Preparation and Properties of MgO-TiO$_2$-CeO$_2$-ZrO$_2$ Composite Materials

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Abstract. The paper mainly expounds the properties, synthesis, application and development of the nano materials and nano ZrO$_2$ materials, emphasize to introduce the process of preparing MgO-TiO$_2$-CeO$_2$-ZrO$_2$ by using the hydrothermal synthesis method and start a series of characterization and testing on them such as the thermogravimetric analysis, infrared spectroscopy, ultraviolet spectroscopy, XRD, scanning electron microscopy (SEM), and the testing and characterization data were collected and analyzed. Due to the special structure of zirconia, which at the same time with oxidizing and reducing, so it can be as a catalyst or catalyst carrier, after some particle doped its catalytic performance is more obvious and improve, nano zirconia in the future will be boarded the greater dance, and also with more metal particles doped excellent performance have been excavated the potential of nano zirconia.

1. Introduction
The research of nano zirconia particles has been developed rapidly, in which the grain, porosity, phase or the combination of the two is the main influence factor, and the grain size is more prominent in these factors [1-6]. People use a variety of chemical and physical methods for preparation of two zirconia nano materials, physical methods from the traditional physical and chemical method to put it, and then to the chemical method, and the preparation method is novel, have good morphology[7-10]; there are many methods of scientific research personnel by two zirconia on a variety of business the improvement makes nano-ZrO$_2$ doped composite, or modified materials have been widely developed and broaden their application fields[11-13]. ZrO$_2$ nano composite material has the properties of small size, which in high temperature, strong acid conditions can keep intact, two nanometer zirconia all of these properties are in the high temperature resistant material and ceramic insulation, showed the characteristics of catalytic materials, and using nano-ZrO$_2$ doped by Ti$^{4+}$, Mg$^{2+}$, Ce$^{4+}$ to form composite environmental friendly material is rarely reported[14-16], this study uses zirconium oxychloride as raw materials by hydrothermal preparation of nano-ZrO$_2$, and Ti$^{4+}$, Mg$^{2+}$, Ce$^{4+}$ doped to ZrO$_2$ powder, and the material preparation the preparation process, microstructure and catalytic performance of organic dyes were tested and characterized.
2. Experimental

According to MgO-TiO$_2$-CeO$_2$-ZrO$_2$ take an appropriate amount of ZrOCl$_2$, Ce (SO$_4$)$_2$·4H$_2$O, C$_{10}$H$_{20}$BrN, TiCl$_3$, MgCl$_2$·6H$_2$O, NH$_3$·H$_2$O, according to the calculated amount of a sufficient amount of ZrOCl$_2$ and CTAB, and will be mixed, the amount of ammonia added amount of distilled water, adjust the pH value to 7-8. the ZrOCl$_2$ and CTAB into the pH value of ammonia solution in 7~8 and 2 hours magnetic stirring and ultrasonic 1 hour. The mixing solution is put into a reaction kettle to react after 24 h at 80 ℃, and then washed with distilled water and anhydrous ethanol without foam. The product is dried and ground into ZrO$_2$ powder. Said to take a certain amount of ZrO$_2$, respectively, with the high sulfate containing Ce$^{4+}$, containing Mg$^{2+}$ magnesium chloride, containing Ti$^{4+}$ of titanium chloride solution mixed, and by a certain proportion of 22 mixed. Mix the solution into the pH value of 7-8 of ammonia in the magnetic stirring for 2 hours, and then the mixing of the solution mixed into the reaction kettle seal, placed under high temperature and high pressure for 24 hours. After removing the reaction solution, filtering, washing, drying, finally get the product.

By ZS90 analysis of grain size analysis potential instrument size distribution of the powders prepared by particle, using ARL X-ray diffractometer (XRD, Cu Kα, λ=1.5406Å) on the sample phase analysis, TA-84005 type infrared analyzer (FIR) spectra of powder was observed by scanning electron microscope, SEM observation of powder microstructure, UV-VIS spectrophotometer to measure the effect of photocatalytic degradation of organic dye.

3. Results and discussion

From figure 1, we can see the obvious characteristic absorption peak of 3410 cm$^{-1}$, 1320 cm$^{-1}$, 1620 cm$^{-1}$, 840 cm$^{-1}$ and 800 cm$^{-1}$, by the experimental results. The above is the most wide large absorption at 3410 cm$^{-1}$ peak, may be early samples or test for the sample surface to absorb the moisture in the air; the samples prepared in which already contains small amount of crystal water in the preparation of samples adding hydroxyl in ethanol, this interaction will three a the absorption peak at 3410 cm$^{-1}$ in the relatively wide. At 1620 cm$^{-1}$ and 1320 cm$^{-1}$, the absorption peak is due to the symmetric stretching vibration peak of hydroxyl group, and the peak at 400 cm$^{-1}$ to 900 cm$^{-1}$ wave number is due to the expansion of the Zr-O and Ce-O bonds. With the sintering process of a little bit of temperature rise, the original more sharp diffraction peaks disappear, the original more broad diffraction peaks, gradually narrowed disappear, the whole map is smooth. When the sample is heated to 700 ℃, all the infrared diffraction peaks mentioned before are basically disappeared. The samples contain water, nitrate and organic matter and other impurities have been completely volatile or decomposition, the whole process of the formation of the whole crystal complete. Only the absorption peak can be attributed to M-O (M = Ti$^{4+}$, Mg$^{2+}$, Ce$^{4+}$) the characteristic peak of stretching vibration, by 700 ℃ of sintered 2 hours powder has no impurity phases, Ti$^{4+}$, Mg$^{2+}$ and Ce$^{4+}$ have entered the zirconia framework or at least in the composite zirconia surface.

![Figure.1 Infrared spectra of different metals samples](image-url)
Figure 2 is a sample XRD, were doped samples of different XRD diagrams, because the experiment need to test in 2-3, as in the 10 ℃ case results, we can see from the figure roughly doped samples appeared the diffraction peaks, indicating Ti$^{4+}$, Mg$^{2+}$, Ce$^{4+}$ doping changed crystal the structure of ZrO$_2$, pure zirconia is amorphous peaks after multiple doping to crystal structure.

![XRD diffraction patterns of the samples](image)

**Figure.2** XRD diffraction patterns of the samples

Figure 3 shows that with the increase of temperature, the weight of the sample in the early stage of TG decreased gradually, curve down fast, steep slope is the main and impurities in the sample evaporation and decomposition result of sample weight decreased sharply with the increase of the temperature of crystallization in water samples. Weightlessness stage 200 ℃ is mainly due to the organic matter in the sample, the nitrate or metal particles of intense redox caused that the decomposition of organic matter in this process, the combustion reaction occurs, the intermediate product and pyrolysis gaseous products by volatilization, this process occurs, Ti$^{4+}$, Mg$^{2+}$, Ce$^{4+}$ into the ZrO$_2$ lattice. The crystal structure of ZrO$_2$ has changed. 400 ℃ after the curve gradually leveled off, that the weight of the sample...
is not much change, stable, basically maintained the original weight of 75% to complete the reaction, the sample structure has been finalized. It is showed that all the metal elements are in the framework of zirconia.

Figure 4 shows that ZrO$_2$ prepared nanoparticles are small particles, particle agglomeration between the few and the shape of spherical, particle size distribution is uniform, compared with the pure ZrO$_2$ particles combine more closely, block structure is more obvious, more uniform particle size distribution, particle binding between more closely, more aggregate distribution, more uniform, in contrast to other group we can see the same as the result of. So we can see that the doping of multi metal elements will change the density of the ZrO$_2$ structure, and the bulk crystal is more uniform.

Study on the performance of dye catalytic degradation of organic matter: experimental samples take the right amount of added amount of methyl orange solution, in the sun light irradiation 10 h, found that the most obvious MgO-TiO$_2$-CeO$_2$-ZrO$_2$ dye removal is the best, secondly, MgO-TiO$_2$-CeO$_2$-ZrO$_2$ shows better catalytic effect, while Mg-ZrO$_2$, pure ZrO$_2$, Ce-ZrO$_2$ is relatively more stable, ultraviolet irradiation MgO-TiO$_2$-CeO$_2$-ZrO$_2$, Ti-Ce-ZrO$_2$, pure ZrO$_2$ samples, obtained as shown in Figure 6:
From figure 6, we know that the undoped ZrO\textsubscript{2} 5 hours was 20 %, and 5 hours after ZrO\textsubscript{2} doped Ti-Ce degraded in 70 %, MgO-TiO\textsubscript{2}-CeO\textsubscript{2}-ZrO\textsubscript{2} was 90 % in 5 hours, consistent with the sun light. The results of UV light in color, the degradation effect of these three kinds of samples within half an hour is not obvious, the effect is obvious at 5 hours after irradiation, MgO-TiO\textsubscript{2}-CeO\textsubscript{2}-ZrO\textsubscript{2} samples have been nearly colorless, indicating mixed the nano ZrO\textsubscript{2} after Mg-Ti-Ce has better catalytic performance, while Mg-ZrO\textsubscript{2}, pure ZrO\textsubscript{2}, Ce-ZrO\textsubscript{2} stability is better.

4. Conclusion
In summary, pure ZrO\textsubscript{2}, MgO-TiO\textsubscript{2}-CeO\textsubscript{2}-ZrO\textsubscript{2} and series of catalytic materials were prepared by hydrothermal synthesis method. The performance of the catalyst was characterized by infrared, scanning electron microscopy, thermogravimetric analysis, XRD analysis, UV irradiation and other tests. The experimental results show that: (1) the target product was successfully synthesized by hydrothermal method, and the density of the doped catalyst was better, and the particle size distribution was more uniform. (2) by hydrothermal preparation of doped catalytic materials than pure zirconia catalyst with better performance, better effect of MgO-TiO\textsubscript{2}-CeO\textsubscript{2}-ZrO\textsubscript{2} degradation of methyl orange under the irradiation of sunlight, the most obvious change in the ultraviolet irradiation for 5 hours, the degradation of methyl orange 90 %, compared to the pure zirconia reduction solutions of 20 % increased by 70 %. This provides an alternative catalytic material for catalytic materials.

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