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One-step synthesis of nanocarbon-decorated MnO_2 with superior activity for indoor formaldehyde removal at room temperature

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ABSTRACT

Indoor formaldehyde (HCHO) pollution receives wide concerns, it is still a challenge to remove low-level HCHO at high gas-hourly space velocity (GHSV) at room temperature required in the indoor environment. Thus, a graphite-like nanocarbon decorated MnO_2 (GLC-MnO_2) was synthesized with a rapid one-step procedure, i.e., a redox reaction between potassium manganese and glucose at 80 °C for 15 min. The as-synthesized GLC-MnO_2 hybrid showed excellent activity for HCHO removal and its mineralization to CO_2 at room temperature. Under the GHSV of 600 L/g_{cat} h, the single-pass removal efficiency was as high as ~92% for 0.5 mg/m^3 HCHO and ~89% for 1.0 mg/m^3 HCHO, which is much higher than those previously achieved by MnO_2-based catalysts. Furthermore, its room-temperature activity was little influenced by the relative humidity in the wide range of 4%–80%. The significantly enhanced catalytic performance of GLC-MnO_2 could be attributed to abundant Mn vacancies and surface adsorbed active oxygen resulted from the coexisted nanocarbon which in-situ formed during preparation of GLC-MnO_2. The presence of nanocarbon may also facilitate electron transfer to form reactive oxidation species for HCHO oxidation. The present study provides a new route to develop efficient catalyst for indoor air pollutants removal.

1. Introduction

Building related illness (BRI) is a widely concerned problem, which is partly caused by the exposure to airborne contaminants such as benzene, toluene and formaldehyde (HCHO) [1–3]. Occupants may suffer from a series of symptoms of diagnosable, including nausea; irritation of eyes, nose and throat; headaches, mental fatigue and even cancer. HCHO is one of the most representative and ubiquitous indoor air pollutants. The International Agency for Research on Cancer (IARC) classified HCHO as carcinogenic to humans (Group 1) based on sufficient evidence in humans and in experimental animals [2,4]. HCHO is an important chemical feedstock. Due to its economic importance and widespread use, many people are exposed to HCHO environmentally and/or occupationally [2].

Hence, in recent years many researchers have tried to develop efficient methods for HCHO removal [5–7]. Among them, catalytic oxidation is considered as the most promising technology without secondary pollution. Supported noble metals (e.g., Pt, Pd, Au and Ag) materials have been widely investigated and showed capability to completely decompose HCHO into CO_2 at room temperature [8–11]. Recently, He's group further increased the activity of supported noble metal (Pt or Pd) with assistance of alkaline metals to improve the dispersion of noble metal on the supporting material [12,13]. However, noble metal catalysts are limited by their high cost and scarcity in the practical application. Alternatively, manganese oxides and other transitional metal oxides have been proven to efficiently decompose HCHO at low temperatures [14,15]. Zhang et al. [16] found that δ-MnO_2 showed the best catalytic activity, achieving almost 100% conversion of 170 ppm HCHO at 80 °C and 35% conversion at 50 °C under the gas hourly space velocity (GHSV) of 100 L/g_{cat} h. Tian et al. [17] synthesized two porous MnO_2 nanomaterials and found the K-OMS-2 nanoparticles could oxidize more than 64% HCHO (460 ppm) into CO_2 at 100 °C and only 10% HCHO converted to CO_2 in the range of 20–40 °C. The poor activity at room temperature hinder the practical application in indoor environment.

Researchers have taken some strategies to promote the catalytic activity of MnO_2, such as doping with transition metals and hybrid carbon. Tang et al. [18] prepared MnO_x-CeO_2 mixed oxide catalyst by several methods and found the MnO_x-CeO_2 obtained by modified co-precipitation method showed ~27% HCHO conversion (HCHO:

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580 ppm) at 60 °C under the GHSV of 21 L/g_{cat} h. Our group [19] synthesized Ce-MnO_2 catalyst with lower Ce/Mn ratio of 1:10, which exhibited the HCHO conversion of ~23% (HCHO: 190 ppm) at 50 °C under the GHSV of 90 L/g_{cat} h. The above transition metal doped MnO_2 achieved complete oxidation of hundreds of ppm HCHO at high temperature (i.e., 100 °C) and low GHSV. Lu et al. [20] assembled the MnO_2 onto the graphene nanosheets forming graphene-MnO_2 hybrid nanostructure, which achieved complete oxidation of HCHO (100 ppm) at 65 °C and 20% at 30 °C under the GHSV of 30 L/g_{cat} h. As a matter of fact, the high concentration HCHO test is far from the real indoor environment, where the HCHO concentration is at low level (e.g., 0.01–1 mg/m^3). Thus, it is more meaningful to evaluate the performance of transition metal oxides such as MnO_2 to remove low-level HCHO at room temperature.

There are few literatures to report the room-temperature degradation of low-concentration HCHO, which is normally encountered in the indoor environment. Shi's group [21] reported that MnO_x coated on honeycomb ceramics exhibited 30% conversion of 1 ppm HCHO under the space velocity of ~48,000 h^{-1} with the total HCHO removal amount of 11.87 mg/g_{cat}. Our group [22] developed the composite MnO_x/granular activated carbon, which achieved 75% conversion of 0.5 mg/m^3 HCHO under the GHSV of 120 L/g_{cat} h during 30 h period. Zhu et al. [19] reported that the Ce-MnO_2 catalyst exhibited the ~53% removal ratio for 0.5 mg/m^3 HCHO under the GHSV of 600 L/g_{cat} h. Wang et al. [23] prepared MnO_x/PET by one-step method, which achieved over 94% conversion of ~0.6 mg/m^3 HCHO within 10 h under the space velocity ~17,000 h^{-1} and relative humidity (RH) ~50%.

To meet the increasing demand on indoor HCHO removal and to improve the activity of catalysts at room temperature and high GHSV condition required by the indoor air cleaning, in the present work, we developed a novel strategy to synthesize a graphite-like nanocarbon decorated-MnO_2 (GLC-MnO_2) hybrid material. The nanocarbon and MnO_2 were simultaneously formed and intermixed by a facile one-step synthesis procedure, i.e., in which potassium permanganate reacted with glucose at 80 °C for 15 min. The GLC-MnO_2 composite material exhibited superior activity at room temperature for low-level (close to real level in indoor environment) HCHO under the high space velocity, reaching ~90% conversion of 0.3–1.0 mg/m^3 HCHO under the GSHV of 600 L/g_{cat} h in a wide range of RH (4–80%).

2. Experimental section

2.1. Synthesis of carbon decorated MnO_2

The carbon decorated-MnO_2 composite was synthesize with a facile reaction between potassium permanganate ($KMnO_4$) with glucose or sucrose. Typically, 1.2 g $KMnO_4$ was first dissolved in 100 mL deionized water in a conical flask to get a purple solution. Then, 0.18 g glucose or 0.34 g sucrose was added into the above purple solution. The conical flask was kept in a water bath at 80 °C for 15 min. Owing to the strong oxidizing property of $KMnO_4$, the glucose or sucrose was oxidized into carbon species, and brown MnO_2 simultaneously formed. The brown precipitate was centrifuged and washed three times with deionized water and then dried in an oven at 105 °C for 12 h. The final products synthesized with glucose and sucrose were referred to as GLC-MnO_2 and AC-MnO_2, respectively.

2.2. Characterization

X-ray diffraction (XRD) analyses were performed on a Rigaku D/max-2500/PC diffractometer (Japan) using Cu Kα radiation by step scanning with a scan rate of 0.2°/s. A field-emission scanning electron microscope (SEM) instrument (S-5500, HITACHI, Japan) was applied to observe the morphology of catalysts. Transmission electron microscopy (TEM) observation was conducted on a JEM-2010F JEOL (Japan) operated at 200 kV. Energy dispersive X-ray spectroscopy (EDX) measurements were performed on a Philips EDAX instrument.

Fourier transform infrared spectroscopy (FTIR) was recorded on a Thermo Nicolet NEXUS-870 spectrophotometer in the wavenumber ranging from 4000–400 cm^{-1}. Raman measurements were carried out with a 532 nm laser and a power of 0.1 mW on a Renishaw Raman spectrophotometer with an inVia reflex optical microscope (Britain). The Brunauer–Emmett–Teller (BET) specific surface area was measured by nitrogen physisorption at liquid nitrogen temperature (77 K) on a Micromeriticis ASAP 2020 analyzer (USA). All the samples were degassed at 250 °C for 4 h before testing. The total specific surface area was determined by a multipoint BET method, and the pore size distributions were calculated using the adsorption branches of N_2 adsorption-desorption isotherms by BJH method. The electron spin resonance (ESR) signals of radicals were examined on a JES-FA200 ESR spectrometer by using 5,5-dimethyl-l-pyrroline N-oxide (DMPO) as a spin-trap reagent for radical measurements. 50 mM DMPO was used to trap the hydroxyl radicals (•OH) and superoxide anion radicals ($\cdot O_2^-$) of the samples (0.12 g/mL), producing the adducts of DMPO-•OH in aqueous suspension and DMPO-O_2^- in methanol suspension, respectively. Electrochemical measurements were carried out with an electrochemistry workstation (PARSTAT2273) in a conventional three-electrode system. A platinum wire was used as a counter electrode; a saturated calomel electrode was used as a reference electrode; and a catalyst modified glassy carbon electrode was used as a working electrode. Before modification, each glassy carbon electrode was sequentially polished with 0.3 and 0.05 μm Al_2O_3 powder, rinsed with water and dried in air. Then 5 mg catalyst powder was mixed with 0.5 wt% Nafion/isopropanol solution. 10 μL of the ink suspension solution was deposited onto the surface of the grassy carbon electrode, and then dried at room temperature. Finally, three electrodes were immersed in 1 M Na_2SO_4 electrolyte for testing. Charge-discharge measurements were performed at a constant current density of 2 mA/cm^2 over the same operating potential range.

X-ray photoelectron spectroscopy (XPS) analyses were performed on a Thermo Scientific ESCALAB 250Xi. The energy positions of the peaks were calibrated by fixing the position of C 1s peak at 284.6 eV. H_2 temperature programmed reduction (H_2-TPR) and O_2 temperature programmed desorption (O_2-TPD) were performed in an AutoChem 2920 instrument (Micromeritics, USA), equipped with a TCD detector. In a typical experiment, ~50 mg sample (40–60 meshes) was placed in a U-type quartz tube. First, the sample was pretreated by helium gas (50 mL/min) for 30 min at 105 °C, then it was cooled down to 40 °C in the helium gas. For H_2-TPR experiment, the sample was reduced by the 5% H_2/Ar (50 mL/min) from 40 to 500 °C with a heating rate of 5 °C/min. The H_2 consumption was detected by the TCD detector. For O_2-TPD experiment, the sample was treated by 5% O_2/Ar (50 mL/min) for 30 min after pretreatment. Then, the sample was purged with helium flow for 30 min to remove the physiosorbed O_2 and stabilize the baseline. Subsequently, the sample was heated from 40 to 800 °C with a heating rate of 5 °C/min in the helium stream (50 mL/min). The O_2 desorption was detected by the TCD detector.

In-situ diffuse reflectance infrared fourier transform spectrometry (DRIFTS) was recorded on a Nicolet 6700 FTIR spectrometer (USA) equipped with a MCT detector and a high temperature reaction chamber with ZeSe windows. The reaction chamber provides all necessary gas in- and outlets and allows for the temperature measurement and control. Catalyst samples were placed in the reaction chamber and the temperatue was controlled at 25 °C. The 30 mL/min of HCHO (~80 ppm) was injected into the chamber with the synthetic air (79% N_2/21% O_2) as the balance gas. The spectra were obtained with a resolution of 4 cm^{-1} and an accumulation of 64 scans, with spectra recorded at time interval of 5 min.