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Modified manganese oxide octahedral molecular sieves M′-OMS-2 (M′ = Co,Ce,Cu) as catalysts in post plasma-catalysis for acetaldehyde degradation

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ABSTRACT

Metal ions-modified cryptomelane-type manganese oxide octahedral molecular sieves M′-OMS-2 (M′ = Co,Ce,Cu) were synthesized and characterized by XRD, BET, EDS, ICP, TEM, XPS, FTIR, H_2-TPR in this work. The obtained materials were supported on Al_2O_3 pellets and investigated for acetaldehyde degradation in a post plasma-catalysis system. The results showed that the introduction of M′-OMS-2/Al_2O_3 catalysts improved acetaldehyde removal efficiency and inhibited ozone formation of plasma significantly, while the intermediates such as acetic acid, amine and nitromethane were suppressed. Co-OMS-2/Al_2O_3 exhibited the best catalytic activity to combine with plasma among all the prepared catalysts. The excellent activity is ascribed to the redox property, oxygen vacancies, oxygen mobility and surface area of catalyst. It can be inferred that, ozone formed in plasma was catalytically dissociated into active oxygen species by metal ions in M′-OMS-2 catalysts and contributed to acetaldehyde oxidation and intermediates removal.

1. Introduction

Volatile organic compounds (VOCs) are considered to be great contributors to environmental pollution and may be toxic to human health. With the increases in emissions, there must be an efficient method for VOCs degradation. Non-thermal plasma (NTP) was widely concerned in last two decades, because it can efficiently oxidize VOCs into carbon dioxide and water at ambient temperature [1]. But this technology also presents some disadvantages, such as the formation of hazardous ozone and low carbon dioxide selectivity [2,3]. To solve these problems, catalysts are usually applied to combine with plasma to form a plasma-catalysis system [4–6].The combination of catalysts and plasma has two ways: when the catalysts are introduced in the discharge zone, it can be called “in plasma-catalysis (IPC)”; when the catalysts are placed downstream of the NTP reactor, it can be named “post plasma-catalysis (PPC)” [7].Compared with IPC, PPC has a simpler structure. And it is much easier for catalysts replacement and beneficial to practical application. In addition, some researchers also found that post plasma-catalysis has less ozone emission than in plasma-catalysis [4]. Therefore, it was well studied in recent years.

Previous studies [8,9] have revealed that manganese oxides could improve VOCs removal efficiency and decompose unwanted byproduct in post plasma-catalysis. However, complete removal of VOCs and ozone for these catalysts is still difficult [9]. We have also reported that quite a few toxic byproducts could still be observed even when MnO_2 catalysts were combined with plasma [10]. Therefore, a more effective catalyst should be developed. On the other hand, as a manganese oxide molecular sieve, cryptomelane (K-OMS-2) has a well-defined 2 × 2 tunnel structure (OMS-2) with K^+ situated in tunnel positions [11]. It presents some excellent properties for catalysis reaction, such as mixed-valency of manganese, easy release of lattice oxygen, mild surface acidity–basicity and porous structure [12]. This material has been proved active in low-temperature catalytic combustion of carbon monoxide and formaldehyde [13,14]. In addition, metal ions (M'^{n+}) can be incorporated into the framework or tunnel sites of cryptomelane to form octahedral molecular sieve M′-OMS-2. These modified metal ions could have an influence on cryptomelane catalytic activity.

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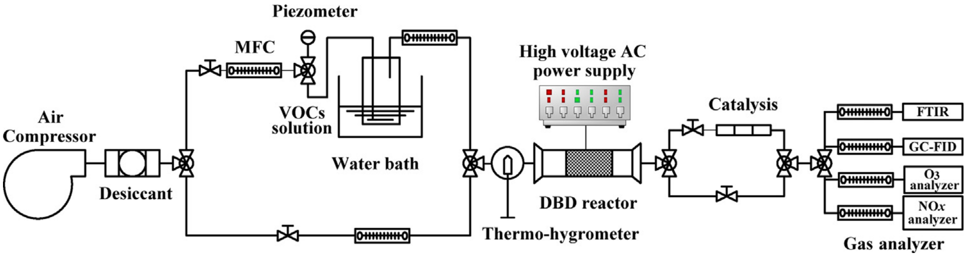

Fig. 1. Experimental set-up of VOCs degradation by plasma-catalysis.

In this work, metal ions-modified cryptomelane-type manganese oxide octahedral molecular sieves M′-OMS-2 (M′ = Co,Ce,Cu) were synthesized and supported on Al_2O_3 pellets. The obtained materials were applied for VOCs degradation in a post plasma-catalysis system. Acetaldehyde was chosen to be removed, because it was one of the principal odor-causing gases from cigarettes [15] and usually used as target pollutant [16,17]. It was found that the introduction of M′-OMS-2/Al_2O_3 catalysts improved acetaldehyde removal efficiency and inhibited ozone formation of plasma significantly. The influence of various metal ions (Co,Ce,Cu) incorporation on M′-OMS-2 catalytic activity was investigated, and the mechanism was also discussed.

2. Experimental set-up

2.1. Catalysts preparation

Cryptomelane (K-OMS-2) was prepared by a reflux method according to literature [18]. $KMnO_4$ solution (13.3 g in 225 ml of distilled water) was added to a mixture of $MnSO_4{\cdot}H_2O$ solution (19.8 g in 67.5 ml distilled water) and concentrated HNO_3 (6.8 ml). The suspension was stirred vigorously and refluxed at 373 K for 24 h. After a filtration, the precipitate was washed with distilled water until neutral pH and dried at 393 K to obtain cryptomelane. In a typical synthesis of M′-OMS-2, 2 g prepared cryptomelane was added to a nitrate salt solution (0.0375 mol Co^{2+}, Cu^{2+}, Ce^{3+} in 50 ml distilled water). The mixture was stirred for 24 h and collected by filtration. The precipitate was washed with water for several times, followed by drying at 353 K for 12 h and calcining at 573 K for 3 h. In order to decrease pressure resistance of catalysts and increase the adsorption of acetaldehyde, M′-OMS-2 was supported on Al_2O_3 pellets (with a diameter of 2 mm). The combination of M’-OMS-2 and Al_2O_3 was a physical mixture by vigorous stir. The details can be described as followed: 3 g of commercial γ-Al_2O_3 pellets and 0.5 g of M′-OMS-2 were mixed together into a 50 ml sealed centrifuge tube. Vibrate the tube manually for 10 minutes, and M′-OMS-2 would be fully stirred with γ-Al_2O_3. Because of porous structure in γ-Al_2O_3, M′-OMS-2 may coat the pores by the adhesion. In this way, M′-OMS-2/γ-Al_2O_3 catalysts were prepared.

2.2. Catalysts characterization

The structure and phase purity of prepared materials were analyzed by X-ray diffraction (D8 ADVANCE, Bruker) with Cu Kα radiation (40 kV, 20 mA). The morphology of M′-OMS-2 samples was observed on a TEM (JEM-2010) instrument with an accelerating voltage of 200 kV. Surface elements analysis of catalysts was determined by energy-dispersive X-ray (EDS). In each sample, six different areas were selected for the EDS analysis, and elements content was calculated by an average value. The chemical composition of catalysts bulk was measured by a coupled plasma-atomic emission spectroscopy (ICP-AES) on an ICAP-6000-Radial instrument. X-ray photoelectron spectroscopy (XPS) data of the samples were obtained from an AXIS-ULTRA-DLD electron spectrometer with Mg and Al radiation at a pressure lower than 10^{-7} Pa. The spectra were calibrated by the carbon peak. Fourier-transform infrared (FT-IR) spectra were recorded in the range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1} on a Nicolet-6700 spectrometer. The samples were mixed with KBr and well grounded before the FT-IR measurement.

The oxygen mobility of M′-OMS-2/Al_2O_3 catalysts was characterized by H_2-TPR. In the experiment, 0.1 g sample was pretreated in high purity nitrogen at 393 K for 2 h, and cooled to room temperature in flow of nitrogen in a fixed bed reactor. And then, the catalyst was heated in a flow of 30 ml/min H_2/N_2 (5 vol.% H_2) mixture with a constant heating rate of 10 K/min. The H_2 consumption was measured by a TCD detector. In addition, surface areas of M′-OMS-2/Al_2O_3 catalysts were determined by BET measurement (Micromeritics, USA, ASAP 2010 M + C).

2.3. Abatement of acetaldehyde by post plasma-catalysis

The experimental set-up of acetaldehyde degradation by post plasma-catalysis was described in Fig. 1. It included an acetaldehyde generator, a plasma-catalysis reactor and an exhaust gas analysis section. Acetaldehyde was evaporated by bubbling with dry compressed air and mixed with air before introduced into

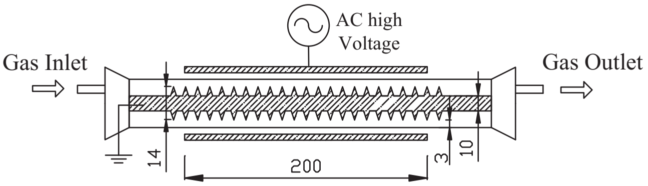

Fig. 2. Schematic overview of NTP reactor.

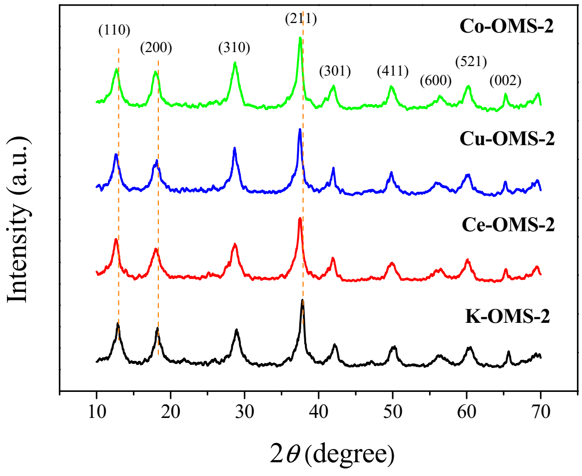

Fig. 3. XRD pattern of M′-OMS-2 samples.