Mechanism of Catalytic Ozonation in $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ Aqueous Suspension for Destruction of Ibuprofen

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Supporting Information

ABSTRACT: Fe_2O_3 and/or Al_2O_3 were supported on mesoporous SBA-15 by wet impregnation and calcinations with AlCl_3 and FeCl_3 as the metal precursor and were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectra (FTIR) of adsorbed pyridine. $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ was found to be highly effective for the mineralization of ibuprofen aqueous solution with ozone. The characterization studies showed that Al-O-Si was formed by the substitution of Al^{3+} for the hydrogen of surface Si-OH groups, not only resulting in high dispersion of Al_2O_3 and Fe_2O_3 on SBA-15, but also inducing the greatest amount of surface Lewis acid sites. By studies of in situ attenuated total reflection FTIR (ATR-FTIR), in situ Raman, and electron spin resonance (ESR) spectra, the chemisorbed ozone was decomposed into surface atomic oxygen species at the Lewis acid sites of Al^{3+} while it was converted into surface adsorbed $\cdot\text{OH}_{\text{ads}}$ and $\text{O}_2^{\cdot-}$ radicals at the Lewis acid sites of Fe^{3+} . The combination of both Lewis acid sites of iron and aluminum onto $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ enhanced the formation of $\cdot\text{OH}_{\text{ads}}$ and $\text{O}_2^{\cdot-}$ radicals, leading to highest reactivity. Mechanisms of catalytic ozonation were proposed for the tested catalysts on the basis of all the experimental information.

INTRODUCTION

Heterogeneous catalytic ozonation has recently gained significant attention as an effective process for the degradation and mineralization of refractory organic pollutants in water.^{1,2} A variety of efficient solid catalysts have been developed for catalytic ozonation, however, these successful results are on a laboratory level. Catalytic ozonation has not been applied widely in the water industry³ because the mechanisms of these processes are still unclear,⁴ including the process of ozone decomposition on the surface of different catalysts and the generation of reactive oxygen species (ROS), key structure factors of catalysts. An in-depth understanding of the mechanism is essential to introduce this technique in water treatment at an industrial scale.

The efficiency of catalytic ozonation and the transformation of pollutants predominantly depend on the behavior of ozone on the surface of the catalysts. However, there is not still any unified mechanism of the process; moreover, many proposed mechanisms are contradictory.⁴ Various metal oxides (Al_2O_3 , Fe_2O_3 , and MnO_2), and metals supported on oxides, are claimed to have catalytic activity in ozonation. Nevertheless, there are contradictory reports on their catalytic activity, which mainly including two possible mechanisms of catalytic ozonation. The one mechanism is that ozone is decomposed into ROS to oxidize organic compound in water; the other one is that both ozone and organic compounds are adsorbed on the catalyst

surface, subsequently interacting between adsorbed species.^{3,4} For example, Al_2O_3 does not reveal any catalytic activity due to not decomposing ozone according to some research,^{5,6} while others report Al_2O_3 is an active catalyst due to the adsorption of organic compounds and ozone on its surface.^{7,8} Also, there are four different hypotheses for the adsorption and decomposition of ozone on Fe-hydroxyoxides.⁹ In addition, in most of the literature,^{10,11} the high efficiency of catalytic ozonation was assigned to the hypothesis of hydroxyl radicals ($\cdot\text{OH}$) generation from ozone decomposition. However, the recent research indicated that catalytic ozonation does not necessarily rely on $\cdot\text{OH}$ formation.^{12,13} These examples show irrefutably that our understanding of the catalytic ozonation in aqueous phase seems to be very poor.

The surface of all the oxides, including metal oxides and metals supported on oxides, is covered by hydroxyls that can have ion exchange properties, and the hydroxyls are considered as the main adsorption centers.^{14,15} Some of them have Lewis acid sites, while others of them have hydrophobic sites. All the above properties depend on the variety of metal in the oxides. Single hydroxyl sites for cation exchange and hydrophobic sites

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are usually found on the surface of silica, while ion-exchange bridged hydroxyl sites and Lewis acid sites are usually found on the surface of Al_2O_3 and Fe_2O_3 .¹⁶ These factors would have great influence on the behavior of ozone on the surface of the oxides, leading to different catalytic activity. However, there was no direct evidence to indicate the process of the interaction between these sites with ozone and what ROS would be involved in aqueous-phase catalytic ozonation.

The objective of this study was to investigate the transformation of ozone over supported metal oxides with different surface hydroxyls and Lewis acid sites, elucidating catalytic ozonation mechanism at the aqueous–solid interface. In the present study, mesoporous SBA-15 silica was used as support. $\text{Al}_2\text{O}_3/\text{SBA-15}$, $\text{Fe}_2\text{O}_3/\text{SBA-15}$, and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ were prepared by impregnation method and characterized by XRD, XPS, and pyridine-FTIR, etc. The reaction processes of ozone were observed at the aqueous–solid interface of four catalysts by in situ attenuated total reflection FTIR (ATR-FTIR) spectroscopy, in situ Raman spectra, electron spin resonance (ESR) spectra, and the determination of ozone. Ibuprofen (IBU), an anti-inflammatory drug with estimated annual global production of several kilotons, has been detected in surface water and wastewater at a range from ng to low $\mu\text{g L}^{-1}$ levels due to its stability for photolysis and biodegradation.^{17,18} Some researchers suggested that IBU may alter the postembryonic development of anuran species in freshwater environs, where IBU is a persistent or seasonal pollutant.¹⁹ Therefore, IBU was selected to evaluate the activity and properties of the catalysts. A preliminary effort to identify a correlation between transformation of ozone onto catalysts and catalytic effect has been undertaken.

■ EXPERIMENTAL SECTION

Chemicals and Reagents. Ibuprofen (IBU) was obtained from TCI Japan (Tokyo, Japan). Its molecular structure is shown in Figure S1 in the Supporting Information (SI). The triblock copolymer $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (Pluronic P123, MW 5800) was purchased from Sigma-Aldrich. Tetraethyl orthosilicate (TEOS), crystallization of aluminumchloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), and deuterioxide (D_2O) were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. (Beijing, China). Spin trap 5-tert-butoxycarbonyl 5-methyl-1-pyrroline *N*-oxide (BMPO) was purchased from DOJINDO Molecular Technologies, Inc. (Shanghai, China). Horseradish peroxidase (POD, specific activity of $>250 \text{ u mg}^{-1}$) was purchased from Amresco (USA). All chemicals were of analytical grade and used as received. Milli-Q water ($18.2 \text{ M}\Omega \cdot \text{cm}$ in resistivity, Millipore) was used throughout the experiments. The solution pH was adjusted with dilute HCl and NaOH solution.

Catalysts Preparation. SBA-15 was synthesized as described previously using triblock copolymer $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (Pluronic P123) as organic template.²⁰ Alumina-coated SBA-15 ($\text{Al}_2\text{O}_3/\text{SBA-15}$) was prepared by the incipient wetness impregnation method with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ as the metal precursor. For example, 0.894 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 10 mL of Milli-Q water. 2 g of SBA-15, dried at 100°C for 12 h, was dispersed into this solution with stirring vigorously for 60 min. The mixture was then dried in an oven at 85°C for 10 h. The impregnation process was repeated three times to obtain the Si/Al atomic ratio of 3, and finally the obtained product was ground, calcined at 550°C for 4 h at a heating rate of 5°C min^{-1} , and then cooled to room temperature naturally.

Furthermore, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ was prepared by an incipient wetness impregnation method with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as the metal precursor. Typically, 1.16 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 6 mL of distilled water, and 2 g of $\text{Al}_2\text{O}_3/\text{SBA-15}$ was added to this solution. After ultrasonic vibration for 60 min, the sample was dried at 80°C for 10 h and finally calcined in a muffle furnace (exposed to static air) at 300°C for 30 min and cooled to room temperature naturally. Following this procedure, the catalysts containing different Fe amounts were prepared with different Fe dosages (3, 6, 12, and 15 wt % Fe with respect to $\text{Al}_2\text{O}_3/\text{SBA-15}$). The catalyst with 12 wt % Fe dosage exhibited the highest activity for catalytic ozonation of IBU, designated by $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$, and was used for all the experiments. As references, $\text{Fe}_2\text{O}_3/\text{SBA-15}$ was prepared under the otherwise identified conditions as that of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$.

Characterization. Powder X-ray diffraction (XRD) of the catalyst was recorded on a Scintag-XDS-2000 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$). The high-resolution transmission electron microscopy (HRTEM) images of the catalysts were obtained using a JEOL-2010 TEM with an acceleration voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) data was taken on an AXIS-Ultra instrument (Kratos Analytical, UK) using monochromatic Al $K\alpha$ radiation (225 W, 15 mA, 15 kV). The point of zero charge (pH_{pzc}) of the catalysts was measured with a Zetasizer Nano (Malvern, UK) with three consistent readings.

Procedures and Analysis. Semi-batch experiments were carried out with a 1.2-L reactor. The reaction temperature was maintained at 20°C . In a typical experiment, 1 L of 10 mg L^{-1} aqueous suspensions of IBU and 1.5 g of catalyst powder were added into the reactor under continuous magnetic stirring. 30 mg of gaseous $\text{O}_3 \text{ L}^{-1}$ oxygen-ozone was bubbled into the reactor through the porous plate of the reactor bottom at a flow rate of 200 mL min^{-1} . The initial pH of reaction suspensions was about 7. The same procedures were carried out for the control experiments of ozone alone and sorption without ozone. Ozone was produced in situ from pure oxygen by a 3S-A5 laboratory ozone generator (Tonglin Technology, China). The residual ozone in the off-gas was absorbed by a KI solution. At given time intervals, a sample was withdrawn. An aliquot of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ was added to the sample to quench the residual aqueous ozone, and the sample was filtered through a Millipore filter (pore size $0.45 \mu\text{m}$) for analysis. The gaseous ozone concentration was measured by an IDEAL-2000 ozone concentration detector (China). The concentration of ozone dissolved in the aqueous phase was determined with the indigo method. IBU was analyzed by means of a 1200 series HPLC (Agilent, USA) equipped with a UV detector at 220 nm and a ZORBAX Eclipse XDB-C₁₈ column ($4.6 \times 150 \text{ mm}$, $5 \mu\text{m}$). The mobile phase was a solution of 60/40 (v/v) acetonitrile–phosphate buffer solution (20 mM, pH = 2.5) and a flow rate of 1 mL min^{-1} . TOC was determined by a Shimadzu TOC-V_{CPH} analyzer. The iron and aluminum contents in the whole particle of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$, after being dissolved by concentrated nitric acid, were detected by inductively coupled plasma optical emission spectrometry (ICP-OES) on an OPTIMA 2000 (PerkinElmer Co., USA). Moreover, the released metallic ions from the catalysts in reaction process also were determined by ICP-OES. Electron spin resonance (ESR) spectra were obtained with a Bruker A300-10/12 ESR spectrometer using BMPO as a spin trap agent at room temperature. All information for FTIR, in situ ATR-FTIR, in situ Raman

spectra, the experiments of O_3 decomposition, the determination of H_2O_2 , the surface Fe^{2+} of the catalysts, gas chromatography–mass spectrometry (GC-MS) analysis, and the preparation of samples is shown in the SI. Each experiment was run in triplicate. Data were the arithmetic mean of three measured values.

RESULTS AND DISCUSSION

Characterization of Catalysts. The low-angle and wide-angle XRD patterns of different supported SBA-15 are shown in SI Figure S2. All the samples exhibited a very strong diffraction peak near 1° , which is identified to be the typical pattern of hexagonal structure attributed to the diffraction plane (100). The other two weaker patterns were indexed to the diffraction plane (110) and (200).²⁰ The results indicated that these samples retained a highly ordered structure of SBA-15 after a loading process. No significant diffraction peaks of Al_2O_3 were observed in either $Al_2O_3@SBA-15$ or $Fe_2O_3/Al_2O_3@SBA-15$, and a weaker peak appeared at 35.65° , which is assigned to α - Fe_2O_3 , in $Fe_2O_3/Al_2O_3@SBA-15$.²¹ In contrast, several stronger peaks for α - Fe_2O_3 (JCPDS card 01-073-2234) appeared in $Fe_2O_3/SBA-15$. TEM images of different samples confirmed this observation (SI Figure S3). All the catalyst samples exhibited well-ordered hexagonal arrays structure with the loading of alumina and iron oxide. There is no aggregated alumina phase in $Al_2O_3@SBA-15$ (SI Figure S3B), despite the high loading content of Al_2O_3 . The result indicated that Al_2O_3 layers were homogeneously coated on the pore walls of SBA-15. Large particles of iron oxide were found on the outer surface of SBA-15, indicating that the iron oxide particles were not well-dispersed. However, the large iron oxide nanoparticles were not observed in $Fe_2O_3/Al_2O_3@SBA-15$, suggesting that the small iron oxide nanoparticles were homogeneously dispersed on the surface of $Al_2O_3@SBA-15$. By XPS measurement, the surface Al and Fe concentrations were 8.53 and 7.97 wt %, which were more than those (7.18 and 6.47 wt %) in bulk for $Fe_2O_3/Al_2O_3@SBA-15$, indicating that most of Al and Fe were supported on the surface of SBA-15. The Fe 2p spectra comprise three peaks with differentiated binding energy values assigned to Fe 2p 3/2 peak (~ 711 eV), satellite peak (~ 718.2 eV), and Fe 2p 1/2 peak (~ 724 eV) (SI Figure S4). The energy separation between Fe 2p 3/2 and Fe 2p 1/2 is more than 13 eV, indicating Fe^{3+} existence.²² In $Fe_2O_3/Al_2O_3@SBA-15$ sample, the Al 2p XPS spectra exhibit two binding energies (BEs) of Al^{3+} at 73.6 and 74.7 eV, assigned to Al–O–Al and Al–O–Si respectively,²³ whereas the Si 2p XPS spectra also exhibited two BEs, 103.4 and 102.3 eV, assigned to Si–O–Si and Al–O–Si, respectively (Figure 1).²³ The same results also were observed in the XPS spectra of $Al_2O_3@SBA-15$ (not data shown). In addition, FTIR spectra also show that the surface Si–OH groups of SBA-15 at 966 cm^{-1} disappeared with the loading of aluminum oxide (SI Figure S5). These data indicated that Al–O–Si was formed by the substitution of Al^{3+} for the hydrogen of surface Si–OH groups, resulting in aluminum oxide homogeneously highly dispersed on the surface of SBA-15, which enhanced the dispersion of iron oxide on the surface of $Al_2O_3@SBA-15$.

The acid sites of different catalysts were determined by FTIR of adsorbed pyridine after degassing at 200°C (Figure 2). Obviously, no peak was observed for SBA-15; two weaker IR bands appeared at 1452 and 1608 cm^{-1} for $Fe_2O_3/SBA-15$ assigned to pyridine adsorbed onto Lewis acid sites.²⁴ $Al_2O_3@SBA-15$ exhibited three strong IR bands at 1452 and 1620 cm^{-1}

Figure 1. Al 2p (A) and Si 2p (B) XPS spectra for $Fe_2O_3/Al_2O_3@SBA-15$.

Figure 2. Infrared spectra of adsorbed pyridine for different samples after outgassing at 200°C : (a) SBA-15, (b) $Fe_2O_3/SBA-15$, (c) $Al_2O_3@SBA-15$, and (d) $Fe_2O_3/Al_2O_3@SBA-15$.

attributed to pyridine adsorbed onto Lewis acid sites and at 1492 cm^{-1} ascribed to pyridine adsorbed onto both Lewis and Brønsted acid sites.²⁴ Furthermore, the three bands became wide and the 1608 cm^{-1} band remained for $Fe_2O_3/Al_2O_3@SBA-15$. The total and strong Lewis acid sites were quantitatively estimated for these catalysts using pyridine adsorption followed by degassing at 200 and 350°C according to the described method (SI Table S1).²⁵ The total acid sites and medium/strong acid sites were 21.7 and $19.2\text{ }\mu\text{mol g}^{-1}$ on the surface of $Fe_2O_3/SBA-15$, while the total Lewis acid sites were 246.2 and $264.3\text{ }\mu\text{mol g}^{-1}$, and medium/strong acid sites were 184.3 and $193.1\text{ }\mu\text{mol g}^{-1}$ for $Al_2O_3@SBA-15$, $Fe_2O_3/Al_2O_3@SBA-15$. The loading of aluminum greatly increased the total acid and medium/strong acid site, which was attributed to the substitution of aluminum for the hydrogen of surface Si–OH group of SBA-15. Dissociative chemisorption of water molecules occurs at Lewis acid sites,²⁶ which was examined by in situ ATR-FTIR experiments in the D_2O solvent with N_2 atmosphere (SI Figure S6). The stretching vibration of the hydrogen-bonded MeO–D was 2499 cm^{-1} , while those of the

hydrogen-bonded D₂O were 2252 and 1064 cm⁻¹. The peak intensities increased according to the following order: SBA-15, Fe₂O₃/SBA-15, Al₂O₃@SBA-15, and Fe₂O₃/Al₂O₃@SBA-15, indicating that the more surface Lewis acid sites resulted in more chemisorbed water. Besides, the presence of Lewis acid sites increased the point of zero charge (pH_{pzc}), increasing the ability of surface hydroxyl groups to dissociate or to be protonated in water.¹⁶ As expected, the pH_{pzc} were 3.1, 3.79, 6.75, and 7.25 for SBA-15, Fe₂O₃/SBA-15, Al₂O₃@SBA-15, and Fe₂O₃/Al₂O₃@SBA-15.

Catalytic Ozonation of IBU. The catalytic activity of various catalysts was evaluated by the degradation of IBU (10 mg L⁻¹) with ozone at an initial pH of 7. Concentrations of 2.8%, 5.7%, 8.0%, and 9.7% of the tested IBU were adsorbed on the surface of Fe₂O₃/Al₂O₃@SBA-15, Al₂O₃@SBA-15, Fe₂O₃/SBA-15, and SBA-15, respectively. The degradation of IBU mainly was attributed to the catalytic ozonation. The degradation rate of IBU was almost the same with ozone alone and catalytic ozonation (SI Figure S7). Ozone decomposition increased in water at pH more than 7, causing more hydroxyl radicals ([•]OH). *tert*-Butanol (TBA) is a strong radical scavenger that has a reaction rate constant of 6 × 10⁸ M⁻¹ s⁻¹ with hydroxyl radicals and only 3 × 10⁻³ M⁻¹ s⁻¹ with ozone. To examine the role of [•]OH and ozone in ozonation, TBA was adopted as the indicator for the radical type reaction. The addition of TBA markedly reduced the degradation of IBU (SI Figure S8), indicating that [•]OH radicals also were involved, and the removal of IBU predominantly came from the oxidation of ozone and [•]OH in ozonation at pH 7. However, the degradation of IBU was less suppressed by the addition TBA in catalytic ozonation than ozone alone. At pH 7, only 2.8% of IBU was adsorbed on the surface of Fe₂O₃/Al₂O₃@SBA-15, as the oxidation reaction of IBU occurred mainly in solution. Because there was no significant amount of TBA adsorbed on the catalyst in aqueous systems, it predominantly scavenged the free [•]OH radicals in solution. The results suggested that the free [•]OH radicals in solution were not main, and the surface reactive oxygen species might play an important role in the catalytic ozonation. However, the TOC removal rate was greatly enhanced in catalytic ozonation (Figure 3). Only 26% of TOC was removed with ozone alone at 60 min, while about 90%, 65%, 48%, and 36% of TOC were removed at the same time in Fe₂O₃/Al₂O₃@SBA-15, Al₂O₃@SBA-15, Fe₂O₃/

SBA-15, and SBA-15 suspensions, respectively. The pH of solution greatly decreased from initial pH 7 to 3.8 (SI Figure S9) in the process of ozonation, indicating the accumulation of organic acids in solution, verifying that most of the organic acids could not be oxidized in ozonation, leading to lower TOC removal. Differently, in the process of catalytic ozonation, the pH changed less than 0.3 in Fe₂O₃/Al₂O₃@SBA-15 suspension, while the pH changed less than 0.7 in the other catalysts suspensions, which was attributed to the faster removal of produced organic acids (SI Figure S9). The results demonstrated that the catalytic activity predominantly depended on the amount of surface Lewis acid sites. There were no Lewis acid sites on the surface of SBA-15, leading to less activity, while the loading of aluminum greatly increased Lewis acid sites, leading to higher activity, and the synergism of aluminum and iron resulted in highest activity of Fe₂O₃/Al₂O₃@SBA-15. The activity of Fe₂O₃/Al₂O₃@SBA-15 did not markedly decrease after six successive cycles of degradation testing, and the crystalline structure of Fe₂O₃/Al₂O₃@SBA-15 remained almost the same as that of the fresh catalyst (SI Figure S10). During the catalytic ozonation, there was no metallic ion release. These results verified that Fe₂O₃/Al₂O₃@SBA-15 is a highly efficient catalyst for the mineralization of IBU in the ozonation process.

Catalytic Ozonation Mechanism. Intermediates of IBU Degradation with Ozonation or Catalytic Ozonation. GC-MS was used to monitor the generation of reaction intermediates during the degradation of IBU in ozonation and catalytic ozonation, respectively. All of the identified compounds were unequivocally identified using the NIST98 library database with fit values higher than 93%. SI Table S2 shows the main intermediates from the degradation of IBU at reaction times of 5 and 20 min. In ozone alone, at 5 min, four intermediates were produced, including 2-methylpropan-1-ol, 2-(3,4-dihydroxyphenyl)-2-hydroxyacetic acid, propane-1,2,3-triol, and *p*-hydroxybenzoic acid, indicating that hydroxylation reaction first occurred on the aromatic ring at para, meta position of 2-methylacetic acid group, and methyl position of acetic acid and propyl group by ozone or [•]OH. At the reaction time of 20 min, *p*-hydroxybenzoic acid remained and other products disappeared, while 2,3-dihydroxy-propanoic acid and 2-hydroxy-3-methylbutyric acid appeared, which were produced by the hydroxylation and carbonylation of aromatic ring at meta position of 2-hydroxyacetic acid group, subsequently some aliphatic acids produced. In Fe₂O₃/Al₂O₃@SBA-15 suspension with ozone, at the reaction time of 5 min in solution, five intermediates appeared, including 2-(3,4-dihydroxyphenyl)-2-hydroxyacetic acid, 2-hydroxy-3-methylbutyric acid, propane-1,2,3-triol, succinic acid, and *p*-hydroxybenzoic acid. Meanwhile, four organic acids were detected on the surface of the catalyst: 2-(3,4-dihydroxyphenyl)-2-hydroxyacetic acid, 3,4,5-trihydroxybenzoic acid, 3,4-dihydroxybutanoic acid, and *p*-hydroxybenzoic acid. At the reaction time of 20 min, in solution, these products disappeared, and only some aliphatic acids, such as 2-hydroxy-propanoic acid, glycolic acid, and malonic acid, were detected. Moreover, on the surface of the catalyst, other acids disappeared, only *p*-hydroxybenzoic acid remained, and malonic acid and 3-hydroxy-hexanedioic acid were produced. The results demonstrate that the catalytic ozonation of IBU proceeds by the simultaneous hydroxylation of different substitute groups, followed by the opening of aromatic rings to form small molecular organic acids or triols into carbon dioxide and water, where the intermediates were

Figure 3. TOC removal during the degradation of IBU in aqueous dispersions of various catalysts with ozone: (a) Fe₂O₃/Al₂O₃@SBA-15, (b) Al₂O₃@SBA-15, (c) Fe₂O₃/SBA-15, (d) SBA-15, and (e) without catalyst. Initial pH = 7.0, initial IBU concentration = 10 mg L⁻¹, catalyst concentration = 1.5 g L⁻¹, gaseous ozone concentration = 30 mg L⁻¹.

produced and disappeared more quickly than those in ozone alone. The results indicate that catalytic ozonation has stronger oxidation performance than ozonation for the further degradation of organic acids intermediates, causing more TOC removal. On the other hand, it was found that most of the aromatic acids and long-chain aliphatic acids were adsorbed on the surface of the catalyst, indicating these intermediates from IBU degradation were oxidized by the surface reaction.

Effect of pH on IBU Degradation. The IBU degradation rate increased with increasing initial pH in ozone alone and in $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ suspension with ozone (SI Figure S11). For ozonation (SI Figure S11A), with initial pH increasing, ozone decomposition increased, resulting in more $\cdot\text{OH}$ formation. The rate constant of the ozone–IBU reaction is $9.6 \text{ M}^{-1} \text{ s}^{-1}$, while that of the $\cdot\text{OH}$ –IBU reaction is $7.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. At initial pH 3, ozone was the main oxidant, leading to lower IBU degradation; while at initial pH 7 and 9, ozone and $\cdot\text{OH}$ were the predominant oxidants, causing more IBU degradation. Correspondingly, TOC removal increased with initial pH increasing, however, the maximum TOC removal was only 40%. Oppositely, in $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ suspension with ozone (SI Figure S11B), TOC removal increased with increasing initial pH from 3.0 to 7.0, but at pH 9, TOC removal rate greatly decreased. The analysis of intermediates verified that most of the organic acids from IBU degradation were adsorbed and oxidized predominantly on the surface of the catalyst at initial pH 7. Considering the pH_{pzc} of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ is about 7.25, the surface of the catalyst was positively charged in the range of $\text{pH} < 7$, while the surface exhibited great negative zeta-potential at pH 9. So organic acid can be adsorbed onto the surface of catalyst by electrostatic attraction at $\text{pH} < 7$, while they hardly had any adsorption on the negatively charged surface at pH 9 due to repulsive force. At $\text{pH} = 9$, the lower TOC removal indicated that the oxidation of organic acids greatly decreased in bulk solution. These results indicated that organic acid degradation predominantly occurred on the surface of the catalyst, indicating where more $\cdot\text{OH}$ and other reactive oxygen species formed.

Characterization of Ozone on the Surface of Different Catalysts. The concentrations of ozone in bulk water and the surface of the catalysts were determined with different reaction times (Figure 4). The concentration of ozone decreased more rapidly in SBA-15 suspension than other suspensions before 20 min, then tended to steady. In contrast, the concentration of ozone continuously decreased in other suspensions with reaction time, and the decay rate of ozone was highest, and ozone completely disappeared at 45 min in $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ suspension. Similar changes of ozone concentration occurred on the surface of the catalysts except SBA-15. The concentration of ozone gradually decreased on the surface of $\text{Fe}_2\text{O}_3/\text{SBA-15}$, $\text{Al}_2\text{O}_3/\text{SBA-15}$, and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$, and the ozone completely disappeared at 60 min on the surface of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$. SBA-15 had the maximum adsorption capacity of ozone, and the concentration of ozone on the surface of SBA-15 did not change within 60 min. The results indicated that the ozone molecule was direct oxidant over SBA-15 suspension, leading to lower reactivity, while more ROS formed in other suspensions with the ozone decomposition. $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ showed the highest ozone decomposition efficiency, resulting in the most ROS formation. In situ ATR-FTIR experiments were carried out in different catalysts suspensions with D_2O (SI Figure S12). In SBA-15 suspension, with increasing ozone bubbling time, the intensities of peaks at

Figure 4. Changes of ozone concentration in bulk water (A) and the adsorbed ozone onto catalysts (B) during the decomposition of ozone in aqueous dispersions of various catalysts: (a) $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$, (b) $\text{Fe}_2\text{O}_3/\text{SBA-15}$, (c) $\text{Al}_2\text{O}_3/\text{SBA-15}$, (d) SBA-15, and (e) without catalyst. Initial $\text{pH} = 7.0$, initial ozone concentration in water = 4.23 mg L^{-1} , catalyst concentration (if used) = 1.5 g L^{-1} .

1064, 2252, and 2499 cm^{-1} hardly had any change, indicating that the surface hydroxyl site (Si-OH) of SBA-15 could not ion exchange with ozone, the ozone was bound by physical absorption onto SBA-15 by hydrogen bond.²⁷ In $\text{Fe}_2\text{O}_3/\text{SBA-15}$ suspension, the intensities of peak at 1064 cm^{-1} did not change, but the intensities of peaks at 2252 and 2499 cm^{-1} decreased gradually, suggesting that the adsorbed water was replaced by ozone. Moreover, in $\text{Al}_2\text{O}_3/\text{SBA-15}$ and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ suspensions, the three peaks decreased gradually, suggesting that the hydroxyl groups in these locations could be ion exchanged with ozone. The results indicated that the surface Lewis acid sites were active sites for adsorption and decomposition of ozone on the surface of the catalysts. Figure 5 shows the Raman spectra of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ and $\text{Al}_2\text{O}_3/\text{SBA-15}$ with ozone aqueous solution. Both samples exhibited a new band appearing at 913 and 938 cm^{-1} , respectively, which was assigned to a surface atomic oxygen species.^{13,28,29} Oppositely, no surface atomic oxygen formed on the surface of SBA-15 and $\text{Fe}_2\text{O}_3/\text{SBA-15}$ with ozone aqueous solution (SI Figure S13). These results indicated that ozone was decomposed into a surface atomic oxygen when it was adsorbed on stronger Lewis acid sites of $\text{Al}_2\text{O}_3/\text{SBA-15}$, while the ozone adsorbed on Lewis acid sites of iron was not converted into the surface atomic oxygen. By ESR spin-trap technique with BMPO, ROS were determined in different catalysts suspensions (Figure 6). Neither $\text{O}_2^{\cdot-}$, nor $\cdot\text{OH}$ signals, were detected in SBA-15 suspension, indicating that the physically sorbed ozone was stable on the surface of SBA-15, confirming that ozone was direct oxidant. The six characteristic peaks of the $\text{BMPO-O}_2^{\cdot-}$ adducts were observed in $\text{Al}_2\text{O}_3/\text{SBA-15}$, $\text{Fe}_2\text{O}_3/\text{SBA-15}$, and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ suspensions. When BMPO was added to catalysts–ozone suspension,

Figure 5. Raman spectra of $\text{Al}_2\text{O}_3/\text{SBA-15}$ (A) and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ (B) aqueous dispersions without (a) and with (b) ozone. Catalyst concentration = 33.3 g L^{-1} , ozone concentration in water = 4.23 mg L^{-1} , initial pH = 7.0.

Figure 6. BMPO spin-trapping ESR spectra recorded in methanol dispersion for $\text{BMPO-HO}_2\bullet/\text{O}_2\bullet^-$ (A) and aqueous dispersion for $\text{BMPO-}\bullet\text{OH}$ (B) with ozone: (a) ozone, (b) SBA-15, (c) $\text{Al}_2\text{O}_3/\text{SBA-15}$, (d) $\text{Fe}_2\text{O}_3/\text{SBA-15}$, and (e) $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$. Initial pH = 7.0, catalyst concentration (if used) = 2 g L^{-1} , initial BMPO concentration = 25 mM , recording time = 3 min.

the $\bullet\text{OH}$ species were not detected in the three suspensions (not data shown), while four characteristic peaks of $\text{BMPO-}\bullet\text{OH}$, 1:2:2:1 quartet pattern, appeared when ozone-

saturated aqueous solution was added to adsorbed BMPO three catalyst suspensions because BMPO possesses positive and negative charges (SI Figure S14), leading to its adsorption onto the surface of the catalysts. These phenomena indicated that the $\bullet\text{OH}$ produced from ozone decomposition mainly was adsorbed on the surface of the catalysts, which was coincident with these results from the effects of initial pH values and TBA scavenger. Moreover, these intensities of $\text{BMPO-}\bullet\text{OH}$ and $\text{BMPO-O}_2\bullet^-$ increased according to the following order of $\text{Al}_2\text{O}_3/\text{SBA-15}$, $\text{Fe}_2\text{O}_3/\text{SBA-15}$, and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$. All the above results indicated that the adsorbed ozone was decomposed into both $\text{O}_2\bullet^-$ in solution and adsorbed $\bullet\text{OH}$ radicals and surface atomic oxygen in $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ suspension with ozone, verifying most of the organic acids were favored to be oxidized on the surface of the catalyst, leading to the lower removal rate of TOC in bulk water at pH 9. Furthermore, the reduction of surface Fe^{3+} to Fe^{2+} was observed with ozone decomposition, and it was greatly enhanced with IBU degradation in $\text{Fe}_2\text{O}_3/\text{SBA-15}$ and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ suspensions. The produced surface Fe^{2+} concentration increased and reached the maximum at about 20 min, then decreased to be oxidized to Fe^{3+} with prolonged reaction time (SI Figure S15). Under the same conditions, the produced H_2O_2 in the suspensions exhibited the same changes (SI Figure S16, curves c and e). The phenomena indicated that the surface multivalent iron took part in the redox reaction of ozone decomposition, enhancing the formation of $\bullet\text{OH}$ and $\text{O}_2\bullet^-$ radicals.

In light of the experimental data and several reviews of the literature,^{1,30–32} a mechanism scheme is proposed for the catalytic decomposition of ozone at the Lewis acids of iron and alumina on SBA-15 (SI Table S3). In this process, ozone replaced the $\equiv\text{Fe}^{3+}\text{-OH}$ groups produced at the surface Lewis acid sites of Fe^{3+} , forming surface adsorbed $\bullet\text{OH}$ ($\bullet\text{OH}_{\text{ads}}$) and $\text{O}_3\bullet^-$ complexing with Fe^{3+} ; subsequently, the free electron transferred from $\text{O}_3\bullet^-$ to the surface Fe^{3+} to generate the surface Fe^{2+} and $\text{HO}_2\bullet$. It has been reported that the complexation of Fe^{3+} with organic acids can decrease the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox potential.³³ During the catalytic ozonation of IBU, most of the produced organic acids were adsorbed on the surface of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$, complexing with the surface Fe^{3+} , enhancing the reaction rate of the surface Fe^{3+} with $\text{O}_3\bullet^-$, resulting in more surface Fe^{2+} and $\text{HO}_2\bullet$ production. The more $\text{HO}_2\bullet$ reacted with each other, producing more H_2O_2 , causing the consistency of H_2O_2 and Fe^{2+} concentration. With the adsorbed organic acids degradation, the complexation of Fe^{3+} with organic acid decreased, leading to the lower surface Fe^{2+} and H_2O_2 formation. Moreover, H_2O_2 also reacted with the surface Fe^{2+} to form $\bullet\text{OH}$ and the surface Fe^{3+} , leading to the decrease of the Fe^{2+} and H_2O_2 . On other hand, ozone replaced the $\equiv\text{Al}^{3+}\text{-OH}$ groups produced at the surface Lewis acid sites of Al^{3+} forming surface atomic oxygen. Subsequently, the active surface atomic oxygen species could react with water to form $\bullet\text{OH}_{\text{ads}}$ and hydrogen peroxide (H_2O_2) due to its stronger oxidizing potential of 2.43 V.³² As expected (SI Figure S16), smaller amounts of H_2O_2 were produced in ozone alone and SBA-15 suspension with ozone, while H_2O_2 production was greatly increased according to the following order $\text{Fe}_2\text{O}_3/\text{SBA-15}$, $\text{Al}_2\text{O}_3/\text{SBA-15}$, and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ suspensions. The concentration of H_2O_2 increased up to about 20 min when IBU was completely degraded, and then decreased with reaction time, which was contributed to the radical chain reactions. Because most of the intermediates from IBU

degradation were organic acids, which could not be oxidized by $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$, the excess $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ reacted with H_2O_2 , besides the surface Fe^{2+} , decreasing H_2O_2 concentration in water. These results confirmed the conjecture about the reaction of surface atomic oxygen with water. The results suggested that the ozone adsorbed onto the Lewis sites of iron was predominantly decomposed into $\text{OH}_{\text{ads}}^\bullet$ and $\text{O}_2^{\bullet-}$ radicals, and the combination of both Lewis sites of iron and aluminum enhanced the formation of $\text{OH}_{\text{ads}}^\bullet$ and $\text{O}_2^{\bullet-}$ radicals in $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ suspension. Therefore, the main ROS were aqueous O_3 and surface adsorbed O_3 in SBA-15 suspension; $\text{OH}_{\text{ads}}^\bullet$ and $\text{O}_2^{\bullet-}$ were predominant in $\text{Fe}_2\text{O}_3/\text{SBA-15}$ suspension; while the surface atomic oxygen was ROS, resulting in higher reactivity in $\text{Al}_2\text{O}_3/\text{SBA-15}$ suspension. Nevertheless, ROS included surface oxygen atom, $\text{OH}_{\text{ads}}^\bullet$ and $\text{O}_2^{\bullet-}$ leading to highest reactivity in $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$. These findings could supply the evidence for the development of new catalysts and adjusting of catalytic ozonation for water purification.

■ ASSOCIATED CONTENT

■ Supporting Information

Details about the experiments: FTIR measurement, in situ ATR-FTIR spectroscopy, in situ Raman spectra, the decomposition of ozone in different catalysts suspensions, determination of H_2O_2 , determination of the surface Fe^{2+} of the catalysts, GC-MS analysis, and the preparation of samples. Structure of IBU and BMPO, XRD patterns, TEM images, XPS Fe 2p spectra, FTIR and in situ ATR-FTIR spectra, IBU degradation in different processes, stability of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ in catalytic ozonation process, effect of initial pH on IBU and TOC removal in ozonation alone and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ suspension with ozone, in situ Raman spectra of SBA-15 and $\text{Fe}_2\text{O}_3/\text{SBA-15}$ with and without ozone, concentration of Fe^{2+} on the surface of $\text{Fe}_2\text{O}_3/\text{SBA-15}$ and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ under different conditions, concentration of H_2O_2 formation during the degradation of IBU, intermediates from IBU degradation in ozone alone and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ suspensions with ozone detected by GC-MS at different reaction times, and a mechanism scheme for the catalytic ozonation in $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SBA-15}$ suspension. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ Notes

The authors declare no competing financial interest.

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