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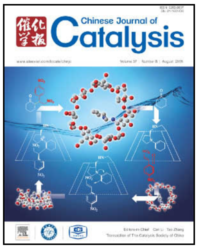

Review

Catalytic removal of volatile organic compounds using ordered porous transition metal oxide and supported noble metal catalysts

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ABSTRACT

Most of volatile organic compounds (VOCs) are harmful to the atmosphere and human health. Catalytic combustion is an effective way to eliminate VOCs. The key issue is the availability of high performance catalysts. Many catalysts including transition metal oxides, mixed metal oxides, and supported noble metals have been developed. Among these catalysts, the porous ones attract much attention. In this review, we focus on recent advances in the synthesis of ordered mesoporous and macroporous transition metal oxides, perovskites, and supported noble metal catalysts and their catalytic oxidation of VOCs. The porous catalysts outperformed their bulk counterparts. This excellent catalytic performance was due to their high surface areas, high concentration of adsorbed oxygen species, low temperature reducibility, strong interaction between noble metal and support and highly dispersed noble metal nanoparticles and unique porous structures. Catalytic oxidation of carbon monoxide over typical catalysts was also discussed. We made conclusive remarks and proposed future work for the removal of VOCs.

1. Introduction

Volatile organic compounds (VOCs) have a high vapor pressure and low water solubility and most of them are major contributors to air pollution due to their toxic nature or as a precursor of ozone or photochemical smog [1,2]. A large variety of VOCs are emitted from industrial and transportation (outdoor sources) and household (indoor sources) activities, such as power generation, vehicle emission, solvent use, and from office supplies and restaurant and domestic cooking. Most VOCs are harmful to the atmosphere and human beings [3,4]. VOCs include alkanes, olefins, alcohols, ketones, aldehydes, aromatics, paraffins, and halogenated hydrocarbons [5]. Among the most common and toxic VOCs are formaldehyde, benzene, toluene, propene, phenol, and acetone.

The removal of these emitted VOCs is a crucial topic in environmental protection. The conventional approach to dispose of highly concentrated VOC streams is thermal incineration. However, this needs to be operated at high temperatures (800–1200 °C) and requires a high operating cost. Furthermore, undesirable byproducts such as nitrogen oxides are produced in the incineration. In contrast, catalytic combustion or oxidation is an effective and feasible technology for VOC removal, which can be operated with dilute VOC effluent

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streams (< 1 %) and at low temperatures (< 600 °C). Thus, this has been widely investigated in recent years. Current efforts for this technology concentrate on developing efficient and low cost catalysts which can catalyze the complete oxidation of VOCs into CO_2 and H_2O at low temperatures [6]. Two classes of catalysts, supported noble metals and transition metal oxides (TMOs), are the most promising materials for VOC combustion [7–11]. Supported noble metal catalysts, in spite of their more expensive costs, are preferred because of their high specific activities at low temperatures [12–18]. Regarding metal oxide catalysts, pure transition metal oxides, mixed transition metal oxides, and perovskites are recognized as efficient low cost catalysts for VOCs combustion [19–28].

It is accepted that the catalytic activity of a metal oxide is associated with its surface area, pore structure, oxygen nonstoichiometry, and reducibility [29]. These factors are determined by the preparation method. The preservation of high surface area is critical because the reaction rate is proportional to the surface area [30]. A good approach for increasing the surface area is to have a metal oxide material fabricated as an ordered porous structure. Porous materials are classified into three types in terms of the pore diameter: microporous (below 2 nm), mesoporous (2–50 nm), and macroporous (above 50 nm) [31]. The fabrication of porous materials, especially the creation of ordered meso- or macroporous materials, has been extensively investigated in the past years. Template methods, which imply a more or less direct replication of the pore system from the template, is one promising synthetic pathways to create porous materials, especially ordered porous materials [32].

The preparation of transition metal oxides by nanocasting procedures makes it possible to obtain nanopore-structured materials which are difficult to achieve using surfactant-usage techniques. This constitutes an additional advantage of the hard template route over the soft template route [33]. The first nanopore-structured transition metal oxide synthesized with mesostructured silica materials was Cr_2O_3 using SBA-15 as template [34]. Tian and coworkers obtained nanospheres of In_2O_3 and Co_3O_4 prepared from 3D-caged mesoporous silica (SBA-16) that showed ordered patterns in TEM images [35]. Nanopore-structured CeO_2 with a BET surface area of 198 m^2/g was prepared using a KIT-6 silica as template by Laha et al. [36]. Recently, Guan and coworkers [37] reported a general reaction container effect in the nanocasting synthesis of a series of mesoporous metal oxides.

Mesopores and micropores help to impart a high surface area and pore volume in a material. They provide numerous active sites and size selectivity for molecules. These small pores can then be coupled with larger macropores that improve mass transfer through the structure to overcome the diffusion limitation present in purely micro-/mesoporous materials. Novel approaches for the synthesis of hierarchically functional materials have been developed in recent years. One such class of materials are the three dimensionally ordered macroporous (3DOM) solids. The general process of fabricating 3DOM structures is simple: (1) form a colloidal crystal of close packed spheres with a uniform size; (2) fill the interstitial space with a fluid precursor capable of solidification, and (3) remove the template to obtain a porous inverse replica [38]. The colloidal crystal templates used for the generation of 3DOM materials were prepared from monodispersed silica or polymer spheres, including polystyrene (PS) and poly(methyl methacrylate) (PMMA). The spheres can be arranged into close packed structures by several methods [39]. For example, using metal nitrates or acetates as precursor and well-aligned PMMA or PS microspheres as the hard template, 3DOM-structured $La_{1-x}Sr_xFeO_3$ (surface area 24–49 m^2/g) [40], $LaMnO_3$ [41], and $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ (surface area 24 m^2/g) [42] were prepared. Zhao and coworkers adopted PMMA as the template to generate 3DOM-structured $LaFeO_3$-supported Au (surface area 32 m^2/g) [43], $Ce_{0.8}Zr_{0.2}O_2$-supported Au (surface area 58 m^2/g) [44] and $LaCo_xFe_{1-x}O_3$ (x = 0–0.5) [45] catalysts, which showed superior performance for the catalytic oxidation of soot. In the past years, Dai's group has investigated the controlled preparation and physicochemical properties of porous Co_3O_4 [46,47], MnO_x [46,48], Cr_2O_3 [49,50], Fe_2O_3 [51], γ-Al_2O_3 [52], $LaMnO_3$ [53,54,55], $LaCoO_3$ [56], La_2CuO_4 [57], $InVO_4$ [58], $SrFeO_{3-\delta}$ [59], and $BiVO_4$ [60] using the silica-templating or surfactant-assisted PMMA-templating strategy. These authors pointed out that the good catalytic performance of the materials obtained for VOC combustion was associated with the large surface area and unique pore structure.

In this review, the correlation between surface area, pore structure, metal dispersion and catalytic performance of the porous materials that leads to the identification of the catalytic active sites is discussed. Due to the explosion of the publications in this field and limited by space, only two kinds of ordered porous materials associated with the issue of VOC combustion are discussed: (1) ordered mesoporous transition metal oxide (TMOs) and supported noble metal catalysts; and (2) ordered macroporous transition metal oxide (TMOs) and supported noble metal catalysts.

2. Recent advances in the synthesis and application of ordered porous transition metal oxides and supported noble metal catalysts

2.1. Ordered mesoporous transition metal oxide catalysts

The utilization of mesoporous TMOs as the catalyst for VOC combustion has attracted attention in the past years because of their low cost, stable structure and, especially, excellent catalytic performance. Great achievements have so far been obtained [61–63].

Compositionally identical TMOs with different pore structures have been reported in the literature. For example, one dimensional (1D)-MnO_2, two dimensional (2D)-MnO_2 and three dimensional (3D)-MnO_2 with different structures were synthesized using the hydrothermal and nanocasting methods, respectively. The catalytic activity for ethanol oxidation over different MnO_2 catalysts decreased in the order of 3D-MnO_2 > 2D-MnO_2 > 1D-MnO_2. The apparent activation energy over 3D-MnO_2 was the lowest (28.2 kJ/mol), which was much lower than over 2D-MnO_2 (33.6 kJ/mol) and 1D-MnO_2 (52.8 kJ/mol). A mesoporous MnO_2 catalyst, especially 3D-MnO_2, had the best