Calcination Effects of Fe Modified MoS$_2$-Carbon Composites for the Improved Degradation Performances of Rhodamine B

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Abstract. The pure MoS$_2$-carbon composites (MoS$_2$-C) and Fe modified MoS$_2$-carbon composites (Fe/MoS$_2$-C) were successfully synthesized through a facile two-step hydrothermal method by adding soft template of CTAB and applied as piezocatalysts to degrade Rhodamine B. The as-obtained catalysts were characterized by the X-ray diffraction (XRD) and scanning electron microscope (SEM). The results indicated the hybrids have large surface area, mesoporous structure, more edges and unsaturated S atoms. By comparing the muffle furnace samples (open air calcination) with the tube furnace one (closed Ar calcination), Fe/MoS$_2$-C catalysts with tube furnace show the higher degradation activities (12.8% versus 5.8%). The possible degradation mechanisms are also discussed.

1.Introduction

The piezoelectric catalytic effect could convert mechanical energy into chemical energy, that is, the surface of the piezoelectric material will introduce charges due to the piezoelectric effect under the action of external mechanical force. Then these charges could participate in the corresponding chemical reactions. In general, piezoelectric polarization may have two ways for the degradation of organic pollutants. Ultrasonic process produces strong oxidizing H$^+$ and •OH groups and results in the degradation of dyes in the reaction solution. For example, the piezocatalytic performance of MoS$_2$ could be promoted by loading with metal (e.g. Fe and Au) nanoparticles $^1$. The synthesis processes have great influences on the catalytic degradation performance of MoS$_2$ $^2$. Different preparation processes of MoS$_2$-C may cause varied MoS$_2$ thin layer thickness and active site distribution. Therefore, in this article, Fe modified MoS$_2$ nanosheets were synthesized with different metal loading under different preparation atmospheres. The calcination effects of Fe modified MoS$_2$ carbon composites (Fe/MoS$_2$-C) were characterized with SEM and N$_2$ adsorption. The structure differences of varied calcination conditions were analyzed and the degradation mechanisms of Fe modified MoS$_2$ carbon composites were also discussed.
2. Experimental

2.1. Chemicals.
Ammonium molybdate tetrahydrate (AR, >99.9%), thioacetamide (AR, >98%) and hexadecyl trimethyl ammonium bromide (CTAB, >99%) were commercially purchased from the Aladdin Bio-Chem Technology, Shanghai. Rhodamine B (RhB, AR) and iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, >99%) were analytical grade and purchased from Tianjin Guangfu Chemical Co. Ltd. All chemicals were used without further purification, and deionized water was used throughout in this study.

2.2. Synthesis of catalysts.
The Fe modified MoS₂ nanosheets were synthesized as following. For typical synthesis processes, 1 mmol of ammonium molybdate tetrahydrate (1.236 g), 30 mmol of thioacetamide (2.254 g), 3 mmol of CTAB (1.093 g) and 1 mmol Fe(NO₃)₃·9H₂O (0.4039 g) were dispersed into 70 mL of deionized water and stirred vigorously for 30 min. Then, the mixture was transferred to a stainless-steel autoclave lined with Teflon and heated at 180 °C for 24 h. The as-prepared product was obtained after washing and vacuum drying. The sample was obtained by calcination at 500 °C for 3 h (heating rate of 1 °C/min) under the Ar atmosphere in tube furnace or in air with muffle furnace. The final product was denoted as Fe/MoS₂-C. MoS₂ nanosheets were prepared without addition of Fe precursor, which was denoted as pure MoS₂.

2.3. Characterization.
The Fe modified MoS₂ nanosheets were characterized by X-ray diffraction with Cu Ka radiation (0.154 nm) as the X-ray source. The scanning electron microscopy (SEM) was done on a Hitachi S-4800. N₂ sorption-desorption isotherms were used to calculate the BET surface area, pore size distribution and the total pore volume with Micromeritics Tristar 3000 sorptometer.

2.4. Catalytic degradation of Rhodamine B.
The piezocatalytic degradation of Rhodamine B was conducted in a glass reactor with cylindrical jacket (30 mg/L). First, the ultrasonic irradiation source was an ultrasonic generator (SciCernt, China) with titanium probe transducer (20 kHz, set power output 100 W). For the degradation of Rhodamine B, the pulse mode of sonication was set to 3.0 s on and 3.0 s off (solution temperature 20 ± 2 °C). For a typical degradation of RhB, 0.06 g of denoted catalyst was added into prepared 200 mL RhB solution. After stirring for 2 min, the solution was ultrasonicated at pulse mode mentioned before and samples (1 mL) were collected and analyzed with a UV–visible spectrophotometer (UV-1800 PC, Jinghua, China) at 554 nm.

3. Results and discussion

3.1. Characterization of Fe/MoS₂-C and related catalysts.
Fig.1 shows the XRD patterns of MoS₂, MoS₂/C and Fe/MoS₂-C calcined with different conditions. The diffraction peaks could be assigned to typical characterization peaks of MoS₂. The (002), (100), (103) and (110) peaks of Fe/MoS₂-C calcined in the muffle furnace are clearly visible. In contrast, the (103) peaks of pure MoS₂/C calcined in the tube furnace are not obvious. The diffraction peaks for Fe/MoS₂-C calcined in the tube furnace could be observed and assigned to (002), (100), (103), and (110) reflections. These results were also reported with previous studies, which indicates the successful iron modification for the MoS₂-C composites. The iron component is uniformly dispersed in the MoS₂ and carbon matrix.

From the SEM images of Fig.2 A and B, Fe/MoS₂-C calcined in air with muffle furnace consisted of abundant cross-linked ultrathin nanosheets. The particles are clustered together and the gaps between the particles could be observed. The spherical MoS₂ nanosheets are small, uniform and closely arranged. The SEM images of Fig.2 C and D show similar grown dense and evenly morphology for
Figure 1. XRD patterns of MoS\textsubscript{2}/C and Fe/MoS\textsubscript{2}-C calcined with different conditions (in air with muffle and in Ar with tube).

The Fe-doped MoS\textsubscript{2}-C calcined in a tube furnace. The particle size of Fe-doped MoS\textsubscript{2}-C calcined in a tube furnace is quite similar and uniform compared with Fe-doped MoS\textsubscript{2}-C calcined in a muffle furnace.

Figure 2. The scanning electron microscopy (SEM) images of Fe/MoS\textsubscript{2}-C calcined in air with muffle furnace (A, B) and in Ar with tube furnace (C, D).

3.2. Comparison of carbon addition under different calcination conditions.

Figure 3 shows the degradation comparisons of MoS\textsubscript{2}-C and Fe/MoS\textsubscript{2}-C calcined with different conditions (in air with muffle furnace versus in Ar with tube furnace). The catalytic performance of
MoS2-C calcined in tube was better than that of MoS2-C calcined in muffle (25.2% versus 12.8%). Since the carbon component could be removed from MoS2-C under air condition in muffle furnace, MoS2-C calcined in tube have higher carbon weight ratio compared to MoS2-C calcined in muffle. The addition of carbon might increase the catalytic performance of MoS2-C, which due to the improved electron transmission capability of MoS2-C composites. The degradation performances of Fe/MoS2-C were quite similar under Ar in tube furnace and air in muffle furnace (7.7% versus 5.8%). Hence, the calcination effects were not obvious when iron components were added into MoS2-C under different calcination conditions. This might be due to the Fe components could enhance the degradation of RhB even without carbon addition, which reduced the calcination difference between Ar and air.

![Figure 3. Degradation comparisons of MoS2-C calcined in air with muffle furnace and in Ar with tube furnace (A), and Fe/MoS2-C calcined in air with muffle furnace and in Ar with tube furnace (B).](image)

4. Conclusions
In summary, Fe modified MoS2-carbon composites were successfully prepared and used as piezocatalyst for the degradation of RhB. The addition of carbon could increase the degradation efficiency for Ar calcination condition.

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