Catalytic ozonation of chlorinated carboxylic acids with $Ru/CeO_2–TiO_2$ catalyst in the aqueous system

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The catalytic mineralization of chloroacetic acid (CAA) and chlorosuccinic acid (CSA) by ozone with $Ru/CeO_2–TiO_2$ solid catalyst in aqueous systems was studied. The catalyst significantly improves the oxidation and degradation at acidic pH. More than 80 to 90% of the converted CAA and CSA are mineralized during the reaction. The chloride is nearly completely released along with the decomposition of CAA and CSA.
The catalytic oxidation of CAA and CSA and conversion of total organic carbon can be simply simulated with a pseudo-first-order behavior with little dependence on the concentration of the dissolved ozone in the aqueous systems, which is maintained in sufficient quantity during the reaction. The catalytic ozonation displays a higher ozone use efficiency than ozonation alone. CSA is apparently easier to degrade than CAA. The chloride ion in the solution has little detrimental influence on the catalytic effects under our experimental conditions. The oxidation of 2 mM CAA is apparently stopped after about 50 min when the CAA concentration decreases to about 0.6 mM and the pH value of the system is lower than the pK_a of CAA. The explanation is that in very dilute systems with pH values lower than the pK_a, the low-concentration of CAA ions slows the adsorption and reaction rates. The near-total elimination of CAA at low concentrations can be achieved only if the pH value is increased above the pK_a. The results demonstrate that catalytic ozonation is an effective and promising method for the oxidation and elimination of chlorocarboxylic acids.

Catalysis combined with the ozonation process (catalytic ozonation) can improve the oxidation and degradation of organic contaminant compounds, especially small carboxylic acids that cannot be easily attacked by conventional oxidation processes. The process provides a promising new kind of water treatment method.[1] It can be conducted under ambient conditions, and may be easily applied in real water treatment situations without any auxiliary thermal or light systems. Some research about the catalysts,[2–5] the effects on model molecules[6–10] and real wastewater treatment[11,12] have appeared during the last few years.

Chlorinated organic chemicals existing in the wastewater and groundwater systems are normally difficult to remove with conventional biological technologies. It is important and necessary to investigate more efficient methods to decompose and totally eliminate such chlorinated organic pollutants in aqueous systems.

In this article, the oxidation and decomposition of small chlorinated carboxylic acids by heterogeneous catalytic ozonation in an aqueous system is studied. The catalyst used is the $CeO_2–TiO_2$ support with 2% Ru. It was synthesized in our laboratory and has been proven[13] to be active and stable during the catalytic ozonation of succinic acid (SA) in an aqueous system, without any leaching problems such as those encountered using some oxide catalysts such as MnO_2, Fe_2O_3, *etc.* Chloroacetic acid (CAA) and chlorosuccinic acid (CSA) were chosen to test the feasibility of such a mixed metal oxide $CeO_2–TiO_2$ (support for Ru) for the ozonation and elimination of small chlorinated organic acids.

Experimental

Catalyst

The synthesis of 2% wt $Ru/CeO_2–TiO_2$ catalyst (simply named as CT-2R) has been described elsewhere.[13] Characterization showed the cubic structure of the catalyst. The BET surface area is about 85 $m^2 \cdot g^{-1}$. The pH of the point of zero charge (pH_{pzc}) of the $CeO_2–TiO_2$ support is about 5.7

Reaction

Ozonation and catalytic ozonation were carried out at room temperature and ambient pressure in a semi-continuously flowing system,[3] in which the gas with ozone, generated from a Lab 76 ozonizer (Trailigaz), was passed continuously through 1000 mL of an aqueous solution of the objective organic compounds in the absence and the presence of suspended catalyst powder. In the standard procedure for the catalytic ozonation, the ozone was introduced into the reactor immediately after 0.8 $g \cdot L^{-1}$ of CT-2R catalyst was added into the solution. The "time zero" was taken at the point when the first bubble was seen in the reactor, with simultaneous magnetic stirring. The flow rate of the ozone gas introduced into the reactor was about 15.6 $L \cdot h^{-1}$. Ozone was controlled at 1275 ± 25 mg $O_3 \cdot h^{-1}$ in all experimental series. The pH value of the reaction systems was adjusted with concentrated HNO_3 and NaOH solutions, in the range of 2.6–3.6.

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Analysis

Samples taken from the reaction systems were analyzed for the concentration of chlorocarboxylic acids, total organic carbon (TOC), chloride ions and the amount of ozone dissolved in the solution system after separation of the catalyst by filtration on a 0.45 μm filter. Nitrite ions were added to the sample immediately to quench possible further reaction by residual ozone. Chloroacetic acid and chlorosuccinic acid were both detected by HPLC with a UV detector, using a Supelco gel C-610H column with an aqueous solution of phosphoric acid (0.1%) as the eluent. TOC was determined on a Shimadzu TOC 5000 apparatus. The concentration of chloride ions in the solution was measured with the spectrophotometric method at 480 nm, using a solution of mercuric thiocyanate and ferric ions, based on the liberation of the colored ferric thiocyanate after mercuric chloride formation. The concentration of ozone dissolved in the solution was measured by the spectrophotometric carmin indigo method.[14] The ozone concentration in the gas at the inlet and outlet was measured with the iodometric method. The ozone consumption during the reaction process was obtained according to the ozone balance in the systems.

Results and discussion

The experimental results on the conversion of the chlorocarboxylic acid, the production of chloride ions as well as the removal of TOC during ozonation alone and catalytic ozonation in acidic systems, in the absence and presence of the CT-2R catalyst, are shown in Fig. 1 and 2 for CAA and CSA, respectively. It can be seen from the figures that ozonation alone has a very small effect on the degradation of chlorinated carboxylic acids in acidic systems under our experimental conditions. Not more than 10% of 2 mM CAA and 20% of 1 mM CSA are converted during 1 h ozonation, and TOC conversion efficiencies (into CO_2) are less than 5% and 10%, respectively, for the two systems.

The presence of the CT-2R catalyst in the ozonation system improves oxidation and degradation efficiencies as seen from Fig. 1 and 2. The CAA and CSA conversion efficiencies are higher than 55% and 80%, respectively, after only 30 min reaction, and the TOC conversion efficiency reaches 45% and 60%, respectively.

A stoichiometric increase in the concentration of chloride ions in solution, along with the decomposition of CAA and CSA during the catalytic ozonation, was also observed (Fig. 1 and 2). This means that chloride is nearly completely released during the catalytic oxidation and no other chlorinated organic intermediates or byproducts were formed during the reactions. Furthermore, it can also be seen from Fig. 1 and 2 that the elimination of TOC during catalytic ozonation is very similar to that of CAA and CSA. More than 90% of CAA and 80% of CSA converted are totally mineralized. This suggests that not very many intermediates and byproducts are produced, especially for the smaller CAA molecule.

It has been found that the adsorption efficiencies by the catalyst are about 5% of 2 mM CAA and 10% of 1 mM CSA, in the absence of ozone under our experimental conditions. So the removal efficiencies cannot be due to adsorption effects. In addition, oxygen passing through the system instead of ozone has no oxidative effect in the presence of the CT-2R catalyst.

Fig. 3 shows the concentration of dissolved ozone during the ozonation and catalytic ozonation of CAA and CSA. The higher efficiency processes (in the presence of the catalyst) have lower ozone concentration than the less efficient ozonation process. This means that the high reaction efficiency is not due to the evolution of the ozone concentration. The improvement in the elimination efficiencies by the catalyst absolutely arises from the catalytic oxidation effect, which in turn consumes much ozone and decreases the ozone concentration in the aqueous systems.

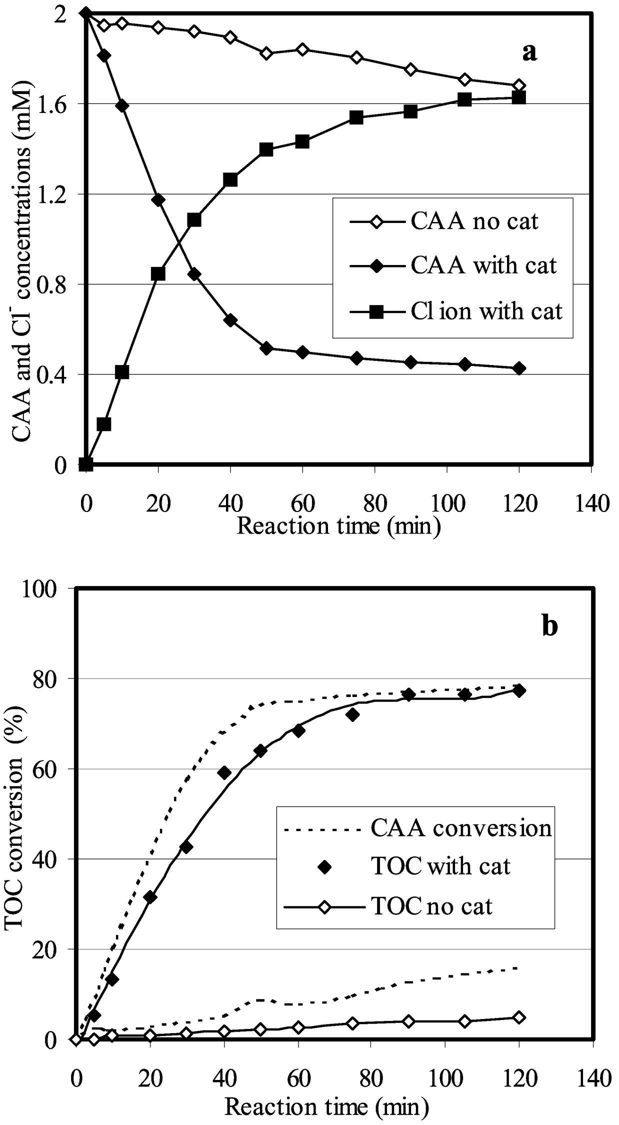

Fig. 1 Conversion of chloroacetic acid (CAA) and TOC, and production of chloride ions during ozonation alone and in catalytic ozonation with the CT-2R catalyst. Room temperature, initial pH: 3.1, catalyst amount: 0.8 $g \cdot L^{-1}$, CAA initial concentration: 2.0 mM, introduced O_3 flow rate: 1275 ± 25 $mg \cdot h^{-1}$. (a) CAA and Cl^- concentrations; (b) TOC conversion.

These results demonstrate that the CT-2R catalyst is very active towards oxidation and degradation of small chlorocarboxylic acids like CAA and CSA.

From Fig. 3, it is seen that the ozone concentration in the aqueous systems increases with time during the catalytic ozonation. This indicates that ozone dissolution is not the limiting step and the ozone concentrations in the systems are sufficient for the oxidation and degradation reactions. Furthermore, the experimental results showed that a stirring speed above 500 rpm has little influence on the reaction. These reveal that the reaction rates are not limited by external mass transfer under our experimental conditions.

Fig. 4 shows the pseudo-first-order conversion of CAA, CSA and TOC during catalytic ozonation processes under our experimental conditions. For the oxidation of CAA, the pseudo-first-order behavior is obtained during the first 50 min. After 50 min, the reaction is apparently stopped and

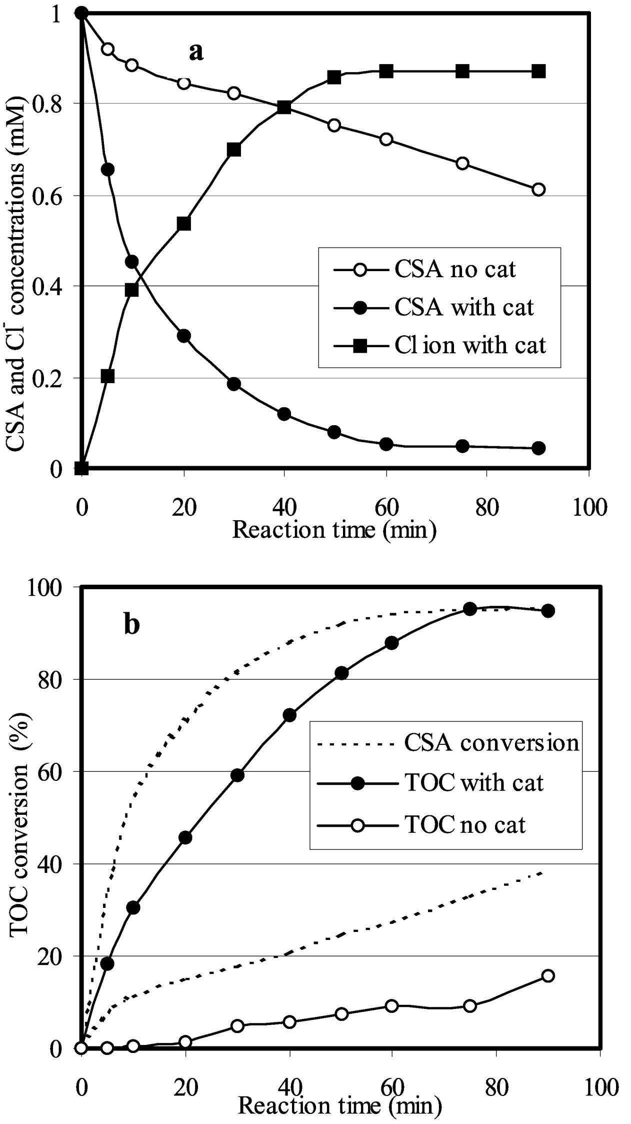

Fig. 2 Conversion of chlorosuccinic acid (CSA) and TOC, and production of chloride ions during ozonation alone and in catalytic ozonation with the CT-2R catalyst. Room temperature, initial pH: 3.1, catalyst amount: 0.8 g·L^{-1}, CSA initial concentration: 1.0 mM, introduced O_3 flow rate: 1275 ± 25 mg·h^{-1}. (a) CSA and Cl^- concentrations; (b) TOC conversion.

the CAA concentration does not decrease very much even after a further 1 h of reaction (see Fig. 1). For the oxidation and degradation of CSA, the pseudo-first-order behavior is obtained only after 10 min. This is probably because processes such as, ozone activation and CSA adsorption on the catalyst have not reached equilibrium and thus the system during the first 10 min is quite complex. A similar situation has also been observed for the catalytic ozonation of succinic acid with the same catalyst, in which the kinetics simulation was possible only after 20 min.[15]

From Fig. 4, the apparent rate constant of CAA and CSA conversion is 0.0282 and 0.0428 min^{-1}, and that of TOC elimination is 0.0206 and 0.0351 min^{-1}, respectively. The pseudo-first-order simulation reveals that the apparent reaction rates of catalytic ozonation of CSA and CAA and conversion of TOC are not very dependent on the concentration of the dissolved ozone under our experimental conditions, when the ozone concentration is in the range of 0.1–0.35 mM, as shown in Fig. 3.

The difference in the time period for the kinetic simulation of catalytic ozonation of CSA and CAA, shown in Fig. 4, results

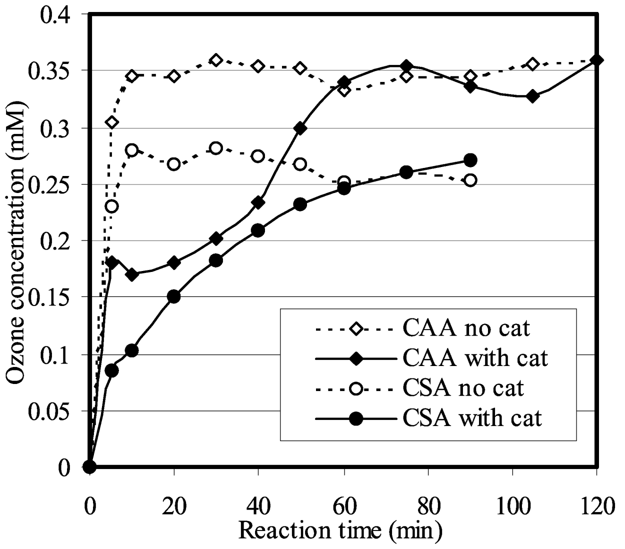

Fig. 3 Evolution of dissolved ozone in the aqueous systems during the ozonation alone (no cat) and in catalytic ozonation (with cat) of CAA and CSA.

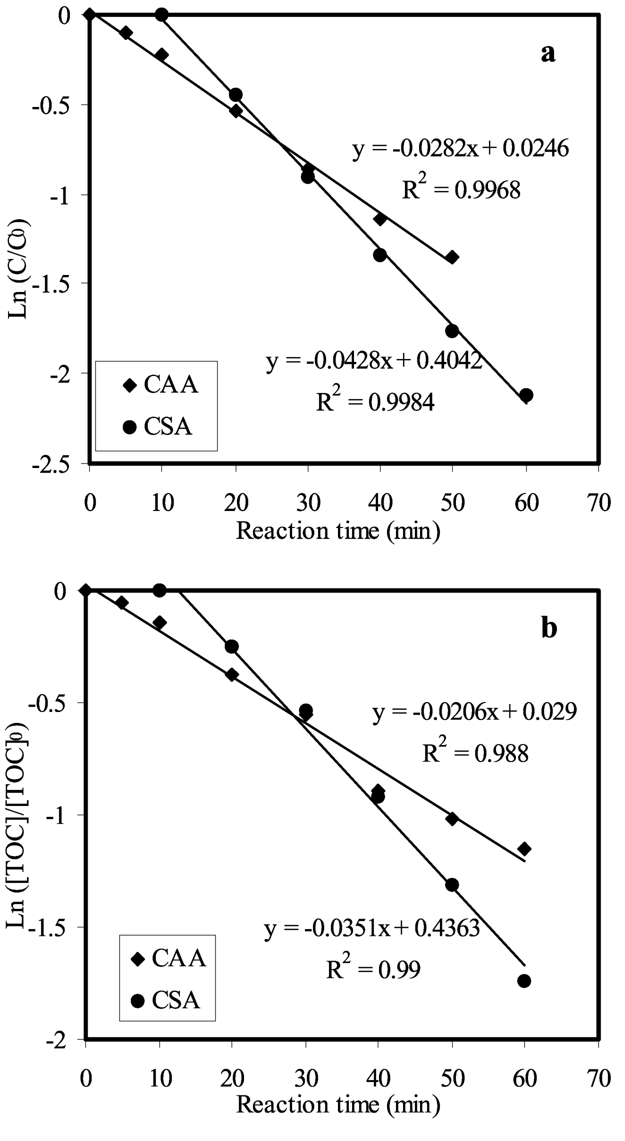

Fig. 4 The pseudo-first-order conversion of CAA, CSA and TOC during catalytic ozonation. Conditions are the same as those in Fig. 1 and 2. (a) CAA and CSA conversion; (b) TOC conversion.

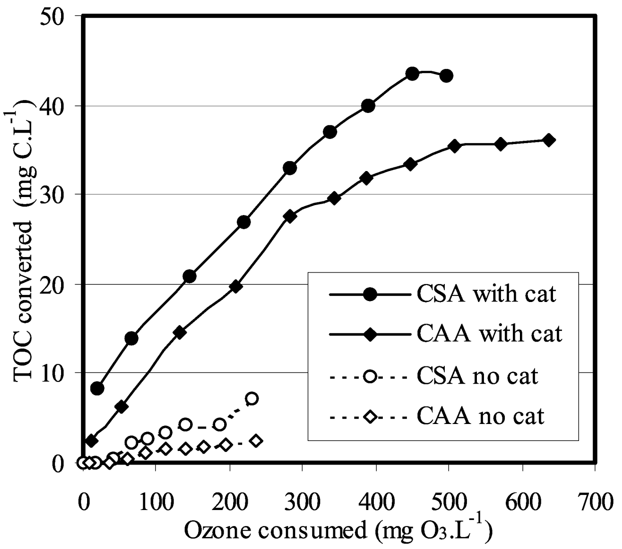

Fig. 5 The relation between TOC conversion and ozone consumption during ozonation alone and in catalytic ozonation of CAA and CSA with the CT-2R catalyst.

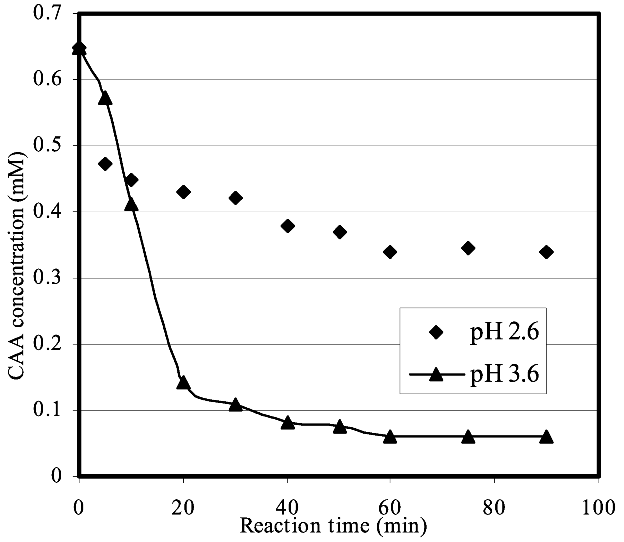

Fig. 6 Catalytic ozonation of low concentration CAA with pH values higher and lower than the pK_a of CAA. Room temperature, catalyst amount: 0.8 g·L^{-1}, introduced O$_3$ flow rate: 1275 ± 25 mg·h^{-1}, CAA initial concentration: 0.65 mM.

from the different molecular structures and interactions of these with the catalyst. Such a selectivity of the catalytic ozonation process towards different organic compounds can also be seen from Fig. 5, which shows the relationship between TOC conversion (in mg C·L^{-1}) and ozone consumption (in mg O$_3$·L^{-1}) during ozonation alone and catalytic ozonation of CAA and CSA. It can be seen from Fig. 5 firstly, that the presence of the catalyst increases the ozone use efficiency compared with ozonation alone, suggesting a beneficial effect of the catalytic ozonation process. Secondly, under the same initial TOC amount (48 mg C·L^{-1}), the relatively bigger molecule, CSA, is easier to mineralize than the smaller one, CAA. This can also be confirmed from the higher rate constants for CSA conversion than those of CAA conversion.

It was shown in Fig. 1 that during the catalytic ozonation of 2 mM CAA, the reaction is nearly stopped after about 50 min when the CAA concentration is about 0.6 mM. Further ozonation for more than 1 h decreases the CAA and TOC concentrations only very slowly.

The CT-2R catalyst has been proved to be active for the ozonation of succinic acid (SA) in our laboratory. The related results have been shown elsewhere.[13,15] So here, SA is used as a model molecule to elucidate the reason for the halt in the reaction during the catalytic ozonation of CAA. The introduction of inorganic chloride ions at concentrations not higher than 2 mM into the catalytic ozonation system of SA has an insignificant influence on the oxidation and conversion of SA and TOC. This is good news for applications of such catalysts in real water systems where chloride ions are commonly found. This also means that the halt in the catalytic conversion of CAA and TOC after about 50 min of reaction is not caused by the chloride ions released from the decomposition of CAA molecules. After 1 h catalytic ozonation of 2 mM CAA, 1 mM SA was introduced into the system and was found to be efficiently converted. This means that the stop of the conversion of CAA was not due to the deactivation of the catalyst.

The pH measurement showed that after 50 min, the pH value of the CAA system decreased from 3.1 to 2.7. The latter is lower than the pK_a of CAA (2.85). Further experiments were performed to study the pH effect on such systems. Fig. 6 shows CAA conversion in relatively low initial concentration (0.65 mM) systems with initial pH above (pH 3.6) and below (pH 2.6) the pK_a of CAA, under similar experimental conditions as in Fig. 1 with the CT-2R catalyst. Although the adsorption efficiency under both pH conditions is similar at about 15%, a very big difference during the catalytic ozonation is observed. In the system with pH value lower than the pK_a, the CAA conversion is very slow after the initial decrease, which was mainly due to adsorption. After 90 min, the apparent removal efficiency of CAA is not more than 50%. But in the system with pH value higher than the pK_a, the reaction is obvious. After 30 min, the conversion efficiency of CAA is higher than 80%. This demonstrates that the change in pH near the pK_a influences the catalytic ozonation process very strongly.

Furthermore, another experiment with 2 mM CAA initial concentration at pH 2.6 (below the pK_a) was carried out. It displays similar CAA and TOC removals as those at pH 3.1 in Fig. 1. This reveals that the change in pH above and below the pK_a in relatively high CAA concentration systems has not such a notable influence on the reaction as in low concentration systems.

Such a pH influence in the low CAA concentration systems is mainly due to different reaction kinetics and mechanisms, which are dependent on the pH value above and below the pK_a of CAA. In the low CAA concentration systems with pH value higher than the pK_a, CAA molecules exist mainly in the basic form (represented with CAA$^-$). Additionally, the catalyst surface would be positively charged if the pH value is much lower than the pH$_{pzc}$ of the catalyst. In this way, the relatively higher CAA$^-$ concentration would be favorable for adsorption and subsequent catalytic oxidation between the adsorbed CAA$^-$ and the active oxidation species on the catalyst surface. When the pH of the system decreases below the pK_a, the CAA mostly exist as uncharged molecules. In the systems with relatively low CAA concentration, the concentration of CAA$^-$ ions must be very small, which would slow the adsorption rate. The adsorption of organic species on the catalyst would become an important factor, and probably the limiting step during the catalytic ozonation. But if the CAA concentration is relatively high, the concentration of CAA$^-$ ions would correspondingly increase and the apparent reaction rate is still high.

In Fig. 7, the pH value of the 2 mM CAA system after 1 h reaction is adjusted from 2.7 to 3.6. A further decrease in the CAA concentration is then observed. This result proves that the apparent stop of the reaction after about 50 min catalytic ozonation of 2 mM CAA under the experimental conditions is

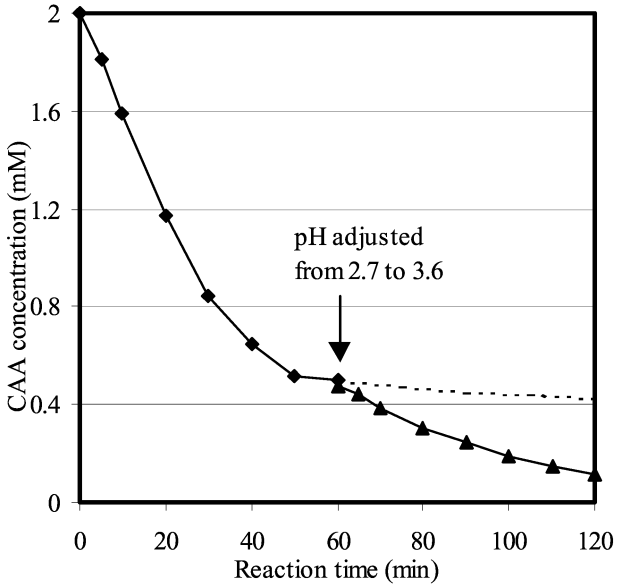

Fig. 7 Catalytic ozonation of CAA (after 1 h, the pH is adjusted from 2.7 to 3.6). Room temperature, initial pH: 3.1, catalyst amount: 0.8 g·L^{-1}, CAA initial concentration: 2.0 mM, introduced O_3 flow rate: 1275 ± 25 mg·h^{-1}.

not due to the deactivation of the catalyst, but the change of reaction kinetics at low CAA concentration when the pH value decreases below the pK_a. So, at low CAA concentrations, the near total decomposition of CAA can be achieved only after the pH value is increased to above the pK_a.

In addition, for the catalytic ozonation of 1 mM CSA, the pH decreases very little from 3.1 to about 3.0, during 90 min of reaction. The stop of the reaction at low concentrations was not observed.

Conclusions

Catalytic ozonation with the CeO_2–TiO_2 support for 2% Ru catalyst is proven to be effective for the total degradation of small chlorocarboxylic acids in aqueous systems. The chloride ion is nearly completely released, and its presence in the solution has little influence on the effectiveness of such a catalyst. The catalytic ozonation presents some selectivity towards different organic molecules. The pH value is very important to the reaction. In the acidic region, it must be controlled carefully in order to achieve the total mineralization of organic pollutants.

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