Research on the Stability of Catalysts Characterized by TG-DTA and ICP

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Abstract. The stability of the catalysts can be verified by the experimental characterization before and after using. In this study, the reusability of Ru and Pd catalysts were investigated in the CWAO process for the treatment of refractory ceramic printing wastewater. By comparing the TG-DTA curves of Ru catalysts after the first, second and third use, the TG curve showed that the mass of the catalyst changed with the temperature. The curve of DTA (Differential Thermal Analysis) showed no significant difference between the endothermic peak and exothermic peak. The DTG curve, combined with the TG curve, represents the endothermic/exothermic state at a certain temperature. Meanwhile, it can also explain the changes of the sample, such as dehydration, decomposition, oxidation, etc., and the curve changes are not obvious during three uses. This shows that the catalyst has good stability. ICP data, concentration difference of Fe, Co, Ce and Ru were 0.261, 1.177, 0.614, 0.0008 mg/L, respectively. ICP data, concentration difference of Fe, Co, Ce and Ru in three times of use of Pd catalyst were 0.547, 0.067, 0.099 and 0.00008 mg/L, respectively. TG-DTA and ICP were used as the characterization methods, and the dissolution concentration of metal ions was used as the evaluation index of catalyst stability. The results show that the Ru-catalysts and Pd-catalysts have good catalytic stability.

1. Introduction

Advanced oxidation processes (AOPs), also known as advanced oxidation processes, mainly oxidizes the unsaturated bond of chroma in dye molecular structure through the strong oxidation ability of free radicals, so that it breaks and loses its chroma ability. At the same time, dye molecules themselves are oxidized into small molecular organics or directly mineralized into inorganic substances, so as to achieve thorough oxidation Purpose of degradation of dye wastewater [1,2]. Catalytic wet air oxidation is an important way of advanced oxidation technology [3-4].

TG-DTA is a method to measure the relationship between the mass of substance and temperature or time under the temperature controlled by program. By analyzing the thermogravimetry curve, we can know the composition, thermal stability, thermal decomposition of the sample and its possible intermediate products and the information related to the quality. Derivative thermogravimetry, also known as derivative thermogravimetry, can be derived from thermogravimetry. It is a technique for recording the first derivative of TG curve to temperature or time. ICP method, full name inductively coupled plasma emitter, can determine the content of metal elements. TG-DTA method and ICP method can be used to characterize the dissolution concentration of metals [5].
2. Experimental part

2.1. Preparation of catalyst
Ru catalyst: Ru-Fe-Co-Ce/FSC (ratio 2:0.5:0.5:3). The proportion of solid to liquid is =1:2. Solid is (FSC carrier, 10.0 g). Liquid (solution, 20.0 g). Total metal ion concentration = 6wt%. Pd catalyst Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3). The solid-liquid ratio was 1:2 by impregnation. Solid is (FSC carrier 10.0 g). Liquid (solution 20.0 g). Total metal ion concentration = 6wt%.

2.2. TG-DTA characterization of catalysts
The temperature difference between the furnace and the sample crucible is different with different heating rate, which leads to measurement error. Generally, when the heating rate is 5 and 10 ℃/min, the effect is small. The heating rate has an effect on the decomposition temperature of the sample. The fast heating rate results in a large thermal lag, and the decomposition start temperature and end temperature increase correspondingly. The difference of decomposition temperature between 1 ℃ /min and 20 ℃ /min is 70 ℃. In the experiment, we usually choose the heating rate of 5 and 10 ℃ /min.

2.3. ICP characterization of water samples
The full name of ICP is inductively coupled plasma emitter. The principle is to determine the dissolution of supported catalyst in wastewater treatment by measuring the dissolution of metal in water sample. The lower the dissolution, the higher the stability of catalyst.

3. Results and discussion

3.1. TG-DTA analysis of Ru-catalysts
TG-DTA of Ru catalyst after three times of use is shown in Figure 1-Figure 3 below.

Figure 1. TG-DTA after the first use of Ru catalyst.
Figure 1 shows that at 150 °C, the weight loss of Ru-Fe-Co-Ce/FSC catalyst after incineration is about 61%. This part of weight is the water absorbed by them when they are exposed to the air. At 150 °C, the water vapor volatilizes and loses. When the incineration temperature was raised to 329 °C, the weight loss of the product was 76.75%, which indicated that during the heating process, the nitrate was heated to decompose into NO$_2$ gas, and the corresponding oxides were formed. The weight loss of calcined catalyst is caused by the volatilized of a small amount of binding water. After incineration, the catalyst did not change at this temperature, indicating that the nitrate before incineration has been transformed into metal oxide. When the temperature increased to 717 °C, the weight loss of catalyst was 99.25%, indicating that some metal oxides were further converted into metal substances.

Figure 2. TG-DTA after the second use of Ru catalyst.

Figure 2 shows that the weight loss of Ru-Fe-Co-Ce/FSC catalyst after use is about 75% after incineration at 150 °C, and 90% when the incineration temperature continues to rise to 383 °C, indicating that in this heating process, nitrate is heated to decompose into NO$_2$ gas, and corresponding oxygenates are generated. When the temperature rises to 688 °C, the weight loss of the catalyst is 99%, indicating that some metal oxides are further converted into metal substances. When the temperature reaches 400 °C, it changes little.
Figure 3. TG-DTA after the third use of Ru catalyst.

Figure 3 shows that the weight loss of Ru-Fe-Co-Ce/FSC catalyst after incineration is about 70%, which is the water absorbed by the catalyst when it is exposed to the air and evaporated at 150 °C. When the incineration temperature is raised to 366 °C, the weight loss is 76%, which shows that in this process, the nitrate is heated to decompose into NO₂ gas, and the corresponding oxides are formed. When the temperature increased to 519 °C, the weight loss of catalyst was 95.15%, indicating that some metal oxides were further converted into metal substances.

From Figure 1 to Figure 3, the curves of TG-DTA are not obvious, which shows that the stability of Ru, Fe, Co, Ce/FSC catalyst is good.

3.2. TG-DTA analysis of Pd catalyst.

TG-DTA of Pd catalyst after three times of use is shown in Figure 4-Figure 6 below.

Figure 4. TG-DTA after the first use of Pd catalysts.
Figure 4 shows that within 150 °C, the weight loss of the used catalyst is about 62.8% after incineration, and 73.95% when the incineration temperature continues to rise to 247 °C, indicating that in this heating process, the nitrate is heated to decompose into NO2 gas, and corresponding oxides are generated. After incineration at 521 °C, the catalyst did not change at this temperature, which indicated that the nitrate before incineration had changed into metal oxide. When the temperature increased to 723 °C, the weight loss of catalyst was 97.70%, indicating that some metal oxides were further converted into metal substances.

Figure 5 shows that the weight loss of Pd-Fe-Co-Ce/FSC catalyst after incineration is about 54.49%, which is the water absorbed by the catalyst exposed to air, and the water vapor evaporates and loses at 150 °C. When the incineration temperature was raised to 363 °C, the weight loss was 78.20%, which indicated that during the heating process, the nitrate was heated to decompose into NO2 gas, and the corresponding oxides were formed. After incineration at 601.5 °C, the catalyst did not change at this temperature, indicating that the nitrates before incineration had been transformed into metal oxides. When the temperature increased to 805 °C, the weight loss of catalyst was 98.90%, indicating that some metal oxides were further converted into metal substances.

Figure 5. TG-DTA of Pd-catalyst after the second use.
Figure 6. TG-DTA after the second use of Pd catalyst.

Figure 6 shows that the weight loss of Pd-Fe-Co-Ce/FSC catalyst after incineration is about 59.30%, which is the water absorbed by the catalyst when it is exposed to the air and evaporated at 150 ℃. When the incineration temperature was raised to 383 ℃, 81.6% of the weight was lost, which indicated that during the heating process, the nitrate was decomposed into NO\textsubscript{2} gas by heating, and the corresponding oxides were formed. The weight loss of calcined catalyst is caused by the volatilized of a small amount of binding water. After incineration, the catalyst did not change at this temperature, indicating that the nitrate before incineration has been transformed into metal oxides. When the temperature increased to 688 ℃, the weight loss of catalyst was 98.48%, indicating that some metal oxides were further converted into metal substances. The drift of DTA line is caused by the lack of samples, and the lack of heat absorption and release peak is caused by the small and slow thermal change.

From Figure 4 to Figure 6, the curves of TG-DTA are not obvious, which shows that the stability of Ru-Fe-Co-Ce/FSC catalyst is good.

3.3. **ICP characterization**

The ICP results of water samples at 120 min under the action of Ru and Pd catalysts are shown in Table 1 and Table 2.

**Table 1. ICP of water sample under the action of Ru-catalysts.**

| Experimental group | Fe    | Co    | Ce    | Pd     |
|-------------------|-------|-------|-------|--------|
| First             | 4.967 | 1.362 | 0.713 | 0.0003 |
| Second            | 3.897 | 0.409 | 0.228 | 0.0012 |
| Third             | 5.228 | 0.185 | 0.099 | 0.0011 |

**Table 2. ICP of water sample under the action of Pd-catalysts.**

| Experimental group | Fe    | Co    | Ce    | Pd     |
|-------------------|-------|-------|-------|--------|
| First             | 3.140 | 0.782 | 0.309 | 0.00062|
| Second            | 2.849 | 0.385 | 0.091 | 0.00066|
| Third             | 3.687 | 0.849 | 0.408 | 0.00074|
It can be seen from Table 1 and Table 2 above that the dissolution of metal ions in the second use of the two catalysts is lower than that in the first use, and slightly higher in the third use than that in the first use. The change of metal dissolution concentration is very small, indicating that the catalyst is relatively stable.

4. Conclusions
The TG-DTA characterization of the catalysts showed that the quality of the catalyst did not change significantly. ICP characterization showed that the concentration of metal in water sample after catalyst use was small. These characteristics show that the noble metal Ru system and Pd System catalysts have good stability.

Acknowledgments
This work was supported by 2019 Lateral Project from Guangzhou College of Technology and Business.

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