Effect of the composition and surface functional groups of Fe-Ni bimetal oxides catalysts in catalytic ozonation process

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ABSTRACT

In this study, Fe-Ni bimetal oxides (Fe-NiO\textsubscript{x}) catalysts were used to activate O\textsubscript{3} in a heterogeneous system. This research focuses on the degradation mechanism of dimethyl phthalate (DMP) by adding Fe-NiO\textsubscript{x} catalyst which activated the O\textsubscript{3} decomposition to generate strong oxidative hydroxyl radicals (\textbullet OH). The experimental results showed that O\textsubscript{3}/Fe-NiO\textsubscript{x} catalyst calcinated under 500 °C achieved 47.75% higher DMP removal efficiency when compared with ozonation of DMP without the catalyst. Besides, control experimental data suggested that the adsorption of DMP was negligible (<4%) for Fe-NiO\textsubscript{x}. Thus, it was concluded that the removal of DMP was due to the catalytic ability of Fe-NiO\textsubscript{x} rather than the adsorption of DMP onto the catalysts. Moreover, the unsatisfactory performance of Fe-NiO\textsubscript{x} catalysts calcinated in the presence of N\textsubscript{2} revealed that O\textsubscript{2} played an important part in affecting the crystalline degree of catalysts during the synthesis process. Meanwhile, the X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR) characterization analysis indicated that calcination temperature was an indispensable factor that influenced the relative content of Ni\textsuperscript{2+} and hydroxyl groups (–OH) in Fe-NiO\textsubscript{x} catalysts. Furthermore, the relative content of Ni\textsuperscript{2+} had a greater effect on catalysts’ activity because of the electron transfer between multivalent metal states.

Key words | bimetallic oxides, dimethyl phthalate, hydroxyl radicals, ozone, nickel ferrite

INTRODUCTION

Nowadays, organic pollutants in wastewater are so complex that it is difficult to remove them by traditional water treatment methods. Some organic pollutants in wastewater may increase health risks when discharged to natural water systems due to their toxicity and persistence (Maddila et al. 2014). Aiming to degrade various organic contaminants, advanced oxidation processes (AOPs) have been investigated extensively by using a series of physical chemistry methods to activate ozone, peroxide, persulfate, and peroxy-monosulfate to produce reactive radicals, such as hydroxyl radicals (\textbullet OH) and sulfate radicals (\textbullet SO\textsubscript{4}).

Recently, heterogeneous catalytic ozonation has attracted increasing attention owing to its potential higher effectiveness in degrading refractory organic pollutants and lower negative influence on water quality (Trapido et al. 1997; Xing et al. 2008; Maddila et al. 2013; Nie et al. 2014). It can be directly applied in real water treatment without any auxiliary thermal or light set-up by adding catalysts into a reaction system in order to enhance the generation of hydroxyl radicals (\textbullet OH), the less selective oxidants (Andreozzi et al. 1996; Legube & Leitner 1999).

Based on previous research, metal elements are commonly used to prepare solid catalysts for heterogeneous
systems because metal oxides can be easily separated from reactant water making it more applicable for practical applications (Sanchez-Polo et al. 2006). As a whole, iron, nickel, copper, and cobalt, etc., are the most common elements used to prepare catalysts (Pines & Reckhow 2003; Zhao et al. 2009; Yuan et al. 2016). For instance, TiO₂, ZnO and MnO₂ have shown excellent catalytic performance in catalytic ozonation (Song et al. 2010). Therefore, the combination of different metal elements to improve the activity of metal oxide catalysts has attracted researchers’ attention. According to previous literatures, the application of bimetallic oxides during the ozonation process is remarkable. Bimetal catalysts, such as Ce-V, Pd-Ce and Fe-Ni, all have high potential in dechlorination or catalysis of ozone and peroxymonosulfate due to their special bimetallic structure (Li et al. 2012; Ren et al. 2012; Maddila et al. 2014; Ren et al. 2015). Moreover, it is reported that the composition and surface groups are changed with different preparation conditions during the synthesis process (Chan & Barteau 2005; de Diego et al. 2005; Mazille et al. 2009).

In this study, the effect of calcination temperature of Fe-Ni bimetal oxides (Fe-NiOₓ) catalysts and the interaction among catalysts, dimethyl phthalate (DMP) and ozone (O₃) were analyzed. DMP was selected as the probe to evaluate the property of the catalysts. The composition and chemical state of different Fe-NiOₓ catalysts were identified by powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. The surface groups were investigated in detail by Fourier transform infrared spectroscopy (FT-IR) while the effect of temperature was determined by thermal gravity analysis (TGA) and derivative thermogravimetric analysis (DTA).

**METHODS**

DMP was purchased from Sigma-Aldrich (USA). Nickel nitrate (Ni(NO₃)₂·6H₂O), ferric nitrate (Fe(NO₃)₃·9H₂O), tert-butyl alcohol (TBA), sodium dihydrogen phosphate (NaH₂PO₄·2H₂O), disodium hydrogen phosphate (Na₂HPO₄·12H₂O) and sodium sulfate (Na₂SO₄) were obtained from Chengdu Kelong Chemical Reagent Company (Chengdu, China). The fresh eggs were bought from a local market (Chengdu, China). All chemicals were analytical grade and the experimental solutions were prepared with ultra-pure water. The solution pH was adjusted by NaH₂PO₄-Na₂HPO₄ buffer.

Fe-NiOₓ catalysts were prepared by the sol-gel process with egg white (Maensiri et al. 2007; Ren et al. 2012). Aqueous solution of nickel nitrate and ferric nitrate was slowly added into fresh egg white with constant stirring. The sol mixture was heated by a water bath at 80 °C for half an hour and then placed in a furnace until the dried precursor was obtained. The dried precursor was ground up and calcined for 2 hours by blowing air. Finally, the product was crushed into powder by agate mortar. Catalysts were calcined at 400, 500, and 600 °C with mol ratio c(Fe³⁺) : c(Ni²⁺) = 1:4.

The composition of metal oxides in catalysts was observed by XRD using a DX-1000 diffract meter. The chemical state of elements was analyzed by Auger electron spectroscopy with a XSAM 800 system. Surface elemental stoichiometry was determined from XPS spectral area ratios. Surface groups on catalysts were identified by FT-IR which was recorded on a Nicolet 6700 spectrometer in the range of 400–4,000 cm⁻¹ using the KBr disk method. The influence of temperature was investigated by TGA using a Mettler Toledo TGA/DSC2 and the heating rate was 10 °C/min.

The ozonation experiments were performed at room temperature (18 ± 1 °C) in a 500 mL flat-bottomed flask. Ozone was synthesized by an ozone generator (HTU-500SE, Azco Industries Limited, Canada) using dry oxygen as the supply gas. The ozone concentration in water was determined using a UV-vis spectrophotometer (UV-1800, Mapada Instruments, China) (Valdes et al. 2008). The pH was adjusted to 7.1 by phosphate buffer. Then 0.05 g catalyst powder and 0.5 mL DMP stock solution (440 mg/L) were immediately added to the ozone solution (0.5 mg/L). A magnetic stirrer was used to ensure maximum contact of substrates. Samples were immediately quenched into excess Na₂SO₃ solution to remove residual ozone after withdrawal from the reactor at different time intervals.

The concentration of DMP was analyzed by a high-performance liquid chromatograph (HPLC, Waters e2695) equipped with a Waters C18 column and UV detector at 228 nm. The mobile phase (1.0 mL/min) was a mixture of methanol and ultra-pure water (V/V = 50/50). The
experiments aiming to investigate O₃ decomposition were carried out under the same control conditions without DMP in the system. At given time intervals, the concentration of residual ozone in the aqueous solution was measured using the indigo method (Bader & Hoigne 1984).

RESULTS AND DISCUSSION

XPS characterization

Figure 1 shows the XPS spectra of Fe (a), Ni (b) and O (c) in catalysts calcinated at 400, 500, and 600°C before and after ozonation. The binding energy at 710.9 and 724.8 eV in Figure 1(a) was assigned to NiFe₂O₄ (Ren et al. 2012). As there was no significant change after the reaction, the results indicated that the iron ion did not experience redox reaction.

In Figure 1(b), the high-resolution Ni2p spectra displayed Ni²⁺ at 861.4 eV and Ni³⁺ at 855.4 eV (Wang et al. 2010; Ren et al. 2012). Catalysts calcinated at 500°C with air had the highest ratio of Ni²⁺ before reaction and it decreased from 74.26% to 49.31% after reaction. The change between Ni²⁺ and Ni³⁺ could have resulted from the oxidation condition provided by O₃ in the system (Ren et al. 2015). The electron transfer between Ni²⁺ and Ni³⁺ which indicated the involvement of the Ni²⁺-Ni³⁺-Ni²⁺ redox process during the reaction explained the reason why the catalysts could enhance catalytic ozonation (Ren et al. 2012).

Figure 1 | XPS spectra of different catalysts before and after experiments: (a) Fe, (b) Ni, (c) O.
From Figure 1(c), it was revealed that O1s spectra was characterized with three peaks: the peak at the lower binding energy (529.4–530.0 eV) was ascribed to lattice oxygen; the peak at 531.25–531.8 eV was assigned to the hydroxyl groups (–OH) and the peak at the higher binding energy (above 533.0 eV) was associated with adsorbed molecular water (Machocki et al. 2004; Dai et al. 2012). The ratio of –OH in catalysts with air blown rose from 30.30% to 37.75%, when calcination temperature increased. After reaction, the ratio in the catalysts calcinated under 500 °C decreased from 35.17% to 30.96% and a new peak appeared due to adsorbed molecular water.

Overall, the Figure 1 results showed that though the relative ratio of –OH in the catalysts calcinated at 500 °C by blowing N2 was very high, all peaks were much weaker, which suggested that there were less metal oxides in the catalysts. Thus, it could be inferred that O2 played an important role in the formation of NiFe2O4 and –OH.

**TGA characterization**

In order to investigate the effect of temperature of catalysts on its decomposition and crystallization, the precursor was subjected to TGA-DTA. In Figure 2, continuous weight loss is shown, owing to the combustion of the organic matter and the loss of trapped water in the egg white during the catalysts synthesis. The peaks of the DTA curve were observed when the organic matter in the precursor burnt out (Maensiri et al. 2007). When the temperature rose to 600 °C, the wave disappeared because all the organic matter was burnt out.

**XRD characterization**

The XRD pattern of all Fe-NiOx catalysts is shown in Figure 3. It shows that catalysts calcinated at 500 and 600 °C had NiFe2O4, NiO and Ni2O3 phases. And the peaks at 2θ = 37.4°, 43.4° and 63.1° were sharper under rising calcination temperature, which suggested that Fe-Ni mixed oxides were crystallized better (Muruganandham & Wu 2008). However, the catalysts synthesized at 500 °C under N2 atmosphere had weaker intensity of peaks because the combustion of organic matter in the precursor was incomplete in the absence of O2. To combine with Figure 1 though, the ratio of every phase was nearly the same, the different crystalline degree of catalysts under various calcination temperatures influenced the catalytic performance. Thus, it was proved that calcination temperature affected the crystalline state of metal oxides and O2 played an important role in their formation process.

**FT-IR characterization**

Figure 4 reveals the FT-IR spectra of catalysts calcinated at 400, 500 and 600 °C before experiments. Three hydroxyl group absorption bands emerged in all curves. The first peak was at 3,425 cm⁻¹, corresponding to the stretching of
the hydrogen-bounded M-OH (M: Fe and Ni) (Lv et al. 2013; Zhao et al. 2013). The second peak was between 1,628 and 1,640 cm\(^{-1}\) due to the bending vibrations of the associated water (Maddila et al. 2014) and the third peak was at nearly 3,205 cm\(^{-1}\) reflecting the hydrogen-bonded water (Zhao et al. 2013). Additionally, the absorption band around 600 cm\(^{-1}\) corresponded to the intrinsic stretching variations of metal elements at tetrahedral sites in NiFe\(_2\)O\(_4\) (Florea et al. 2013). In contrast, the peak intensities of catalysts prepared with N\(_2\) were weaker, which indicated that O\(_2\) had a significant impact on the formation of surface groups.

### Catalytic ability of Fe-NiO\(_x\) oxides

The catalytic activity experiments within 10 min were carried out with different catalysts and the results are presented in Figure 5. It is noted that the removal efficiency of DMP was significantly enhanced with the addition of Fe-NiO\(_x\) catalysts calcinated at 500 \(^\circ\)C, which achieved nearly 86.83% DMP degraded in 10 min in the Fe-NiO\(_x\)/O\(_3\)/DMP system. Only 47% and 46% DMP was degraded with catalysts calcinated at 400 \(^\circ\)C and 600 \(^\circ\)C under the same experimental conditions. Meanwhile, approximately 44% of DMP was removed during the ozonation process activated by the catalysts prepared with N\(_2\).

Both results of catalysts calcinated at 400 and 500 \(^\circ\)C in Figures 3 and 4 indicated that the better crystalline degree of catalysts led to more DMP being degraded. Besides, results of catalysts calcinated at 500 and 600 \(^\circ\)C in XPS analysis showed that the catalysts calcinated at 500 \(^\circ\)C had more Ni\(^{2+}\) which contributed to stronger catalytic power on O\(_3\) activation.

As has been well proven in previous studies, the relationship between catalytic ability and density of –OH on the catalysts surface had a positive linear correlation. To be more specific, –OH reacted with O\(_3\), generating unstable species as the promoter of O\(_3\) chain decomposition and, thus, produced -OH (Yang et al. 2007; Zhang et al. 2008; Sui et al. 2012). Multivalence oxidation states improved interfacial electron transfer which made the organic pollutant degrade rapidly (Xing et al. 2008; Lv et al. 2010). Therefore, it could be inferred that Fe-NiO\(_x\) oxides could catalyze the ozonation process because of the interaction of multivalent Ni and –OH. However, this research result contradicted previous ones which insisted that more –OH led to better degradation results in heterogeneous catalytic process (Yang et al. 2007; Zhang et al. 2008; Sui et al. 2012; Zhao et al. 2015). The Ni\(^{2+}\)-Ni\(^{3+}\) redox process in the system and the electron transfer between them which enhanced the oxidation reaction had led to this phenomenon (Ren et al. 2012).

### Ozone decomposition with Fe-NiO\(_x\) oxides

A series of ozone decomposition experiments was carried out with various catalysts. As shown in Figure 6, all catalysts
significantly promoted ozone decomposition compared to the rate of the O₃ alone system. As the ozone decomposition results followed a similar pattern in Figure 5, catalysts calcinated at 500 °C by blowing air were the most effective with nearly 66.67% O₃ decomposed. Reactive species generated from O₃ chain decomposition were not consumed without pollutant in the system in Figure 5 and this might narrow the rate difference between O₃ decomposition in Figures 5 and 6 (Lv et al. 2010; Zhao et al. 2015).

Active oxidative species in ozonation system

The improvement in DMP degradation was ascribed to the formation of active oxidative species with O₃ decomposed, which had high oxidative ability to remove refractory organic matter (Yang et al. 2009; Huang et al. 2011; Zhao et al. 2013). In order to confirm whether -OH was generated or not during the AOP, TBA was used as radical scavenger because its reaction rate constant with -OH is 6 × 10⁸ M⁻¹ s⁻¹ and with O₃ it is only 3 × 10⁻³ M⁻¹ s⁻¹ (Acero et al. 2001).

As shown in Figure 7, after adding TBA, DMP degradation was significantly inhibited from 86.83% to 27.29% in 10 min with both O₃ and the catalysts calcinated at 500 °C by blowing air in the system. Since TBA had a much higher reaction rate constant with -OH than O₃, the decrease was due to the consumption of -OH caused by TBA. About 39.08% DMP was degraded in 10 min with O₃ alone and it decreased to 22.57% with the addition of TBA. Besides, only adding catalysts into the system resulted in less than 4% DMP being adsorbed with or without TBA experimental conditions.

CONCLUSIONS

Calcination temperature and O₂ were important factors which influenced the crystalline degree and relative content of Ni²⁺ and -OH during the Fe-NiOₓ catalysts synthesis process. Different calcination temperatures led to different precursor decomposition and crystalline process, and O₂ affected the oxidation level of organic matter in the precursor. The beneficial effect on DMP degradation was promoted by the Ni²⁺-Ni³⁺ redox process and -OH. The presence of Ni²⁺ had a much stronger impact because the electron transfer between multivalence could accelerate O₃ decomposition and -OH generation. The degradation process was mainly attributed to the presence of -OH generated from the process of O₃ activated by Fe-NiOₓ catalysts, while the adsorption of DMP could be ignored.

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