

Catalytic wet air oxidation (CWAO) of cationic red GTL over the Fe₂O₃-CeO₂-Bi₂O₃/γ-Al₂O₃ catalyst under mild reaction conditions

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Abstract The catalytic wet air oxidation (CWAO) of cationic red GTL over the Fe₂O₃-CeO₂-Bi₂O₃/γ-Al₂O₃ catalyst was investigated under mild operating conditions in a batch reactor. The catalyst was prepared by wet impregnation, and characterized by N₂ adsorption-desorption (BET measurement), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The effect of the reaction conditions (catalyst loading, reaction temperature, solution concentration and initial solution pH) was studied. The Fe₂O₃-CeO₂-Bi₂O₃/γ-Al₂O₃ catalyst exhibited good catalytic activity and stability in the CWAO of cationic red GTL under atmospheric pressure. When the reaction temperature, the solution concentration and the initial pH of the solution increased, the decolorization efficiency was improved. The apparent activation energy for the reaction was 79 kJ mol⁻¹. Hydroperoxy radicals (HO₂·) and superoxide radicals (O₂^{-·}) appeared as the main reactive species upon the CWAO of cationic red GTL.

Keywords: Catalytic wet air oxidation (CWAO); Cationic red GTL; Iron oxides catalyst

1. Introduction

Industrial wastewaters, originating from the production of textiles, paper printing, plastics, rubber and medicines, often contain highly concentrated, toxic and hazardous organic compounds. Such compounds may cause severe problems to the environment when directly discharged into the water body. Biological treatments, the most widely developed wastewater treatment methods, are not appropriate and effective for the treatment of such wastewaters because of the bactericide properties of refractory compounds (Collado *et al.* 2013). Therefore, the development of effective technologies for destroying such pollutants has gained considerable attention. Advanced oxidation processes (e.g. ozonation, photocatalysis...) demonstrated good removal ability for refractory pollutants at low concentration levels (Liao *et al.* 2014; Wang *et al.* 2015).

Wet air oxidation (WAO) is an effective technology to deal with highly concentrated, toxic and hazardous organic compounds under high pressure (0.5-20 MPa) and at high temperature (125-320 °C) (Luck 1999). The WAO process exhibited high efficiency in the decolorization and COD abatement of industrial wastewaters, while the severe operating conditions to be implemented limit its practical application. In turn, upon catalytic wet air oxidation (CWAO) the operating conditions can be effectively decreased, the pollutant oxidation rate can be increased and the reaction time can be shortened (Kim and Ihm 2011). Commonly, the CWAO could be implemented as a pretreatment of industrial wastewaters before further treatment using the conventional biological processes (Mezohegyi *et al.* 2013). Heterogeneous catalysts have shown good promise since they might be easily separated from the effluent compared to homogeneous catalysts. Many heterogeneous catalysts have been developed in the CWAO of organic compounds, such as noble metal catalysts (Ru, Pt, Pd...) (Barbier Jr. *et al.* 2005; Yang *et al.* 2015; De los Monteros *et al.* 2015), transition metal oxides (CuO, Fe₂O₃, MnO₂ ...) (Das and Bhattacharyya 2014) and carbon materials (Soria-Sánchez *et al.* 2011; Yang *et al.* 2014). In the last decade, some attempts have been made to develop heterogeneous catalysts used under milder conditions for the CWAO. For example, the catalysts (CuO-MoO₃-P₂O₅, Zn_{1.5}PW₁₂O₄₀, Mo-Zn-Al-O, Pt/Ce_xZr_{1-x}O₂...) have been proved to exhibit good catalytic performances under atmospheric pressure (Yang *et al.* 2010; Xu *et al.* 2012; Wang *et al.* 2017).

Iron oxide-supported catalysts, with a high specific surface area and a high density of active sites, were environmental friendly materials and showed good catalytic activity in the CWAO reaction (Quintanilla *et al.* 2007). Moreover, it was also found that Bi and Ce promoted the performance of the catalysts and exhibited good stability in the CWAO reaction (Zhu *et al.* 2006). In the paper, Fe, Ce and Bi oxides were combined and supported on γ-Al₂O₃ to enhance the catalyst performances in the CWAO under mild reaction conditions. Cationic red GTL, widely used in the textile industry, was selected as a model molecule. The impact of the reaction conditions (catalyst loading, reaction

temperature, solution concentration and initial pH value of the solution) was studied, and a possible mechanism was tentatively proposed for the CWAO of cationic red GTL over the Fe₂O₃-CeO₂-Bi₂O₃/γ-Al₂O₃ catalyst.

2. Experimental

2.1. Materials

Cationic red GTL was purchased from Tianjin Fuchen Fine Chemical Plant (China). Its chemical structure was shown in the literature (Xu *et al.* 2012). Other reagents used for the different experiments were all of analytical grade. γ-Al₂O₃ was purchased from Aladdin Industrial Corporation and used as a support. The crystallite size was ca. 10 nm.

2.2 Catalyst preparation

The catalysts were prepared by wet impregnation. Firstly, Bi(NO₃)₃·5H₂O was dissolved in dilute nitric acid, and then Fe(NO₃)₃·9H₂O and Ce(NO₃)₃·6H₂O were added into the solution under vigorous stirring. Secondly, the γ-Al₂O₃ support was loaded above the solution. The mixture was kept under sonication for 30 min, and then impregnated at room temperature overnight. The resulting solid was dried at 110 °C overnight and calcined at 400 °C for 3 h under flowing air (400 mL min⁻¹) to get the Fe₂O₃-CeO₂-Bi₂O₃/γ-Al₂O₃ catalyst. The corresponding Fe₂O₃/γ-Al₂O₃ and Fe₂O₃-CeO₂/γ-Al₂O₃ catalysts were prepared following a similar process. The Fe, Ce and Bi loadings on the γ-Al₂O₃ were ca. 3.5, 2.4 and 1.8 wt.% for all catalysts, respectively.

2.3. Catalyst characterization

The specific surface area of the samples was measured by N₂ adsorption at 77 K using an Autosorb IQ-MP system. Before the analysis, the samples were outgassed at 250 °C for 4h. X-ray diffraction (XRD) analysis was carried out on a Bruker D8 X-ray diffractometer in the range 20-80° using a Cu Kα radiation source (λ=0.15406 nm) and a scanning speed of 40 min⁻¹. X-ray photoelectron spectroscopy (XPS) study was performed on a PHI 5400 ESCA analyzer using an Al Kα X-ray source (hν=1486.60 eV). The C1s peak (Eb=284.60 eV), originating from the surface contamination, was used as a reference for the calibration of the binding energies. The pH at the point of zero charge (pH_{PZC}) of the catalysts was measured according to the method developed by the literature (Noh and Schwarz 1990).

2.4. CWAO reaction

The CWAO experiments were carried out under atmospheric pressure in a glass batch reactor. It was kept into a water bath in order to maintain the stable temperature during the experiment, and equipped with a magnetic stirrer to insure good mass transformation. 250mL of a cationic red GTL solution (100 mg L⁻¹, pH0=5.4) was added into the reactor, while pure O₂ (200 mL min⁻¹) was continuously bubbled into the reactor under vigorous stirring. After heating the reactor up to the desired temperature, a fixed amount catalyst was

introduced into the reactor, and this time was defined as the “zero” time. In parallel, in order to evaluate the adsorption capacity of the catalysts, the same experiments were performed under N₂ bubbling. Upon reaction, the samples were periodically withdrawn from the reactor. After being filtrated with a 0.22 μm filter to eliminate any solid catalyst particles, the liquid samples were analyzed with a UV-vis spectrophotometer and measured at 530 nm. The evaluation of the catalytic activity was based on the measurement of the decolorization efficiency (%) and calculated as follows:

$$\text{Decolorization} = \frac{c_0 - c_t}{c_0} \times 100$$

where c₀ and c_t were the initial and final concentration of cationic red GTL, respectively. Moreover, the effluents from the reactor were further analyzed by ICP at the end of the reaction to check for any possible leaching of Fe, Ce, Bi and Al from the catalysts.

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. BET and pH_{PZC}

The specific surface areas of the different samples were summarized in Table 1. The γ-Al₂O₃ support had a pretty large specific surface area ca. 166 m² g⁻¹. Compared to the bare support, the specific surface areas of the catalysts only slightly decreased, indicating that the impregnation of the active components did not significantly affect the accessibility of the porous structure of the support. As shown in Table 1, the pH_{PZC} of the catalysts slightly decreased compared to the bare γ-Al₂O₃ support. Such differences could potentially alter the catalysts surface charge upon reaction and subsequently affect the dye adsorption on the catalyst surface (Karpel *et al.* 2005).

3.1.2 XRD

The XRD patterns of the bare γ-Al₂O₃ support and the different catalysts were shown in Fig.1. The support was characterized by three main typical diffraction lines at 37.6°, 45.9° and 67.0°. These peaks were also observed for all catalysts and the intensity of the peaks had not change, indicating that the impregnation of the active phase and the calcination pretreatment did not significantly affect the crystalline structure of the support. In addition, very weak and quite broad diffraction peaks characteristic of the α-Fe₂O₃ phase were observed at 32.8° and 53.8° in the XRD pattern of Fe₂O₃/γ-Al₂O₃ catalyst, indicating that iron was present as small α-Fe₂O₃ particles well-dispersed on the support. It was observed that the diffraction peaks further decreased in intensity and almost disappeared from the XRD patterns, when Ce and Bi was impregnated together with Fe. The observation indicated that the addition of Ce and Bi further promoted the dispersion of α-Fe₂O₃ particles. Moreover, no diffraction peak characteristic of Ce and Bi was ever observed on the XRD patterns of Fe₂O₃-CeO₂/γ-Al₂O₃ and Fe₂O₃-CeO₂-Bi₂O₃/γ-Al₂O₃ catalysts, probably because of the low loadings of Ce and Bi.

3.1.3 XPS

The surface composition of the catalysts and the chemical state of the different active components in the catalysts were determined with XPS, and the spectra for Fe, Ce and Bi were shown in Fig.2 in the case of the $\text{Fe}_2\text{O}_3\text{-CeO}_2\text{-Bi}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst. By comparison with the spectra obtained for $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{-CeO}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts, we observed that the binding energy of Fe 2p_{3/2} was slightly shifted toward lower binding energies upon the addition of Ce and Bi, indicating a change in the chemical state of Fe. To get deeper insights into the change, the Fe 2p_{3/2} spectra were fitted with two bands, i.e. a main peak ca. 711.0 eV, attributed to $\text{Fe}^{3+}\text{-O}$, and a smaller peak ca. 709.5 eV assigned to $\text{Fe}^{2+}\text{-O}$ (Descostes *et al.* 2000; Guo *et al.* 2010). Accordingly, the fraction of $\text{Fe}^{2+}\text{-O}$ increased and were 5.43 to 8.74 and 11.09 at.% for $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3\text{-CeO}_2/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{-CeO}_2\text{-Bi}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts, respectively (Table 1). In addition, XPS spectra of Ce3d and Bi4f were observed, and assigned to CeO_2 and Bi_2O_3 , in agreement with the preparation process of the catalysts.

3.2. CWAO of cationic red GTL under atmospheric pressure

3.2.1 Impact of the different catalysts

As shown in Fig.3, the decolorization efficiency upon the WAO of cationic red GTL, in the absence of any catalyst, was almost zero even after 240 min of reaction at 70 °C under O_2 bubbling. In conclusion, cationic red GTL was shown to be stable under the applied reaction conditions in the absence of any catalyst. Under N_2 bubbling, the adsorption of cationic red GTL on the $\gamma\text{-Al}_2\text{O}_3$ support and the different catalysts was assessed under the same reaction conditions. It was observed that the fraction of cationic red GTL adsorbed on the samples (ca. 20%) was quite significant and almost the same in all cases, in agreement with the literature (Xu *et al.* 2012). Indeed, the special surface area (ca. $160\text{ m}^2\text{ g}^{-1}$) and the pH_{PZC} (ca. 8.0) of all the samples were very similar. The high fraction of cationic red GTL adsorbed on the samples could be explained by the high surface exposed by the catalysts.

Under O_2 bubbling, the Al_2O_3 support alone was shown to be totally inactive. On the opposite, the different catalysts exhibited good decolorization performances. After 240 min reaction run, the percentage of decolorization reached to 32%, 38% and 46% over $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3\text{-CeO}_2/\gamma\text{-Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{-CeO}_2\text{-Bi}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts at 70°C, respectively. The decolorization of cationic red GTL could be attributed to the action of the adsorption and activity of catalysts. The addition of Ce and Bi effectively improved the decolorization efficiency of the $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst, and the $\text{Fe}_2\text{O}_3\text{-CeO}_2\text{-Bi}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst exhibited the best catalytic performance in the CWAO reaction. Moreover, no leaching of Fe, Ce, Bi or Al was ever detected upon completion of the reaction, indicating that the catalyst was stable under the applied reaction conditions. In addition, we observed in all cases that the total organic carbon (TOC) of the effluents never decreased, indicating that cationic red GTL was only

oxidized into some intermediates that could not be mineralized to CO_2 and H_2O under such mild operating conditions. The intermediates were identified by HPLC to be mainly hydroquinone and 1-chloro-3-nitro-benzene.

3.3. Insights into the reaction mechanism

While it is well accepted in the literatures that the CWAO of organic compounds proceeds via a free radical mechanism, the nature of the active oxygen species involved in the process (e.g. superoxide, hydroperoxyl) is still a question of debate depending on the reaction conditions and the catalyst (Barbier *et al.* 1998; Yang *et al.* 2015). To determine better the nature of the active species involved in the CWAO of cationic red GTL over the $\text{Fe}_2\text{O}_3\text{-CeO}_2\text{-Bi}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst under atmosphere pressure, a series of experiments was performed in the presence of different radical scavengers. Tert-butyl alcohol (TBA) and p-benzoquinone (BQ) were used as scavengers for $\text{OH}\cdot$ and $\text{HO}_2\cdot/\text{O}_2^{\cdot-}$ radicals, respectively. Parachlorobenzoic acid (p-CBA) was also used as an indicator for the presence of $\text{OH}\cdot$ radicals since it would be readily oxidized if such radicals would be produced upon the CWAO of cationic red GTL (Rosenfeldt *et al.* 2006).

Looking at the possible involvement of the hydroxyl radicals, two different experiments were performed in the presence p-CBA and TBA, respectively. As shown in Fig.4, it was found that: (1) p-CBA did not be oxidized upon CWAO, while the decolorization of cationic red GTL reached to 30% after 240 min reaction; (2) the decolorization of cationic red GTL reached to 41% even in the presence of TBA. Both of these results clearly indicated that no $\text{OH}\cdot$ radicals were generated and involved in the CWAO of cationic red GTL over the $\text{Fe}_2\text{O}_3\text{-CeO}_2\text{-Bi}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst. Moreover, in Fig.8 the presence of BQ induced a decrease of the decolorization efficiency from 45 to 22%. The result demonstrated that $\text{HO}_2\cdot/\text{O}_2^{\cdot-}$ radicals were involved as the main reactive oxygen species in the CWAO of cationic red GTL over the $\text{Fe}_2\text{O}_3\text{-CeO}_2\text{-Bi}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst.

4. Results and discussion

Iron oxide supported catalysts were investigated in the CWAO of cationic red GTL under atmospheric pressure. The iron catalysts showed a good decolorization efficiency, which was clearly enhanced by the addition of Ce and Bi. Indeed, the addition of Ce and Bi improved the iron dispersion and increased the fraction of iron present as Fe^{2+} in the catalyst. The decolorization efficiency was also enhanced with the higher adsorption of cationic red GTL on the catalyst surface in the CWAO. Superoxide and hydroperoxyl radicals ($\text{HO}_2\cdot/\text{O}_2^{\cdot-}$) were identified as the main reactive oxygen species in the CWAO of cationic red GTL over the $\text{Fe}_2\text{O}_3\text{-CeO}_2\text{-Bi}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst. Finally, we proposed that superoxides radicals could be produced from the reactive adsorption oxygen on the Fe^{2+} centers.

Table 1. The structure of the samples.

Samples	Surface area(m ² /g)	pH _{pzc}	Fe ²⁺ (at.%)	Fe ³⁺ at.%)
γ-Al ₂ O ₃	166	8.22	—	—
Fe ₂ O ₃ /γ-Al ₂ O ₃	163	7.64	5.43	94.57
Fe ₂ O ₃ -CeO ₂ /γ-Al ₂ O ₃	160	7.78	8.74	91.26
Fe ₂ O ₃ -CeO ₂ -Bi ₂ O ₃ /γ-Al ₂ O ₃	157	7.94	11.09	88.91

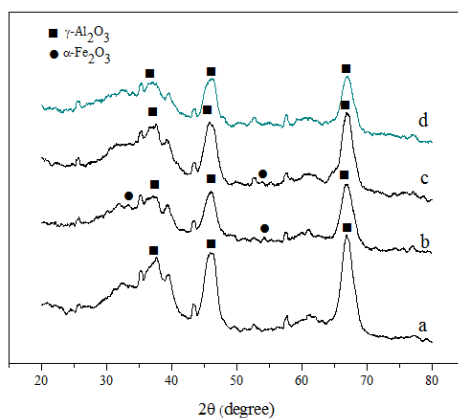


Figure 1. XRD patterns of the support and catalysts.

(a: γ-Al₂O₃, b: Fe₂O₃/γ-Al₂O₃, c: Fe₂O₃-CeO₂/γ-Al₂O₃, d: Fe₂O₃-CeO₂-Bi₂O₃/γ-Al₂O₃)

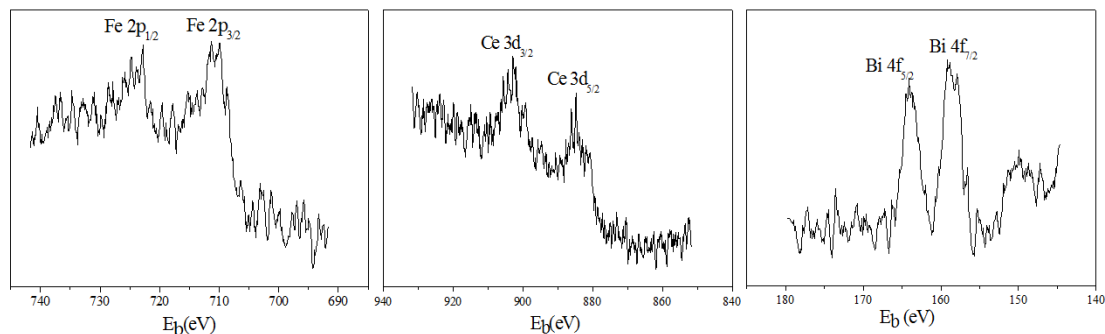


Figure 2. XPS spectra of Fe₂O₃-CeO₂-Bi₂O₃/γ-Al₂O₃ catalyst.

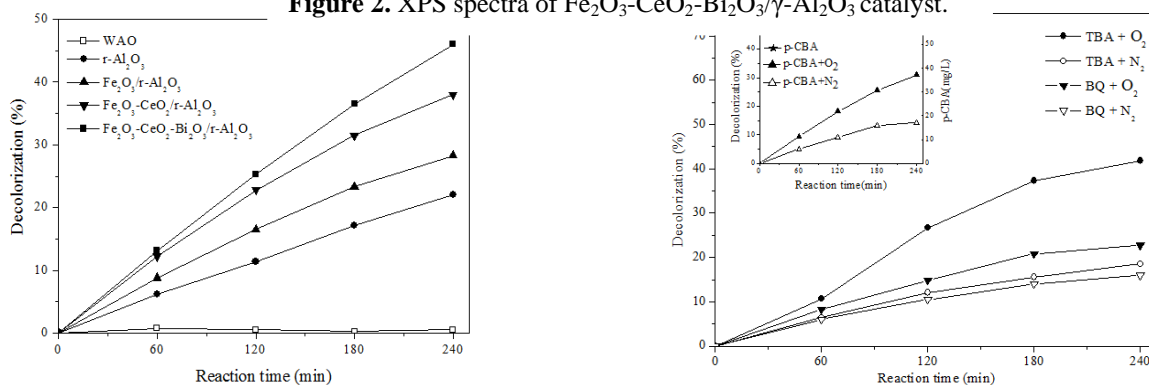


Figure 3. The decolorization efficiency of cationic red GTL in the CWAO over the different catalysts under atmosphere pressure. ([Dye]₀=100 mg/L, [Catalyst]=2.0 g/L, O₂=200 mL/min, T=70 °C)

Figure 4. Effect of scavenging agents on the decolorization efficiency of cationic red GTL in the CWAO over Fe₂O₃-CeO₂-Bi₂O₃/γ-Al₂O₃ catalyst under atmosphere pressure. ([Dye]₀=100 mg/L; [Catalyst]=2.0 g/L; O₂=200 mL/min; T=70 °C)

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