The Highly Efficient Degradation on Nitrobenzene by Using Nano-copper-cobalt Bimetallic Oxide as Heterogeneous Fenton Catalysts: Efficiency, Dynamic and Mechanism

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Abstract: The nano-copper-cobalt bimetallic composite oxide (NCC) has been synthesized under hydrothermal conditions, which was further characterized by SEM, TEM-EDS, XRD, XPS and FTIR-ATR. NCC was used as heterogeneous Fenton catalyst to degrade nitrobenzene (NB). During the degradation process, H2O2 can be activated efficiently by NCC, and NB was degraded rapidly with high efficiency among wide pH range (3-9). In detail, NB with concentration of 10 mg/L (pH=7) can be completely degraded within 45 min at room temperature, in which the amount of NCC was 2.5 g/L, and that of H2O2 was 0.8 mol/L. OH∙ was the main active reactive oxidation species (ROS), which was verified by free radical quenching experiments and benzoic acid (BA) probe experiments. The stability of NCC has been proved by executing four cycling experiments, and no obvious decrease can be found on its degradation ratio. Finally, the degradation mechanism was proposed in terms of their interface pictures. This work paves a new way for the application of NCC as heterogeneous Fenton catalysts.

1. Introduction
As an important raw material in industry, agriculture and medicine, nitrobenzene (NB) has been used with large amount in the production processes [1-4]. So far, NB has widely monitored in the environment as carcinogenic pollutant. It can possess high toxicity although its concentration is relative low, which can threaten the human health and ecological environment [4]. For example, NB can exhibit acute toxicity against macrobranchium nipponense when the concentration is higher than 0.039 mg/L [1], and it can also possess genetic toxicity against soybean root tip cells [5]. Therefore, the removal of NB pollutant seems urgent. But due to the strong electron-withdrawing group -NO2 on benzene, the NB is chemically stable, which leads to the difficulty in the degradation of NB with chemical oxidization or biological methods [6]. Advanced oxidation process (AOPs) is a promising method with high degradation and mineralizing efficiencies [7,8]. Among various AOPs, Fenton water treating technology has captured special interests owing to high catalytic activity of Fe(II) on H2O2. However, Fenton reaction could only be used in small pH range, besides, the large amount of by-product iron also give rise to new problem [9]. In view of these limits, heterogeneous Fenton reactions appeared. In this system, pyrite [10], metals with zero valences [11], bimetallic composites [12-15], supported solids (CuFe/SBA-15) [16] were used as catalysts, in which H2O2 was activated to...
produce reactive oxidation species (ROS) to the degenerate the target substrates. To our disappointment, in most of the heterogeneous Fenton reactions, some disadvantages such as small pH ranges, low catalytic activities, difficulties of catalyst recovery, high metal dissolution rates still haven’t been well solved. There is still a big challenge in solving the problems of heterogeneous Fenton reactions. Bimetallic oxide will be a good candidate in overcoming these problems. Previous reports have indicated that the catalytic activities of bimetallic composite catalysts were more advantageous than those of monometal catalysts. For instance, bimetallic composite catalyst CuFeO$_2$ can exhibit higher catalytic ability on bisphenol A (BPA) than mere Cu$_2$O and Fe$_3$O$_4$ [14]. To our knowledge, Cu, Co have been adopted as catalysts in the corresponding Fenton reactions [17,18], but the work about Cu/Co bimetallic composite catalyst is still in its infancy. In this work, Cu/Co nano-copper-cobalt bimetallic composite oxide (NCC) has been synthesized under hydrothermal conditions, which was used as heterogeneous Fenton catalyst to degrade nitrobenzene (NB). Furthermore, the chemical stability of NMCC, the effect of reaction condition on degradation dynamic were investigated, and finally, the degradation mechanism was proposed. This work will promote the application of NCC as heterogeneous Fenton catalysts due to its high activity and stability.

2. Experimental section

2.1. Materials and physical measurement

All chemicals were analytical reagent obtained from commercial resource and used without further purification. The thickness of needle water-based filter membrane was 0.22 um, and all the solutions were prepared using Milli-Q water (>18.2MΩ·cm, Millipore). Powder XRD patterns (Philips X’Pert-MPD diffractometer with CuKα radiation, λ =1.54056 Å) were conducted to determine the components of catalysts. The morphologies, sizes, crystalline phases and surface elements were investigated by field emission scanning electron microscopy (SEM) spectrometer and STEM-EDS (JEM-3200FS). Valence states of catalysts were monitored by X-ray photoelectron spectroscopy (XPS). IR spectra were recorded on a FTIR-ATR iS50 FTIR spectrophotometer (4000-400 cm$^{-1}$) on powdered sample spread on KBr plate. The components of metals in NCC were determined by ICP-MS (NexION 2000 ICP-MS, PerkinElmer).

2.2. Preparation of NCC

Cu/Co nano-copper-cobalt bimetallic composite oxide (NCC) was synthesized by hydrothermal method. Cu(NO$_3$)$_2$·3H$_2$O(0.01 mol) and Co(NO$_3$)$_2$·6H$_2$O (0.01 mol) were dissolved in ultrapure water, then NaOH (3.3mol/L) was added to produce suspension. After stirring for several minutes, the mixture was treated under ultrasonic condition for 10 min to yield colloid-like suspension. Afterwards, the sample was kept stirring for 8 min, and n-propionaldehyde was added to prevent oxidation. After continuous stirring for 2 min, the mixture was transferred to a Teflon-lined autoclave, which was heated at 200 °C for 48 h. Then the autoclave was cooled to room temperature. The sample was filtrated and washed with ultrapure water for several times, and dried at 80 °C for 4 h. Cu$_2$O, CoO$_2$/Co(OH)$_2$, Fe/Co composite were synthesized with the same method.

2.3. Fenton degradation experiment

The concentration of NB is 10 mg/L, which is stored at low temperature of 3-4 °C. Heterogeneous Fenton reactions were executed in 200 mL conical flask in batch mode. After the pH was adjusted in the reaction range, NCC and H$_2$O$_2$ were added into NB solutions (100 mL) to carry out the degradation process at room temperature. The degraded samples were extracted at certain intervals, and absolute methanol was used to quench the reaction. The extracted samples were filtrated by 0.22 μm needle water-based filter membrane, and the NB concentrations were monitored by HPLC. The catalysts were recovered from the precipitation layer of liquid, which were washed with ultrapure water and dried at ambient condition for re-usage.
The concentration of benzoic acid (BA) is 1g/L, which is stored at low temperature of 3-4 °C. Under the same reaction processes, the degraded samples were extracted at certain intervals, similarly, absolute methanol was used to quench the reaction. The extracted samples were treated the same method, and the concentrations of p-hydroxybenzoic acid (p-HBA) were determined by HPLC. In the radical quenching experiment, tetr-butyl alcohol (TBA) was used to quench the reactive oxidation species ·OH. TBA was added before the addition of H2O2, and the NB degradation experiments were repeated. All the results can be recurred in the acceptable error range.

2.4. Analytic method
The concentrations of NB, p-HBA were determined by HPLC (waters 2665) equipped with waters 2998UV detector. The conditions of chromatographic column were as follows: symmetry C18 5μm, 4.6×250 mm column, mobile phase: methanol and 0.1% acetic acid solution, the mobile phase ratio of NB: 70:30, detection wave length: 255 nm, appearance time: 2.709s, velocity of flow: 1mL/min, the volume of injected sample: 50μL. The concentrations of p-HBA were determined qualitatively by using BA as probe [19], based on which the concentrations of hydroxyl radicals were measured. The ratio of p-HBA: m-HBA:o–HBA is 1.2:2.3:1.7 [20]. The amounts of NCC, metals in the solution were recorded by ICP-MS (NEXION 2000 ICP-MS, PerkinElmer). The concentrations of Cu, Co ions were calculated according to their peak strength.

3. Results and discussion

3.1. Characterization of NCC catalysts
The crystalline phases of all catalysts were verified by XRD patterns (Figure 1a). Upon comparison with the standard PDF cards, the catalyst prepared using Cu(NO3)2·3H2O as starting material was Cu2O, and that synthesized by Co(NO3)2·6H2O was CoO2/Co(OH)2. The product was CuFeO2 when the starting materials were Cu(NO3)2·3H2O and Fe(NO3)3·9H2O. Interestingly, the products prepared by Cu(NO3)2·3H2O and Co(NO3)2·6H2O were mixture of Cu2O, CuO, CoO2, Co(OH)2, CoO, and the good agreement with PDF cards suggest their good purities. The IR spectra in the range of 4000-450 cm-1 hint the presence of surface chemical bonds (Figure 1b). In detail, the peak at 3626 cm-1 of NCC and CoO2/Co(OH)2 are assigned to the stretching vibrations of isolated OH specie, which stems from the Co(OH)2 [20]. The peak at 539 cm-1 is the characteristic vibration of Co-O bond [21], and those at 1564, 1466 cm-1 are attributed to the adsorbed waters.
Figure 2. (a,b) SEM images and (c-f) STEM images of NCC

The morphologies of NCC catalysts were observed by SEM and TEM-EDS analysis (Figure 2). NCC catalysts were layer-like with ordered lattice stripes, and the sizes of NCC were in the nanometer range. However, the plate-like surfaces were partly or fully covered by some flocculus, or the flocculus was observed lonely (Figure 2d, 2e). This phenomenon indicated that the heterogeneities of elements. Furthermore, the edges of NCC particles were irregular, suggesting the presence of some defects in their lattices (Figure 2f). These defects were the reason for their more active sizes and higher catalytic activities. Judging from XRD and EDS results, the plate-like particles might be the mixtures of Co-based species, and the flocculus was the mixtures of Cu-based species.
Figure 3. XPS binding energy spectra of NCC (a), XPS full spectrum (b), O-1s (c) Co-2p, (d) Cu-2p

XPS measurements can provide some surface chemical information of NCC. As indicated by Figure 3a, the binding energies at 934.0, 780.4, 530.8, 284.4 eV were the characteristic bands of Cu-2p, Co-2p, O-1s and C-1s, respectively, which further proved the presence of Cu, Co and O elements. The C might originate from the propionic aldehyde, which was introduced in the instrument or in the preparation of catalysts. Besides, two shoulder peaks at 530.96 and 531.78 eV were assigned to the O-1s orbital, and this O element could stem from lattice O of catalysts, C-O or absorbed H2O. The XPS spectrum of Co-2p in Figure 3c (780.20, 781.02 and 781.92 eV) suggested that the valence of Co element were +2 and +4 (ratio: 1.52:1) [22, 23]. This assignment was consistent with literatures, and mixed valence between +3 and +4 in CoO2 can be observed. The binding energies of Cu-2p can be seen in Figure 3d (932.49, 933.39 and 934.70 eV), which can be attributed to the vibration of Cu2O and CuO[24,25]. And the valence of Cu was +1 and +2 with ratio of 1:1.97. The XPS results were in agreement with XRD patterns.

ICP-MS measurement can give quantitative metal components of NCC. As illustrated by Table 1, the Cu/Co molar ratio in NCC was generally the same with that of starting materials. But some differences can be seen in EDS and XPS results, which again proved the heterogeneities of elements. The mass fractions of Co and Cu were 14.79% and 14.48%, which hinted that the high metal content in NCC catalysts.

| Metal element  | M(Co:Cu) | m(Co)/% | m(Cu)/% |
|----------------|----------|---------|---------|
| Cu/Co composite | 1.022:1  | 14.79   | 14.48   |
3.2. Catalytic performances

![Graph](image)

Figure 4. Effect of different systems on NB degradation. Conditions: room temperature, 2.5 g/L of catalyst, 0.8 mol/L of H$_2$O$_2$, pH=7, NB concentration 10 mg/L.

The catalytic performances of different catalysts in the degradation of NB were depicted in Figure 4. As indicated by Figure 4a, the degradation ratio of NB only using H$_2$O$_2$ was 17.55% in 60 min without the catalysts. And a 8.19% decrease of NB in 60 min can be obtained when only NCC was used without H$_2$O$_2$, which might be led by adsorption of NB on surfaces of catalysts. However, rapid efficient degradation can be achieved by using NCC/H$_2$O$_2$ system (100% degradation ratio in 45 min), which validated that NCC/H$_2$O$_2$ was a good candidate for NB degradation. Comparably, the catalytic performances of other catalysts including Cu$_2$O, CuFeO$_2$ were relatively lower, which were generally as low as that of H$_2$O$_2$. Besides, the Fe-Co composites, CoO$_2$/Co(OH)$_2$ catalysts exhibited the degradation ratios of 35.41% and 78.36%. Conclusion could be drawn that the Co-containing catalysts exhibited higher catalytic performances, hinting the importance of Co in the catalytic process. Finally, the presence of mixed valence states such as Cu(I)/Cu(II), Co(II)/Co(IV) will give rise to better catalytic performances, suggesting that the mixed valence states could also serve as co-catalytic effect in NCC/H$_2$O$_2$ system (the detail discussion can be seen in Section 3.6).

3.3. NB degradation dynamics

![Graph](image)

Figure 5. Kinetics of oxidative degradation of NB by NCC/H$_2$O$_2$ system. Conditions: room temperature, 2.5 g/L of catalyst, 0.8 mol/L of H$_2$O$_2$, pH=7, NB concentration degree 10 mg/L.

The reaction kinetics were discussed in terms of ln($C_t/C_0$) vs time curve (Figure 5). The good linear relationship between ln($C_t/C_0$) and time can be obtained. Judging from Figure 5, The NB degradation was a first order reaction with dynamic equation of ln($C_t/C_0$) = -kt, where t is the reaction time, k is the
apparent rate constant, $C_t$ and $C_0$ are the concentrations at the beginning and the time of extracting sample. The quasi-first order reaction dynamic mode can be fitted with linear regression coefficient ($R$) of 0.99 and $K$ of 0.112 min$^{-1}$. Compared with the literatures [26-28], NCC/H$_2$O$_2$ catalytic system exhibited higher catalytic activities.

Figure 6. Response curves of different NCC and H$_2$O$_2$ amounts for NB degradation. Conditions: room temperature, pH=$7$, NB concentration 10mg / L

3.1. The effect of NCC/H$_2$O$_2$ amounts Figure 6 illustrated the effect of NCC/ H$_2$O$_2$ amount on degradation rate of NB. To our interests, the degradation efficiency was improved with the increasing amount of NCC/H$_2$O$_2$ amounts. The degradation ratio in 60 min was 60.68% when the using amounts of H$_2$O$_2$ and NCC were 0.40 mol/L and 0.5 g/L. And the degradation ratio didn’t improve obviously (64.62%, 64.62% and 69.19%) when increasing the H$_2$O$_2$ amounts from 0.80, 1.20 to 1.50mol/L. This trend can be explained as the limited NCC amount can only activate small amount of H$_2$O$_2$, therefore, the $\cdot$OH will react with additional H$_2$O$_2$ to reduce the amount of ROS, as a result, the degradation efficiency was affected. So a conclusion could be drawn that amount of active sites on catalysts will determine the degradation efficiency. As verified by Figure 6b-d, under the same H$_2$O$_2$ amount, the degradation ratio was enhanced by increasing NCC amounts. When the amounts of NCC/H$_2$O$_2$ were 2.5g/L, 0.8mol/L and 2.5g/L, 1.20mol/L, no further improvement of degradation ratio can be obtained. So the ideal using amount of NCC/ H$_2$O$_2$ on degradation of 10mg/L NB was 2.5g/L NCC and 0.8mol/L H$_2$O$_2$. 
3.3.2. The pH conditions

The effect of pH condition on the NB degradation and the pH change using NCC/ H$_2$O$_2$ system was depicted in Figure 7. The pH condition was adjusted by NaOH and H$_2$SO$_4$ during the reaction. Out of our expectation, the NB degradation could not be affected greatly by pH environments. NB can be completely degraded in wide pH range including acid, neutral and basic conditions. Thus, NCC/ H$_2$O$_2$ catalytic system can degrade NB in a wide pH range. Specially, faster degradation rate can be achieved at pH=7, which is the best initial pH value. This reaction condition was more advantageous than those in other heterogeneous Fenton reactions [29]. Setting pH=7 as the initial pH value, we monitored the pH change during the NB degradation using NCC/ H$_2$O$_2$ catalytic system, as shown in Figure 6b. After the addition of NCC catalysts, pH increased obviously firstly, which was led by the generation of isolated OH$^-$ species from Co(OH)$_2$. In all the degradation process, both slight increase and decrease can be observed in pH values, and the pH ended at 6.32 when the reaction was completed (45 min). The lower pH might be caused by the presence and their further mineralization of short alkyl chain carboxylic species.

![Figure 7](image1.png)

**Figure 7.** (a) Effect of different initial pH values on NB degradation. (b) pH value curve during degradation of pH=7. Conditions: room temperature, 2.5 g/L of catalyst, 0.8 mol/L of H$_2$O$_2$, NB concentration degree 10mg/L.

![Figure 8](image2.png)

**Figure 8.** Effect of different initial NB concentrations on their degradation. Conditions: room temperature, 2.5 g/L of catalyst, 0.8 mol/L of H$_2$O$_2$, pH=7.
3.3.3. The effect of NB concentration The effect of NB concentrations on their degradation rates was displayed in Figure 8. To our interest, although the NB concentrations increased, NCC/H$_2$O$_2$ catalytic system can also fully degraded them, which illustrated the high catalytic performance of NCC. Furthermore, the rate constant $k$ was calculated when the NB concentrations increased from 10 to 20, 40 and 60mg/L. The results suggested that $k$ decreased with increasing NB concentrations. This can be easily explained as follows: when the amounts of NCC and H$_2$O$_2$ were fixed, the amount of active $\cdot$OH in the system was also fixed, therefore, the possibilities of NB attacked by ROS in certain time and volume will be lowered, as a result, the reaction rate will decrease.

3.4. The identification of ROS

![Figure 9](image_url)

Figure 9. (a) TBA quenching experiments on NCC/system. (b) BA probe experiments qualitatively quantify the accumulation of $\cdot$OH in the degradation process. Conditions: room temperature, 2.5 g/L of catalyst, 0.8 mol/L of H$_2$O$_2$, pH=7, NB concentration 10mg/L, BA concentration 1g/L.

As indicated by the previous literatures, the ROS of heterogeneous catalytic system containing H$_2$O$_2$ is $\cdot$OH, which was also treated as the main ROS of organic pollutant degradation in the acid or neutral solutions [10,11,30]. Tert.-butyl alcohol (TBA) can quench the $\cdot$OH specie with high efficiency[31-33], and the rate constants of the reactions of TBA, methanol and NB with $\cdot$OH specie were $K=6.0\times10^8$ m$^{-1}$s$^{-1}$, $9.7\times10^8$ m$^{-1}$s$^{-1}$, $3.9\times10^9$ m$^{-1}$s$^{-1}$, respectively[33]. In this work, excess TBA (1mol/L) was also added into the NCC/H$_2$O$_2$ catalytic system to quench the $\cdot$OH radicals, and the effect of TBA on the NB degradation was given in Figure 9a. As expected, the degradation result with the presence of TBA was the same with that containing only NCC. Therefore, TBA has inhibited the catalytic reaction efficiently, and conclusion could be drawn that the main ROS in the NCC/H$_2$O$_2$ catalytic system was $\cdot$OH. Furthermore, benzoic acid (BA) was used as probe to validate this conclusion. It’s well accepted that the BA can react with $\cdot$OH to generate p-HBA, o-HBA, m-HBA and other products, and the sensitivity of p-HBA was higher than other isomers [34]. The reaction equation was as follows:

$$\text{BA} + \cdot\text{OH} \rightarrow \text{p-HBA} + \text{o-HBA} + \text{m-HBA} + \text{other products}$$

Here, the percentage of p-HBA, o-HBA, m-HBA accounted as high as 90±5%[19]. So, semi-quantitative analysis on $\cdot$OH by monitoring the p-HBA can be executed. The rate constant of BA reacting with $\cdot$OH was $K=5.9\times10^9$ m$^{-1}$s$^{-1}$[35]. The HPLC measurements on products of BA probe experiments confirmed the presence of p-HBA (Figure 9b), which further verified the ROS of NB degradation using NCC/H$_2$O$_2$ catalytic system was $\cdot$OH. Besides, the generation rate of $\cdot$OH was close to NB degradation rate. In a word, TBA quenching experiment together with BA probing experiment verified that the main ROS of this degradation reaction was $\cdot$OH.
3.5. Stabilities of NCC catalysts

Figure 10. Reaction rate curve of NCC on NB degradation with different re-using cycles

The stability of catalyst is an important issue in the design of new catalysts, which will determine their real application in industrial production. Their stabilities in heterogeneous Fenton system must also be considered. In this work, the NCC catalysts were recovered from the precipitation in the bottom, and stability experiments for four cycles were conducted under the same conditions. As shown in Figure 10, the NB degradation ratio was weakened slightly after several cycles with the apparent reaction constant $K$ decreasing from 0.112 to 0.0926 min$^{-1}$. But the NB solution (10mg/L) can also be degraded completely in 45 min, suggesting good recyclability of NCC catalyst. On the other hand, metal ions in the recycled solutions after reacting for 60 min were monitored by ICP-MS, upon which the dissolved rate was calculated. As disclosed by Table 2, the dissolved rates of Cu, Co ions were small, and no Cu ions have dissolved in the solution. The recycling stability and dissolved experiments proved the good stability of NCC catalyst. Finally, in the NCC/ $H_2O_2$ catalytic degradation system, heterogeneous Fenton reaction dominated the process, which can be explained as a micro-reaction in their interfaces [35].

| Recycling times | Dissolved rate of Cu/% | Dissolved rate of Co/% |
|----------------|------------------------|-----------------------|
| 1              | 0                      | 0.45                  |
| 2              | 0                      | 0.36                  |
| 3              | 0.0026                 | 0.51                  |
| 4              | 0.00035                | 0.56                  |

3.6. Reaction mechanism in the interface

As discussed in the above, $\cdot$OH species was responsible for the NB degradation, which occurred on the surface of catalyst. XPS measurements on recovered NCC were conducted to obtain their surface chemical contents and valence states (Figure 11). Compared with the initial XPS spectra of NCC catalyst, a part of Cu(II) was oxidized into Cu(II), and some Co(IV) were transferred into Co(II). This valence state changes hinted the role of Cu(I)/Co(IV) in the degradation process, and the Cu(II)/Co(II) active sites can activate $H_2O_2$ to generate $\cdot$OH, $\cdot$OH$_2$ species. It’s worth mentioning that the surface O content in the NCC lattice decreased, which might be led by the hydroxylation of NCC in the degradation process.
Based on the above experimental facts, the possible surface reaction mechanism of NB degradation using NCC/H₂O₂ catalytic system was proposed, as depicted in Figure 12. In the heterogeneous system containing catalyst, H₂O₂ and substrate, NB and H₂O₂ will absorb on the active sites of catalyst firstly. Afterwards, the interaction between strong reductive Cu(I) and H₂O₂ will give rise to Cu(II) and -OH. And the -OH will attack substrate to degrade NB (equation 1 and 10). At the same time, the initial and newly produced Cu(II) active sites can react with H₂O₂ to generate Cu(II)-H₂O₂ complexes via substituting the surface waters, among which intra-molecular electron transfer will occur to re-generate the Cu(I) (equation 2, Cu(I)/Cu(II) cycle was complete). Similar reactions will also happen on Co active sites (equation 6-9, Co(IV)/Co(II) cycle was complete). Because the reduction of Co(IV) by Cu(I) was thermally favorable, another cycle will present (equation 5).

\[
\text{Cu}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{2+}(-\text{OH}^-) + \cdot\text{OH} \quad (1)
\]

\[
\text{Cu}^{2+}(-\text{OH}) + \text{H}_2\text{O}_2 \rightarrow \left(\text{Cu}^{2+} \cdot \text{H}_2\text{O}_2\right)(-\text{OH}) \rightarrow \text{Cu}^+ + \text{H}_2\text{O} + \cdot\text{HO}_2 \quad (2)
\]

\[
\text{Cu}^{2+}(-\text{OH}) + \cdot\text{HO}_2 \rightarrow \text{Cu}^+ + \text{H}_2\text{O} + \text{O}_2 \quad (3)
\]

\[
\text{Cu}^{2+}(-\text{OH}) + \text{O}_2^- \rightarrow \text{Cu}^+ + \text{OH}^- + \text{O}_2 \quad (4)
\]

\[
\text{Cu}^+ + \text{Co}^{4+} \rightarrow \text{Cu}^{2+} + \text{Co}^{2+} \quad (5)
\]

\[
\text{Co}^{4+}(-\text{OH}) + \text{H}_2\text{O}_2 \rightarrow \left(\text{Co}^{4+} \cdot \text{H}_2\text{O}_2\right)(-\text{OH}) \rightarrow \text{Co}^{2+} + \text{H}_2\text{O} + \cdot\text{HO}_2 \quad (6)
\]

\[
\text{Co}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Co}^{4+}(-\text{OH}) + \cdot\text{OH} \quad (7)
\]

\[
\text{Co}^{4+}(-\text{OH}) + \cdot\text{HO}_2 \rightarrow \text{Co}^{2+} + \text{H}_2\text{O} + \text{O}_2 \quad (8)
\]

\[
\text{Co}^{4+}(-\text{OH}) + \text{O}_2^- \rightarrow \text{Co}^{2+} + \text{OH}^- + \text{O}_2 \quad (9)
\]
4. Conclusion

In summary, the nano-copper-cobalt bimetallic composite oxide (NCC) has been synthesized under hydrothermal conditions, which was used as heterogeneous Fenton catalyst to degrade nitrobenzene (NB). The high catalytic activities stemmed from the Cu/Co bis-active sites of NCC. The degradation mechanism based on the surface reactions was proposed. NB can be degraded rapidly among wide pH range (3-9) in the NCC/ H₂O₂ catalytic system. In detail, NB with concentration of 10 mg/L (pH=7) can be completely degraded within 45min at room temperature, in which the amount of NCC was 2.5g/L, and that of H₂O₂ was 0.8mol/L. NCC catalysts possessed high chemical stabilities and high recyclabilities, which can be potentially used as heterogeneous Fenton catalysts.

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