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MnO₂-nanowire@NiO-nanosheet core-shell hybrid nanostructure derived interfacial Effect for promoting catalytic oxidation activity

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ABSTRACT

Nanostructure-derived interfacial effect plays a great role in enhancing catalytic activities. Herein, a MnO₂ nanowires@NiO nanosheets core-shell hybrid nanostructure was successfully prepared by uniformly decorating NiO nanosheets on the one-dimensional MnO₂ nanowires. The physico-chemical properties of the MnO₂ and MnO₂@NiO were characterized by using XRD, BET, SEM, H₂-TPR and XPS techniques. Compared to the single MnO₂ nanowires, the MnO₂@NiO nanocomposite with better low-temperature reducibility and more active surface oxygen species exhibited much better performance in complete oxidation of benzene, giving the temperatures for 100% benzene conversion of 320 °C under the conditions of 1000 ppm benzene in air and space velocity of 120,000 mL g⁻¹ h⁻¹ while the value over pure MnO₂ was 380 °C. The novel hetero-interface constructed between MnO₂ and NiO core-shell nanostructures might make a great contribution on this significantly promoting effect.

1. Introduction

Due to the rapid industrialization and urbanization in developing countries, the air pollution becomes more serious than that previously experienced by the developed nations. Volatile organic compounds (VOCs) emitted from the combustion of fuels, chemical industries and organic solvent consumptions are very popular air pollution all over the world, which have become a great threat for our living environment and human being's health [1–3]. Recently, some extremely severe and persistent environmental problems like haze and ozone pollution happened in China are highly associated with VOCs emissions [4–7]. Developing green chemical processes is highly desirable but now it still needs to find a suitable solution to deal with the current VOCs issue. Catalytic combustion has been proved to be a perfect technique for abatement of VOCs by converting them to non-toxic CO₂ and H₂O. In the past decades, noble metal based catalysts have been applied in the catalytic combustion reactions like automotive catalytic converters and VOCs combustion reactors [8–13]. However, the widely application of noble metal based catalysts is still limited because of some drawbacks like high price, sintering problem and poisoning tendency. In the past few years, some low-cost general metal oxides like MnO₂, Co₃O₄, NiO, ABO₃ (perovskite oxide) have been found to be active for catalytic oxidation of VOCs [14–18]. Compared to the noble metal catalysts, the

activities of low-cost metal oxides are still low so that it has great potential to be improved.

Up to now, a lot of efforts like constructing novel nanostructures and developing porosity have been made for promoting the poor activities of low-cost metal oxides. Among them, the multi-components based oxides usually perform much better than the single oxides which provides an efficient way for establishing highly active catalysts. Two strategies have been applied for developing multi-components based oxides: one is generating solid oxides and another is constructing hetero-interfaces. For solid oxide composites, different metal ions will occupy the related sites in the same crystal structure like MxCo_{3-x}O₄ (M = Mn, Zn and Ni etc) spinel oxide [19–22], ABO₃ perovskite [23–25] and metal-doped CeO₂ [26,27] etc. Due to the diversities of different metal ions, some clear defects will be generated for enhancing the activities of catalyst. Besides, developing the hetero-interfaces between different metal oxides like ZnCo₂O₄@CeO₂ [28], CeO₂@MnO_x [29] and MnO₂@Co₃O₄ [30], provides another way for promoting catalytic performances. Such Putla et al.'s study [29], they used CeO₂ nanocubes as a core to decorate uniform MnO_x nanoparticles shell and the CeO₂@MnO_x composite with novel hetero-interfaces exhibited much better activities in diesel soot oxidation and benzylamine oxidation. Therefore, it is very significant to construct hetero-interface for making advanced high-performance catalysts.

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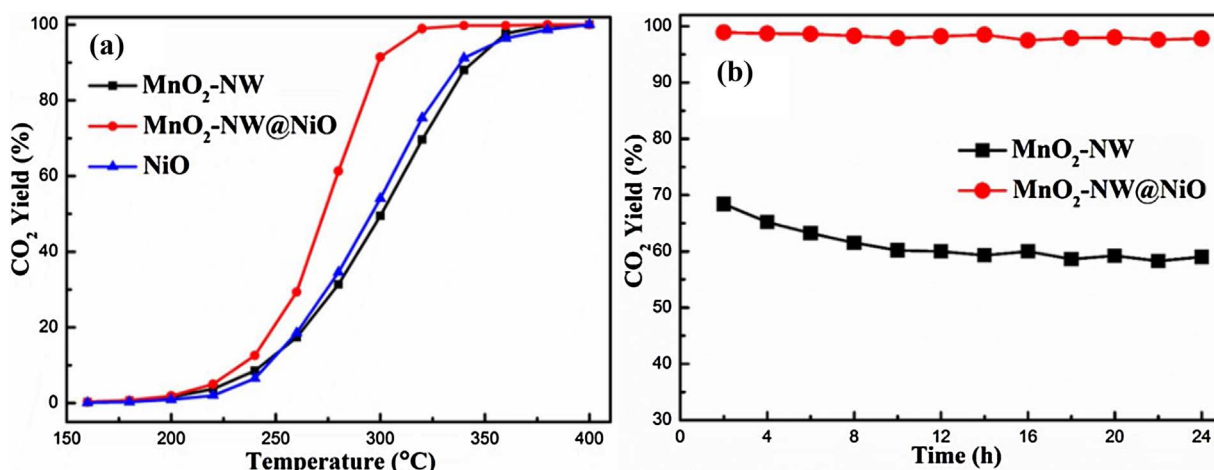


Fig. 1. (a) Catalytic performance MnO₂-NW, NiO and MnO₂-NW@NiO for the abatement of benzene; (b) time-on-stream at 320 °C of MnO₂-NW and MnO₂-NW@NiO (benzene concentration = 1000 ppm in air, and WHSV = 120,000 mL g⁻¹ h⁻¹).

In this study, environment-friendly MnO₂ nanowire was firstly synthesized and then used as a core substance for coating uniform NiO nanosheets shell layer. Because of the numerous hetero-interface between MnO₂ and NiO, the surface chemical properties like reducibility and oxygen species distribution were greatly modified. Compared to the original MnO₂ nanowires, this novel MnO₂@NiO heterogeneous structure showed much better activity in catalytic removal of carcinogenic benzene.

2. Experimental

2.1. Catalysts preparation

A hydrothermal process was applied for synthesizing uniform MnO₂ nanowires [31]. Typically, a solution with volume of 180 mL containing 15 mmol KMnO₄ and 15 mmol NH₄Cl was prepared and then transferred into a 200 mL Teflon-lined autoclave. After hydrothermal treatment at 200 °C for 24 h, the powder was collected by washing and filtering, and then dried at 90 °C for one night. The NiO decoration was carried out by a low-temperature hydrothermal method according to our previous study [30]. Briefly, 0.05 mol Ni(NO₃)₂ and 0.25 mol urea were dissolved in 100 mL solution with water/alcohol volume ratio of 1/1. Then, 500 mg as-prepared MnO₂ powder was added and the obtained solution was put into an 80 °C water bath with strong stirring for 2 h reaction. The powder was filtered and washed then dried at 90 °C for one night. Before catalytic test and characterization, both original MnO₂ nanowires and NiO decorated composite were annealed at 350 °C for 2 h under ambient atmosphere. Moreover, the preparation of pure NiO was followed by the coating process without adding MnO₂. The final samples were denoted as MnO₂-NW, NiO and MnO₂-NW@NiO, respectively.

2.2. Catalysts characterization

A Panalytical X'Pert PRO system was used to do the X-ray powder diffraction (XRD) analysis with 2θ range of 5–90°. Nitrogen adsorption-desorption isotherms were measured at 77 K on an automatic surface analyzer (SSA-7300, Beijing Builder Electronic Technology, China). The morphologies of as-prepared catalysts were determined on a scanning electron microscopy (SEM, JEOL JSM-7001F, Japan). Hydrogen-temperature programmed reduction (H₂-TPR) analysis was carried out in an automated catalyst characterization system (Autochem 2920, Micromeritics, USA). In each test, about 30 mg catalyst was loaded in a U-shaped quartz reactor and the temperature was raised to 750 °C with a ramp of 10 °C min⁻¹ under 5% H₂ in Ar (25 mL min⁻¹). The surface species was analyzed by doing the X-ray

photoelectron spectroscopy (XPS) on an electron spectrometer (XLESCALAB 250Xi, VG Scientific) and all spectra was calibrated by the standard carbon 1s peak at 284.6 eV.

2.3. Catalytic test

Catalytic oxidation test was operated in a continuous flow fixed-bed reactor (i.d. 6 mm) with a weight hourly space velocity (WHSV) of 120,000 mL g⁻¹ h⁻¹. The catalyst usage was 50 mg (40–60 mesh), which was further mixed with 300 mg of quartz sands (40–60 mesh) and placed in the reactor with quartz wool on both sides. The reactant gas was 1000 ppm benzene in air from gas cylinder (Standard gas, Beijing Hua Yuan Gas Chemical Ltd., China). All related gas components were analyzed with a gas chromatograph (Shimadzu GC-2014) integrated with two flame ionization detectors (FID) where one is applied to analysis hydrocarbons, and another one is used to detect CO₂ and CO (CO_x was converted into methane for FID detection with a methanizer). The separations of hydrocarbon and CO_x from target gas exhaust were carried out on a capillary column (Stabilwax-DA, 0.53 mm × 0.5 mm × 30 m) and a Poropak-N column (80/100 mesh 3.2 mm × 2.1 mm × 1.0 m), respectively. The results showed only CO₂ and H₂O were found in the downstream gas products and the carbon balance can be above 99.5%.

3. Results and discussion

3.1. Catalytic performance

Due to the presence of the delocalized electrons, benzene is particularly stable and difficult to oxidize completely, and even low-level benzene exposure may cause serious health problems like cancer and aplastic anaemia [32,33]. Without catalysts, no obvious oxidation reaction could take place under 400 °C so that applying catalysts for removing carcinogenic benzene is highly desirable. As shown in Fig. 1a, the conversion of benzene to non-toxic CO₂ increased with developing the reaction temperature and the complete oxidation can be achieved below 400 °C. For single MnO₂ nanowires, the reaction temperatures for 10% (T_{10%}), 50% (T_{50%}) and 100% (T_{100%}) conversion are 243, 301 and 380 °C, respectively, as listed in Table 1. Over pure NiO, the activity for benzene oxidation is very similar to the performance on pure MnO₂ nanowires. But after coating with NiO species, the MnO₂@NiO core-shell nano-composite oxide presented much better activity, demonstrating the great enhancement of the NiO species. The complete oxidation of benzene can be achieved below 320 °C at a weight hourly space velocity (WHSV) of 120,000 mL g⁻¹ h⁻¹, which is 60 and 80 °C lower than the original single MnO₂ nanowires and single NiO,

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