

Catalytic mechanism and reaction pathway of acetone ammoximation to acetone oxime over TS-1

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Abstract—A series of two-step reactions and several special experiments were designed and carried out to discover the reaction pathway of acetone ammoximation to acetone oxime over titanium silicalites-1 (TS-1) employing 25 wt% ammonia and 30 wt% hydrogen peroxide as the ammoximation agents. The experimental results show that the acetone oxime can form even if there is no direct contact between acetone and TS-1 catalysts, indicating the hydroxylamine route may be the most important catalytic mechanism for the reaction. HPLC, GC/MS and ion chromatography characterization results show that hydrogen peroxide can oxidize acetone oxime to acetone, nitrite and nitrate in the presence of TS-1. In addition, nitrite and nitrate can form in the reaction of H_2O_2 and NH_3 over TS-1. Based on these results, a possible overall reaction pathway of acetone ammoximation over TS-1 has been proposed.

Key words: Acetone, Acetone Oxime, Ammoximation, TS-1, Hydrogen Peroxide

INTRODUCTION

Acetone oxime is an excellent deoxidant that is widely used as corrosion inhibitor and passivator in boiler instead of N_2H_4 because of its low toxicity, low environmental pollution and high deoxidization effect [1]. Conventionally, acetone oxime is produced mainly by the hydroxylamine method. First, nitride reacts with acid to give hydroxylamine salt such as hydroxylamine sulphate, hydroxylamine hydrochloride and hydroxylamine phosphate. Then, the formed hydroxylamine salt reacts with acetone to produce acetone oxime. The conventional route involves multiple reaction steps, hazardous chemicals like oleum, halides or oxides of nitrogen and, more seriously, a large amount of low-value by-products like ammonium sulfate are produced. In recent years, a new catalytic process for the manufacture of oximes has been developed in liquid phase over titanium silicate, especially TS-1, employing NH_3 and H_2O_2 as the ammoximation agents [2,3], which becomes increasingly important because it is an efficient and environmental friendly route. Liang et al. [1] studied the effects of reaction conditions (solvents, reaction temperature, catalyst amount, the molar ratio of NH_3 /acetone) on the conversion and selectivity of the reaction. Zhang et al. [4] mainly studied the liquid-phase adsorption of ketones on TS-1 and the direct ammoximation reactions of these ketones with H_2O_2 and NH_3 catalyzed by TS-1. The purpose of their works was to find out whether the reaction mainly occurred inside or outside the cavity of the zeolite, and it was hoped that the results could shed light on the reaction mechanism. However, no experiments were designed to prove the reaction mechanism of acetone ammoximation over TS-1. The intrinsic kinetics of the acetone ammoximation reaction over TS-1 was

studied in our previous work [5]. To date, however, there is a lack of an in-depth understanding of the catalytic mechanism and reaction pathway of the reaction.

Recently, a number of studies of the catalytic mechanism of cyclohexanone ammoximation over TS-1 have been made [6-15], and two main viewpoints about the catalytic mechanism of the reaction were illustrated. One opinion is the imine route [6-10]: cyclohexanone first reacts with ammonia to form an unstable imine intermediate adsorbed on the TS-1 catalyst, and then the imine reacts with H_2O_2 over TS-1 to form cyclohexanone oxime. The other is the hydroxylamine route [11-15]: ammonia first reacts with H_2O_2 over TS-1 to form hydroxylamine intermediate, and then hydroxylamine reacts with cyclohexanone to give cyclohexanone oxime.

In the present work, we first assumed that acetone ammoximation over TS-1 followed the same catalytic mechanism as the case of cyclohexanone ammoximation, and a series of experiments were designed and carried out to confirm the mechanism. The reaction products were carefully characterized by HPLC, GC/MS and ion chromatography to develop a reaction pathway of acetone ammoximation over TS-1.

EXPERIMENTAL

1. Materials

TS-1 catalyst (average particle size, 200 nm; surface area, $95\text{ m}^2\text{g}^{-1}$; the Si/Ti mass ratio, 9) was provided by Baling Petrochemical Company, SINOPEC. Acetone, 30 wt% hydrogen peroxide, 25 wt% ammonia, *t*-butanol and acetone oxime in analytical grade were all obtained commercially and used as received. Methanol ($>99.9\%$ Chromatography Grade) was supplied by Yuwang Group and pure water by Hangzhou Wahaha Group (China). Deionized water (electrical conductivity $<12\text{ }\mu\text{s}\cdot\text{cm}^{-1}$) was self made with RO membrane.

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2. Ammonoxidation Experiments

The ammonoxidation of acetone to acetone oxime was carried out in a 125 mL four-necked flask equipped with a condenser, a thermometer and a stirrer. After TS-1 catalysts and acetone in *t*-butanol solution were introduced into the four-necked flask, the system was heated to a desired temperature under stirring. The reaction temperature was maintained by means of a super thermostatic water bath in which the reactor was immersed. When the temperature reached the set value, 30 wt% hydrogen peroxide and 25 wt% ammonia were pumped into the reactor separately at a certain flow rate by two peristaltic pumps (Baoding Lange constant-flow pump Co., Ltd, China). When the reaction was finished, the catalysts were separated from the mixture by centrifugation. The products were analyzed by an HPLC system (Agilent 1100 Series, USA) equipped with a diode array detector (DAD) and an auto-sampler. Chromatographic separations were performed at 35 °C using a ZORBAX Eclipse XDB-C18, 5 μm, 4.6 mm×250 mm column. A mobile phase composed of 25% methanol and 75% water at a flow rate of 1 mL·min⁻¹ was used. Acetone conversion and acetone oxime selectivity were calculated based on the concentrations of acetone and acetone oxime, according to Eqs. (1) and (2), respectively.

$$X = \frac{C_{acetone(0)} - C_{acetone(P)}}{C_{acetone(0)}} \times 100\% \quad (1)$$

$$S = \frac{C_{AO}}{C_{acetone(0)} - C_{acetone(P)}} \times 100\% \quad (2)$$

Where X is the acetone conversion (%), S the acetone oxime selectivity (%), $C_{acetone(0)}$ the initial acetone concentration (mol·L⁻¹), $C_{acetone(P)}$ the acetone concentration in the resulting reaction mixture (mol·L⁻¹), and C_{AO} the concentration of acetone oxime in the resulting reaction mixture (mol·L⁻¹).

RESULTS AND DISCUSSION

1. Investigation of Catalytic Mechanism

Inspired by the cyclohexanone ammonoxidation over TS-1 [6-15], two probable catalytic mechanisms of acetone ammonoxidation to acetone oxime over TS-1 are proposed. The first is the imine route: this path involves an imine intermediate adsorbed on the catalyst surface which reacts with hydrogen peroxide over TS-1 to give acetone oxime, as shown in Fig. 1. The second is the hydroxylamine route: ammonia is oxidized by hydrogen peroxide over TS-1 to hydroxylamine intermediate, which further reacts with acetone in the homogeneous phase to form acetone oxime, as shown in Fig. 2. To confirm which route plays the key role, a two-step experiment was designed based on the fact that the active site of TS-1 catalyst is

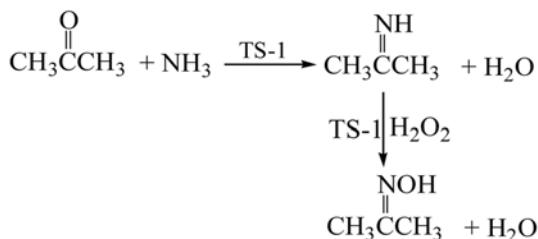


Fig. 1. Mechanism of acetone oxime formation via imine route.

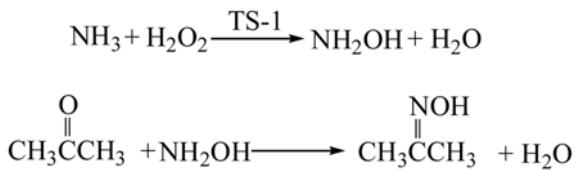


Fig. 2. Mechanism of acetone oxime formation via hydroxylamine route.

different in the two routes. To investigate the temperature effect of the first step, three tests were carried out at temperature of 30, 50 and 70 °C, respectively, while the second step reaction temperature was kept at 70 °C.

In the two-step experiments, after 30 g *t*-butanol and 1.2 g TS-1 were added into a four-necked flask, the flask was heated to a desired temperature under stirring. The reaction remained for further 10 min after 20.6 g 30 wt% hydrogen peroxide and 22.6 g 25 wt% ammonia were fed continuously into the reactor at 0.63 mL·min⁻¹ and 0.83 mL·min⁻¹ by two peristaltic pumps, separately. Then, the resulting reaction mixture of the first step was centrifuged to separate TS-1 catalyst, and the reaction mixture was put back into the reactor to react with 8.7 g acetone for 60 min at 70 °C.

In this way, there will be no TS-1 catalysts in the second step experiment. If the catalytic reaction mechanism is the hydroxylamine route, acetone oxime will be produced since there is no direct interaction between the acetone and TS-1. Instead, if the catalytic reaction mechanism is the imine route, acetone oxime will not form due to the absence of TS-1.

The results of the two-step experiments presented in Fig. 3 show that acetone oxime is evidently formed in the second step in which no direct contact between acetone and TS-1 occurs. Therefore, the reaction mechanism of acetone ammonoxidation over TS-1 may mainly follows the hydroxylamine route while the imine route may play only a side role. It can be found that acetone oxime yield increases with reaction temperature in the first step, indicating that the first step of the reaction is a typical catalytic stage that produces a reactive

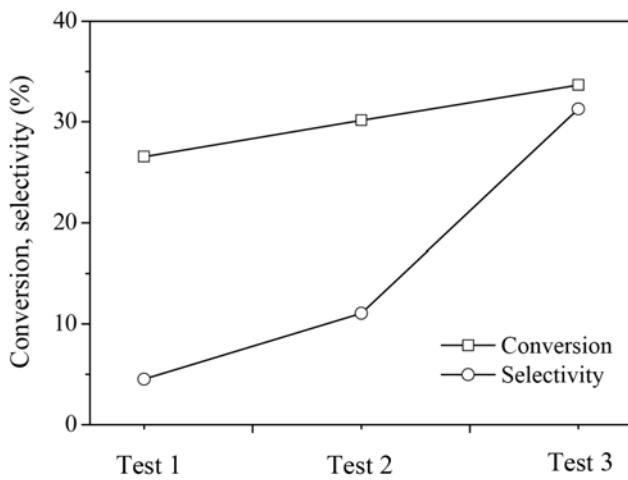


Fig. 3. Acetone conversion and acetone oxime selectivity of three two-step tests. Reaction conditions: 1.2 g TS-1, 8.7 g acetone, 30 g *t*-butanol, 20.6 g 30 wt% H₂O₂ and 22.6 g 25 wt% ammonia.

intermediate. Meanwhile, unambiguous experimental evidence showed there was not a homogeneous catalysis to give oxime in ketone ammoximation [15], which could be due to the titanium leaching caused by oxidant or solvent [16]. Therefore, the extra-framework titanium dissolution in the reaction mixture of acetone ammoximation has no effect on the judgment about the catalytic mechanism.

In the three tests carried out with this procedure, acetone conversion and acetone oxime selectivity are very low, obviously lower than the reported values [1]. For example, the conversion is only 33.7% and the selectivity is only 31.3% in Test 3. This is probably because only part of the key intermediate hydroxylamine can react with acetone in the second step experiment, and part of them adsorbed on the TS-1 catalyst are separated away from the reaction mixture or decomposed or oxidized to form typical inorganic by-products (nitrite and nitrate) during the tests.

2. Investigation of Side Reactions

2-1. The Side Reaction between Acetone Oxime and H_2O_2

The results of single-factor optimization experiments showed that the conversion of acetone could not reach 100% even if the amount of used hydrogen peroxide or ammonia was far more than that of acetone. Therefore, we suppose that a certain portion of the reaction products were possibly converted back to acetone, resulting in the decrease of conversion. In this reaction system, the reaction products contain acetone oxime, nitrate, nitrite and small amounts of unidentified compounds, in which only acetone oxime is a good reducing agent, while hydrogen peroxide is a good oxidant [17,18]. So it is most likely that hydrogen peroxide reacts with acetone oxime to generate acetone, leading to the lower conversion of acetone. To confirm this hypothesis, the following experiments were designed.

Step 1: The reaction between hydrogen peroxide and acetone oxime was performed in a glass reactor at 70 °C for an hour. Only 1.2 g TS-1, 30 g *t*-butanol, 20.6 g 30 wt% hydrogen peroxide and 2.1 g acetone oxime were added into the reaction system.

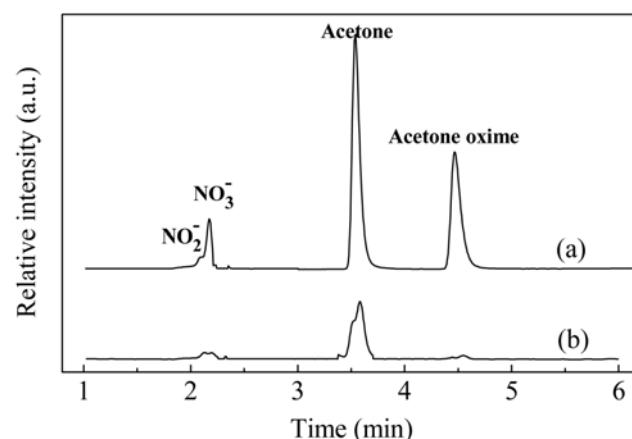


Fig. 4. HPLC analysis of (a) the mixture of reagent grade acetone, acetone oxime, nitrite and nitrate and (b) the reaction products formed between H_2O_2 and acetone oxime over TS-1 in step 1.

Step 2: TS-1 of the first step was separated via centrifugation and the liquid phase was analyzed by HPLC.

Step 3: The liquid phase was extracted repeatedly with the hexane, and the extraction phase was analyzed by GC/MS while the extraction raffinate was analyzed by ion chromatography.

The HPLC results are shown in Fig. 4. It is proved that acetone forms as acetone oxime reacts with hydrogen peroxide over TS-1. At the same time, small quantities of nitrite and nitrate ions are also produced as observed from the results. The results indicate that hydrogen peroxide can oxidize acetone oxime to acetone, nitrite and nitrate in the presence of TS-1. To seek further evidence for the formation of acetone, nitrite and nitrate, the reaction mixture was analyzed by GC/MS and ion chromatography, respectively.

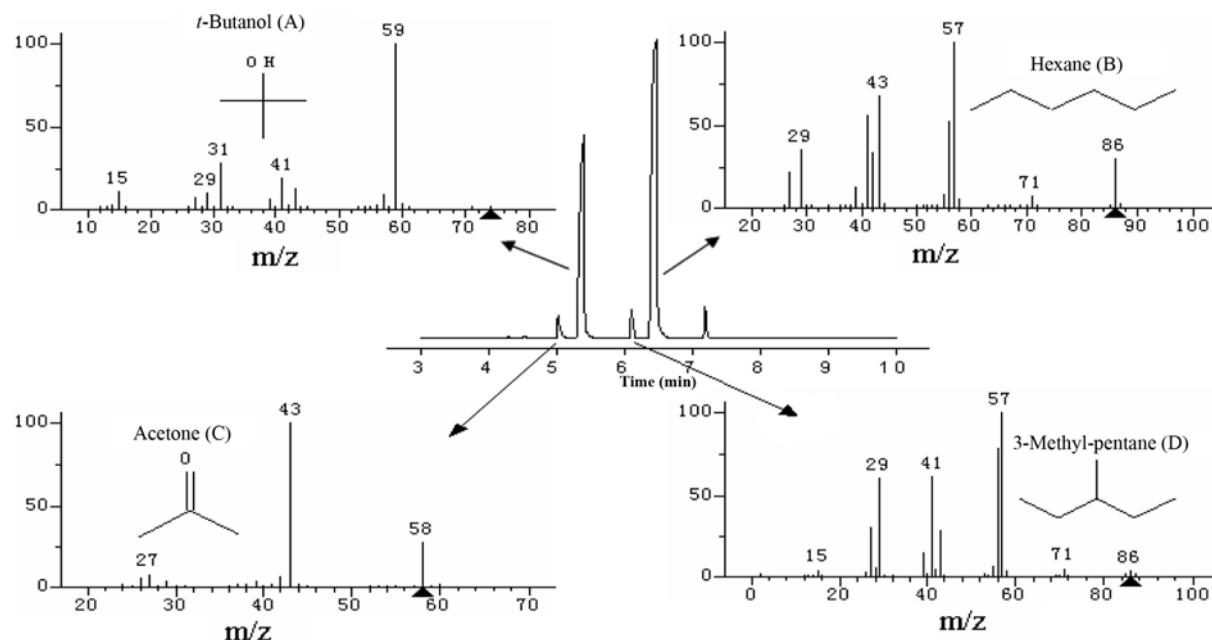


Fig. 5. GC/MS spectra and mass fragmentation of the extraction phase of the reaction mixture formed between H_2O_2 and acetone oxime over TS-1 in step 1.

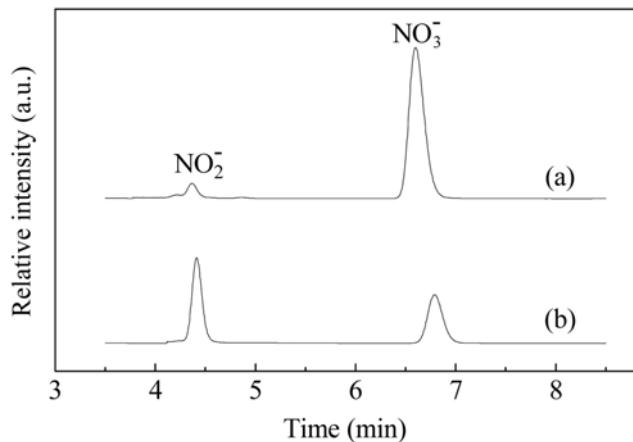


Fig. 6. Ion chromatography analysis of (a) the extraction raffinate of the reaction mixture formed between H_2O_2 and acetone oxime over TS-1 in step 1 and (b) the reagent grade nitrite and nitrate.

As shown in Fig. 5, four substances were detected using GC/MS. By comparing the molecular ions and mass fragments with those in the GC/MS Wiley 275 library, four compounds are identified as follows: *t*-butanol (A), hexane (B), acetone (C), 3-methyl-pentane (D). A is the reaction solvent, B and D root in the extraction reagent, and C is the product of hydrogen peroxide and acetone oxime over TS-1. Fig. 6 presents the analysis results of ion chromatography. By comparing the ion chromatography apex of the reagent grade nitrite and nitrate and the reaction mixture of hydrogen peroxide and acetone oxime over TS-1, it is confirmed the presence of NO_2^- and NO_3^- . These results prove the appearance of acetone, nitrite and nitrate in the reaction mixture of hydrogen peroxide and acetone oxime over TS-1, which are in good agreement with the HPLC analysis.

To prove the requirement of TS-1 for the oxidation of acetone oxime to form acetone, the reaction between hydrogen peroxide and acetone oxime was carried out in a glass reactor without TS-1

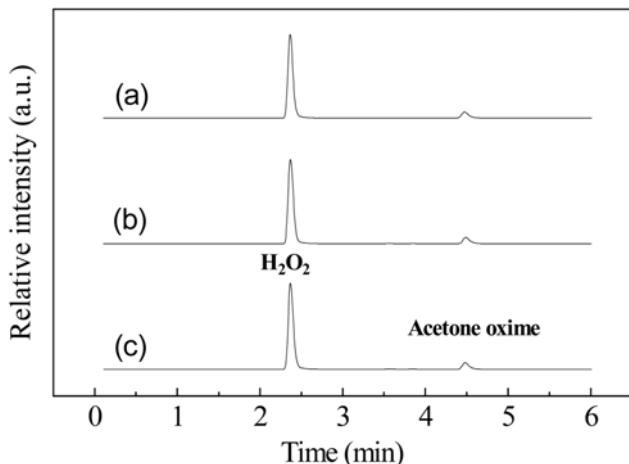


Fig. 7. HPLC analysis of the reaction mixture of H_2O_2 and acetone oxime without TS-1 at different reaction time of (a) 20 min; (b) 40 min; (c) 60 min.

at 70 °C. Other reaction conditions were as follows: 20.6 g 30 wt% hydrogen peroxide, 2.1 g acetone oxime, 30 g *t*-butanol. Fig. 7 gives the HPLC analysis results of the resulting reaction mixture. The characteristic peaks of hydrogen peroxide and acetone oxime in reaction mixture almost have no change when the reaction time is increased from 20 min to 60 min, and no characteristic peak of acetone is observed. Together with the results shown in Fig. 4, it can be concluded that hydrogen peroxide cannot oxidize acetone oxime to form acetone without the presence of TS-1.

2-2. The Side Reaction between NH_3 and H_2O_2

It is reported that there are two possible ways to produce NO_2^- in the reaction of cyclohexanone ammonium [15]. One is hydrogen peroxide reacts with ammonia to form hydroxylamine over TS-1, and then hydroxylamine is oxidized by hydrogen peroxide to give NO_2^- . The other is hydrogen peroxide reacts with ammonia directly to NO_2^- without TS-1. To prove whether there is the same process in the reaction of acetone ammonium to give NO_2^- , we carried out the following control experiments to determine through which route NO_2^- was produced.

After 30 g *t*-butanol, 20.6 g 30 wt% hydrogen peroxide and 22.6 g 25 wt% ammonia were added into the reaction system, we carried out the reaction between hydrogen peroxide and ammonia in a glass reactor at 70 °C without/with the presence of TS-1 catalyst.

As shown in Fig. 8(b), there is no response of NO_2^- , indicating that no NO_2^- was generated in the reaction mixture of H_2O_2 and NH_3 in the absence of TS-1. Whereas, there is an evident response of NO_2^- in Fig. 8(a), suggesting that NO_2^- was generated from NH_2OH , which was formed in the reaction mixture of H_2O_2 and NH_3 over TS-1. To prove whether TS-1 is necessary for the oxidation of NH_2OH , the following experiments were designed.

First, a reaction between H_2O_2 and NH_3 over TS-1 was carried out in a glass reactor at 70 °C under stirring. Other reaction conditions were as follows: 15 g 30 wt% hydrogen peroxide, 22.6 g 25 wt% NH_3 , 1.2 g TS-1, 30 g *t*-butanol. After the separation of TS-1 via centrifugation, the resulting reaction mixture was analyzed by HPLC, and the result is shown in Fig. 9(c).

Second, the above liquid phase was divided equally into two parts,

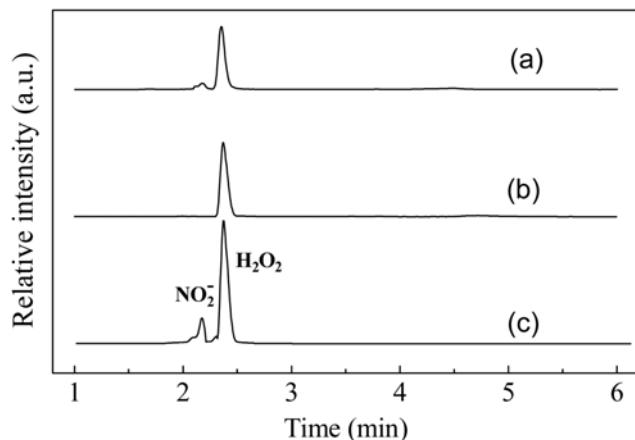


Fig. 8. HPLC analysis of (a) the reaction mixture of H_2O_2 and ammonia over TS-1, (b) the reaction mixture of H_2O_2 and ammonia without TS-1 and (c) the reagent grade H_2O_2 and nitrite.

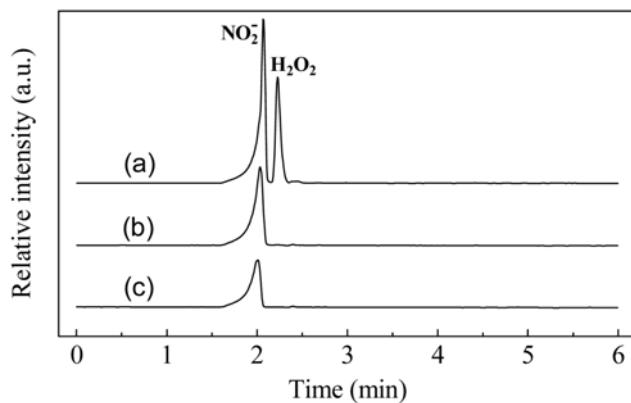


Fig. 9. HPLC analysis of (a) the reaction products of H_2O_2 and the liquid phase part of (c) without TS-1, (b) the reaction products of H_2O_2 and liquid phase part of (c) over TS-1 and (c) the reaction products of H_2O_2 and NH_3 over TS-1.

and then reacted separately with 5 g 30 wt% H_2O_2 without or with 1.2 g TS-1 at 70 °C under stirring. The resulting reaction mixtures were all analyzed by HPLC after the separation of TS-1 via centrifugation, and the results are shown in Fig. 9(a) and Fig. 9(b), respectively.

It is obvious that the response value of NO_2^- in Fig. 9(a) is higher than that in Fig. 9(c), indicating that NH_2OH can be oxidized to NO_2^- in the absence of TS-1. The response value of NO_2^- in Fig. 9(b) is lower than that in Fig. 9(a), possibly because some H_2O_2 reacted with NH_3 over TS-1 to form NH_2OH . Meanwhile, NO_2^- is oxidized to NO_3^- by H_2O_2 [15].

3. Reaction Pathway of Acetone Ammoximation over TS-1

According to the above discussion, a possible overall reaction pathway of liquid phase acetone ammoximation over TS-1 is proposed as represented in Fig. 10. As can be seen, there is a main reaction to form acetone oxime via a hydroxylamine route. At the same time, there are several side reactions: acetone oxime reacts with H_2O_2 over TS-1 to form acetone, nitrite and nitrate; H_2O_2 oxidizes hydroxylamine to nitrite and nitrate in the absence of TS-1; and hydrogen peroxide decomposes to water and oxygen, which is always possible in alkali conditions [15].

CONCLUSIONS

We first confirmed that the hydroxylamine route may be the most

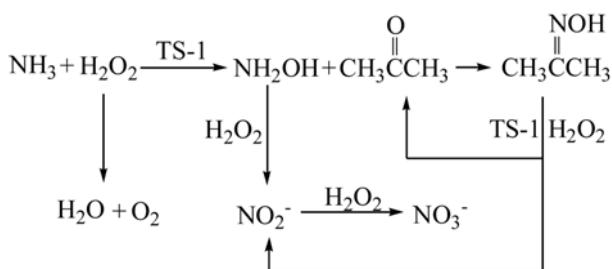


Fig. 10. Reaction pathway of acetone ammoximation over TS-1 in liquid phase.

important catalytic mechanism for the liquid phase acetone ammoximation over TS-1 through a series of two-step tests. Then we demonstrated the presence of a consecutive reaction between H_2O_2 and acetone oxime over TS-1 to form acetone, a parallel reaction between H_2O_2 and NH_3 over TS-1 during the process of acetone ammoximation to acetone oxime over TS-1 by careful characterization of reaction products with HPLC, GC/MS and ion chromatography, and got a reaction pathway of the reaction in liquid phase.

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