesis of the KIT-6 template involves several steps: The uniform dispersion of the precursor (polyethylene oxide–polypropylene oxide–polyethylene, P123) in a water bath at 50 °C under stirring, the addition of an inducer (H_2SO_4, 1-butanol), polymerization (tetraethyl orthosilicate, TOES) under stirring at 35 °C, thermal treatment in a Teflon-lined autoclave at 100 °C for 24 h, filtration and drying, and calcination. The hard template method is used to successfully synthesize mesoporous materials by introducing the precursor solution into the channels of the hard template (SBA-15, KIT-6 or FDU-1) and calcination to form nanochannel crystal oxides. The big challenge of ordered mesoporous catalysts derived from the hard template route is determining how to completely fill the mesoporous channels of the hard template with the precursor solution so that the obtained target products possess regular pore structures and continued channels.

2.2. Macroporous or Mesoporous Composite Oxides

Generally speaking, the colloidal crystal template method is the most commonly employed to synthesize 3DOM materials. The precursor solution infiltrates sufficiently into the microsphere gaps for achieving the filling replication to obtain the regularly arranged large pore walls. The materials derived from such a route display a high degree of pore order and a well-controlled porosity that is a replica of the template. This method includes the following four steps: (ⅰ) Monodisperse PMMA microspheres are first synthesized by the emulsion-free polymerization, colloidal crystal templates are then obtained by the constant-temperature suspension method; (ⅱ) according to the stoichiometry of each metal element in the target product, the product is configured into a homogeneous solution that dissolves the metal source, citric acid, and surfactant (e.g., triblock copolymer P123, F127, *L*-lysine, *L*-tryptophan, or xylitol); (ⅲ) the PMMA hard template is impregnated in the precursor solution for a certain time and dried; and (iv) the sample is calcined in a tubular furnace under a N_2 atmosphere at low temperatures, in which the amorphous carbon formed due to partial carbonization of PMMA is served as a harder and heat-resistant template. Then, the above sample is further calcined in air at high temperatures to obtain the 3DOM material with a high surface area and a good pore structure. The precursor solution infiltrates the colloidal gap through the capillary action and must satisfy the following points: (i) The solution soaks the template fully without dissolving the template to avoid destroying ordered arrangement of the structure; (ii) the appropriate precursor solution concentration should be ensured to fabricate a three-dimensionally macroporous skeleton with good mechanical strength, but the liquid with a high concentration with a high density has difficulty infiltrating into the narrow channels; (ⅲ) metal precursor solutions should be of mild reactivity to let the liquid enter the voids flexibly, and the metal precursors with strong reactivity may interact with the functional groups on the template surface or moisture in the air to avoid the infiltration of the precursor solutions; and (ⅳ) the melting point of the dried metal oxide precursor must be higher than decomposition temperature of the template in air. It is relatively available to prepare the 3DOM metal oxide using metal alkoxide as precursor. However, metal salts (nitrates, acetates, and chlorides) are cheap and available compared with most of the metal alcohols, especially the low-valence transition metals and rare-earth metals. Yan et al. [44] synthesized a series of 3DOM transition-metal oxides (Fe_2O_3, Cr_2O_3, Mn_2O_3, and Co_3O_4) using the PMMA-template and impregnation methods with the transition-metal nitrate or acetate as precursor and ethanol or acetic acid as solvent. Precursor solution was deposited into the template gaps via the impregnation and evaporation routes. Since the melting point of nitrate or acetate is low, oxalate ions are introduced and react with the metal ions to form oxalates with higher melting points. The oxalates are decomposed directly to obtain 3DOM metal oxides, with the template being removed at high temperatures simultaneously. Sadakane et al. [45] prepared the 3DOM Fe_2O_3, Cr_2O_3, Mn_2O_3, Mn_3O_4, and Co_3O_4 using the PMMA-templating method with metal nitrates as precursors. Zhao and coworkers [46] carbonized the surface carboxyl-modified PMMA-templates in an inert atmosphere and calcined at 700 °C to generate the 3DOM $La_{1-x}K_xCoO_3$ catalysts. Dai and coworkers [18][19] carried out a number of valuable works on this topic, and prepared various 3DOM-structured materials (e.g., Cr_2O_3, Fe_2O_3, Mn_2O_3, Co_3O_4, TiO_2, CeO_2, $LaMnO_3$, $LaSrCoO_3$, and $LaMnAl_{11}O_{19}$) with high surface areas through the surfactant-aided PMMA-templating approaches. These authors claimed two kinds of the as-prepared macroporous walls with regular nano-bulk materials or accumulation of NPs. The macroporous walls which consisted of NPs accumulation displayed an irregular mesoporous structure and exhibited higher pore capacity than nano-bulk walls. The NPs accumulation walls showed high catalytic activity similar to the small-sized NPs. It is difficult to obtain porous crystalline structure of perovskite-type oxides via the colloidal crystals template route after they are calcined at high temperatures (above 1000 °C). However, one group successfully synthesized 3DOM $LaMnAl_{11}O_{19}$ using a two-step calcination method via a PMMA-template route at 1100 °C [20]. The samples were first calcined in a N_2 atmosphere at 400 °C to form a hard and heat-resistant partially carbonized framework to maintain a good pore structure. Then, the well-ordered pore hexaaluminate crystal phase was slowly formed after the high-temperature calcination at 1100 °C in an air atmosphere.

The mesoporous structure was obtained by introducing metal salt solution into the pores of the hard template (KIT-6, SBA-15, or FUD-1) to achieve the solid-to-solid replication (i.e., so-called “nanocasting”). The big challenge in synthesizing ordered mesoporous catalysts via the hard template route is determining how to completely fill the mesoporous channels with metal precursors to ensure consistency and stability, so as to obtain the target products with well-ordered regular structures and continuous porous channels. The 3D ordered mesoporous (3DOMeso) CrO_x was prepared by the solvent-free and two-step calcination methods with KIT-6 as template [21]. Chromium nitrate was first melted in a sealed autoclave with a melting point of 60 °C and filled mesoporous channels of the KIT-6 template. The pressure in the autoclave increased with the decomposition of metal salts in the channel above 125 °C, which was beneficial for filling the channels of KIT-6 by the molten salts. The 3DOMeso Fe_2O_3 [22] and 3DOMeso Co_3O_4 [23] were fabricated by the vacuum-assisted nanocasting method with the alcohol solution of metal nitrate as the precursor source and KIT-6 or SBA-16 as the template. The hard-template powders were first treated under vacuum and airtight conditions, and then the metal nitrate alcohol solution of an appropriate concentration was added until no obvious superfluous solution was prospected. The 3DOMeso oxide was generated after the silicon template was removed with 10 vol% HF aqueous solution. The 3DOMeso MnO_2 [24] was fabricated via an ultrasound-assisted SBA-16 template route with a high surface area of 266 m^2/g. Ultrasonic treatment expelled the gas effectively and promoted the liquid–solid mass transfer and the metal precursors dispersion to maximize the filling of silicon channels, with the lowest possibility of forming oxides outside the silicon template. Well-ordered 3DOMesoporous frameworks are associated with the precursor solution concentration, since a diluted salt solution is too low to fully fill the template channel after drying.

2.3. Supported Metal Oxides or Noble Metals

High surface areas of ordered macro- or mesopores and increased surface oxygen species concentrations are beneficial for constructing bifunctional catalysts with high dispersion of the active phase(s) via supporting metal oxides or noble metals NPs. The particle sizes of noble metals mainly affect exposure of the active sites and utilization of the noble metals. Noble metal NPs exhibit good low-temperature catalytic activities, which is associated with their small particle sizes and good ability to flexibly activate reactant molecules. However, noble metal NPs can be agglomerated to big particles during the reaction process at high temperatures, thus resulting in poor thermal stability and irreversible catalyst deactivation. The coordinative environment of the noble metals is also the key factor influencing catalytic efficiencies of the supported noble metal catalysts, especially the oxidation states of noble metals and the strong interaction between the noble metal and the support. The strategies to regulate the coordinative environment of the noble metals mainly involve selection of the pretreatment atmosphere, modification of the noble metal NPs, and adjustment in physicochemical property of the support. Transition-metal oxides possess multiple metal oxidation states, and phase transition takes place after treatments at different temperatures. A suitable support is very important due to dispersing the active components of metals and increasing stability, selectivities, and activities of the supported noble metal catalysts. The well-developed catalysts with 3D porous structures favor adsorption and diffusion of the reactants and O_2 molecules, and the large surface areas can efficiently disperse noble metal and/or metal oxide NPs to improve catalytic activities and thermal stability of the supported materials.

Ordered porous materials possess the advantages of stabilizing metal or metal oxide NPs, increasing surface active sites, and improving ultrahigh NPs dispersion [47], as compared with micron-scale bulk samples. The traditional methods of loading metal NPs include the incipient wetness impregnation and adsorption. Dai and coworkers developed a novel strategy to generate a series of uniform-sized noble metals NPs supported on 3DOM-structured high-surface-area materials (e.g., Au–Pd–Co/3DOM Mn_2O_3 [25], Au–Pd–CoO/3DOM Co_3O_4 [26], CoPd/3DOM CeO_2 [27], AuPd/3DOM $CoCr_2O_4$ [48], AuPd/3DOM $La_{0.6}Sr_{0.4}MnO_3$ [49], PdPt/3DOM $LaMnAl_{11}O_{19}$ [20][50], and PdPt/MnO_x/3DOM $CoFe_2O_4$ [51]) by the PVA- or PVP-protected reduction and surfactant-assisted PMMA-templating approaches. For example, this group prepared the supported Au–Pd–M (M = Cr, Mn, Fe, and Co) catalysts by the acid-modified PVA-protected N_2-bubbling reduction method [25][26]. The mixed solutions of PVA, HCl, chlorate, $HAuCl_4$, and $NaPdCl_4$ after magnetic stirring were used as the noble metal precursor. The sodium borohydride was quickly introduced into the precursor solution as a reducing agent to prohibit the growth and agglomeration of Au–Pd–M NPs. The as-prepared 3DOM oxide was well-wetted via ultrasonic-assisted dispersion in a mixture solution with mild N_2 bubbling. After being washed with deionized water and ethanol before drying and calcination in furnace, the supported Au–Pd–M NPs possessed well-controlled particle sizes, ultrahigh dispersion, and stabilized metal NPs. Very recently, the same group developed a novel in situ noble-metal-embedded fabrication approach to synthesize Pt-embedded 3DOM Mn_2O_3 via the PMMA-templating and ethylene glycol reduction routes [52]. The Pt-embedded 3DOM Mn_2O_3 materials were fabricated by the one-step calcination method via the mixing of Pt-ethylene glycol solution and manganese nitrate precursor solution (which was dissolved in methanol). Part of the Pt NPs (with a size of 3.6–4.4 nm) were embedded in the skeleton of 3DOM Mn_2O_3, which exhibited an excellent thermal stability in the durative on-stream reaction, as compared with the sample derived from the gas-bubble-aided colloid adsorption route. On this basis, the same research group also successfully obtained the PtRu-embedded 3DOM $Ce_{0.7}Zr_{0.3}O_2$ catalysts with excellent thermal stability by adopting the PMMA-templating and ethylene-glycol-reduction approaches [53]. The embedded PtRu catalysts preserved changeless performance for toluene oxidation after thermal treatment at 800 °C, since the thermally treated sample showed a slight size increase of the average PtRu NPs from 4.2 to 6.7 nm, which was attributed to the embedded architecture to facilitate generation of a larger number of Pt-O-Ce-like bonds to stabilize the noble metals. However, the supported PtRu sample prepared by the colloidal adsorption method displayed a remarkable loss of

PtRu surface area with an average enlarged PtRu size from 5.1 to 17.3 nm under the similar reaction conditions, resulting in a sharp decline in catalytic activity.

References

1. Pfefferle, L.D.; Pfefferle, W.C. Catalysis in combustion. Catal. Rev. 1987, 29, 219–267.
2. Wei, L.; Wang, Z.W.; Liu, Y.X.; Guo, G.S.; Dai, H.X.; Cui, S.P.; Deng, J.G. Support promotion effect on the SO2 and K+ co-poisoning resistance of MnO2/TiO2 for NH3-SCR of NO. J. Hazard. Mater. 2021, 416, 126117.
3. Gremminger, A.T.; Pereira de Carvalho, H.W.; Popescu, R.; Grunwaldt, J.-D.; Deutschmann, O. Influence of gas composition on activity and durability of bimetallic Pd-Pt/Al2O3 catalysts for total oxidation of methane. Catal. Today 2015, 258, 470–480.
4. Öcal, M.; Oukaci, R.; Marcelin, G.; Jang, B.W.-L.; Spivey, J.J. Steady-state isotopic transient kinetic analysis on Pd-supported hexaaluminates used for methane combustion in the presence and absence of NO. Catal. Today 2000, 59, 205–217.
5. Raza, J.; Khoja, A.H.; Anwar, M.; Saleem, F.; Naqvi, S.R.; Liaquat, R.; Hassan, M.; Javaid, R.; Qazi, U.Y.; Lumbers, B. Methane decomposition for hydrogen production: A comprehensive review on catalyst selection and reactor systems. Renew. Sust. Energ. Rev. 2022, 168, 112774.
6. Wang, Y.G.; Ren, J.W.; Wang, Y.Q.; Zhang, F.Y.; Liu, X.H.; Guo, Y.; Lu, G.Z. Nanocasted synthesis of mesoporous LaCoO3 perovskite with extremely high surface area and excellent activity in methane combustion. J. Phys. Chem. C 2008, 112, 15293–15298.
7. Chen, J.H.; Arandiyan, H.; Gao, X.; Li, J.H. Recent advances in catalysts for methane combustion. Catal. Surv. Asia 2015, 19, 140–171.
8. Tang, X.F.; Li, J.H.; Hao, J.M. Synthesis and characterization of spinel Co3O4 octahedra enclosed by the facets. Mater. Res. Bull. 2008, 43, 2912–2918.
9. Li, J.H.; Liang, X.; Xu, S.C.; Hao, J.M. Catalytic performance of manganese cobalt oxides on methane combustion at low temperature. Appl. Catal. B 2009, 90, 307–312.
10. Chen, J.H.; Zhang, X.Y.; Arandiyan, H.; Peng, Y.; Chang, H.Z.; Li, J.H. Low temperature complete combustion of methane over cobalt chromium oxides catalysts. Catal. Today 2013, 201, 12–18.
11. Zhu, Y.F.; Tan, R.Q.; Feng, J.; Ji, S.S.; Cao, L.L. The reaction and poisoning mechanism of SO2 and perovskite LaCoO3 film model catalysts. Appl. Catal. A 2001, 209, 71–77.
12. Huang, H.F.; Sun, Z.; Lu, H.F.; Shen, L.Q.; Chen, Y.F. Study on the poisoning tolerance and stability of perovskite catalysts for catalytic combustion of volatile organic compounds. React. Kinet. Mechan. Catal. 2010, 101, 417–427.

13. Cheng, J.; Wang, H.L.; Hao, Z.P.; Wang, S.B. Catalytic combustion of methane over cobalt doped lanthanum stannate pyrochlore oxide. Catal. Commun. 2008, 9, 690–695.
14. Cheng, J.; Li, J.J.; Ma, C.Y.; Hao, Z.P. Catalytic combustion of methane over La2TM0.3Zr1.7O7−δ (TM = Mn, Fe, and Co) pyrochlore oxides. Catal. Commun. 2009, 10, 1170–1173.
15. Aitbekova, A.; Zhou, C.; Stone, M.L.; Lezama-Pacheco, J.S.; Yang, A.-C.; Hoffman, A.S.; Goodman, E.D.; Huber, P.; Stebbins, J.F.; Bustillo, K.C.; et al. Templated encapsulation of platinum-based catalysts promotes high-temperature stability to 1100 °C. Nat. Mater. 2022, 21, 1290–1297.
16. Bartley, J.K.; Dimitratos, N.; Edwards, J.K.; Kiely, C.J.; Taylor, S.H. A Career in catalysis: Graham J. Hutchings. ACS Catal. 2021, 11, 5916–5933.
17. Agarwal, N.; Freakley, S.J.; McVicker, R.U.; Althahban, S.M.; Dimitratos, N.; He, Q.; Morgan, D.J.; Jenkins, R.L.; Willock, D.J.; Taylor, S.H.; et al. Aqueous Au-Pd colloids catalyze selective CH4 oxidation to CH3OH with O2 under mild conditions. Science 2017, 358, 223–227.
18. Dai, H.X.; Hou, Z.Q.; Zhang, X.; Zhang, K.F. Catalytic performance of regularly morphological and porous catalysts for the oxidation of volatile organic compounds. J. Beijing Univ. Technol. 2019, 45, 1095–1114.
19. Dai, H.X.; Deng, J.G.; Xia, Y.S.; Zhang, R.Z.; Zhang, L. Hard-templating fabrication and catalytic applications of three-dimensionally ordered meso-and macroporous transition-metal oxides. Inorg. Chem. Ind. 2012, 44, 55–58.
20. Xu, P.; Zhang, X.; Zhao, X.T.; Yang, J.; Hou, Z.Q.; Bai, L.; Chang, H.Q.; Liu, Y.X.; Deng, J.G.; Guo, G.S.; et al. Preparation, characterization, and catalytic performance of PdPt/3DOM LaMnAl11O19 for the combustion of methane. Appl. Catal. A 2018, 562, 284–293.
21. Xia, Y.S.; Dai, H.X.; Jiang, H.Y.; Deng, J.G.; He, H.; Au, C.T. Mesoporous chromia with ordered three-dimensional structures for the complete oxidation of toluene and ethyl acetate. Environ. Sci. Technol. 2009, 43, 8355–8360.
22. Xia, Y.S.; Dai, H.X.; Jiang, H.Y.; Zhang, L.; Deng, J.G.; Liu, Y.X. Three-dimensionally ordered and wormhole-like mesoporous iron oxide catalysts highly active for the oxidation of acetone and methanol. J. Hazard. Mater. 2011, 186, 84–91.
23. Xia, Y.S.; Dai, H.X.; Jiang, H.Y.; Zhang, L. Three-dimensional ordered mesoporous cobalt oxides: Highly active catalysts for the oxidation of toluene and methanol. Catal. Commun. 2010, 11, 1171–1175.
24. Deng, J.G.; Zhang, L.; Dai, H.X.; Xia, Y.S.; Jiang, H.Y.; Zhang, H.; He, H. Ultrasound-assisted nanocasting fabrication of ordered mesoporous MnO2 and Co3O4 with high surface areas and polycrystalline walls. J. Phys. Chem. C 2010, 114, 2694–2700.

25. Xie, S.H.; Liu, Y.X.; Deng, J.G.; Zhao, X.T.; Yang, J.; Zhang, K.F.; Han, Z.; Arandiyan, H.; Dai, H.X. Effect of transition metal doping on the catalytic performance of Au–Pd/3DOM Mn2O3 for the oxidation of methane and o-xylene. Appl. Catal. B 2017, 206, 221–232.
26. Xie, S.H.; Liu, Y.X.; Deng, J.G.; Zang, S.M.; Zhang, Z.H.; Arandiyan, H.; Dai, H.X. Efficient removal of methane over cobalt-monoxide-doped AuPd nanocatalysts. Environ. Sci. Technol. 2017, 51, 2271–2279.
27. Xie, S.H.; Liu, Y.X.; Deng, J.G.; Zhao, X.T.; Yang, J.; Zhang, K.F.; Han, Z.; Dai, H.X. Three-dimensionally ordered macroporous CeO2-supported nanoparticles: Highly active catalysts for methane oxidation. J. Catal. 2016, 342, 17–26.
28. Wu, Z.X.; Deng, J.G.; Liu, Y.X.; Xie, S.H.; Jiang, Y.; Zhao, X.T.; Yang, J.; Arandiyan, H.; Guo, G.S.; Dai, H.X. Three-dimensionally ordered mesoporous Co3O4-supported Au–Pd alloy nanoparticles: High-performance catalysts for methane combustion. J. Catal. 2015, 332, 13–24.
29. Zhao, X.T.; Liu, Y.X.; Deng, J.G.; Xu, P.; Yang, J.; Zhang, K.F.; Han, Z.; Dai, H.X. Mesoporous PdxPt alloys: High-performance catalysts for methane combustion. Mol. Catal. 2017, 442, 191–201.
30. Ciuparu, D.; Lyubovsky, M.R.; Altman, E.; Pfefferle, L.D.; Datye, A. Catalytic combustion of methane over palladium-based catalysts. Catal. Rev. 2002, 44, 593–649.
31. Gélin, P.; Primet, M. Complete oxidation of methane at low temperature over noble metal based catalysts: A review. Appl. Catal. B 2002, 39, 1–37.
32. Yang, J.; Guo, Y.B. Nanostructured perovskite oxides as promising substitutes of noble metals catalysts for catalytic combustion of methane. Chin. Chem. Lett. 2018, 29, 252–260.
33. Bashan, V.; Ust, Y. Perovskite catalysts for methane combustion: Applications, design, effects for reactivity and partial oxidation. Int. J. Energy Res. 2019, 43, 7755–7789.
34. Nkinahamira, F.; Yang, R.J.; Zhu, R.S.; Zhang, J.W.; Ren, Z.Y.; Sun, S.L.; Xiong, H.F.; Zeng, Z.Y. Current progress on methods and technologies for catalytic methane activation at low temperatures. Adv. Sci. 2022, 2204566.
35. Arandiyan, H.; Wang, Y.; Sun, H.Y.; Rezaei, M.; Dai, H.X. Ordered meso- and macroporous perovskite oxide catalysts for emerging applications. Chem. Commun. 2018, 54, 6484–6502.
36. Zhang, C.X.; Zhao, P.Y.; Liu, S.X.; Yu, K. Three-dimensionally ordered macroporous perovskite materials for environmental applications. Chin. J. Catal. 2019, 40, 1324–1338.
37. Velev, O.D.; Jede, T.A.; Lobo, R.F.; Lenhoff, A.M. Porous silica via colloidal crystallization. Nature 1997, 389, 447–448.
38. Harkins, W.D. A general theory of the mechanism of emulsion polymerization. J. Am. Chem. Soc. 1947, 69, 1428–1444.

39. Jiang, S.; Sudol, E.D.; Dimonie, V.L.; El-Aasser, M.S. Seeding as a means of controlling particle size in dispersion polymerization. J. Appl. Polym. Sci. 2008, 108, 4096–4107.
40. Hartlen, K.D.; Athanasopoulos, A.P.T.; Kitaev, V. Facile preparation of highly monodisperse small silica spheres (15 to >200 nm) suitable for colloidal templating and formation of ordered arrays. Langmuir 2008, 24, 1714–1720.
41. Lin, J.; Zhao, L.S.; Zheng, Y.; Xiao, Y.H.; Yu, G.T.; Zheng, Y.; Chen, W.; Jiang, L.L. Facile strategy to extend stability of simple component-alumina-supported palladium catalysts for efficient methane combustion. ACS Appl. Mater. Interfaces 2020, 12, 56095–56107.
42. Lin, J.; Chen, Y.L.; Liu, X.J.; Chen, X.H.; Zheng, Y.; Huang, F.; Xiao, Y.H.; Zheng, Y.; Jiang, L.L. Microstructural property regulation and performance in methane combustion reaction of ordered mesoporous alumina supported palladium-cobalt bimetallic catalysts. Appl. Catal. B 2020, 263, 118269.
43. Ryoo, R.; Joo, S.H.; Jun, S. Synthesis of highly ordered carbon molecular sieves via template-mediated structural transformation. J. Phys. Chem. B 1999, 103, 7743–7746.
44. Yan, H.W.; Blanford, C.F.; Holland, B.T.; Smyrl, W.H.; Stein, A. General synthesis of periodic macroporous solids by templated salt precipitation and chemical conversion. Chem. Mater. 2000, 12, 1134–1141.
45. Sadakane, M.; Horiuchi, T.; Kato, N.; Takahashi, C.; Ueda, W. F Facile preparation of three-dimensionally ordered macroporous alumina, iron oxide, chromium oxide, manganese oxide, and their mixed-metal oxides with high porosity. Chem. Mater. 2007, 19, 5779–5785.
46. Xu, J.F.; Liu, J.; Zhao, Z.; Xu, C.M.; Zheng, J.X.; Duan, A.J.; Jiang, G.Y. Easy synthesis of three-dimensionally ordered macroporous La1−xKxCoO3 catalysts and their high activities for the catalytic combustion of soot. J. Catal. 2011, 282, 1–12.
47. Arandiyan, H.; Dai, H.X.; Deng, J.G.; Wang, Y.; Sun, H.Y.; Xie, S.H.; Bai, B.Y.; Liu, Y.X.; Ji, K.M.; Li, J.H. Three-dimensionally ordered macroporous La0.6Sr0.4MnO3 supported Ag nanoparticles for the combustion of methane. J. Phys. Chem. C 2014, 118, 14913–14928.
48. Wang, Z.W.; Deng, J.G.; Liu, Y.X.; Yang, H.G.; Xie, S.H.; Wu, Z.X.; Dai, H.X. Three-dimensionally ordered macroporous CoCr2O4-supported Au–Pd alloy nanoparticles: Highly active catalysts for methane combustion. Catal. Today 2017, 281, 467–476.
49. Wang, Y.; Arandiyan, H.; Scott, J.; Akia, M.; Dai, H.X.; Deng, J.G.; Aguey-Zinsou, K.-F.; Amal, R. High performance Au–Pd supported on 3D hybrid strontium-substituted lanthanum manganite perovskite catalyst for methane combustion. ACS Catal. 2016, 6, 6935–6947.
50. Xu, P.; Zhao, X.T.; Zhang, X.; Bai, L.; Chang, H.Q.; Liu, Y.X.; Deng, J.G.; Guo, G.S.; Dai, H.X. Three-dimensionally ordered macroporous LaMnAl11O19- supported Pd nanocatalysts highly active for methane combustion. Mol. Catal. 2017, 439, 200–210.

51. Li, X.Y.; Liu, Y.X.; Deng, J.G.; Xie, S.H.; Zhao, X.T.; Zhang, Y.; Zhang, K.F.; Arandiyan, H.; Guo, G.S.; Dai, H.X. Enhanced catalytic performance for methane combustion of 3DOM $CoFe_2O_4$ by co-loading MnOxand Pd–Pt alloy nanoparticles. Appl. Surf. Sci. 2017, 403, 590–600.
52. Pei, W.B.; Liu, Y.X.; Deng, J.G.; Zhang, K.F.; Hou, Z.Q.; Zhao, X.T.; Dai, H.X. Partially embedding Pt nanoparticles in the skeleton of 3DOM Mn_2O_3: An effective strategy for enhancing catalytic stability in toluene combustion. Appl. Catal. B 2019, 256, 117814.
53. Pei, W.B.; Dai, L.Y.; Liu, Y.X.; Deng, J.G.; Jing, L.; Zhang, K.F.; Hou, Z.Q.; Han, Z.; Rastegarpanah, A.; Dai, H.X. PtRu nanoparticles partially embedded in the 3DOM $Ce_{0.7}Zr_{0.3}O_2$ skeleton: Active and stable catalysts for toluene combustion. J. Catal. 2020, 385, 274–288.

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