Ammoximation of cyclohexanone in acetic acid using titanium silicalite-1 catalyst: Activity and reaction pathway

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Abstract

The activity of titanium silicalite (TS-1) and the reaction pathway for the ammoximation of cyclohexanone to produce cyclohexanone oxime were studied using acetic acid as a solvent at 60 °C. The effect of solvent, sources of nitrogen, water content and the active site stability were also evaluated. It was found that, in the reaction using acetic acid as a solvent, the ammoximation of cyclohexanone proceeded mainly via the oxidation of imine, which was primarily formed in situ by the condensation of ketone with ammonia. In addition, the ammonium salts of weak acids, such as acetate, citrate and carbonate, can be used as nitrogen sources for the ammoximation in acetic acid. Water was shown to inhibit the formation of imine, and also prevent the side reactions. Moreover, TS-1 possessed an excellent stability, and can be reused without significant loss of activity.
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1. Introduction

Titanium-containing zeolites are found to be efficient catalysts for the selective oxidation of a large number of organic substrates, such as alkanes, alkenes, alcohols, aromatics and phenol [1–5]. The liquid-phase ammoximation of ketone over titanium zeolites to synthesise oxime is another important process attracting industrial interests. As cyclohexanone oxime is the key intermediate for the manufacture of caprolactam through Beckmann rearrangement, the ammoximation of cyclohexanone using NH_3 and H_2O_2 is widely investigated [6–14]. Compared with the current commercial processes, liquid-phase ammoximation of cyclohexanone over titanium-containing zeolites can be carried out in one step, without use of environmentally undesirable chemicals, and only small amounts of by-products formed by homogeneous reactions are obtained [11]. This is because the oxime can only be produced by the reaction of substrate(s) with titanium active sites, which is previously generated by an interaction of the framework titanium with H_2O_2 [9,13]. A clear clarification of the reaction pathway for this reaction is not only scientifically valuable, but also industrially important.

Since early 1990s, a debate on the reaction pathway for the ammoximation of ketone has widely become interesting. In order to explain the formation of peroxydicyclohexylimine, Thangaraj et al. [6] have proposed a mechanism that the ammoximation proceeds through an unstable intermediate, imine. This mechanism is similar to that reported for the gas-phase ammoximation of cyclohexanone in the presence of NH_3 and O_2 [15], and has been supported by IR spectroscopy which proves the formation of adsorbed imine species on the surface of TS-1 [16]. The imine intermediate is then oxidised by the titanium active sites to an oxime. Despite the restricted diffusion of cyclohexanone and its oxime in the medium pore zeolites, an excellent catalytic performance was observed by several groups using TS-1 [6–8]. This is later drawn into recent conclusion that the reaction proceeds via the oxidation of ammonia to hydroxylamine, which subsequently reacts with the ketone to form a corresponding oxime [12–14].

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In this work, acetic acid that was recently reported to improve the catalytic activity for cyclohexane oxidation [17], was used as a solvent in the ammoximation of cyclohexanone. Comparing with the reaction using water, an enhanced catalytic activity was also observed in the reaction using acetic acid as a solvent. The results from this study also suggest that, in the presence of acetic acid, the reaction pathway was different from the well-accepted pathway that observed in the reaction using water and other nucleophilic solvents. The difference in the reaction mechanism accordingly effects the product selectivity, and the causes of such observation were discussed.

2. Experimental procedure

Na-free TS-1 were synthesised using a procedure modified from that report in literature [18]. Tetrabutyl orthotitanate (2.36 g) was mixed with deionised water at 5 °C, followed by 30% hydrogen peroxide solution (4.29 g) under stirring for 30 min. Then, 25% ammonia solution (8.34 g at 5 °C) was added and stirred. The solution was left overnight at room temperature. The solution was then heated at 80–90 °C for 30 min. Ammonia solution was added until the last solution has just as much weight as before heating. After that this solution was added into the mixture of deionised water (9.36 g), tetrapropylammonium bromine (TPABr, 3.08 g) and Ludox (10.81 g) under vigorous stirring. The mixture was stirred for a day and the final yellow gel with a molar composition of 15 TPABr:3.8 TiO_2:94 SiO_2:2168 H_2O:212 NH_3:12.3 H_2O_2 was loaded in the autoclave and crystallised at 185 °C. After 5 days, the synthetic zeolite was filtered, washed and calcined at 550 °C with a heating rate of 2 °C/min. Calcination was carried out in dry air for 5 h and the sample was left to cool in the furnace under stream of nitrogen. After cooling, the calcined sample was repeatedly washed by 5 M of sulphuric acid until non-framework titanium species cannot be detected by a colour change upon dropping hydrogen peroxide. Finally, the sample was calcined again in air at 550 °C for 4 h. The TS-1 catalyst was then characterised using XRD, XRF, SEM and FTIR. Surface area of the TS-1 catalyst was determined by nitrogen adsorption technique.

Catalytic studies of cyclohexanone ammoximation were carried out in a micro batch reactor (10 ml) using 0.04 g of TS-1. Typically, cyclohexanone (0.38 g) was added to 28% (w/w) ammonia solution (0.73 g) and solvent (2.4 ml). The mixture was then heated to the reaction temperature under vigorous stirring. Finally, 30% (w/w) hydrogen peroxide solution (0.53 g) was added into the mixture. The molar ratio of the feed used in the reaction was as follows: ketone:NH_3:H_2O_2 = 1:1.5:1.2. After a period of time, the reaction was halted by removing heat and quenching in an ice bath. 2-Propanol (4 ml) was then added to homogenise the reaction mixture. The solution was filtered and analysed by GC-FID with DB-FFAP capillary column (0.25 mm × 30 m). The separation temperature was started from 110 to 170 °C

with a heating rate of 20 °C/min. Helium was used as a carrier gas at a linear velocity of 28 cm/s.

3. Results and discussion

3.1. Catalyst characterisation

X-ray diffraction and scanning electron microscope show that TS-1 sample is a well-defined, crystalline microporous material. The TS-1 sample with large and uniform crystallite size (5 μm × 20 μm) was chosen in this study. Although a reduced activity could be expected from the restricted diffusion of cyclohexanone in TS-1 channels, using catalyst with large primary crystals can ensure that the observed catalytic activity was mainly derived from that in the pore of TS-1. The catalyst also showed a characteristic adsorption of tetrahedrally coordinated Ti–O–Si at ~960 cm^{-1}. Elemental analysis by X-ray fluorescence showed that a constant Si/Ti ~26 was obtained after repeatedly washing with 5 M sulphuric acid. The specific surface area of 358 m^2/g was obtained by nitrogen adsorption at 77 K.

3.2. Catalytic activity

The ammoximation of cyclohexanone over TS-1 is shown in Fig. 1. It can be seen that the reaction using acetic acid as a solvent give a higher conversion than that using water. As previously discussed elsewhere [17], this can be attributed to the fact that peracetic acid was generated in the reaction using acetic acid as a solvent. The peracetic acid can further react with titanium tetrahedral producing peroxo-complex in a manner similar to that generated from hydrogen peroxide. The fact that the peracetic acid is more hydrophobic than the hydrogen peroxide, the peroxo-complex formed by peracetic acid (a softer ligand) would be relatively more stable. Therefore, higher amounts of active sites are available for the reaction. Additionally, the active site formed by peracetic acid would possess a better oxidising activity due to its higher electron density. These would lead to an improved activity for cyclohexanone conversion when acetic acid was used as a solvent.

3.3. Product selectivity

However, selectivity of cyclohexanone oxime in the reaction using acetic acid as a solvent was lower than that using water. Other products confirmed by GC–MS are 2-oxepanone and acetyl cyclohexanone oxime. The first could be formed by "Baeyer–Villiger Rearrangement" when cyclohexanone react directly with peracetic acid in the presence of acid [19]. As TS-1 possesses the medium pore size (~5.5 Å), it is unlikely that 2-oxepanone, a seven membered ring, is generated in the pore of TS-1. It may be postulated that 2-oxepanone was generated homogeneously in the liquid-phase without aid of TS-1. The second by-product, acetyl cyclohexanone
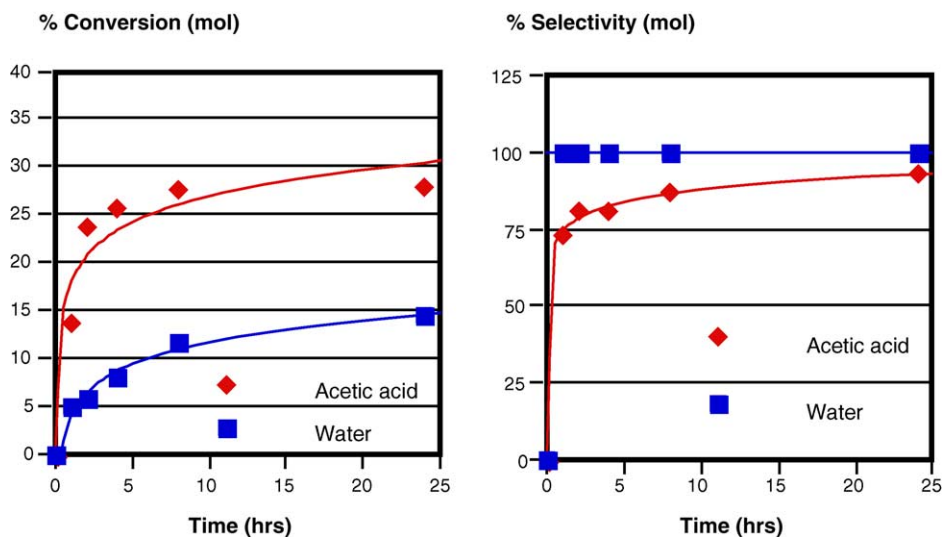
Fig. 1. Conversion of cyclohexanone and selectivity of cyclohexanone oxime from the reaction using acetic acid and water as solvent (reaction condition: at 60 °C, cyclohexanone 0.38 g, ammonia solution (28%, w/w) 0.73 g, hydrogen peroxide solution (30%, w/w) 0.53 g, solvent 2.4 ml, TS-1 0.04 g).

oxime, could be possibly generated either from (i) a simple condensation of cyclohexanone oxime formed in the reaction with acetic acid or (ii) an oxidative coupling of cyclohexanone oxime with acetic acid in the presence of hydrogen peroxide and TS-1. In order to verify the above possibilities, the path (i) was tested by heating and stirring cyclohexanone oxime with acetic acid without hydrogen peroxide and TS-1 for 4 h. While the path (ii) was tested in the presence of hydrogen peroxide and TS-1. It was found that acetyl cyclohexanone oxime cannot be generated by path (i) test. However, the reaction tested for path (ii) produce notably amounts of acetyl cyclohexanone oxime. Consequently, it seems that acetyl cyclohexanone oxime was generated by coupling of cyclohexanone oxime with acetyl radical, which is presum-

ably decomposed from the acetyl peroxo-titanium complex. The acetyl peroxo-titanium species were earlier suggested [17] to be formed by an interaction of tetrahedral titanium with peracetic acid and their decomposition would lead to the generation of active oxidising species [20] as proposed in Fig. 2. Typically, the decomposition of peroxo-titanium species (a) may well be driven by the reaction with hydrogen peroxide to give acetic acid (or water). However, thermal decomposition to give acetyl radical (or hydrogen radical) could also take place. Fig. 3 demonstrates the formation of 2-oxepanone and acetyl cyclohexanone oxime. In addition to the oxidised products, adducts from aldol condensation are also observed from the reaction using acetic acid as a solvent. This is probably due to the decreased pH of the media, which
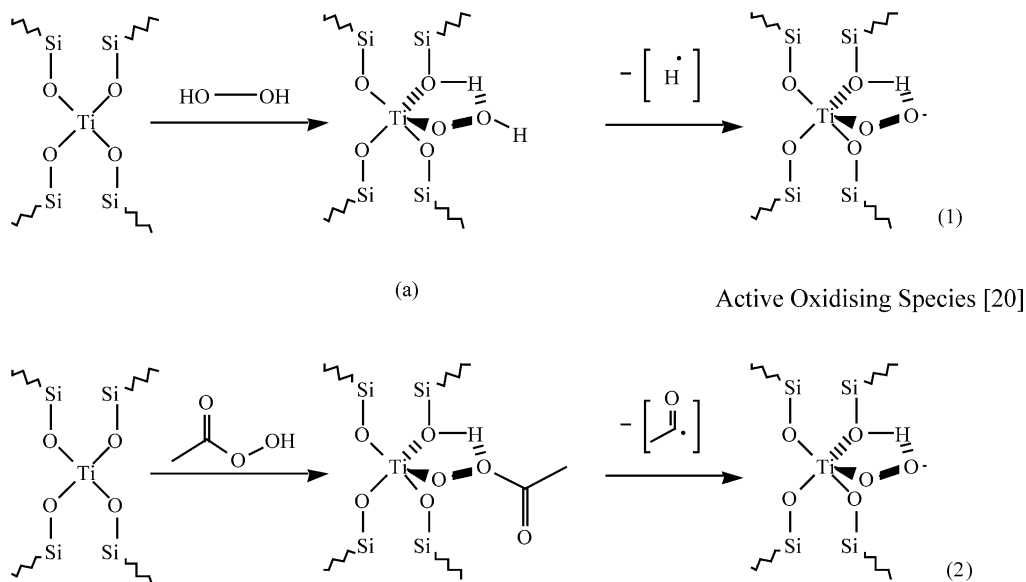

Fig. 2. A proposed reaction pathway for the formation of active oxidising species in the reaction using (1) water and (2) acetic acid as solvent.
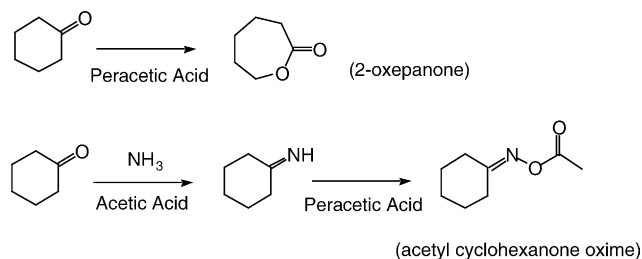
Fig. 3. Formation of 2-oxepanone and acetyl cyclohexanone oxime.

readily promotes acid-catalysed condensation of cyclohexanone.

Despite the conversion was increased by increasing amount of catalysts used, the selectivity of cyclohexanone oxime was not significantly changed (Fig. 4). This is because, in presence of acetic acid, 2-oxepanone (the major byproduct) was generated by the homogeneous reaction of cyclohexanone with peracetic acid, as discussed earlier. When the amount of catalyst was increased, more peracetic acid can also be obtained. Therefore, yield of both cyclohexanone oxime and 2-oxepanone would be increased without a marked change in product selectivity.

In the reaction using water as a solvent, peracetic acid was not present and hydrogen peroxide alone is not effective for the Baeyer–Villiger reaction. Therefore, there is no 2-oxepanone and also acetyl cyclohexanone oxime produced. Thus, selectivity of cyclohexanone oxime in the reaction using water as a solvent is considerably high.

3.4. Active sites and its stability

Since peracetic acid, generated in situ from hydrogen peroxide and acetic acid, can be a strong oxidising agent, one may argue that the observed activity may well be derived solely from the homogeneous reaction. Moreover, the strong interaction of peracetic acid with the titanium active sites
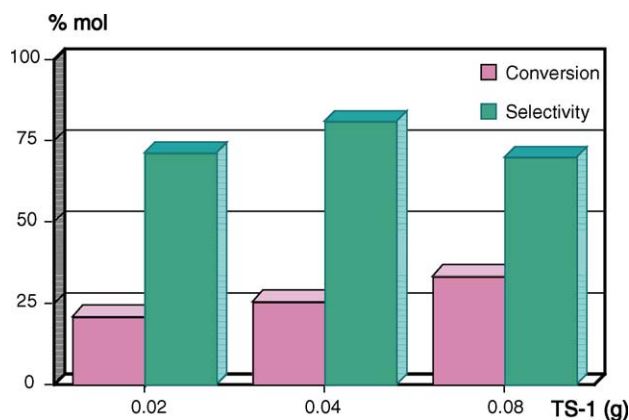

Fig. 4. Effect of catalyst loading on conversion of cyclohexanone and selectivity of cyclohexanone oxime (reaction condition: at 60 °C, cyclohexanone 0.38 g, ammonia solution (28%, w/w) 0.73 g and hydrogen peroxide solution (30%, w/w) 0.53 g, acetic acid 2.4 ml, reaction time 4 h, TS-1 0.02, 0.04 and 0.08 g as catalyst).

Table 1
Conversion of cyclohexanone and yield of products (mol%) from the reactions without catalyst, with tetrabutyl orthotitanate and with reused TS-1 as catalysts

Catalyst	TS-1	None	Ti(OBu)$_4$	Reused TS-1
Conversion of cyclohexane	47.8	31.7	31.1	55.3
Yield of cyclohexane oxime	37.8	17.8	22.2	46.1
Yield of 2-oxepanone	3.0	4.8	2.9	4.1
Aldol products	2.0	4.0	–	1.9
Yield of acetyl cyclohexane oxime	2.5	1.1	1.6	0.9
Yield of coupling products	2.5	3.9	3.5	2.0

Reaction condition: Temperature 60 °C, cyclohexanone 0.38 g, ammonia solution (28%, w/w) 0.73 g and hydrogen peroxide solution (30%, w/w) 0.53 g, acetic acid 2.4 ml, reaction time 6 h, titanium-containing zeolites 0.04 g as catalyst (or equivalent mol of titanium species).

could result in the dissolution of titanium as peroxo-complex into acetic acid. The leached Ti species may also be responsible for some parts of the observed activity as suggested elsewhere [21]. To verify the above possibility, the ammoximation of cyclohexanone without TS-1 was tested, together with that using tetrabutyl orthotitanate as a catalyst.

From Table 1, it was found that part of the observed activity was also contributed from the homogeneous oxidation by peracetic acid. However, in addition to the oxidised products, adducts from aldol condensation were increasingly promoted. Thus, a poor selectivity of cyclohexanone oxime was obtained in the reaction without catalyst. In contradiction the presence of TS-1 catalyst leads to a better activity and selectivity of the oxidised products. This is not only because TS-1 can promote the formation of peracetic acid [17], but also due to the presence of active oxidising species formed by the peracetic acid and the titanium framework. Hence, the activity towards oxidation is enhanced, as compared to that without catalyst. When an equivalent mole of tetrabutyl orthotitanate was used instead of TS-1, a similar result to the non-catalysed reaction was also observed. Therefore, it is clear that the enhanced ammoximation activities are mainly derived from neither the homogeneous reaction nor the leached titanium species, if applicable.

Although the tetrahedral titanium framework of TS-1 is relatively stable, the strong interaction of peracetic acid with the titanium framework could lead to the leaching of titanium active sites into the solution. This was indeed observed in the oxidation of cyclohexane using acetic acid as a solvent [17]. According to this study, the homogeneous titanium species has no significant effect on the ammoximation of cyclohexanone in acetic acid. Nevertheless, leaching of titanium active sites during the reaction is not preferable and has become one of the major drawbacks for industrial applications. Actually, such circumstance is not the case for the ammoximation of cyclohexanone. No notable amount of dissolved titanium was detected in the solution (by UV–vis adsorption) and when the catalyst was reused without thermal regeneration, the activity of TS-1 is even enhanced (Table 1). The cause of the slightly improved activity of the reused TS-1 cannot be evaluated at this stage. However, a better stability of TS-1 in acetic acid

is probably derived from the presence of nitrogen sources, which would increase pH of the solution and, hence, suppress the dissolution of the framework titanium species.

3.5. Mechanistic study

Unless the reaction pathway proceed via oxidation of ammonia to produce primarily hydroxylamine, the enhanced activity in the reaction using acetic acid may well be resulted from the enhanced formation of cyclohexanone imine. The formation of imine was previously evidenced by an absorption band at $\sim 1653 \, cm^{-1}$ when ammonia and cyclohexanone was introduced to Ti-mordenite at $60\,°C$ [12]. As the amount of cyclohexanone imine is increased, the oxidation of cyclohexanone imine would also be accelerated, resulting in a higher yield of cyclohexanone oxime in the reaction using acetic acid, as compared to that using water.

From the mechanistic point of view, the condensation of cyclohexanone with ammonia in acetic acid would be favoured because cyclohexanone imine formation is facilitated at pH approximately 4–5 or in the presence of acid catalyst [22]. However, a recent report [14] demonstrated that in the reaction using water, hydroxylamine was primarily formed. These possibilities can be readily tested either by the reaction of ammonia with only cyclohexanone prior to the addition of TS-1 and hydrogen peroxide (test I), or the reaction of only ammonia with catalyst and hydrogen peroxide, followed by catalyst removal and cyclohexanone addition (test II). The test I can be employed to verify the hypothesis that ammoximation proceeds via condensation of cyclohexanone with ammonia. On the other hand, the hypothesis for hydroxylamine formation can be demonstrated by the test II.

From Table 2, it shows that cyclohexanone oxime can be only formed in test I when acetic acid is used as a solvent. Thus, the condensation of cyclohexanone with ammonia in homogeneous phase is facilitated in the presence of acetic acid (test I). It is also possible that the cyclohexanone imine could interact with a relatively hydrophobic active site, formed by complexation of peracetic acid and the framework titanium. Therefore, the oxidation of the imine to the oxime could be expected. In contrast, when acetic acid is used as a solvent, ammonia was protonated in test II and may not be readily oxidised to hydroxylamine. Conclusively, in the reaction using acetic acid as a solvent, only the pathway proceeded via the condensation of cyclohexanone with ammo-
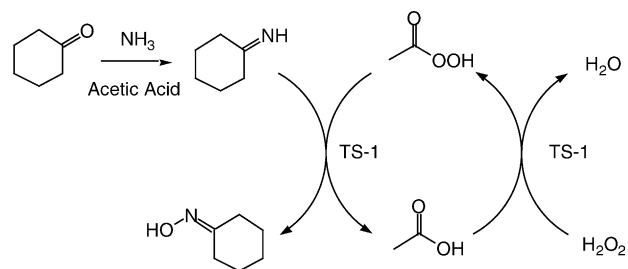

Fig. 5. Proposed reaction pathway for cyclohexanone ammoximation using acetic acid as a solvent.

nia should be responsible for the formation of cyclohexanone oxime. Fig. 5 illustrates the reaction pathway, which is proposed from the results observed in this study.

In the reaction using water as a solvent, on the other hand, cyclohexanone oxime can be formed by both tests. Since ammonia was not readily protonated in the reaction using water as a solvent, it can directly react with the active sites to produce hydroxylamine. The observed smaller yield of cyclohexanone oxime in test II may be derived from (i) an incomplete formation of hydroxylamine when the catalyst was removed, and/or (ii) the oxidation of hydroxylamine to nitrite and nitrate species [14] before cyclohexanone was added.

3.6. Ammonium salts as reagents

The fact that the observed catalytic pathway is inconsistent with the pervious report when acetic acid is used as a solvent can be accounted for a poor activity of protonated ammonia towards the oxidation. However, such species are readily active for condensation with cyclohexanone. This can be further investigated using various types of ammonium salts as sources of nitrogen. It is reasonable to postulate that in the reaction using acetic acid as a solvent, ammonium acetate is formed. This salt must be able to react with cyclohexanone, which is indeed observed together with other weakly acid salts as shown in Table 3.

When weakly acid salts, such as ammonium acetate, citrate and carbonate, were used as reagent in the presence

Table 2
Yield of cyclohexanone oxime (mol%) from reaction pathway testing

Test	Solvent	
	Water	Acetic acid
Typical reaction	8.1	20.8
Test I (imine pathway)	7.4	14.9
Test II (hydroxylamine pathway)	1.7	0.27

Reaction condition: Temperature $60\,°C$, cyclohexanone 0.38 g, ammonia solution (28%, w/w) 0.73 g and hydrogen peroxide solution (30%, w/w) 0.53 g, Solvent 2.4 ml, TS-1 0.04 g, reaction time: 2 h/4 h (step 1/step 2).

Table 3
Yield of cyclohexanone oxime (mol%) from reaction using ammonium salts as reagent

Reagent	Solvent	
	Water	Acetic acid
Ammonia solution (NH_4OH)	8.1	20.8
Ammonium acetate (NH_4OAc)	0.68	21.5
Ammonium citrate (($NH_4)_2HC_6H_5O_7$)	0.47	6.6
Ammonium carbonate (($NH_4)_2CO_3$)	6.3	8.3
Ammonium oxalate (($NH_4)_2C_2O_4$)	Trace	1.8
Ammonium chloride (NH_4Cl)	Trace	Trace
Ammonium sulphate (($NH_4)_2SO_4$)	Trace	Trace

Reaction condition: Temperature $60\,°C$, cyclohexanone 0.38 g, hydrogen peroxide solution (30%, w/w) 0.53 g, solvent 2.4 ml, TS-1 0.04 g, reaction time 4 h.

of acetic acid, cyclohexanone oxime was indeed generated. Particularly, there is no significant difference between the reaction using ammonia solution and that using ammonium acetate as reagent. This confirms that ammonium salts is quite active for ammoximation. A relatively lower activity was observed when ammonium citrate was used as reagent. This is because ammonium citrate is a salt of hydroxy polyacid, therefore it can be somewhat dissociated in acetic acid. Consequently, reactivity for the reaction with cyclohexanone to generate cyclohexanone imine is relatively lower than the reaction using ammonium acetate. For ammonium carbonate, yield of cyclohexanone oxime in the reaction using acetic acid, was lower than that expected. This may be resulted from the fact that ammonium carbonate reacts vigorously with acetic acid producing carbon dioxide, ammonia and exhaust heat. Under this circumstance, a rapid vaporisation of carbon dioxide may well lead to the loss of ammonia. This could reduce the rate of condensation with cyclohexanone resulting in a lower production of cyclohexanone oxime as observed.

On the other hand, in the reaction using water as a solvent, the use of ammonium acetate and citrate show much lower activity than that of ammonia solution. This can be resulted from the fact that ammonium acetate and citrate could be highly dissociated in the water. Accordingly, ammonia is mostly present in a protonated form. The lone pair electrons of ammonia could be deactivated and either the reaction with cyclohexanone to form cyclohexanone imine or the direct oxidation to hydroxylamine were inhibited in the reaction using water as a solvent. Nevertheless, this is not the case for ammonium carbonate. As being a salt of weak carbonic acid, it can be readily decomposed to give ammonia at reaction temperature. Therefore, the activity of ammonium carbonate in water is somewhat similar to the ammonia solution.

The ammonium salts of strong acid such as, ammonium oxalate, ammonium chloride and ammonium sulphate, cannot be used as reagent in both reactions using acetic acid and water as solvent. This is because the K_a of the conjugated acid of ammonium salts is high. Consequently, the salt is highly dissociated, leading to the deactivation of the lone pair electrons of ammonia. Therefore, the strongly protonated ammonia is not efficient for both condensation with cyclohexanone to produce cyclohexanone imine and oxidation to give hydroxylamine.

3.7. Effect of water content

According to the above discussion, the condensation of cyclohexanone with ammonia becomes an essential step for the ammoximation. This step could be notably interfered by the pH of the solution and also by the presence of water. It is expected that less amount of water present in the reaction shall lead to a better activity. As hydrogen peroxide solution was used as an oxidising agent, the presence of water cannot be avoided. Nevertheless, the effect of water can be investigated by adding dried zeolite A (a water adsorbent) into the system.
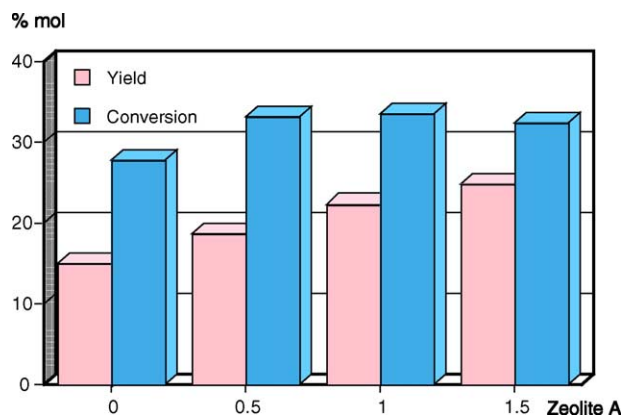

Fig. 6. Effect of water content on the yield of cyclohexanone oxime and conversion of cyclohexanone (reaction condition: at 60 °C, cyclohexanone 0.38 g, ammonia solution (28%, w/w) 0.73 g and hydrogen peroxide solution (30%, w/w) 0.53 g, acetic acid 2.4 ml, TS-1 0.04 g, reaction time 4 h, added 0.5, 1.0 and 1.5 g of zeolite).

From Fig. 6, it was clearly shown that the conversion of cyclohexanone and the yield of cyclohexanone oxime was increased with the amount of zeolite A added. The zeolite A, which is highly hydrophilic and possesses small pore size, can readily adsorb water. This would facilitate the condensation of ammonia with cyclohexanone to give the corresponding imine since water was removed from the system. As the formation of the imine is promoted, a higher yield of cyclohexanone oxime can be expected. In addition, the yield of 2-oxepanone and acetyl cyclohexanone oxime (by-products) were decreased when zeolite A was added. This is probably because cyclohexanone and peracetic acid are largely consumed by the ammoximation process. Hence, the direct reaction of peracetic acid with cyclohexanone or the coupling of cyclohexanone oxime with acetyl radical would be limited. Accordingly, a higher selectivity of cyclohexanone oxime was also obtained when zeolite A was added.

4. Conclusion

Ammoximation activity of cyclohexanone is enhanced in the reaction using acetic acid as a solvent. However, selectivity of the corresponding oxime is reduced due to formation of by-products, 2-oxepanone, acetyl cyclohexanone oxime and aldol adducts. Together with the strong oxidising species like peracetic acid, the tetrahedrally coordinated titaniums are active species and they are relatively stable. Leaching of active sites was not observed in this reaction, presumably due to the presence of ammonia in the system. However, further investigation using larger amounts of catalysts or testing in a continuous process should be made to really prove on this. Nevertheless, this study shows that soluble titanium species plays no role in ammoximation of cyclohexanone using acetic acid as a solvent.

The mechanistic study shows that there are two possible pathways for the ammoximation of cyclohexanone. In the

reaction using water as a solvent, the oxidation of ammonia to produce hydroxylamine, followed by its condensation of cyclohexanone seems to be favoured. However, only the pathway proceeded via the condensation of cyclohexanone with ammonia is responsible for the formation of cyclohexanone oxime in the reaction using acetic acid as a solvent. This also leads to an improved catalytic activity because the formation of cyclohexanone imine, an oxime precursor, is enhanced in presence of acetic acid. In addition, peracetic acid, which is formed in situ, can be served as a better oxidising agent, as compared to the hydrogen peroxide alone. However, the reaction using acetic acid as a solvent shows a lower cyclohexanone oxime selectivity because peracetic acid can directly react with the reactant and the product to produce two other by-products, 2-oxepanone and acetyl cyclohexanone oxime, respectively. From the economic point of view, this could be a major obstacle to an industrial development even though high conversion is obtained.

In the reaction using acetic acid as a solvent, it is also evident that the source of nitrogen can be obtained from ammonium salts of the weak acid, such as acetate, citrate and carbonate. These species are active for the formation of imine. However, this is not the case for the reaction using water because the reaction pathway involves ammonia oxidation. The protonated ammonia is inactive for the oxidation to hydroxylamine and the reaction in water can be carried out only with ammonia in slightly basic solution. The presence of water in the reaction using acetic acid does not only inhibit the ammoximation activity, but also facilitate the formation of by-products. Hence, selectivity of cyclohexanone oxime is improved when water is removed from the system.

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