



Catalytic oxidation of gaseous benzene with ozone over zeolite-supported metal oxide nanoparticles at room temperature

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ARTICLE INFO

Article history:

Received 31 October 2014

Received in revised form 10 January 2015

Accepted 14 January 2015

Available online 9 February 2015

Keywords:

Metal oxides

MnO₂/ZSM-5

Catalytic ozonation

Benzene

CO₂ selectivity

ABSTRACT

To improve the capacity for complete oxidation of gaseous benzene by catalytic ozonation, a series of metal oxides catalysts (Mn, Co, Ni, Cu, Zn and Ce) were prepared by impregnation method using ZSM-5 zeolite as the support. The developed metal oxides were highly dispersed in nanosize on the support. Among them, MnO₂/ZSM-5 showed the best activity toward catalytic ozonation of benzene. Benzene can be completely removed even at room temperature and CO₂ selectivity reached 84.7%. MnO₂/ZSM-5 was quite effective due to the production of highly reactive oxidizing species from ozone decomposition. The activities toward benzene catalytic ozonation are closely related to the capacity for ozone decomposition.

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1. Introduction

Volatile organic compounds (VOCs) cause a major air pollution concern since they are involved in various undesirable processes such as: (a) production of photochemical oxidants like ozone in the troposphere that may be toxic to humans and (b) contribution to sick buildings syndrome [1]. Great efforts have been made to remove VOCs before their emission using adsorption [2], absorption, photocatalysis [3,4], biological degradation [5], plasma catalysis [6] and catalytic combustion [7] and some emerging combined processes [8–10]. Among them, catalytic combustion has been intensively studied and used in industrial application. However, it can only proceed at high temperature, which needs heating equipment and energy consumption with the risk of explosion. In addition, the catalysts easily get deactivated due to sintering at high temperature. Thus, it is highly desirable to catalytic oxidation of VOCs at low temperature, preferentially at room temperature.

Catalytic oxidation has been successfully achieved under the help of ozone since it greatly decreases the apparent activation

energy [11]. This process is generally called as catalytic ozonation [12] or ozone-catalytic oxidation [13]. Many of the gaseous streams involved in industrial processes contain VOC at very low concentrations [14] while catalytic oxidation is not suitable for high-concentration VOCs [15]. Catalytic ozonation provides an efficient solution for the abatement of these diluted VOCs. It has been used to destroy toluene [16], benzene [12,17–20], formaldehyde [21], and acetone [22]. Although catalytic ozonation has been proved to be an effective method for VOCs oxidation, there are still some big issues such as catalytic deactivation and poor capacity for the complete mineralization of VOCs. The catalysts quickly got deactivated due to the accumulation of organic intermediates such as weakly bound formic acid and strongly bound surface formate and carboxylates on the catalyst surface [12,17,23,24]. In addition, only partial of mineralized VOCs was converted into CO₂, while much of them was oxidized into toxic CO [17,24]. Some attempts have been made to promote VOCs oxidation and prevent the deactivation of catalyst by the modification of catalyst, supports and operating parameters; however, CO₂ selectivity was still not satisfactory [17,24–26]. These issues greatly prevent the industrial application of catalytic ozonation.

In this study, a series of metal oxide catalysts (Mn, Co, Cu, Ni, Zn and Ce) were prepared by impregnation method using ZSM-5 as the support. The porous ZSM-5 provides high surface area not only for the dispersion of metal oxides during the preparation of catalyst,

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but also for the strong adsorption of benzene and ozone during the reaction. The prepared catalysts were characterized by field scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction, X-ray photoelectron spectroscopy (XPS), inductively coupled plasma (ICP) and Brunauer–Emmett–Teller (BET) surface area. They were used for catalytic ozonation of benzene at room temperature. The catalytic performance over metal oxides was compared to find out the reasons accounting for the good activity toward benzene catalytic ozonation.

2. Materials and methods

2.1. Catalyst preparation

Six percent metal oxide (Mn, Co, Cu, Ni, Zn and Ce) were supported on H-ZSM-5 zeolite (Si/Al = 200, Nankai University Catalyst Co., Ltd) by impregnation method. The acetate precursor was dissolved in deionized water, and the ZSM-5 powder was added into the solution under stirring. After impregnation for 12 h, the slurry was dried in oven at 110 °C for 12 h, and then the dried catalyst was further calcined at 550 °C for 3 h. The obtained powders of catalysts were grounded, tableted, crushed and sieved to 20–40 mesh.

2.2. Catalyst characterization

The morphology of the catalysts was recorded on a Quanta 400F field SEM and FEI Tecnai G2 Spirit TEM. Phase structures were analyzed by XRD (Empyrean, PANalytical) using Cu K α radiation (1.5406 Å). The Mn valence states in the samples were determined by XPS on a spectrometer (ESCALAB 250, Thermo Fisher Scientific) performed with a monochromatic Al K α X-ray source. During XPS measurements, the base pressure of the sample chamber was kept below 2.0×10^{-9} Mbar. Emission lines were calibrated with the C 1s signal at 284.8 eV. The surface area and pore volumes were obtained from a N $_2$ adsorption/desorption analysis conducted at 77 K on a Micromeritics Tristar II 3020 system. The specific surface area was calculated by the BET method. The t-plot method was used to determine the micropore and external surface area as well as the micropore volume. The mesopore volume was derived from the adsorption isotherm according to the Barrett–Joyner–Halenda (BJH) model. The loading of metal was measured by ICP (4300 DV, Perkin Elmer, USA).

2.3. Catalytic test

The schematic diagram of the experimental setup is shown in Fig. 1. Catalytic ozonation of benzene was carried out in a fixed-bed flow reactor at room temperature (25 ± 1 °C). The setup constituted of three parts: gas distribution, reaction and gas analysis system. The gas from a zero air generator is dry and free of CO, CO $_2$ and hydrocarbon. It was used to bubble water and benzene liquid to generate water and benzene vapor, respectively. Ozone was supplied by an ozone generator. The desired benzene and ozone concentration, together with the humidity level, can be obtained by regulating the flow through the mass flow controllers (S49, Horibametron). Benzene, ozone, water vapor and balanced dry air were fully mixed before entering the reactor. The glass tubular reactor (i.d. 11 mm) with 1 g of MnO $_2$ /ZSM-5 catalysts was placed in a water bath at 25 °C. The flow rate through the reactor is 1 L/min, corresponding to a gas hourly space velocity (GHSV) of 4.8×10^4 h $^{-1}$. The inlet benzene, ozone concentration and relative humidity (RH) was fixed at 30 ppm, 450 ppm and 50%, respectively. The concentrations of benzene, CO and CO $_2$ formed from benzene oxidation were monitored on-line by a gas chromatograph (GC 2014, Shimadzu) equipped with two flame-ionization detectors (FID). One FID equipped with an Rt-Q-BOND PLOT column (30 m \times 0.25 mm

i.d, film thickness 10 μ m) was used for benzene analysis, and the injection and detector temperatures were 100 and 250 °C, respectively. The other FID equipped with a packed column (TDX-01, 3 m \times 3 mm) was followed by a methanizer and used to determine the concentrations of CO and CO $_2$. The GC/FID system was calibrated using the standard gas. The gas samples from the reactor system were on-line feed to GC by an automatic gas sampling valve. Residual ozone in gas flow was eliminated by potassium iodide before being introduced into GC to avoid the possible damage of chromatographic column and interference on analysis results. Ozone concentration was measured by an ozone analyzer (202, 2B Technology). CO $_2$ selectivity was defined as the ratio of benzene oxidized into CO $_2$ to the total removed benzene.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. SEM and TEM

The SEM images of the as-synthesized samples were presented in Fig. 2. The particles of all the samples are rod-like. The average particle size is ca. 500 nm in diameter for all samples. The morphology of MnO $_2$ /ZSM-5 and CuO/ZSM-5 (Fig. 2a and d) was rather uniform and their zeolite structure was well kept after metal loading. The other catalysts were slightly agglomerated, as shown in Fig. 2b, c, e and f. The TEM images of the samples were presented in Fig. 3. MnO $_2$ (Fig. 3a), CuO (Fig. 3d) and CeO $_2$ (Fig. 3e) nanoparticles are highly and uniformly dispersed on ZSM-5 with size in the range 10–30 nm while the size of other metal oxides were not uniform.

3.1.2. Surface area and porosity

The textural properties of the prepared samples are listed in Table 1. The BET surface area of ZSM-5 reached a high level of 373.2 m 2 /g, which is very important for the high dispersion of metal oxide nanoparticles, as observed by TEM in Fig. 3. The introduction of metal oxides would lead to the slight reduction of BET surface area, as shown in Table 1, probably due to the blockage of the pores, especially the micropores. The surface area of the catalysts followed the order: ZSM-5 > CuO/ZSM-5 > CoO/ZSM-5 > CeO $_2$ /ZSM-5 > NiO/ZSM-5 > MnO $_2$ /ZSM-5 > ZnO/ZSM-5; on the contrary, their mesopore volume was slightly increased except ZnO/ZSM-5. The pore size of mesopores ranges from 2 to 50 nm. Some of the macropores of ZSM-5 were filled by metal oxides on the supported ZSM-5, leading to the increased amount of mesopores. Compared with Fig. 3 and Table 1, larger mesoporous volume can be observed over supported ZSM-5 with the metal oxides of larger particle size. The actual loadings of metals were added in Table 1. They are a little lower than the theoretic values due to the loss of metal during the preparation.

3.1.3. XPS

Since the prepared transition metal oxides (Mn, Co, Cu and Ni) exhibit better catalytic activity (shown in Fig. 6) and generally have diverse valence states, XPS was employed to investigate their valence. Their XPS spectra are displayed in Fig. 4. The XPS spectra of Mn 2p are shown in Fig. 4a. Two distinct peaks at binding energies (BEs) of 642.9 and 654.3 eV with the spin-orbital splitting of 11.4 eV appeared in the Mn 2p core-level spectrum, indicating that the obtained MnO $_x$ mainly exists in MnO $_2$ [27,28]. In some study, the oxidation states of MnO $_x$ were 3+ or the mixture of 2+–4+, probably due to their difference in MnO $_x$ loading amount, preparation method or structural properties of supports. The XPS spectra of Co 2p are shown in Fig. 4b. The Co 2p $_{3/2}$ binding energy appears at near 780.4 eV, which is ascribed to Co $^{2+}$ [29,30]. The XPS spectra of Cu 2p are shown in Fig. 4c. The Cu 2p $_{3/2}$ binding energy appears at near 934.5 eV, which is ascribed to Cu $^{2+}$ [31]. The XPS spectra of Ni 2p

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