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The mechanism of catalyst deactivation and by-product formation in acetone ammoximation catalyzed by hollow titanium silicalite

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ABSTRACT

The deactivation mechanism of hollow titanium silicalite (HTS) in aqueous ammoximation of acetone was investigated. Amines and polynitro-compounds, formed by alkaline autocatalytic and oxidative coupling reaction respectively, were determined to be the main by-products. The results showed that deactivation of HTS could be caused by two main reasons: (1) slow deactivation due to by-product amines adsorbed on the active sites of catalyst surface; (2) rapid deactivation in the late period due to by-products, mainly 2,3-dimethyl-2,3-dinitrobutane (DMNB), filling and blocking the pores of catalyst.

1. Introduction

Since first reported in 1980s, the outstanding performance of titanium silicalite for catalytic oxidation has been attracting wide attention [1]. Typical reactions included olefin epoxidations, ketone ammoxidations, aromatics hydroxylations, alkane oxidations, alcohol oxidations, etc. [2–7]. As a novel titanosilicate, the titanium silicalite with hollow structure (branded by HTS, having large intraparticle voids) prepared by dissolution-recrystallization process demonstrated the performance of catalytic oxidation superior to conventional TS-1 zeolite [8–11]. Recently, the HTS catalyst has been successfully applied by SINOPEC for cyclohexanone oxime production (70 kt/year) via cyclohexanone ammoximation [12].

Acetone oxime with low toxicity and high deoxidization ability was widely used to replace carcinogenic N_2H_4 as corrosion inhibitor and passivator in boilers. The conventional synthesis of acetone oxime not only went through multiple steps involving the use of hazardous chemicals, but also produced large quantities of by-products. According to the literature, a new synthetic route of acetone oxime by ammoximation of acetone with H_2O_2 and NH_3 employing TS-1 zeolite as catalyst could provide high efficiency and produce few by-products [13,14].

Study on deactivation of catalyst is very important to industrial application. The deactivation of TS-1 zeolite in preparing ketone oxime by ammoximation has been investigated by several researches. Petrini et al. [15] suggested that the deactivation of TS-1 zeolite in conversion of cyclohexanone to cyclohexanone oxime could be caused by three reasons: (1) slow dissolution of the zeolite framework with accumulation of Ti on external surface; (2) direct loss of Ti from the framework and (3) blocking of the pore by by-products. Zhang et al. [16] investigated the deactivation behavior of TS-1 zeolite in cyclohexanone ammoximation, and found the formation of polycylic aromatics and/or polyalkenes in internal surface of catalyst to be key reason causing the deactivation. Liu et al. [17] investigated the stability of TS-1 catalyst in cyclohexanone ammoximation, and found that the deactivation of TS-1 was mainly due to the block of the zeolite pores by deposits. Besides, there was also tendency to change the structure of Ti framework, but no obvious evidences in destroying the crystal structure of the spent TS-1. Sun [18] found that the main reason causing the deactivation of TS-1 zeolite in cyclohexanone ammoximation was the dissolution loss of zeolite caused by ammonia. They expressed that the dissolution of zeolites was related to the polarity and ammonia

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Abbreviations: TS-1, titanium silicalite-1; HTS, hollow titanium silicalite; *t*-BuOH, tertiary butanol; DMNB, 2, 3-dimethyl-2, 3-dinitrobutane; AMPO, 4-amino-4-methyl-2-pentanone; HMPO, 4-hydroxy-4-methyl-2-pentanone; TMPDO, 2,2,6,6-tetramethylpiperidinyl-4-one; 4-hydroxyimino-TMPD, 4-hydroxyimino-2,2,6,6-tetramethylpiperidine.

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content of reaction mixture, the addition of auxiliary containing silicon could effectively inhibit the loss of zeolite in basic circumstance and significantly expand the duration of stable performance of zeolite. Jiang et al. [19] investigated the reaction of cyclohexanone ammoximation catalyzed by TS-1 zeolite, and found the loss of silicon 50 ~ 60 μg/g from catalyst framework by dissolution. The continual addition of the auxiliary silicon could effectively inhibit the dissolve run-off of framework silicon, and expand the lifetime of catalyst without negative effects on the performance of catalytic reaction. Choudhary et al. [20] proposed that the poisoning of TS-1 by ammonia decreased the conversion of styrene epoxidation reaction.

For the reaction of acetone ammoximation on TS-1 zeolite, however, current studies are mainly focusing on the conversion, selectivity and productivity, while the deactivation of TS-1 catalyst still remain to be investigated.

In this work, the deactivation of HTS catalyst in the reaction of acetone ammoximation with H_2O_2 was investigated. Based on the characterization of fresh and deactivated catalysts by various methods, and the identification of impurities from both reaction liquid and deactivated catalyst surface by GC–MS and NMR, the mechanism of HTS deactivation and by-products formation was discussed in detail.

2. Experimental

2.1. Material

Industrial HTS catalyst containing 3.0% ~ 3.5% Ti was provided by SINOPEC. Reagents *t*-BuOH (99%), CH_2Cl_2 (99.5%), $CHCl_3$ (99%), HNO_3 (65%) and TMPDO (97%) were analytical grade. Ammonia solution (NH_3, 25%), hydrogen peroxide solution (H_2O_2, 28%) and acetone (99.5%) were industrial grade.

2.2. Operation procedure

Continuous operation was conducted in a 5 L slurry bed reactor connecting with a ceramic membrane separator. At the beginning, 300 g HTS zeolite, 1000 g acetone and 2500 g solvents with the molar ratios of NH_3:acetone = 1.17:1 and H_2O_2:acetone = 1.1:1 were filled into the reactor. During the operation, the premixed solution with the molar ratios of H_2O_2:acetone = 1.1:1, solvent:acetone = 2.5:1 and NH_3:acetone = 1.08:1 was continually sent to the reactor at rate of 25 ~ 32 mL/min. The operation conditions were 343 ~ 348 K, 0.1~0.25 MPa and 70 min resident time. Once the reactor system reached steady-state in a half hour, products were sampled at different operation times for GC analysis. Reaction solution was removed by ceramic membrane separation when reaction was finished. The used catalyst was boiled in deionized water at 348 K for 1 h, and then collected for characterization. The boiled liquid was extracted by CH_2Cl_2 for determination of by-products by GC–MS.

Batch operation was carried out to verify the influence of by-products on reaction. 35 g HTS catalyst, 105 g deionized water, 1.81 mol acetone and 1.45 mol ammonia were added into a 500 mL flask in a hot water bath at 343 K. Then, 1.32 mol of ammonia and 1.54 mol of H_2O_2 were dropped into the flask with stirring in 1 h. After another half hour reaction, the catalyst was separated by centrifugation and the liquid solution was collected for GC analysis.

2.3. Samples analysis

The samples of reactants and products were analyzed by Agilent 6890N GC. By-products were identified by Agilent 6890N/5937N GC–MS. Some of by-products were identified by Brucker AVANCE 400 NMR using DMSO-d_6 as solvent and TMS as internal standard.

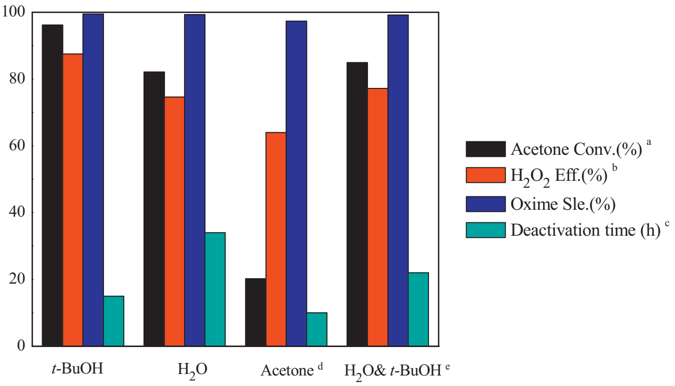


Fig. 1. Influence of solvent on the acetone ammoximation. [a]For the liquid sampled after 0.5 h continual reaction; [b]molar ratio of acetoxime to H_2O_2; [c]the continual operation time until acetone conversion was less than 60%; [d]extra amount of acetone as solvent; [e]H_2O: *t*-BuOH = 1:1 (wt).

2.4. Characterization techniques

The UV–vis spectra were recorded on a Perkin-Elmer Lambda 950 spectrometer, $BaSO_4$ being used as a reference. Powder X-ray diffraction patterns were recorded at RT on a Bruker-AXS D8 Advance diffractometer using nickel-filtered Cu Kα radiation. Micromeritic ASAP 2020M system was used to measure nitrogen adsorption–desorption isotherms of samples.

3. Results and discussion

3.1. Acetone ammoximation

Data in Fig. 1 showed the results of acetone ammoximation in various solvents. One can see that solvent property had significant effects on acetone conversion, H_2O_2 efficiency and catalyst deactivation, even though all solvents gave high selectivity of product oxime (more than 97%). With using *t*-BuOH as solvent, both acetone conversion and H_2O_2 efficiency were high, but the time causing catalysts deactivation was less than 15 h. With using H_2O as solvent, the time deactivating catalyst became longer although acetone conversion and H_2O_2 efficiency decreased a little, indicating the positive effect of water on the maintenance of catalyst reactivity. In the case of *t*-BuOH–H_2O mixture as solvent, the time causing deactivation was longer than that of single *t*-BuOH solvent but shorter than single water solvent. According to solvent polarity, it was concluded that an increase of solvent polarity could extend the lifetime of catalyst but decrease the initial conversion of acetone and the efficiency of H_2O_2. In addition, with the existence of excessive acetone as solvent, the H_2O_2 efficiency was much lower, the time deactivating catalyst became shorter, and also a little decrease of oxime selectivity was observed which could be caused by self-condensation of excessive acetone [21].

After comprehensive consideration to the solvent effects on reaction process, water was finally chosen as a preferable solvent. Fig. 2 showed the change of acetone conversion in water solvent with continual operation time. As seen, the conversion was slowly reduced during 30 h, and then decreased quickly with further increase of time, suggesting that the loss of catalyst reactivity before 30 h might be caused losing of active sites whereas the rapid decrease of reactivity after 30 h could be caused by blocking pores of catalyst. It was interesting to find that 2,3-dimethyl-2,3-dinitrobutane (DMNB) was generated in large

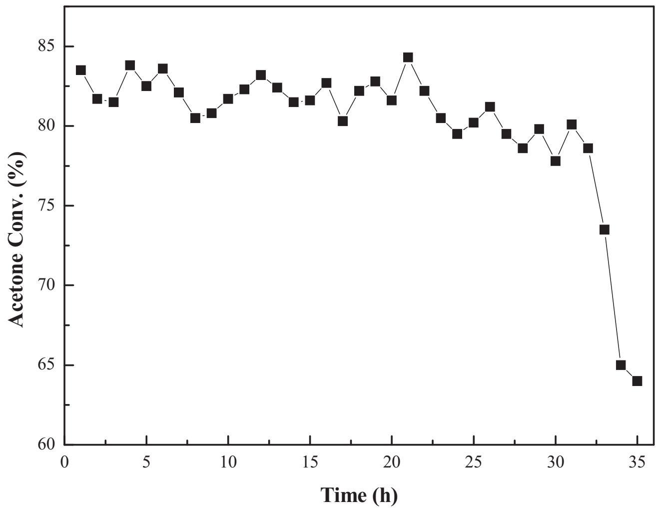


Fig. 2. The conversion of acetone using water as solvent at 343 ∼ 348 K, 0.1 ∼ 0.25 MPa, and 70 min resident time, and feeding rate of mixed feed at 25 ∼ 32 mL/min.

amount after 30 h reaction even though acetone conversion decreased quickly.

3.2. By-products analysis

Various by-products were collected from the reaction liquids and/or the surface of deactivated catalyst. Because of slightly soluble in water (0.013% wt. at 293 K), significant amount of DMNB was easily collected from the reaction liquids in the later period of reaction. The collected DMNB sample was analyzed by NMR, giving the data of ^{1}H NMR δ: 1.71 (s), and ^{13}C NMR δ: 23.0, 91.5. Boiled liquid of deactivated catalyst was extracted by CH_2Cl_2 and then analyzed by GC–MS to determine other by-products. As presented in Table 1, several amines with relatively high content were determined. In fact, these amines were also observed in the CH_2Cl_2 extract of reaction liquid. According to literature [22–26], 4-hydroxyimino-TMPD had stronger basicity than ammonia (pK_b of 4-hydroxyimino-TMPD and ammonia are 2.7 and 4.8, respectively) and a little larger size compared with HTS zeolite with an MFI structure (0.53 nm × 0.56 nm for straight channel and 0.51 nm × 0.55 nm for sinusoidal channel). Understanding these properties of by-products could provide an insight to the mechanism of catalyst deactivation and by-products formation.

3.3. Catalyst characterization

As examined by X-ray diffraction (Fig. 3), HTS exhibited almost the same main diffraction peaks as normal TS-1, indicating that HTS is with MFI topological structure. In UV–vis spectra (Fig. 4), HTS exhibited sharp absorption at 210 nm, characteristic of framework, isolated tetrahedral, which was widely accepted as the active center in TS-1. Another strong absorption at 325 nm belongs to anatase. By the way, one could see that XRD and UV–vis spectra had little changed from fresh HTS to deactivated HTS, indicating that framework and topological structure of deactivated HTS had little changed.

As characterized by TEM and SEM before, the particles of HTS contain large intra-particle voids (mesoporosity and/or macroporosity), which was quite different from those of TS-1 [10,27,28]. Textural properties of HTS were measured by nitrogen gas adsorption and desorption isotherm (Fig. 5). Unlike conventional TS-1, HTS exhibited one pronounced hysteresis loop with an abrupt closure

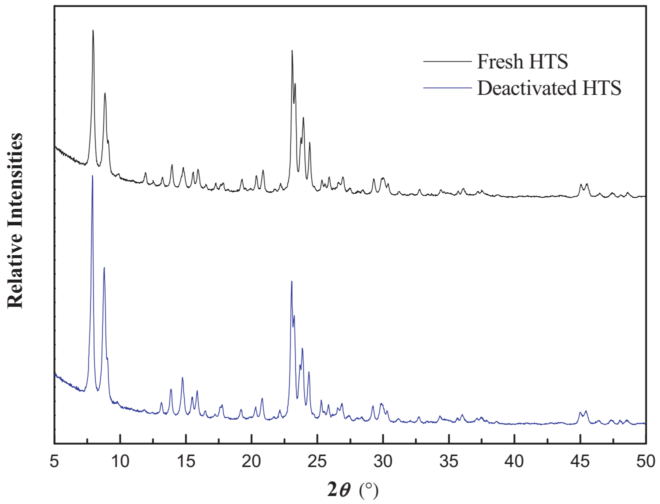


Fig. 3. The XRD patterns of HTS samples. Deactivated HTS: catalyst separated from reaction system of water as solvent after 34 h continual operation.

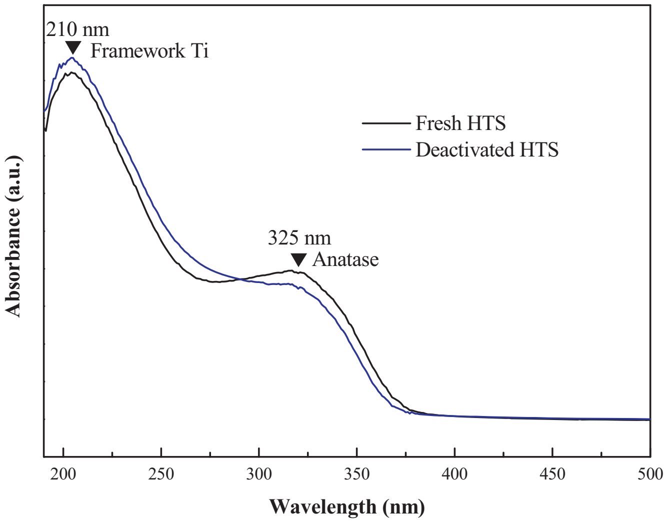


Fig. 4. UV–vis spectra of HTS samples.

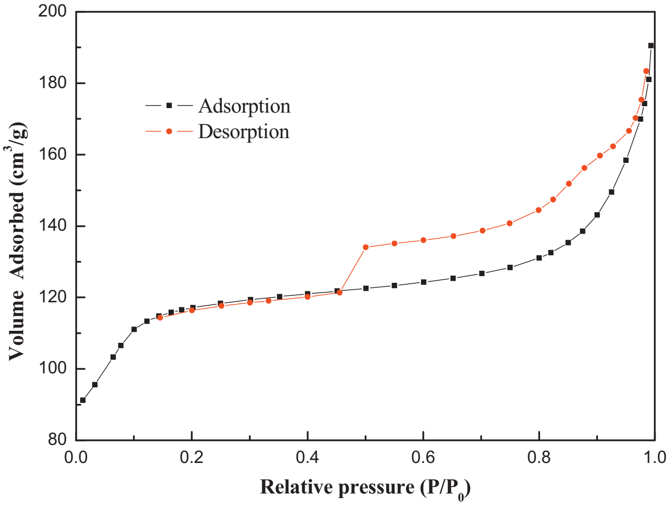
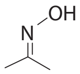
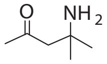
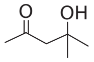
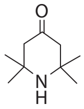
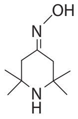


Fig. 5. Nitrogen adsorption isotherm of fresh HTS sample.

Table 1
Major by-products extracted from boiled liquid of deactivated catalyst with CH_2Cl_2.

Molecular weight	Compound	Formula	Molecular size[a] (nm)	GC-content (%)	GC–MS data[b]
73	Acetone oxime		0.49	51.87	73 (M^+, 100), 58 (54), 31 (20)
115	AMPO		0.66	4.90	100 (M^+-CH_3, 12), 100 (12), 58 (100), 43 (25)
116	HMPO		0.68	2.89	101 (M^+-CH_3, 22), 59 (50), 43 (100)
155	TMPDO		0.67	2.38	155 (M^+, 6), 140 (100), 98 (21), 83 (80), 58 (59), 42 (56)
170	4-hydroxyimino -TMPD		0.75	19.17	170 (M^+, 18), 155 (35), 122 (7), 98 (20), 58 (100), 42 (23)
	Others			18.79	

[a] Molecular size, distance between the furthest two atoms, was carried out in HyperChem software (HyberCube Inc., Version 7.5), energy minimization using geometry optimization.
[b] Electron energy of mass spectrometer was 70 eV and peaks before 2.0 min of gas chromatography was excluded to ignore solvent effect.

on the desorption branch, also indicating the presence of intraparticle voids.

The data in Table 2 showed that the surface area and volume of micropore decreased significantly from fresh catalyst to deactivated catalyst, indicating that pores of deactivated catalyst were blocked by large number of impurities or products. In comparison with fresh catalyst, the surface area of the deactivated catalyst after calcination was almost fully recovered, indicating that the framework of catalyst might be not destroyed.

4. Possible mechanism

4.1. Catalyst deactivation

To interpret the deactivation of catalyst, the mechanism of main reaction was first explained here. Two possible mechanisms of acetone ammoximation over TS-1 zeolite were proposed [29]. As illustrated in Scheme 1, the first route involved the formation of intermediate hydroxylamine by oxidation of ammonia with hydrogen peroxide, and then the hydroxylamine reacted with acetone in homogeneous phase to form acetone oxime; the second route involved the formation of intermediate imine which reacted with hydrogen peroxide over TS-1 zeolite to produce acetone oxime. In both cases, the adsorption of reactants on active sites to form intermediates was a key step. Therefore, the internal surface of catalyst was a determining factor for the main reaction process because most of active sites were located in the internal surface of TS-1 zeolite [30–32].

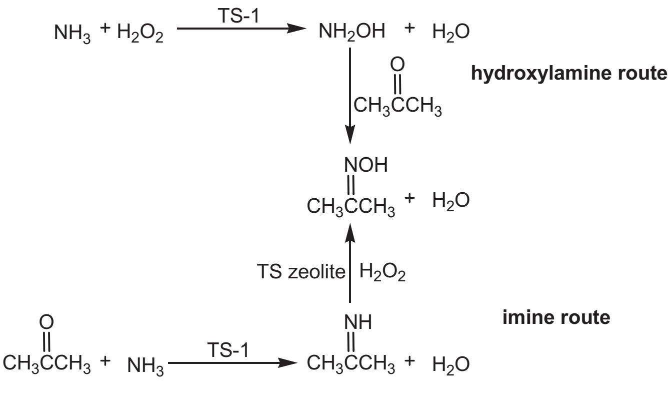
At the same time, amines as by-products with strong basicity could also adsorb on active sites of HTS catalyst, competing with imine intermediate as well as ammonia and hydrogen peroxide. In addition, amines adsorbed on internal surface of catalyst could not easily diffuse out of catalyst pores due to their larger size, and gradually accumulated to block the pore channels of catalyst. On the other hand, the amines formed in the reaction liquid could hardly diffuse into pores of catalyst, and could deposit on channel mouth and external surface of catalyst, which gave rise to another way to decrease active sites. As a part of compensation, these amines could be partly removed from external surface and channel mouth of catalyst by solvents with strong polarity. But overall, the gradual decrease of active sites for reactants and intermediates due to amines adsorption and deposition caused the slow deactivation of HTS catalyst, evidenced by the gradual decrease of acetone conversion in Fig. 1.

In the case of water as solvent, the reaction in the later period could generate large amount of DMNB to deposit on internal and external surface of catalyst. Consequently, blocking of catalyst pores accompanied by the substantial reduction of pore surface area and volume caused the rapid deactivation of catalyst. Based on

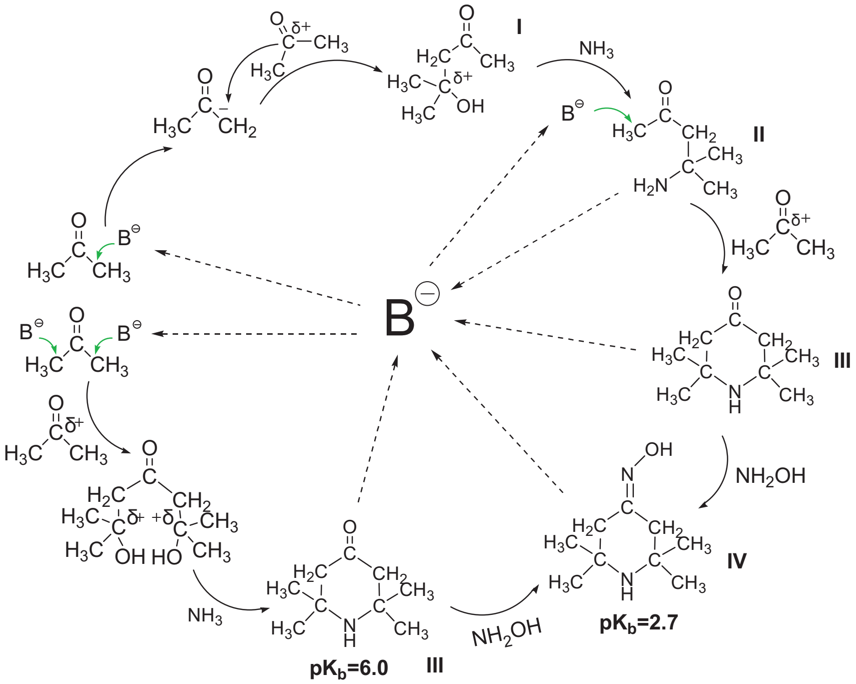
Table 2
BET specific surface area of HTS catalyst with different treatments.

Catalyst[a]	Fresh	Deactivated	Calcined[d]
Total surface area[b]	404.6	359.7	407.4
Micropore surface area[b]	296.1	196.0	318.8
Micropore volume[c]	0.13	0.08	0.14

[a] Catalyst separated from reaction system of water as solvent after 34 h continual operation.
[b] m^2/g.
[c] cm^3/g.
[d] Calcined temperature: 823 K.



Scheme 1. Mechanism of acetone ammoximation to acetone oxime.



Scheme 2. Formation of amine by-products though an autocatalytic reaction.

quantitative differences, DMNB played the main role in rapid deactivation of catalyst, although amine and other by-products might also contribute to the rapid deactivation to some extent.

4.2. By-products formation

The proposed mechanism on formation of by-products was illustrated in Scheme 2. As seen, HMPO (I) could be formed by condensation of acetone at the beginning, which was a classical reaction under alkaline condition [19]. Compared to cyclohexanone and butanone with electron-donating groups (two methylene for cyclohexanone and one methyl for butanone), the condensation of acetone was more easier to occur, because methyl of acetone was easier to lose hydrogen to form carbanion under alkaline condition. Adding ammonia to HMPO could form AMPO (II) [33]. TMPDO (III) could be formed by condensation of acetone and ammonia as well as condensation of acetone and AMPO under alkaline condition either. The main amine by-product 4-hydroxyimino-TMPD could be formed by reaction of TMPDO and hydroxylamine, which was used to generate acetone oxime when considering the hydroxylamine route for acetone ammoximation. Thus, TMPDO not only adsorbed on the active sites of HTS catalyst, but also competed with acetone to consume hydroxylamine, causing the decrease of acetone conversion. Furthermore, generation of amines increased the alkalinity of reaction liquid to promote the by-reactions featured as an alkali autocatalytic process, leading to the increase of acetone conversion but the decrease of acetone oxime selectivity in certain extent.

To verify the effect of the amine by-products on the ammoximation reaction, an additional experiment was conducted with adding some TMPDO into the reactant mixture at the beginning. The influence of TMPDO acetone ammoximation was illustrated in Fig. 6. One could see that both the acetone conversion and oxime selectivity were decreased with adding TMPDO into the reaction. In other words, TMPDO acting as a contributor to catalyst deactivation had significant influence on acetone ammoximation. In addition, other by-products, especially 4-hydroxyimino-TMPD and DMNB were significantly increased in this process, indicating that TMPDO could not only cause a loss of reactivity, but also might be favorable to the formation of other amines as by-products.

In comparison with the formation of by-product nitrocompound (2-nitrobutane) in butanone ammoximation [34], large amount of polynitro-compound (DMNB) instead of nitrocompound was produced in acetone ammoximation, indicating the different mechanism of by-products formation. The formation of DMNB in acetone ammoximation might experience a free radical addition and coupling process as depicted in Scheme 3. It had been proposed that as active intermediates for TS-1 zeolite, titanium hydroperoxyl intermediates could decompose H_2O_2 by oxidation via formation of hydroperoxyl radical ($^{\bullet}OOH$), and alkali condition might favor this process [35,36]. In the later stage of acetone ammoximation, parts of active sites were covered with amines and other by-products, giving little room for hydrogen peroxide to form active intermediates, thus excess hydrogen peroxide (compared to the limited active sites) was oxidized to $^{\bullet}OOH$, and DMNB was generated as soon as the formation of $^{\bullet}OOH$. As showed in Scheme 3, $^{\bullet}OOH$ could first add to C-atom of C=N to form the

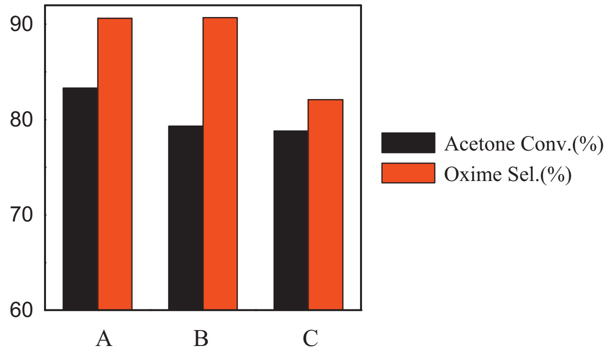
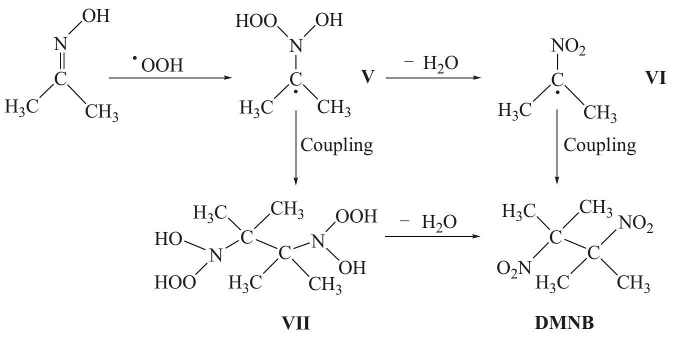


Fig. 6. The influence of adding TMPDO to the reactants on conversion of acetone. (A: no addition of TMPDO; B: 0.35 g TMPDO added; C: 1.75 g TMPDO added). Conditions: 105 g deionized water as solvent; 35 g HTS catalyst; 1.81 mol of acetone, 2.77 mol of NH_3, 1.54 mol of H_2O_2; procedure: NH_3 and H_2O_2 were dropped into the batch reactor with stirring in 1 h.



Scheme 3. Formation of DMNB though a free radical reaction.

relatively stable intermediate (V), and then coupling and dehydration of (V) could produce DMNB. It should be mentioned that DMNB could be mainly formed on the internal surface of catalyst because acetone oxime could easily enter into catalyst pores and •OOH was formed on internal surface. Polynitro-compounds were not found in cyclohexanone and butanone system mainly because of lacking strong alkaline condition and the relative big space steric hindrance. DMNB could accumulate inside the pore channels of catalyst due to its slight solubility in aqueous reaction mixture, gradually block the channels, and finally cause deep deactivation of HTS catalyst.

To verify the mechanism of DMNB formation, the extra experiment was conducted in batch reactor with using water as solvent, HTS zeolite as catalyst, acetone oxime and hydrogen peroxide as raw material. In the absence of HTS zeolite, DMNB was not observed, in the existence of HTS, however, the yield of DMNB increased rapidly with increasing the concentration of alkali (adjusting the pH by adding sodium hydroxide or ammonia) and the amount of hydrogen peroxide, giving a maximal DMNB yield of 43.2% as reported before [37]. The results showed that the formation of DMNB should experience a catalytic process and was closely related to solution alkalinity and hydrogen peroxide, which might explained why DMNB was obviously increased with adding TMPDO to reaction mixture.

5. Conclusions

Two main mechanisms causing HTS catalyst deactivation in acetone ammoximation using water as solvent were proposed. First one involved the adsorption of amines such as 4-hydroxyimino-TMPD with strong alkalinity on active sites to cause slow deactivation of catalyst. Second one featured as the blocking of catalyst pores mainly by DMNB to cause a rapid deactivation of catalyst. For the first time, polynitro-compound was found in the reaction of ketone ammoximation. Formation of amines and DMNB experienced an alkali autocatalytic reaction and radical oxidative coupling reaction, respectively.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.01.003.

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