Synergistic Catalytic Effects of Fe-Based Bimetallic Nanocatalyst and Non-thermal Plasma on Removal of Acetaldehyde

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Abstract. Acetaldehyde is a typical volatile organic compound (VOC) releasing from food waste. Fe-based bimetallic nanocatalyst combined with non-thermal plasma (NTP) for acetaldehyde catalytic oxidation is an efficient and energy-saving method. The pore structure parameters of FeCoOₓ/TiO₂, FeCeOₓ/TiO₂ and FeMnOₓ/TiO₂ bimetal nanocatalysts were analyzed quantitatively by N₂ adsorption-desorption test. The phase composition and active element valence of three Fe-based bimetallic nanocatalysts were analyzed and compared by XRD. The experimental data showed the microporous and mesoporous structures of FeCoOₓ bimetal oxides were more complete, and the elemental dispersibility was better. In the non-thermal plasma-catalyst (NTPC) system, the introduction of Fe-based bimetallic nanocatalyst significantly improved the catalytic efficiency of acetaldehyde and catalytic selectivity of CO₂. FeCoOₓ/TiO₂ had the best performance among these three nanocatalysts with acetaldehyde catalytic conversion rate reaching 87.5% and CO₂ selectivity higher than 90%, under the specific energy density (SPD) of 180 J L⁻¹, which was less than half of the energy consumption in a single non-thermal plasma catalytic reaction. By optimizing the microstructure and elemental composition of Fe-based bimetallic nanocatalyst, it is expected to be an effective method to improve catalytic performance, which is also a promising approach for improving VOCs removal efficiency and reducing energy consumption.

1. Introduction
Volatile organic compounds (VOCs), as important components of air pollutants, have become the focus of the atmospheric environment study all over the world[1, 2]. Acetaldehyde, as a typical VOC component of food waste exhaust, not only affects the ecological environment, but also causes people's strong discomfort and seriously endangers human health. Reducing the content of acetaldehyde can effectively improve health and quality of life[3]. Various methods, including adsorption, catalytic oxidation and photocatalytic, have been used to reduce high concentration of VOCs from waste gas. Traditional methods are not suitable for the removal of low concentration VOCs. The overall catalytic efficiency of the traditional process does not reach the active window due to VOCs concentration low, resulting in a sharp increase in the reaction cost of VOCs per unit concentration[4]. Therefore, it is necessary to develop alternative technologies to make up for the defects of traditional technologies and successfully remove low-concentration VOCs from food wastes.
Non-thermal plasma (NTP) technology provides an advanced method for the efficient removal of VOCs[5]. Oxygen and other oxidants produced by plasma can oxidize low-concentration VOCs in food waste. In the process of VOCs removal using NTP technology, the production of highly reactive and toxic by-products such as O₃ and NOₓ are considered a problem[2]. O₃ is the most undesirable by-product in NTP exhaust emissions, and its thermal stability is above 250°C. Thus O₃ has strong oxidation[6]. The residual O₃ can damage equipment or harm human health. VOCs can be removed by the combination of catalyst and NTP, and the concentration of undesirable by-products produced by NTP catalysis can be reduced. The formation concentration of O₃ depends on the location of catalyst in NTP catalytic reactor. It can be divided into two types according to the relative positions between catalyst and the plasma area: catalyst positioning in the plasma area is called in plasma catalysis (IPC), and catalyst positioning in the downstream of the plasma area is called post-plasma catalysis (PPC)[7]. PPC technology has high performance of O₃ removal. In PPC process, various catalysts or carriers are widely used to remove VOCs, such as zeolite, TiO₂, SiO₂ and Al₂O₃[4]. A variety of different types of active metal elements have been fully used as the main active materials for catalytic oxidation of VOCs, such as noble metals of Pt, Pd, Au, Ag, and transition metal elements of Mn, Fe, Co, Ni and Cu[4, 5, 8]. These active metal elements are used as doping components of the catalyst to provide additional catalytic active sites. Iron, a cheap metal, is widely used as an impregnating material for VOCs removal. Meanwhile, due to the high temperature window of VOCs catalytic reaction, the practical applications of high-temperature catalysts are limited to automobiles and factories. Thus, the high cost of operating temperatures limits the applicability of catalytic processes for the removal of VOCs from food waste[3]. In view of this, PPC technology combined with Fe-based catalysts has potential applications in the removal of low-concentration VOCs from food waste.

In this study, we established a non-thermal plasma-catalyst (NTPC) system to remove VOCs from food waste. In order to improve the economic feasibility, Fe-based bimetal nanocatalysts were developed to combine with NTP to obtain higher catalytic activity for typical VOCs in food waste and to work under lower energy consumption. Fe-based bimetal nanocatalysts supported by nano-TiO₂ doped with Co, Ce or Mn were prepared by ultrasonic assisted hydrothermal method. The effect of Specific power density (SPD) on VOCs in food waste was evaluated by comparing the removal efficiency of acetaldehyde in NTPC system, the catalytic selectivity of CO₂, and the generation concentration of O₃ and NOₓ.

2. Materials and Methods

2.1. Fe-based Bimetallic Nonacatalysts Preparation

Three different Fe-based bimetal nanocatalysts were prepared by ultrasound-assisted hydrothermal method. Fe(NO₃)₃·9H₂O (analytically pure 99.9%, Macklin, China), Co(NO₃)₂·6H₂O (analytically pure 99.99%, Macklin, China), Ce(NO₃)₃·6H₂O (analytically pure 99.9%, Macklin, China), and Mn(NO₃)₃·6H₂O (analytically pure 98%, Macklin, China) were used as precursors of iron oxides, cobalt oxides, cerium oxides, and manganese oxides, respectively. The nano-TiO₂ particles as the catalyst carrier were prepared with the precursor tetra-butyl ortho-titanate (PTE). Fe(NO₃)₃·9H₂O and Co(NO₃)₂·6H₂O were dissolved orderly into deionized water at room temperature. Under the condition of ultrasonic wave and continuous magnetic agitation, appropriate amount of ethanol was added. The stainless steel autoclave with polytetrafluoroethylene (PTFE) lining was heated at 175°C for 12 hours. Then the autoclave was cooled to the ambient temperature and the TBOT was added to the above mixed solution. Under the action of ultrasonic wave, it was continuously stirred until the precipitation formed. The autoclave was aged for 4 hours at 175°C again. Finally, the mixture was collected after repeated centrifugal washing. The precipitation was dried at 135°C for 10 h and calcined at 450°C for 3.5 h. The nanocatalysts prepared were ground and sieved for the catalytic reaction of VOCs and the physicochemical properties analysis of catalyst microstructure. The obtained nanocatalyst was named FeCoOₓ/TiO₂ with a molar ratio of Fe:Co:Ti at 1.5:1.0:17.5. FeCeOₓ/TiO₂ or
FeMnO$_x$/TiO$_2$ nanocatalysts was prepared by substituting Ce(NO$_3$)$_3$·6H$_2$O or Mn(NO$_3$)$_3$·6H$_2$O for Co(NO$_3$)$_2$·6H$_2$O, respectively.

2.2. Fe-based Bimetallic Nonacatalysts Characterization
The surface area and pore size distributions of three Fe-based bimetallic nonacatalysts were tested using a Tristar II(3020) micropore analyzer (Maxon, Illinois, USA). The adsorption isotherm of N$_2$ on the nanocatalyst was measured at 77 K after vacuum degassing at 623 K for 10 h. Brunner-emettteller (BET) and Barrett Joyner Halenda (BJH) were used to calculate the specific surface area and pore size distribution of the nanocatalysts, respectively. The characteristic peaks of X-ray diffraction (XRD) were tested by the D-8 Advance Analyzer (Bruker, Frankfurt, Germany). Under the radiation of Mo K$_\alpha$, the diffraction intensity was 10°~ 90°, the step length was 0.02°, and the point counting time was 1 s. The characteristic peaks of the XRD patterns were compared with the ICDD data to distinguish the elemental phases in the nanocatalysts.

2.3. Experimental setup
The NTPC system schematic diagram was shown in Figure 1, including a gas generator of aldehyde, NTP catalytic reactor and exhaust detection. Carrier gas N$_2$ is supplied from the standard gas in the cylinder. All gas flows were regulated by the mass flow controller. Aldehyde was generated from the evaporator by pumping a certain amount of liquid aldehyde regularly. The concentration of aldehyde in the reaction gas mixer was adjusted by modifying the carrier gas flow rate. A certain amount of water vapor was pumped into the gas mixing chamber with an internal volume of 10 L to control the relative humidity of the reaction gas, which was monitored by the humidity meter. Before each concentration test, the aldehyde concentration in the mixing chamber were stable for 30 minutes.

Figure 1. Schematic diagram of NTPC system. 1, O$_2$ standard gas; 2, N$_2$ standard gas; 3, mass flowmeter; 4, shutdown valve; 5, injection pump shutdown valve; 6, evaporator; 7, water carrier; 8, gas mixer; 9, non-thermal plasma reactor; 10, nanocatalysts; 11, power generator; 12, flue gas analyzer; 13, record system; 14, gas washing bottle.

The plasma reactor was designed by dielectric barrier discharge (DBD) with quartz tube as discharge barrier. The length of the quartz tube was 300 mm, the inner diameter was 10.8 mm, and the wall thickness 0.6 mm. A copper rod with a diameter of 3.2 mm and a length of 300 mm was placed in the center of the quartz tube as the high voltage electrode of the DBD plasma reactor. And a piece of copper mesh with width of 25 mm was wrapped on the outer wall of quartz tube as the low voltage electrode. CTP-2000(Nanjing Suman) AC power converter was the discharge energy generator with accurate control of voltage, current and frequency. The gas hourly space velocity (GHSV) was 300000 mL·(g·h)$^{-1}$, and the mass of Fe-based bimetallic nonacatalyst used during activity test was 0.2 g in 40-80 mesh.

The import and export concentrations of aldehyde in the reactor were measured by Ultra Ray 3000 VOCs analyser (RAE, California, USA). CO$_2$ (CO$_2$ and CO) conversion rate were supervised by a portable special gas analyzer TD500-SH (Shouhe, Beijing, China). The removal efficiency (Re), CO$_2$ selectivity ($S_{CO2}$) were calculated as follows:
Re = \frac{[C_2H_4O]_{in} - [C_2H_4O]_{out}}{[C_2H_4O]_{in}} \times 100\% \quad (1)

SCO_2 = \frac{[CO]}{[CO]_2} \times 100\% \quad (2)

Where \([C_2H_4O]_{in}\) and \([C_2H_4O]_{out}\) were the import and export concentrations of aldehyde, respectively. \([CO]\) and \([CO_2]\) were the concentrations of CO and CO_2 downstream of NTPC reactor. In order to ensure the accuracy of the experimental results, each condition was repeated more than three times.

3. Results and Discussion

3.1. Characterization of Fe-based Bimetallic Nonacatalysts

Figure 2 exhibited the pore structure characteristics of the three Fe-based bimetallic catalysts in terms of specific surface area (S_a), total pore volume (V_p) and average pore size (D_p). The results of S_a, V_p and D_p showed that FeCoO_x/TiO_2 had better pore structure characteristics than FeCeO_x/TiO_2 and FeMnO_x/TiO_2. The S_a of FeCoO_x/TiO_2 was 36.8% higher than that of FeCeO_x/TiO_2 and 73.8% higher than that of FeMnO_x/TiO_2. In the V_p comparison, the V_p of FeCoO_x/TiO_2 was 21.5% and 25.5% larger than that of FeCeO_x/TiO_2 and FeMnO_x/TiO_2, respectively. The D_p of FeCoO_x/TiO_2 was 39.6% lower than that of FeCeO_x/TiO_2 and 54.9% lower than that of FeMnO_x/TiO_2. It could be proposed that the bimetallic oxides of FeCoO_x, FeCeO_x and FeMnO_x could be well dispersed on the surface of nano-TiO_2 carrier. It could be seen that the bimetal oxide of FeCoO_x had more significant effects on promoting micropore formation, increasing S_a and V_p, and reducing D_p. Although Fe-based bimetal oxides of FeCoO_x, FeCeO_x and FeMnO_x caused some changes in S_a, V_p and D_p of nanocatalyst, the pore structure characteristics data remained at the same order of magnitude. This was due to the large proportion of mesopore in the nanocatalysts[3]. Although the formation of micropores could improve the pore structure characteristics, it was inhibited to some extent by the presence of mesopores in nanocatalyst[1].

The XRD results of Fe-based bimetallic nanocatalysts were shown in Figure 3. The different phase compositions of the three nanocatalysts were searched and matched by MDI Jade 6.5 software. In the XRD results of FeCoO_x/TiO_2, FeCeO_x/TiO_2 and FeMnO_x/TiO_2, anatase TiO_2 showed strong and significant diffraction peaks at 2θ = 25.3°, 37.8°, 43.0°, 53.9°, 62.7°, 68.8°, 70.3°, and 75.1°, corresponding to the typical diffraction peaks in XRD pattern of ICDD[9]. However, in different nanocatalysts, the diffraction angles of characteristic peaks of anatase TiO_2 were not the same. The results showed that compared with FeCeO_x/TiO_2 and FeMnO_x/TiO_2, the diffraction peaks of nano-TiO_2 in FeCoO_x/TiO_2 sample were weaker and wider, indicating the FeCoO_x doping reduced the crystallinity of TiO_2. In FeCoO_x/TiO_2 nanocatalyst, the diffraction angles of anatase TiO_2 peaks were also the smallest. This could be due to the stronger interaction between FeCoO_x and nano-TiO_2 than that between FeCeO_x (FeMnO_x) and nano-TiO_2[8]. There were no obvious characteristic peak reflection of FeO_x, CoO_x, CeO_x and MnO_x in the test samples, indicating high dispersion of active substances on the nanocatalyst surface. It could also be due to forming particles that are too small to be recognized[10].
3.2. Aldehyde Catalytic Efficiency and CO₂ Selectivity

Under the same experimental conditions, the effects of different SPD on catalytic oxidation of aldehyde were studied. As shown in Figure 4, Fe-based bimetallic nanocatalysts could further promote plasma catalysis of aldehyde. The catalytic conversion of aldehyde was over 80% at about SPD 500 J·L⁻¹ in single plasma catalytic reaction. After adding Fe-based bimetallic nanocatalysts, the removal rate of aldehyde was significantly improved. FeCoOₓ/TiO₂ sample had the best performance among these three nanocatalysts. Under the condition of SPD 180 J·L⁻¹, its catalytic oxidation rate reached 87.5%, which was less than half of the energy consumption in single plasma catalytic reaction.

In addition, compared with the single plasma-catalysis reaction, the combination of NTP with Fe-based bimetallic nanocatalysts also significantly improved the CO₂ selectivity, as shown in Figure 5. The selectivity of CO₂ at 500 J·L⁻¹ was only 61.3% in a single plasma catalytic reaction. In contrast, under the condition of SPD 500 J·L⁻¹, FeCoOₓ/TiO₂ sample showed the CO₂ selectivity of 93.6%. Therefore, it could be concluded that aldehyde was more easily degraded and completely oxidized to CO₂ under the catalytic reaction of plasma coupled with Fe-based bimetallic nanocatalysts. These results also showed that Fe-based bimetallic nanocatalysts played an important role in the catalytic oxidation of VOCs and the formation of oxidation products, which could also improve the energy utilization efficiency.

4. Conclusions

The catalytic performance of Fe-based bimetallic nanocatalysts combined with NTP on aldehyde catalytic oxidation was systematically studied by catalyst characterization analysis and catalytic efficiency comparison. The results of N₂ adsorption-desorption experiments showed that Fe-based bimetallic oxides of FeCoOₓ, FeCeOₓ, and FeMnOₓ changed Sₐ, Vₚ, and Dₚ of nanocatalysts, but the data were at the same order of magnitude. XRD results exhibited the three Fe-based bimetallic nanocatalyst all had strong and obvious diffraction peaks of anatase TiO₂. The active species of FeOₓ, CoOₓ, Co₂O₃, and MnOₓ had high dispersity on the catalyst surface.
In the catalytic performance tests, the introduction of Fe-based bimetallic nanocatalysts could significantly improve the catalytic conversion rate of aldehyde. At about SPD 180 J·L⁻¹, the removal efficiency of FeCoOₓ/TiO₂ nanocatalyst for aldehyde reached 87.5%, which was less than half of the energy consumption in single plasma catalytic reaction. Meanwhile, FeCoOₓ/TiO₂ nanocatalyst also showed the best CO₂ selectivity, reaching over 90%. In general, we obtained a clearer understanding of the catalytic performance of Fe-based bimetallic nanocatalysts in combination with NTP for the catalytic oxidation of aldehyde, and proposed a new direction for optimizing the composition of nanocatalysts to improve the catalytic efficiency and selectivity of VOCs.

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