Characterization of Various MnOx Doped CSAC and Its Application for Efficient Catalysis of Hydrogen Peroxide

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Abstract. In the present work, the experiments of catalytic decomposition of hydrogen peroxide (H₂O₂) were carried out by using a series of prepared catalysts doped the coconut shell activated carbon (CSAC) under Fenton-like system. The relevant catalysts were prepared by the modified impregnation method. The effects of various catalysts had also been studied in the reaction system. The rate of catalytic decomposition of H₂O₂ was measured at regular time intervals. Besides, the optimum catalysts were characterized by SEM, EDX, BET, and XRD instruments. And it was demonstrated that the rich Mn₃O₄ and K₂₀Mn₈O₁₆ were beneficial for the catalytic activity, which may account for its superior catalytic efficiency.

1. Introduction
In the modern society, volatile organic compounds (VOCs) have been greatly involved in the severe environmental pollution in some countries [1]. It is currently essential to control and remove the emissioned VOCs. Compared with conventional technologies, wet scrubber under advanced oxidation processes (AOP) provide new attempt for VOCs elimination with Fenton-like system[2-6]. But it is obvious that the capacity of ·OH generating from H₂O₂ decomposition is different from the prepared catalysts resulting from the surface energy of transition metal[7]. The paper aims to make some efforts into paving the way for the following degradation of gaseous toluene and the elimination of excessive H₂O₂.

2. Materials and methods
2.1. Catalyst preparation
The required catalysts were prepared by the modified impregnation method via the following steps: the CSAC were sieved with 180 mesh, and then were to remove the ash. The dried CSAC were added into the deionized water, and the pH value of the system was slowly adjusted to 11.0 via the addition of ammonia (NH₃·H₂O) drop by drop. Meanwhile, the transition metal was dissolved into deionized water, and the obtained solution was gradually put into the suspension of CSAC and water by the peristaltic pump under magnetic stirring, respectively. The system was proceeded for 20 min by the ultrasonic wave again. After 12 h, the suspension was filtered and subsequently washed with the deionized water.
for several times until pH value of the solution reached to 7.0-8.0. The sample was dried for 12 h at 378 K and calcined in muffle furnace at 674 K for 4 h. Finally, the desired catalyst was obtained to carry out the following experiments.

2.2. Experimental procedures
One glass beaker (100 mL) with diameter of 5 cm was used as the reaction vessel and placed on a magnetic stirrer. In the typical experiment, 100 mL of 5% (wt%) H2O2 solution was poured into the beaker. The prepared catalyst was added into the solution and well mixed by the magnetic stirrer with the suitable speed, respectively.

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. SEM and EDS
The morphology and microstructure of the prepared catalysts can be characterized by scanning electron microscopy (SEM). The typical SEM images of undoped and doped CSAC were illustrated in Figure 1(a-d). And the qualitative and quantitative analysis of element types and contents of microzone materials are characterized can be characterized by Energy Dispersive Spectrometer (EDS), as shown in Figure 1(e-h). It could be clearly seen that the undoped CSAC appears as a loose agglomeration. After doping, the pore structure of some regions was found by the SEM. As shown in Figure 1, the SEM images of the Figure 1(b), Figure 1(c) and Figure 1(d) were significantly different from the Figure 1(a). The difference might be ascribed to the oxidation reaction between KMnO4 and CSAC, which could probably bring about new pore structure on the surface. It was illustrated in Figure 1(e-h) that MnOx particles were highly dispersed on the supports, like Figure 1(f) and Figure 1(g). The dispersed particles should be ascribed to the high surface area of CSAC. MnCl2/CSAC catalyst (Figure 1(h)) had uniform distribution of MnCl2 probably due to the washing loss of the precipitates during the catalyst preparation. Besides, no doping metals was observed probably because the metals were doped into CSAC but not on the surface[8].

Figure 1. SEM images and EDS spectroscopy of undoped and doped CSAC: CSAC (a/e),
KMnO₄/CSAC (b/f), Modified-KMnO₄/CSAC (c/g), MnCl₂/CSAC (d/h), respectively.

Table 1. Element types and contents of the catalysts in Figure 1(f, g, h).

| Element | KMnO₄/CSAC Wt% | KMnO₄/CSAC At% | Modified-KMnO₄/CSAC Wt% | Modified-KMnO₄/CSAC At% | MnCl₂/CSAC Wt% | MnCl₂/CSAC At% |
|---------|----------------|----------------|--------------------------|--------------------------|----------------|----------------|
| C       | 51.54          | 66.88          | K                        | 8.66                     | K              | 4.26           |
| O       | 21.43          | 20.88          | Mn                        | 30.52                    | O              | 10.69          |
| Mn K    | 15.57          | 4.42           | C                        | 33.2                     | K              | 5.13           |
| Zn K    | 2.7            | 0.64           | O                        | 21.38                    | Mn            | 25.71          |
| F K     | 8.75           | 7.18           | F                        | 5.93                     | F              | 6.00           |
| Total   | 100            |                | Total                    | 100                      | Total         | 100            |

From Table 1, it was clearly observed that the element Mn was doped on the surface of CSAC, respectively. Compared with Figure 1(f) and Figure 1(h), modified-KMnO₄ (Figure 1(g)) had much larger Mn amount 30.52% than others 15.57% and 14.62%. And it was consistent with Figure 2 that the element Mn well existed in the selected catalysts.

3.1.2. BET

For the raw CSAC, the BET specific surface area reached 1,771.05 m²/g, which was less larger than that of the other doped CSAC. They were seen 1766.44, 1719.79 and 1699.30 m²/g, respectively. To some extent, the specific surface area could improve the absorption capacity of transition metal. The adsorption cumulative volumes of pores were obtained by the Barrett-Joyner Halenda (BJH) model. They were 0.39, 0.34 0.33 and 0.33 cm³/g. The presence of transition metal probably blocked the pores of CSAC and promoted the growth of particles, which well agreed with the results of average particle size and reduction of specific surface area.

3.1.3. XRD

As shown in Figure 2, XRD patterns of both modified KMnO₄/CSAC and MnCl₂/CSAC catalysts exhibited relatively poor crystallinity. The small diffraction peak seen at around 23.966° and 43.037° were the characteristic peaks of CSAC, which could be assigned to the (2 0 1) and (3 0 4) lattice plane, respectively. The characteristic diffraction peaks of Mn₃O₄ were located around 36.102° and 43.037° were ascribed to the (3 0 4) lattice planes of Mn₃O₄ structure. The diffraction peak became much widened, indicating that Mn₃O₄ particles were well dispersed on CSAC. This was well consistent with the results of the EDS images. However, the Mn₃O₄ characteristic diffraction peaks of MnCl₂ doped the CSAC could be easily neglected due to the very low relative intensity. The result furthermore implied that Mn₃O₄ structure of MnCl₂/CSAC had poor crystallinity. Besides, it was noted that one sharpened and intense diffraction peak observed at around 12.763° was the characteristic peaks of K₂-xMn₈O₁₆, which could be assigned to the (1 1 0) lattice plane.

Figure 2. XRD patterns of the undoped CSAC, doped KMnO₄ catalyst, modified KMnO₄ catalyst and MnCl₂ catalyst.
3.2. Tests of $\text{H}_2\text{O}_2$ decomposition

3.2.1. Effect of various catalyst precursors

The Figure 3 showed $\text{H}_2\text{O}_2$ decomposition rate over various catalysts. Among the prepared photocatalysts, KMnO$_4$/CSAC achieved the highest $\text{H}_2\text{O}_2$ catalysis efficiency. FeSO$_4$/CSAC, NiCl$_2$/CSAC, MnCl$_2$/CSAC and CSAC had similar $\text{H}_2\text{O}_2$ decomposition efficiency. Compared with CoCl$_2$/CSAC, the precursor KMnO$_4$ could obviously promote the $\text{H}_2\text{O}_2$ decomposition. However, other precursors performed similar $\text{H}_2\text{O}_2$ decomposition tendency with the control test (the CK group), which had no trantion metal incorporated into pore structure of CSAC. The purpose was to exclude the influence of the metal factors upon the decomposition of the hydrogen peroxide.

3.2.2. Effect of MnO$_x$

The effect of various MnO$_x$ upon catalysis decomposition of $\text{H}_2\text{O}_2$ was indicated in Figure 4. Compared with unmodified and modified KMnO$_4$, MnCl$_2$/CSAC had similar performance with the control test (the CK group). The above curve presented the steady tendency towards the $\text{H}_2\text{O}_2$ decomposition. But for the KMnO$_4$ and modified KMnO$_4$ coped CSAC, the rate of $\text{H}_2\text{O}_2$ decomposition increased rapidly with respect to time. The process further implied that they could enhance $\text{H}_2\text{O}_2$ decomposition to some degree[9].

![Figure 3. Evaluation of different precursors on $\text{H}_2\text{O}_2$ decomposition: TM/CSAC (0.1 g/L) at room temperature.](image1)

![Figure 4. Evaluation of various MnO$_x$ on $\text{H}_2\text{O}_2$ decomposition: MnO$_x$/CSAC(0.1 g/L) at room temperature.](image2)

4. Conclusions

A series of efficient transition metal catalysts were synthesized by modified impregnation method. MnO$_x$/CSAC catalysts show much better catalytic activity for $\text{H}_2\text{O}_2$ degradation compared with other prepared catalysts. The optimum catalyst will be potential for removing the VOCs economically and efficiently, due to simplicity synthesis, low cost, high stability and excellent catalytic performance. However, the efficiency of the catalyst in treating VOCs needs to be verified by experiments.

Acknowledgements

The authors gratefully appreciated the financial support of the Open Research Fund of State Key Laboratory of Coking Coal Exploitation and Comprehensive Utilization, China Pingmei Shenma Group (Grant NO. 41040220171106-6).

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