Kinetics of s catalyzed oxidation of Zinc heteropolyate of Supercritical water of POPs

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Abstract: The kinetics of persistent organic pollutants (POPs) degradation has been the focus of wastewater treatment in recent years, and supercritical water oxidation is a green and efficient organic waste treatment method developed in recent years. The kinetics of degradation of POPs by catalytic oxidation of near-critical water zinc heteropolysate was studied. The reaction order, apparent activation energy and the feedback of three factors to catalytic degradation were measured. In this experiment, under the conditions of temperature 280~360℃, pressure 6.9~ 20.3MPa and reaction time 5~30min, using Zn$_{1.2}$PW$_{12}$O$_{40}$ as catalyst and hydrogen peroxide as oxygen source, the kinetics of supercritical water catalytic oxidation of 4,4'-dibromobiphenyl was studied. Through MATLAB software fitting data, it was found that: Using zinc phosphotungstate Zn$_{1.5}$PW$_{12}$O$_{40}$ catalyst, 4,4'-dibromobiphenyl reaction order is 1.70, apparent activation energy is 44.04 kJ/mol, therefore, phosphotungstate as catalyst can reduce the activation energy of POPs oxidative degradation in near-critical water.

1. The Introduction
When water is in the high-temperature and high-pressure state above the critical point (374℃, 22.1Mpa), it is called Supercritical critical water. Supercritical water has variable density, low surface tension, low viscosity and high diffusion coefficient. Supercritical water oxidation technology can be used in the treatment of various toxic substances and waste water. There are many reports on the development and application of supercritical water oxidation technology. The main treatment objects include: phenol, trichloroacetalddehyde, nitrobenzene, tert-butanol, naphthol, diaminoethylene dioxide, cyanogen and melamine, DDT, polychlorinated biphenyl, dioxins, explosive wastewater, papermaking wastewater, organic fermentation wastewater, nitrification process wastewater, organophosphorus pesticides and plastics and so on. Supercritical water oxidation technology has high treatment efficiency and low treatment cost. It is economically and technically feasible and has a broad development prospect. Supercritical water oxidation (swo) is a green and efficient method for the treatment of organic waste developed in recent years. Listed in the national key technology of one of the big six "energy and the environment", the SCWO listed as the most promising waste disposal technology, the scientist Paul w. Hart said: "given the SCWO method has many advantages, and use it to replace the incineration method is full of vitality."

The research group mainly studied the kinetics of the catalytic degradation of persistent organic pollutants (POPs) by zinc heteropoly acid in supercritical water, and determined the feedback of three factors, including reaction order, apparent activation energy and pre-index factor, on the catalytic degradation. Our research group has studied the kinetics of POPs catalytic oxidation in supercritical water with Mn$_2$O$_3$ as catalyst. Through this experiment, we can also get the effect of different catalysts on POPs degradation.
2. The experiment content

2.1 Experimental instruments

High-pressure reaction kettle: Hai 'an huada petroleum instrument co., LTD
High efficiency and energy saving industrial resistance furnace: 10kw, Kaifeng teda electric furnace technology co., LTD
Electric thermostatic blast drying oven: dgg-9070b, Shanghai senxin industrial instrument co., LTD
Electronic balance: ab104-n, mettler Toledo instrument Shanghai co., LTD
Ultrasonic cleaner: QT10260, Tianjin ripu electronic instrument co., LTD
Vacuum pump: 2xz-2, Shanghai vacuum pump factory
Muffle furnace: sxl-1208, Shanghai jinghong experimental equipment co., LTD
Digital regulator: XMTD, Shanghai huihai electrical equipment co., LTD
Integrated thermal analyzer: STA 409 PC, neisch instrument company, Germany
X ray diffractometer: D'max-2200, science corporation, Japan

2.2 The raw material

4,4'-dibromobiphenyl: yantai jiumu chemical co., LTD
Hydrogen peroxide solution: analytically pure, Shanghai sinopyrine chemical reagent co. LTD
Adjacent Philippine rowling: analytically pure, Shanghai haoshen chemical reagent co., LTD
Potassium dichromate: analytically pure, Shanghai haoshen chemical reagent co. LTD
Hexahydrate, ammonium ferric sulfate (II) :Shanghai try his four chemical co., LTD
Silver sulfate: analytically pure: Shanghai fine chemical materials research institute
Concentrated sulfuric acid: analytically pure, Shanghai sinopyrine chemical reagent co. LTD

7. Hydrated ferrous sulfate: Shanghai shanhai engineering group experiment no.2 plant
Artificial zeolite: 20~40 mesh, Shanghai reagent 5 factory
Deionized water: made in laboratory

2.3 The experimental process

2.3.1 preparation of catalysts

Zn1.2PW12O40 catalyst was prepared with heteropoly acid as precursor and natural cellulose as template. The solid of 1.6g Zn(AC)2 was dissolved in 30ml ethanol, and the solution was mixed with 0.3mol/l H3PW12O40 water solution. The solution was stirred for 1 hour at 80℃. After that, some filter paper was soaked in the mixture for 6 hours.

2.3.2 oxidative degradation of 4,4'-DBB

The intermittent agitation-free high-pressure stainless steel reactor was used as a device for the oxidation and degradation of 4,4'-DBB, with a volume of 100ml. The liquid product was calculated according to the K2Cr2O7 method in national standard 11914-89, and the chemical oxygen demand (COD) value was taken as the evaluation index.

2.3.3 determination of chemical oxygen demand (COD)

Accurately absorb 20.00ml of evenly stirred sample (if the sample is less than 20.00ml, it can be diluted to 20.00ml).10.00mlK2Cr2O7 standard solution, put it in a reflux conical bottle containing grinding port, then add several small zeolites or glass beads, mix the ingredients in conical bottle evenly through shock. Start the timer from the boiling of the liquid, reheat and reflux for 2h.

If the COD value of the water sample is too high, you can first take 1/10 of the required volume in the above steps for measurement, and then gradually reduce the content of the water sample, until the measured solution is not green, the volume of the water sample used at this time should be the required volume for analysis of the water sample. In the process of water sample dilution, the volume of water sample absorbed shall not be less than 5.00ml. For water samples with high COD value,
progressive dilution and multiple dilution can be carried out. If the content of Cl- in the water sample is greater than 30mg/L, 0.4g HgSO₄ should be placed in the reflux conical flask first, and then 20.00ml water sample or diluted water sample should be added for determination.

After reflux, the liquid was cooled to room temperature, and the outer wall of the condensing tube was washed with 90ml deionized water, and the reflux conical bottle was removed. If the total volume of the liquid is too large, the titration end point will be fuzzy, affecting the determination results. So the total volume of the solution should be less than 140 milliliters.

After the solution is thoroughly cooled, drop 3 drops of ferrous spirit indicator and titrate the sample through the standard solution of ferrous ammonium sulfate. When the color of the solution changes from yellow to turquoise to reddish brown, record the volume of the titrant used.

20.00ml deionized water was taken for the above steps as the blank contrast experiment, and the volume of titrant used in the blank test was accurately recorded.

Calculate the COD value of the water sample

\[
\text{COD}_\text{(O}_2, \text{mg/L}) = (V_0 - V_1) \times C \times 8 \times 1000 / V
\]

Where: C -- concentration of titrant, namely the standard solution of ammonium ferrous sulfate, mol/L;

\( V_0 \) -- the volume of the standard solution of ammonium ferrous sulfate required for blank experiment, ml;

\( V_1 \) -- volume of the standard solution of ammonium ferrous sulfate required for water sample determination, ml;

\( V \) -- volume of water sample used in the experiment, ml;

2.3.4 establishment of kinetics equation of degradation reaction

Firstly, the experimental data are preprocessed to improve the fitting accuracy. Then experimental data input to the main interface, in the use of MATLAB simulation toolbox (MATLAB7.0→Start→Toolboxes→CurveFitting Tool) for data processing, customized nonlinear fitting, as shown in figure 1.

3. Results and discussion

3.1 kinetic analysis of non-catalytic cracking reaction

The experimental data of non-catalytic degradation reaction kinetics are shown in table 1.

| Residence time /min | COD (mg/L) |
|---------------------|------------|
|                     | 320°C      | 340°C      | 350°C      | 360°C      |
| 5                   | 347.2      | 283        | 239.5      | 214.8      |
| 10                  | 228        | 154.2      | 122.5      | 98.7       |
| 15                  | 157.2      | 119.2      | 89.5       | 67.3       |
Because the oxidation reaction in the near critical state of water produces more intermediate products, reflecting a more complex situation, easy to be affected by many factors and interference. The power exponential equation method is not affected by the intermediate reaction and the products, but only depends on the concentration of reactants and the reaction temperature. Therefore, the power exponential equation method is adopted in this paper for the kinetic study of the reaction. In the process of this reaction, the organic matter content can be characterized by chemical oxygen demand, so the content of pollutants in the macroscopic dynamics study can be characterized by chemical oxygen demand after the reaction, and the change of chemical oxygen demand can be characterized by the oxidation reaction process. Thus, the following dynamic expression can be obtained:

\[ -\frac{d(COD)}{dt} = k_1[COD]^a[H_2O_2]^b \]  

(1)

Where: \( a, b \) respectively represent the reaction series of COD and H\(_2\)O\(_2\).

Since the oxidant (H\(_2\)O\(_2\)) is excessive in the near critical water oxidation reaction, the concentration of the oxidant [H\(_2\)O\(_2\)] in the reaction process can be considered as a constant, so [H\(_2\)O\(_2\)]\(^b\) can be incorporated into \( k_1 \), then equation (1) is converted into

\[ -\frac{d(COD)}{dt} = k [COD]^a \]  

(2)

After the determination of initial chemical oxygen demand \([COD]_0=3628 \text{ mg/L}\), the initial conditions were applied: \( t=0, [COD]_0=3628 \text{ mg/L} \), and when \( a \neq 1 \), the integral of equation (2) was:

\[ [COD] = 3628[1 + 3628^{\frac{1}{a}} k(a-1)t]^{\frac{1}{a}} \]  

(3)

According to the experimental data in table 1, equation (3) is fitted to get figure 2. Through regression analysis, \( a=1.71 \) can be obtained, and the reaction rate under different temperatures is constant \( k \). The specific data are shown in table 2.

| Table 2 Relationship between temperature and reaction rate constant |
|---|
| T/℃ | 320 | 340 | 350 | 360 |
| k×10^4 | 1.057 | 1.358 | 1.655 | 1.915 |

(a)  
(b)
According to the Arrhenius formula,\[ k = Ae^{\frac{E_a}{RT}} \] (4)

Arrhenius formula can be converted into the following formula:
\[ \ln k = -\frac{E_a}{RT} + \ln A \] (5)

Where A is the preexponential factor and Ea is the reaction activation energy.

Lnk and \((-T^{-1} \times 10^3)\) were used to draw the figure, and the results were shown in figure 3. According to the slope of the line, the reaction activation energy \(E_a = 46.56 \text{ kJ/mol}\), and the preexponential factor \(A = 13.09\).

3.2 Kinetic analysis of Zn\(_{1.2}\)PW catalytic degradation reaction
The experimental data of Zn1.2PW catalytic degradation reaction kinetics are shown in table 3.

| Table 3 kinetic data of Zn\(_{1.2}\)PW\(_{12}\)O\(_{40}\) catalytic degradation reaction |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Residence time /min            | COD (mg/L)      |                 |                 |                 |
|                                | 320°C           | 340°C           | 350°C           | 360°C           |
| 5                               | 223.2           | 159             | 123.7           | 109.7           |
| 10                              | 101.2           | 67              | 61.8            | 54.2            |
| 15                              | 55.9            | 37.5            | 29.4            | 17.9            |
| 20                              | 36.64           | 21.8            | 12.5            | 6.2             |
| 25                              | 19.8            | 17.6            | 8.9             | 1.6             |
| 30                              | 14.5            | 10.8            | 3.6             | 0               |
Under the catalysis of near-critical water oxidation, the following kinetic expression is obtained:

\[- \frac{d[COD]}{dt} = k_a [COD]^a [H_2O_2]^b [M]^c \]  \hspace{1cm} (6)

In the formula, a, b and c respectively represent the reaction series of COD, H_2O_2 and M (catalyst). Because hydrogen peroxide oxidant is excessive in the process of oxidation of near-critical water, the concentration of this oxidant is usually set as a constant value. The quantity of M is a fixed value, that is, [M]c, so [H2O2] b and [M]c can be incorporated into k1, then equation (6) is transformed into

\[- \frac{d[COD]}{dt} = k [COD]^a \]  \hspace{1cm} (7)

In the regression study of equation (7), figure 4 can be obtained, and then a value (a=1.79) can be obtained through calculation, and then the value of the reaction rate constant k at different temperatures can be calculated, as shown in table 4.

![Figure 4 Zn_{1.5}PW_{12}O_{40} catalyzed kinetic data fitting chart](image)

(a) 320°C (b) 340°C (c) 350°C (d) 360°C

| T/°C | kx10³ |
|------|--------|
| 320  | 6.633  |
| 340  | 8.695  |
| 350  | 10.37  |
| 360  | 11.57  |

LNK and (-t⁻¹ \times 10³) were used to draw the figure, and the results are shown in figure 9. According to the slope of the line, the reaction activation energy Ea= 44.04 kJ/mol could be calculated.
4. Conclusion

Under the conditions of temperature 280~360℃, pressure 6.9~20.3mpa and reaction time 5~30min, with Zn$_{1.2}$PW$_{12}$O$_{40}$ as catalyst and hydrogen peroxide as oxygen source, the kinetics of 4,4′-dibromobiphenyl catalyzed by near critical water was studied. Through MATLAB software fitting, it was found that:

1. Without catalyst, the reaction order of 4,4′-dibromobiphenyl is 1.71, with apparent activation energy of 46.56 kJ/mol.
2. Zinc phosphotungstate Zn$_{1.5}$PW$_{12}$O$_{40}$ catalyst was used. The reaction order of 4,4′-dibromobiphenyl was 1.70 and the apparent activation energy was 44.04 kJ/mol.
3. Phosphotungstate as a catalyst can reduce the activation energy of POPs oxidative degradation in near-critical water, but compared with Mn$_2$O$_3$, the effect on activation energy is not significant.

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