



Catalytic removal of benzene over CeO₂–MnO_x composite oxides prepared by hydrothermal method



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ABSTRACT

A series of CeO₂–MnO_x composite oxides were synthesized through hydrothermal method and the complete catalytic oxidation of benzene were examined. The effects of the Ce_{at}/Mn_{at} atomic ratio on the features of catalyst structure and catalytic behavior were researched. The results exhibited that the catalytic properties of CeO₂–MnO_x composite oxides were higher than pure CeO₂ or MnO_x. When the Ce_{at}/Mn_{at} ratio was 3:7, the catalytic activity reached the best. By means of testing, the data revealed that the synergistic effects existed in the composite oxides, which resulted in the enhancement of catalytic abilities. In the main phase, MnO_x provided available oxygen species and CeO₂ enhanced oxygen mobility. In addition, the nature of oxygen vacancy of catalysts was also studied through positron annihilation spectrum. The results showed that the concentration of oxygen vacancy for CeO₂–MnO_x composite oxides changed comparing with pure CeO₂ or MnO_x, which also caused the activity differences over benzene.

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1. Introduction

Volatile organic compounds (VOCs) produced by industrial manufacturing are an important class of air pollutants. Many environmental problems, such as offensive odors, toxic emissions, ozone formation and petrochemical smog are related to the emissions of VOCs. The reduction of the emissions of VOCs is a very important environmental issue for human health. At present, VOCs are usually removed by thermal oxidation, catalytic oxidation, adsorption and absorption [1]. Among these techniques, catalytic oxidation is regarded as an effective way for VOCs emission control, due to higher destructive efficiency than adsorption, and lower operating temperature and harm reaction by-products than thermal oxidation [2–5]. In addition, catalytic oxidation does not require additional fuel, reducing energy consumption and avoiding the formation of thermal NO_x.

Benzene is a hazardous volatile organic compound presenting in various industries such as chemical, petrochemical, paint and coating and steel manufacture. Catalytic oxidation is regarded as one of the most promising routes for the effective removal of benzene. Supported noble metal catalysts, typically Pd, have been generally preferred for the complete oxidation of benzene due to the higher

activity [1,6–9]. However, the usage of these noble metals is limited due to high cost, low thermal stability and sensitivity to poisoning. Transition metal oxide-based catalysts are suitable alternative because of higher thermal stability and lower price [10]. In certain cases, transition metal oxides can be actually more active than noble metal catalysts [11].

Perovskites, zirconia-based catalysts, manganese and cobalt oxides have been claimed for their effectiveness in VOCs oxidation, among which, manganese oxides are the most active oxide catalysts in VOC oxidation [11–14]. Ceria (CeO₂), as a rare earth oxide, has been extensively investigated in heterogeneous catalysis due to its high oxygen storage capacity. More recently, CeO₂-based mixed oxides have also been employed for VOCs removal [15–17]. CeO₂–MnO_x mixed oxides can be applied as heterogeneous catalysts for the abatement of contaminants in the liquid and gas phases, such as the catalytic reduction of NO and oxidation of acrylic acid and formaldehyde [18–21], which exhibit much higher catalytic activity than those of pure MnO_x and CeO₂.

In this article, we investigate the catalytic behavior of CeO₂–MnO_x composite oxide catalysts prepared via the hydrothermal method through the complete catalytic oxidation of benzene. Their catalytic activities differences are analyzed in detail for different Mn/Ce atomic ratio oxides. The purpose of this study is to discuss the roles of crystal vacancy produced by the formation of solid solution and interaction between CeO₂ and MnO_x in the combustion of benzene.

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2. Experimental

2.1. The preparation of CeO₂–MnO_x composite oxides

The chemicals used in this work, including Ce(NO₃)₃·6H₂O (99%), Mn(NO₃)₂ solution (50%), NaOH (98%), and ethanol, were purchased from Beijing Chemicals Company (Beijing, China). CeO₂–MnO_x composite oxides with different Mn/Ce atomic ratio (Mn/Ce ranging from 1:9 to 9:1) were synthesized by a hydrothermal process. Briefly, Ce(NO₃)₃·6H₂O and Mn(NO₃)₂ in appreciate amounts were dissolved in a 10 mL H₂O and mixed with a 6 M NaOH solution. The solution was then transferred to an autoclave (100 mL) and gradually heated to 120 °C, then kept at the given temperature for 24 h. The precipitates in autoclaves were collected by centrifugation, washed with distilled water and ethanol several times. The obtained materials, labeled as Ce_xMn_{1–x} (where *x* refers to the Ce/(Ce + Mn) atomic ratio) were dried at 80 °C overnight and calcined at 550 °C for 4 h. Pure CeO₂ and MnO_x were also prepared using the similar process as reference.

2.2. Characterization technique

The crystal phase of the materials was characterized on X-ray diffraction (XRD, Philips X'pert PRO) equipped with a Cu K α radiation source ($\lambda = 0.154187$ nm) at a scanning rate of 0.03°/s (2θ from 10° to 90°). The assignment of the crystalline phases was based on the ICSD data base (Mn₂O₃ no. 89-4836; CeO₂ no. 81-0792). The inductively Coupled Plasma (ICP) was tested to measure the contents of Ce and Mn ions. The morphology and structure of samples were observed using transmission electron microscopy (TEM) (JEOL JEM-2010F) with an accelerating voltage of 200 kV.

The BET specific surface area (S_{BET}) was measured by physical adsorption of N₂ at the liquid nitrogen temperature using an Autosorb-1 analyzer (Quantachrome). Before measurement, the samples were degassed at 300 °C for 4 h under vacuum. Surface composition was determined by X-ray photoelectron spectroscopy (XPS) using an ESCALab220i-XL electron spectrometer from VG Scientific with a monochromatic Al K α radiation. The binding energy (BE) was referenced to the C1s line at 284.8 eV from adventitious carbon. Positron annihilation spectrum was tested in order to research the nature of oxygen vacancy in the catalysts.

Hydrogen temperature-programmed reduction (H₂-TPR) was performed with a U-type quartz reactor equipped with Automated Catalyst Characterization System (Autochem 2920, MICROMERIT-ICS). A 50 mg sample (40–60 mesh) was loaded and pretreated with a 5% O₂ and 95% He mixture (30 mL/min) at 150 °C for 1 h and cooled to 50 °C under He flow. The samples were then heated to 900 °C at a rate of 10 °C/min under the flow of a 10% H₂ and 90% Ar mixture (30 mL/min).

2.3. Catalytic activity tests

Activity tests for catalytic oxidation of benzene over Ce_xMn_{1–x} composite catalysts were performed in a continuous-flow fixed-bed reactor under atmospheric pressure, containing 100 mg of catalyst samples (40–60 mesh). A standard reaction gas containing 1000 ppm benzene and 20% O₂ in N₂ was fed with a total flow rate of 100 mL/min. The weight hourly space velocity (WHSV) was typically 60,000 mL g^{–1} h^{–1}. The reactants and the products were analyzed on-line using a GC/MS (Hewlett-Packard 6890N gas chromatograph interfaced to a Hewlett-Packard 5973 N mass selective detector) with a HP-5MS capillary column (30 m \times 0.25 mm \times 0.25 μ m) and another GC (GC112A, Shangfen,

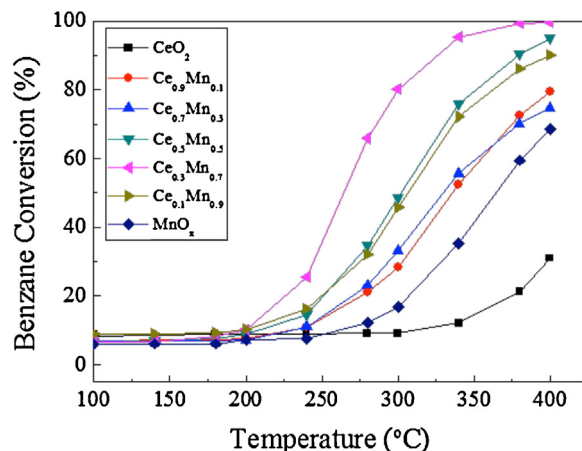


Fig. 1. C₆H₆ conversion (%) over CeO₂, MnO_x and Ce_xMn_{1–x} catalysts as a function of reaction temperature (°C).

China) with a carbon molecule sieve column. The conversion of benzene (X_{benzene} , %) was calculated as follows:

$$X_{\text{benzene}} = \frac{C_{\text{benzene(in)}} - C_{\text{benzene(out)}}}{C_{\text{benzene(in)}}} \times 100\% \quad (1)$$

where $C_{\text{benzene (in)}}$ (ppm) and $C_{\text{benzene (out)}}$ (ppm) are the concentrations of benzene in the inlet and outlet gas, respectively.

3. Results and discussion

3.1. Catalytic oxidation activity of Ce_xMn_{1–x} composite oxides for benzene

The catalytic performances of CeO₂, MnO_x and Ce_xMn_{1–x} catalysts were evaluated in the oxidation of benzene. The catalytic conversion of benzene as a function of the temperature, 100–400 °C, is shown in Fig. 1. It can be acquired that the least active catalyst is CeO₂ followed by MnO_x. Upon addition of Mn to CeO₂, the activity increases monotonically up to a Mn content of 70 at.% and Ce_{0.3}Mn_{0.7} is the most active among all catalysts achieving complete benzene conversion at ca. 375 °C. When the Mn content continuously increases to 90 at.%, Ce_{0.1}Mn_{0.9}, the catalytic activity starts to decrease, even worse than that of Ce_{0.5}Mn_{0.5}, which indicates that the optimum ratio (Ce/Mn) is 3:7 for Ce_xMn_{1–x} catalysts to reach the best benzene conversion. In addition, the MnO_x and CeO₂ catalysts achieve full conversion above 600 °C. They both exhibit the negative activity over benzene comparing with that of Ce_xMn_{1–x}, which is probably related with the formation of the solid solution and the existence of synergistic effect between components for Ce_xMn_{1–x} composite oxides. This illustration will be researched in the following text.

3.2. Characterization of Ce_xMn_{1–x} catalysts

Fig. 2a shows the XRD patterns of the samples in the angular range 20°–70° 2θ . For pure MnO_x, the intensive and sharp diffractions at $2\theta = 23.1^\circ, 32.9^\circ, 38.2^\circ, 45.3^\circ, 49.4^\circ, 55.2^\circ$ and 65.8° could be primarily attributed to Mn₂O₃ (PDF# 89-4836/65-1798). The diffraction peaks at $2\theta = 28.5^\circ, 33.0^\circ, 47.4^\circ, 56.4^\circ$ and 59.2° in the XRD profile of the pure cerium oxide clearly demonstrate the presence of cubic fluorite structure of CeO₂ (PDF# 81-0792). However, the XRD patterns of the Ce_xMn_{1–x} mixed oxide ($x \geq 0.5$) do not show any diffraction of manganese oxides, and only broad reflections due to CeO₂ are observed. This is in good consistent with recent observations that the phase composition of Ce_xMn_{1–x} oxides strongly depended on the molar ratios of manganese and cerium oxides

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