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Ammoximation of cyclohexanone over nanoporous TS-1 using UHP as an oxidant

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Abstract

Ammoximation of cyclohexanone to cyclohexanone oxime has been carried out using ammonia and urea hydrogen peroxide adducts as the oximation reagents. Effect of catalyst concentration, temperature, and molar ratio of reactants and effect of doping TS-1 with Fe has been studied to obtain the optimum conversion of cyclohexanone (CH) and selectivity to cyclohexanone oxime. The catalyst has been characterized employing the techniques of XRD, FT-IR, EDAX, SEM, AAS and Mössbauer spectroscopy with a view to confirm phase purity, stoichiometry, particle size distribution and oxidation state of Fe. The BET surface area of TS-1 catalyst was found to be 680 m^2/g. A maximum conversion of about 70% of cyclohexanone with cyclohexanone oxime selectivity of 99.72% was obtained over TS-1 doped with Fe at a temperature of 40 °C and cyclohexanone to UHP molar ratio of 1:1. Reaction seems to proceed through a redox mechanism and follow hydroxylamine as well as imine routes. According to hydroxylamine route ammonia and UHP react within the TS-1 pores and produce hydroxylamine. The hydroxylamine thus formed reacts with cyclohexanone outside the pores to produce cyclohexanone oxime. In the imine route cyclohexanone and ammonia react to produce cyclohexanone imine, which is oxidized to cyclohexanone oxime. A tentative mechanism for the process has been proposed.

Keywords: Ammoximation; Cyclohexanone; Cyclohexanone oxime

1. Introduction

Oxidation in presence of ammonia of organic compounds having a methyl group in the α-position relative to a double bond or an aromatic ring, to corresponding nitriles, is called ammoxidation [1]. When organic compound is an aldehyde or ketone the process has been referred to as ammoximation and the product is oxime. Ammoximation of cyclohexanone to cyclohexanone oxime is of special importance as it is precursor of caprolactam needed for nylon production. The conventional technology of oxime production is multi-step, energy intensive, environmentally unfavourable and produces ammonium sulphate as by-product, which causes disposal problem. Vapour phase ammoximation over SiO_2/Al_2O_3 catalysts using air as oxidizing agent resulted into poor yield of cyclohexanone oxime and led to many side products [2]. Enichem [3] developed a new liquid phase single step process based on direct ammoximation of cyclohexanone with ammonia and hydrogen peroxide using a ZSM-5 type titanium silicate zeolite named TS-1. This environmental friendly process results into high yield and selectivity of cyclohexanone oxime. Ti, Na-zeolites, Ti, Na-USY, Ti, Na-erinite and Ti, Na-ZSM-5 have also been used as catalyst for ammoximation of cyclohexanone [4]. Besides cyclohexanone, hydroxyaromatic ketones have been subjected to ammoximation over titanium molecular sieves [5]. Ammoximation of cyclohexanone over amorphous SiO_2–TiO_2 [6], no-redox oxides [7], such as amorphous silica and supported titanium silicate [8,9] is also reported.

TS-1 is also used for transformation of styrene-to-styrene oxide using hydrogen peroxide as the oxidizing agent. However, the selectivity of the oxide is low because of its isomerization to phenyl acetaldehyde [10]. Urea hydrogen peroxide adducts (UHP) releases anhydrous hydrogen peroxide in the reaction mixture in a controlled manner, avoids isomerization of styrene

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oxide and increases selectivity towards styrene oxide. Very high selectivity of styrene oxide has been reported by Laha and Kumar [11] using anhydrous urea hydrogen peroxide adduct in the epoxidation of styrene over TS-1 catalyst. TS-1 catalyst and oxygen precursors H_2O_2 are common to epoxidation as well as ammoximation. Although, there are reports on the epoxidation of styrene over TS-1 catalysts using UHP as oxygen precursor, to the best of our knowledge, there is no report on the ammoximation of cyclohexanone using UHP as oxidant. The present problem of ammoximation of cyclohexanone was therefore undertaken with a view to (1) find the suitability of UHP and ammonia as ammoximation reagent, (2) to optimise the process conditions for maximum yield of cyclohexanone oxime, (3) to study the effect of doping TS-1 with Fe, and to (4) predict a suitable reaction mechanism.

2. Experimental

2.1. Synthesis of TS-1 catalyst

To an aqueous solution of 25.25 g of tetrapropyl ammonium hydroxide (TPAOH), 16.75 g of tetraethyl orthosilicate (TEOS) were added slowly under vigorous stirring for 45 min in order to hydrolyze the TEOS. A slight increase in temperature was observed. To the resultant mixture (pH 12.5), a solution of 1.3 g of tetrabutyl orthotitanate (TBOT) in 5 g of dry isopropyl alcohol was added drop wise with stirring for 45 min in order to avoid its instantaneous hydrolysis to stable TiO_2 resulting in poor incorporation of titanium. The clear liquid thus obtained was stirred for 1 h in order to complete the hydrolysis of TEOS and TBOT. Finally 13 g of double distilled water were added slowly to the above mixture and the final gel mixture was stirred for 45 min to remove the alcohol. The crystallization of the gel mixture was carried out into a stainless steel autoclave at 443 K under static condition for 24 h. The autoclave was quenched and solid product was separated by centrifugation at 3600–4000 rpm in 2 h. The product was dried at 393 K for 4–5 h and calcined at 813 K for 16 h. It would be worth mentioning that TBOT was used as the source of Ti instead of the conventional TEOT because the hydrolysis of the former is lower. For the efficient incorporation of Ti in the zeolite framework, the relative rate of hydrolysis of Si-alkoxide (preferably of lower molecular weight) and Ti-alkoxide (preferably with high molecular weight) should be matched as closely as possible. For preparation of Fe-doped TS-1 catalyst, 1 g TS-1 was added to a 10 ml 5% solution of ferric chloride and pH was adjusted to 9 by adding ammonium hydroxide solution. The mixture was stirred for 2 h, filtered washed till free from chloride ions, oven dried and calcined at 813 K.

2.2. Characterization of the catalyst

The physicochemical and catalytic behavior of zeolites can be modified by changing their framework composition [12]. The advent of crystalline titanium silicates with zeolite properties has enlarged the domain of zeolite catalysis in hydroxylation, ammoximation and oxidation reactions [13–19]. The substitution of silica by Ti in the MFI structure (TS-1) was first claimed by Taramasso et al. [12] and titanium silicate-2 (TS-2) with MEL topology was claimed by Reddy et al. [13].

The characterization of the sample was carried out using X-ray diffraction studies (Rigaku), infrared spectroscopy (Shimadzu), atomic adsorption spectroscopy, EDAX and SEM (JEOL JSM-5600) and BET surface area (Quanta chrome autosorb (1.24) instrument).

The Mössbauer measurements are carried out in the conventional transmission geometry in the constant acceleration mode. The Wiessel make velocity drive, LND make proportional counter and the ORTEC–MCS was used in the system. The source used was Co-57 in Rh matrix of ∼6 mCi strength. The spectrometer is calibrated with respect to the natural iron. The spectrum is fitted with doublet using NORMOS-SITE least-square routine for the hyperfine parameters.

2.3. Ammoximation of cyclohexanone

The catalytic runs were performed in a 250-ml capacity three-necked RB flask fitted with magnetic stirrer, a condenser, a thermometer pocket and the third neck was fitted with a dropping funnel. The whole assembly was housed in a water bath. Known amounts of cyclohexanone and UHP were taken in the flask and ammonia was fed drop wise from the dropping funnel. In a typical batch experiment the water bath was heated to 313 K and 10 g of UHP, 10 g of cyclohexanone, 1 g of catalyst TS-1 were taken in the flask and 10 ml of ammonia (25 wt.%) was fed to the reactor drop wise over a period of 6 h. After 6 h, the reaction mixture was cooled down to room temperature and catalyst separated by filtration. The filtrate was subjected to analysis using a GLC (make: Shimadzu 14B GLC) equipped with FID detector.

3. Results and discussion

The X-ray powder diffraction pattern of the calcined TS-1 zeolites is produced in Fig. 1. It was similar to that of standard ZSM-5 zeolites confirming orthorhombic symmetry and location of Ti in zeolite framework. The FT-IR spectrum of Fe-TS-1

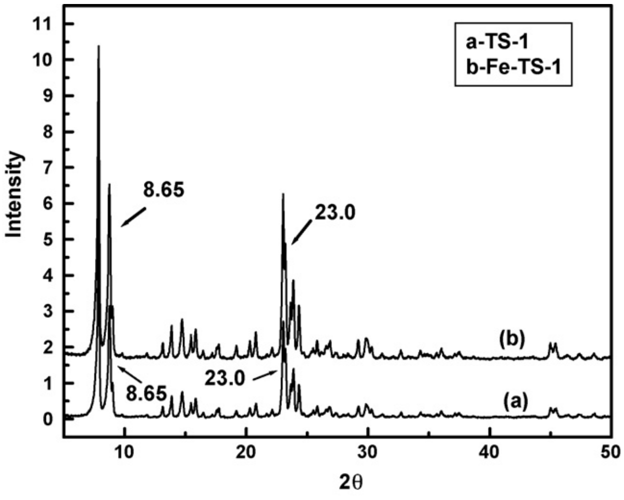


Fig. 1. X-ray diffraction patterns of TS-1 and Fe-TS-1.

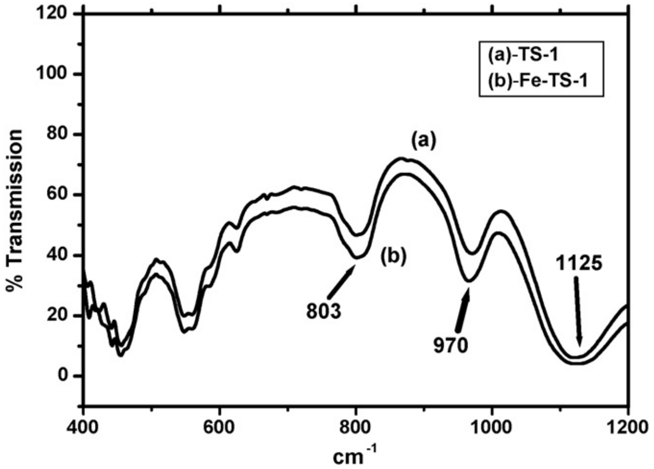


Fig. 2. FT-IR spectra of (a) TS-1 and (b) Fe-TS-1 in the region 500–1000 cm^{-1}.

sample is reproduced in Fig. 2. Absorption bands are observed at 970 and 650 cm^{-1}. The band appeared at 650 cm^{-1} was characteristic of the MFI structure. The IR band observed at 970 cm^{-1} can be attributed to a stretching mode of a [SiO_4] unit bonded to a Ti^{4+} ion (O_3SiOTi)[10]. The BET surface area for TS-1 was found to be 680 m^2/g.

Effect of temperature on the ammoximation of cyclohexanone over TS-1 is shown in Table 1. Conversion increased slowly up to 313 K then sharply reached a maximum of 56.50% at 333 K. However, further increase in temperature led to decrease in conversion. Drop in conversion above 333 K can be attributed to low availability of H_2O_2, perhaps due to fast decomposition of UHP and decreased solubility of H_2O_2 in water. Thus, optimum temperature range of ammoximation with UHP seems to be 313–333 K. Maximum selectivity was also found in the same temperature range.

Table 2 presents the effect of catalyst concentration on the ammoximation of cyclohexanone. It is found that initial increase in the catalyst concentration leads to increase in cyclohexanone conversion until a limiting value is reached. A 10 wt.% catalyst is found to be optimum with cyclohexanone conversion of 56.50% with an oxime selectivity of 99.29%.

The effect of CH/UHP molar ratio on the cyclohexanone conversion and oxime selectivity in depicted in Table 3. A CH/UHP molar ratio of 1 was found to be optimum. Further increase in the ratio led to decreased conversion due to insufficient availability of hydrogen peroxide from UHP. Table 4 presents effect of NH_3/UHP molar ratio on the ammoximation of cyclohexanone over TS-1 catalyst. A NH_3/UHP molar ratio of 1.5 was found to give a maximum conversion of about 56.50% with oxime selectivity of 99.29%. Lower molar ratio of NH_3/UHP (higher UHP/NH_3) destroys part of hydroxylamine responsible for oxime synthesis [12] and lowers the conversion. Higher NH_3/UHP molar ratio (excess of ammonia) decomposes UHP faster decreasing availability of H_2O_2 in the pores for NH_2OH synthesis.

Table 1
Influence of temperature on cyclohexanone ammoximation

	Temperature			
	298	313	333	353
Cyclohexanone				
Conversion (wt.%)	24.13	18.69	56.50	17.45
Product distribution (wt.%)				
Cyclohexanone	75.88	81.31	43.50	82.55
Cyclohexanone oxime	18.53	15.83	55.54	14.54
Others	2.27	0.94	0.40	2.92
Oxime selectivity	89.10	94.41	99.29	83.29

Catalyst = 1 g; CH:NH_3:UHP molar ratio = 1:1.5:1; CH/catalyst weight ratio = 10; reaction duration = 6 h.

Table 2
Influence of catalyst concentration on cyclohexanone ammoximation

	Catalyst concentration (g mol^{-1}) of CH			
	2	5	10	15
Cyclohexanone				
Conversion (wt.%)	47.04	54.57	56.50	54.41
Product distribution (wt.%)				
Cyclohexanone	52.93	54.25	43.50	45.59
Cyclohexanone oxime	33.19	39.68	55.54	44.15
Others	13.88	15.08	0.40	10.40
Oxime selectivity	72.48	86.51	99.29	80.93

Temperature = 333 K; reaction duration = 6 h; CH:NH_3:UHP molar ratio = 1:1.5:1.

Table 3
Influence of CH/UHP molar ratios on the ammoximation of cyclohexanone over TS-1

	CH/UHP molar ratio			
	1:1	1:2	1:3	1:4
Cyclohexanone				
Conversion (wt.%)	56.50	10.77	22.18	15.18
Product distribution (wt.%)				
Cyclohexanone	43.50	89.23	77.82	54.82
Cyclohexanone oxime	55.54	9.53	19.97	14.24
Others	0.40	1.23	2.20	0.93
Oxime selectivity	99.29	88.56	90.06	93.83

Temperature = 333 K; reaction duration = 6 h; CH/catalyst weight ratio = 10; NH_3/UHP molar ratio = 1.5.

Table 4
Influence of NH_3/UHP molar ratios on the ammoximation of cyclohexanone over TS-1

	NH_3/UHP molar ratio			
	0.5	1.0	1.5	2.0
Cyclohexanone				
Conversion (wt.%)	16.64	43.70	56.50	37.06
Product distribution (wt.%)				
Cyclohexanone	83.36	56.29	43.50	62.93
Cyclohexanone oxime	14.79	35.21	55.54	32.62
Others	1.79	8.50	0.40	4.48
Oxime selectivity	89.21	80.55	99.29	87.93

Temperature = 333 K; reaction duration = 6 h; CH/catalyst weight ratio = 10; CH/UHP molar ratio = 1.

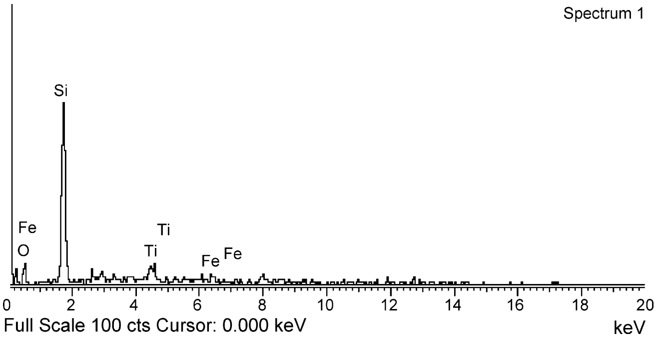


Fig. 3. EDAX spectrum of Fe-doped TS-1.

3.1. *Effect of doping Fe in TS-1*

This study was performed with a view to examine the behaviour and performance of TS-1 by doping it with Fe. The energy dispersive X-ray analysis [EDAX] spectrum of Fe-doped TS-1 is shown in Fig. 3. The chemical analysis by EDAX measurement taken as an average of five different sites over an area of 15 μm × 15 μm shows Si = 37.62%, Ti = 3.21%, oxygen 57.41%, Fe = 1.76% giving Si/Ti atomic ratio to be 11.71. The SEM picture recorded on JEOL JSM-5600 instrument shows particle of uniform shape and size and is reproduced in Fig. 4. Since EDAX only provides local and therefore selective composition of the catalyst a further analysis of the catalyst composition was made with the help of atomic absorption spectroscopy employing Shimadzu-6800 instrument. The Si percentage in TS-1 was found to be 47.5. The Fe and Si percentage in Fe-TS-1 was found to be 0.28 and 43.51 respectively. In order to determine framework and extra framework Fe, we treated the Fe-TS-1 catalyst with a $CaCl_2$ solution buffered at pH 4 by CH_3COOH/CH_3COONa buffer for 1 h, filtered the solid, washed with distilled water and dried. AAS measurement of this sample gave the iron and Si percentage to be 0.29 and 43.63, respectively. Almost same percentage of iron in Fe-TS-1 and $CaCl_2$ leached Fe-TS-1 suggests that whole of the iron is present in the framework and equal amount of Ti has gone into the extra-framework positions.

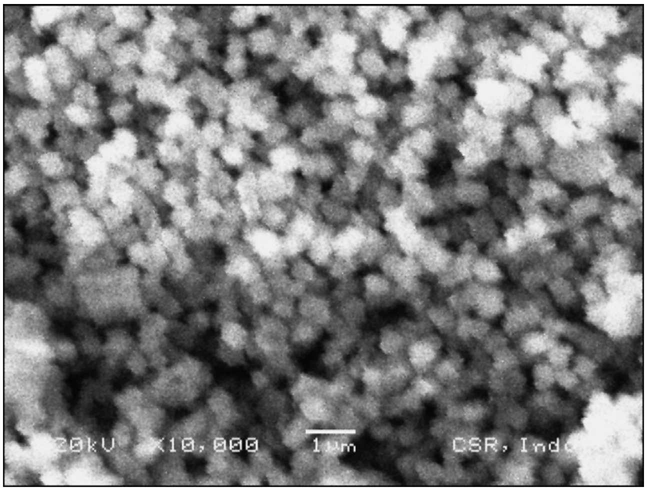


Fig. 4. SEM images of Fe-TS-1.

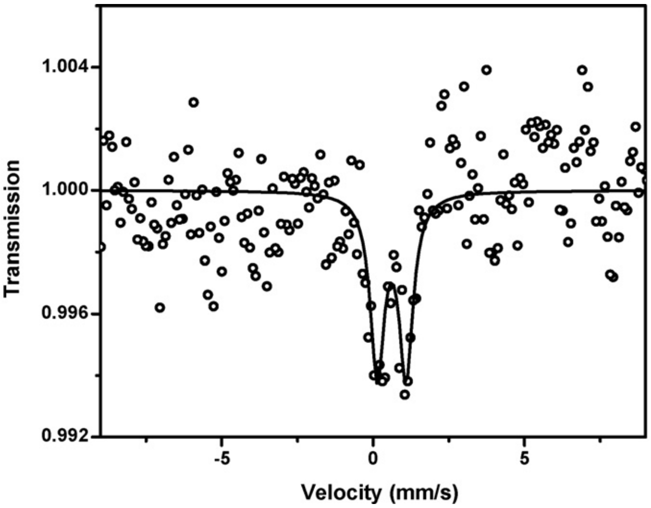


Fig. 5. Mössbauer spectrum of Fe-doped TS-1.

The room temperature Mössbauer spectrum of Fe-doped TS-1 is reproduced in Fig. 5. An isomer shift of 0.622 ± 0.017 mm/s and quadrupole splitting of 0.942 ± 0.030 mm/s is obtained. Even though the obtained line width (0.554 ± 0.057 mm/s) is more than the instrumental line width (∼0.3 mm/s), it is not attempted to fit the data with more than one doublet due to the poor statistics. The obtained isomer shift indicates the presence of Fe in +3 state and the Mössbauer spectra clearly show the non-magnetic nature of the sample.

A comparative performance of Fe-doped Ts-1 with TS-1 is presented in Table 5. Better performance of Fe-doped Ts-1 seems to be due to higher number of active sites and lower redox potential of Fe compared to Ti.

4. Mechanism of the process

TS-1 with MFI structure possess straight and sinusoidal channels with pore size 0.53 nm × 0.56 nm and 0.51 nm × 0.55 nm, respectively, and are large enough to allow passes of C_5–C_6 cyclic ketones [7]. It is also proposed that Ti peroxy species present at the inner as well as outer surface of the catalyst function as active sites [14]. In order to have an idea of the ratio of inner to outer Ti sites we performed ammoximation of

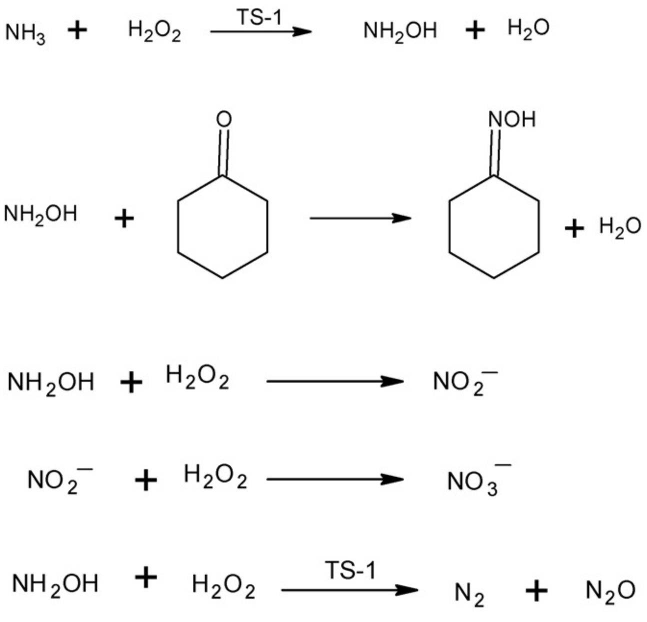
Table 5
A comparative performance of Fe-doped TS-1 with TS-1

	TS-1	Fe-TS-1
Cyclohexanone		
Conversion (wt.%)	56.50	69.89
Product distribution (wt.%)		
Cyclohexanone	43.50	30.11
Cyclohexanone oxime	55.54	69.7
Others	0.40	0.19
Oxime selectivity	99.29	99.72

Temperature = 333 K; reaction duration = 6 h; CH/catalyst weight ratio = 10; $CH:NH_3$:UHP molar ratio = 1:1.5:1.

cyclohexanone in presence of *N*,*N*-diethylaniline and triethylamine and found that poisoning due to triethylamine was many fold larger than that due to *N*,*N*-diethylaniline. This has been attributed to the size of two amines. Triethylamine being smaller in size could enter into the pores and could effectively poison the catalyst. Due to stearic reason, *N*,*N*-diethylaniline could not enter the inner pores and as a result poisoning was not appreciable. This suggests presence of much larger number of Ti sites in the inner pores than on the outer surface of TS-1 crystals. Similar finding has been reported by Takashi and Jappar [6] while studying the poisoning effect of organic amines on ammoximation of cycloheptanone by hydrogen peroxide over TS-1 catalysts. These authors have also studied the reactivity of cyclohexanone and isomeric methylcyclohexanones and isomeric dimethylcyclohexanones and attributed lower reactivity of methyl cyclohexanone to steric restrictions imposed by the methyl groups.

Most of the mechanism suggested for ammoximation of cyclohexanone over TS-1 is based on the fact that ammonia and hydrogen peroxide react inside the pores to produced hydroxylamine which reacts with cyclohexanone outside the pores in the homogeneous phase to produce oxime. This hypothesis is supported by the findings that TS-1 could catalyze ammoximation of ketones [20], with kinetic diameter larger than TS-1 pores and ability of the catalyst to form hydroxylamine from NH_3 and H_2O_2. Interaction between NH_2OH and cyclohexanone molecules has also been proposed. In order to confirm similar type of mechanism applicable in the present work we allowed ammonia and UHP to react over TS-1 at 333 K for 6 h and then cool the reaction mixture to room temperature and filter to separate the catalyst. Cyclohexanone was then added to the filtrate within few hours and formation of cyclohexanone oxime was confirmed. However, the yield was poor, perhaps due to oxidation of hydroxylamine by hydrogen peroxide of UHP to nitrogen oxides. Ammonium hydroxide and UHP were allowed to react for 2 h in a test tube at 313 K over TS-1. The resulting reaction mixture was mixed with a ice cooled mixture of aniline and HCl. The mixture was allowed to stand for few hours when positive colour developed indicating formation of diazonium compound. This test confirmed formation of nitrous oxide due to reaction between NH_2OH and H_2O_2. The above findings are summarized in Scheme 1.



Scheme 1. Ammoximation of cyclohexanone via hydroxylamine route.

According to another mechanism, cyclohexanone and ammonia react to produce cyclohexanone imine, which in turn is oxidized to cyclohexanone oxime. Since negligible yield is obtained without catalysts, the oxygen insertion in the imine seems to be through catalyst via some sort of peroxo compound. To confirm the formation of imine intermediate, we recorded the IR spectra of cyclohexanone in presence of TS-1 as well as cyclohexanone and ammonia mixture in presence of TS-1 and the records in the region 1400–1900 cm^{-1} are reproduced in Fig. 6. The band appeared at 1705 cm^{-1} can be assigned to C=O stretching mode while that appeared at 1635 cm^{-1} can be assigned to C=N stretching mode. These records confirm the formation of imine intermediate in equilibrium with ketone. This mechanism is shown in Scheme 2. As this reaction is to be completed mostly in the pores of the catalyst, its contribution seems to be smaller than that compared to hydroxylamine route which completes out side the pores.

The active sites in the catalysts seem to be framework and extra framework metal sites, which functions through redox mechanism. Extra framework Ti seems to be present in the form TiO_x [21]. Metal sites receive oxygen from UHP; get oxidized to peroxo compound, which in turn transfer oxygen to substrate (NH_3, Cyclohexanone) and get reduced. The cycle is repeated again and again. Better performance of Fe-doped TS-1 can be attributed to higher redox potential of iron compared to titanium.

Thus we conclude that (1) major number of active sites in TS-1 are in the pores, (2) doping TS-1 with Fe simply increases

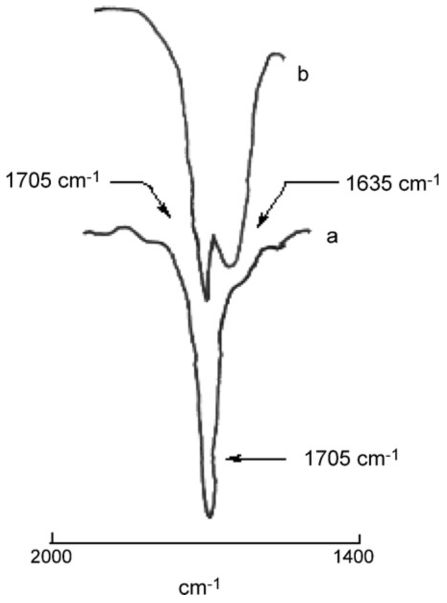
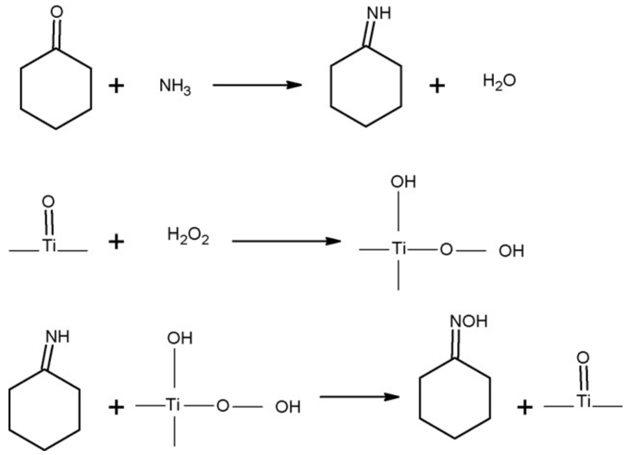


Fig. 6. IR spectra of (a) CH in presence of TS-1 and (b) CH and NH_3 mixture in presence of TS-1 in the region 1400–2000 cm^{-1}.



Scheme 2. Ammoximation of cyclohexanone via imine route.

the number of active sites, and (3) the reaction seems to operate through two routes. According to one mechanism, ammonia and hydrogen peroxide react at the active sites within the pores and produce NH_2OH that reacts with cyclohexanone outside the pore to produce cyclohexanone oxime. In another mechanism cyclohexanone and ammonia react in the solution to produce cyclohexanone imine, which is subsequently oxidised to cyclohexanone oxime. Active centres seem to be framework as well as extra-framework Ti and Fe metal sites, which function through redox mechanism.

5. Conclusion

Ammoximation of cyclohexanone using ammonia and urea hydrogen peroxide adduct has been studied over TS-1 and Fe-doped TS-1 in slurry phase. Doping enhances the performance of TS-1. A maximum yield of 70% of cyclohexanone oxime with selectivity of 99.72% has been achieved over Fe-TS-1. It is also concluded that major number of active sites in TS-1 are in the pores and doping TS-1 with Fe simply increases the number of active sites. The reaction proceeds through hydroxylamine as well as imine routes. According to Hydroxylamine route, ammonia and hydrogen peroxide react at the active sites within pore and produce NH_2OH which reacts with cyclohexanone outside the pore to produce cyclohexanone oxime. In the imine route, CH and ammonia react to produce cyclohexanone imine, which is oxidised by the TS-1 catalytically through cyclohexanone oxime. In both the mechanism the catalyst seems to function as a redox system.

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