

Chapter IV

EPOXIDATION

REACTIONS

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CHAPTER IV: EPOXIDATION REACTIONS

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4.1. Introduction

Epoxidation of alkenes is of considerable importance for the chemical industry especially for the synthesis of chemical intermediates. The electrophilic addition of oxygen to an alkene, to form an epoxide remains one of the greatest challenges in selective oxidation chemistry [1]. Epoxidation reactions of alkenes generally require the presence of a catalyst. However several side reactions such as oxidation in the allylic positions, ring-opening of the epoxides by hydrolysis or solvolysis, epoxide rearrangement or even total breakdown of the C=C bonds, can take place [2,3]. The finding of efficient catalysts for the selective insertion of one oxygen atom from oxygen donors like dioxygen, hydrogen peroxide, alkyl hydroperoxide, sodium hypochlorite or iodosyl benzene into various molecules, under mild conditions therefore remains a topic of investigation for the chemical and biological catalysts [2].

The use of zeolite titanium silicate (TS-1) with MFI structure received much attention for oxidation of many organic substrates under mild reaction conditions with H_2O_2 [4-6]. However the use of TS-1 is limited due to its complicated and laborious synthesis [7], secondly it is only applicable to substrates capable of entering its pores. To overcome these drawbacks many attempts have been made to substitute the zeolite based catalysts by systems containing highly dispersed transition metal cations on various organic or inorganic supports with high surface areas [8] like TiO_2-SiO_2 [9], TiO_2-ZrO_2 [10] etc.

TiO₂ as such is considered to be inactive for the epoxidation, hence the catalysts containing titanium chemically bonded to siloxane ligands are considered to be active [11]. Titanium containing catalysts such as Ti-silicas and Ti-zeolites have been widely used for the alkene epoxidation [12-15] because titanium is capable of generating peroxometal intermediates, which facilitate the oxygen transfer to cyclohexene.

It is also very important for epoxidation catalysts to possess a mesoporous structure in order to facilitate the diffusion of bulky reactants and products [4]. Farias et al [16] also stated that the presence of both Bronsted and Lewis acid sites play a prominent role in epoxidation reactions. Since the mesoporous materials normally possess large surface area and narrow pore size distribution, the use of mesoporous TiO₂ in epoxidation reactions becomes attractive also considering its chemical stability, cost and availability. However the utilization of pure TiO₂ with mesoporous structure in the epoxidation of cyclohexene or cyclooctene has been hardly investigated. T. Streetwong et al [3] studied the catalytic performance of mesoporous TiO₂ and RuO₂/TiO₂ [17] for epoxidation reactions and showed that the synthesized mesoporous TiO₂ and RuO₂/TiO₂ showed better activity and selectivity than the non-mesoporous commercial TiO₂.

In our present work, the catalytic performance of meoporous TiO₂ synthesized by a very simple method (described in section 2.2.3 and 2.2.4) have been investigated for epoxidation of cyclohexene and *cis*-cyclooctene.

4.2. Experimental

4.2.1. Catalyst Synthesis

The following catalysts (Table 4.1) have been investigated for epoxidation of

i) cyclohexene

ii) *cis*-cyclooctene

Table 4.1: Structural properties of synthesized TiO₂ samples

Sr. No.	Code	Method of synthesis	Phase % Anatase	Scherrer crystallite size (nm)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
1	R1	TiCl ₃ : HNO ₃	52	14	42	0.13	9
2	R2	TiCl ₃ (HNO ₃):Tu (1:2)	82	13	66	0.17	11
3	R2a	TiCl ₃ (HNO ₃):Tu (1:4)	34	09	91	0.19	10
4	R3	TiCl ₃ (HNO ₃):Tu:Oa (1:2:1)	100	12	67	0.16	8
5	R3a	TiCl ₃ (HNO ₃):Tu:Oa (1:4:1)	100	08	94	0.23	7
6	Degussa-P25	-	84	21	50	-	-

4.2.2.. Catalyst Characterization

The details of characterization of the samples are discussed earlier in Chapter 2. The representative data of XRD and porosity is shown in Figure 4.1 and 4.2 respectively.

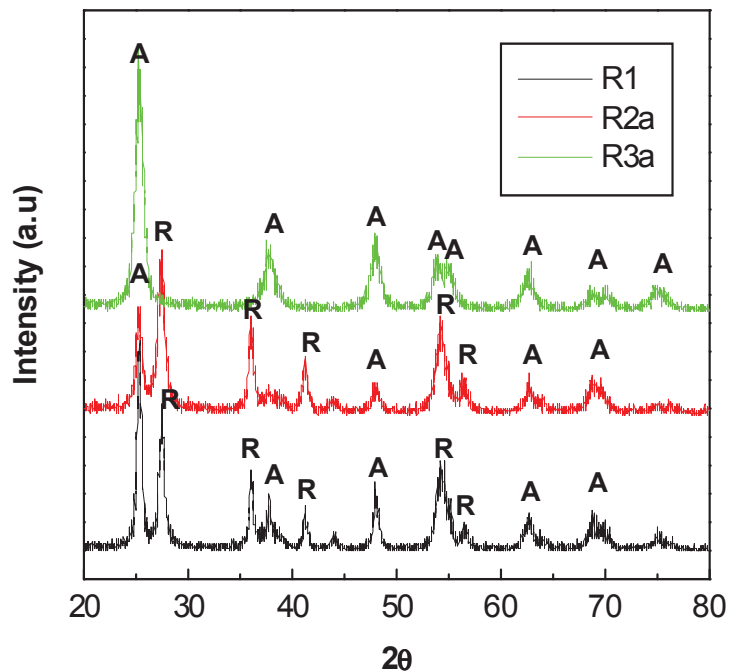


Figure 4.1: XRD patterns of R1 [$\text{TiCl}_3(\text{HNO}_3)$], R2a [$\text{TiCl}_3(\text{HNO}_3)$:Tu (1:4)], and R3a [$\text{TiCl}_3(\text{HNO}_3)$:Tu:Oa (1:4:1)]

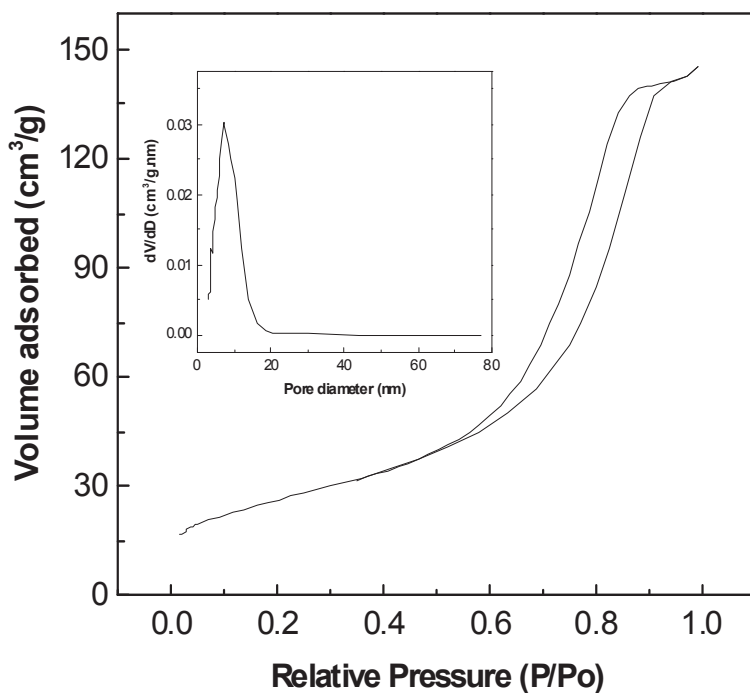
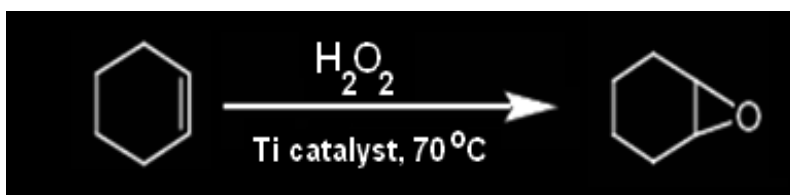


Figure 4.2: N_2 adsorption-desorption isotherm and mesopore size distribution (inset) of the synthesized TiO_2 catalyst R3a [$\text{TiCl}_3(\text{HNO}_3)$:Tu:Oa (1:4:1)]

4.3. Catalytic activity measurement

a) Epoxidation of Cyclohexene (General Procedure)

The catalytic activity test was carried out without precautions against atmospheric air containing oxygen. The catalysts were activated at 383 K for 2 h before the experiments. The epoxidation of cyclohexene reaction (scheme 4.1) was performed in a round bottom flask fitted with a condenser, under atmospheric pressure in air. The temperature of the reaction vessel was maintained using an oil bath, with acetonitrile as solvent and aqueous H₂O₂ as oxidant.



Scheme 4.1: Epoxidation of cyclohexene

After the required time (12 h) the product samples were withdrawn and analyzed periodically on a gas-chromatograph (Agilent 6890N) equipped with a flame ionization detector and a capillary column (5 μm thick cross-linked methyl silicone gum, 0.2 mm × 50 m long). The product samples were also identified by injecting the samples into GC-MS (Shimadzu 2000 A). Conversion of cyclohexene is defined as the weight percentage of cyclohexene consumed. The selectivity to a product is expressed as the amount of a particular product divided by the amount of total products and multiplied by 100.

Table 4.2: Epoxidation of cyclohexene over various TiO₂ samples

Sr. No.	Code	Method	Phase (% Anatase)	Cyclohexene Conversion (%) ^a	% Selectivity Cyclohexene oxide
1	R1	TiCl ₃ : HNO ₃	52	12	44
2	R2	TiCl ₃ (HNO ₃):Tu (1:2)	82	14	52
3	R2a	TiCl ₃ (HNO ₃):Tu (1:4)	34	13	40
4	R3	TiCl ₃ (HNO ₃):Tu:Oa (1:2:1)	100	16	44
5	R3a	TiCl ₃ (HNO ₃):Tu:Oa (1:4:1)	100	24	50
6	Degussa P-25	-	84	10	30

^a Reaction conditions: Cyclohexene (mmol) = 2, H₂O₂ (mmol) = 2, acetonitrile (g) = 1.25, catalyst (g) = 0.025, reaction temperature (°C) = 70, time = 12 h.

It can be seen from Table 4.2 that all the catalysts synthesized are active for epoxidation of cyclohexene and the activity was significantly higher than the well known commercial catalyst Degussa P-25, which showed only 10 % conversion. Among the synthesized catalysts, R3a showed the maximum activity of 24 %. This is a 100 % anatase TiO₂, having comparatively well defined mesoporous structure (Figure 4.2, pore diameter 7 nm) and higher surface area.

On the other hand the similarly prepared anatase TiO₂ (R3) showed significantly lower activity 16 %. This catalyst did not show well defined mesoporous structure, pore radii (Figure 2.6b) and also had lower surface area. The activity results of all the catalysts are summarized in Figure 4.3.

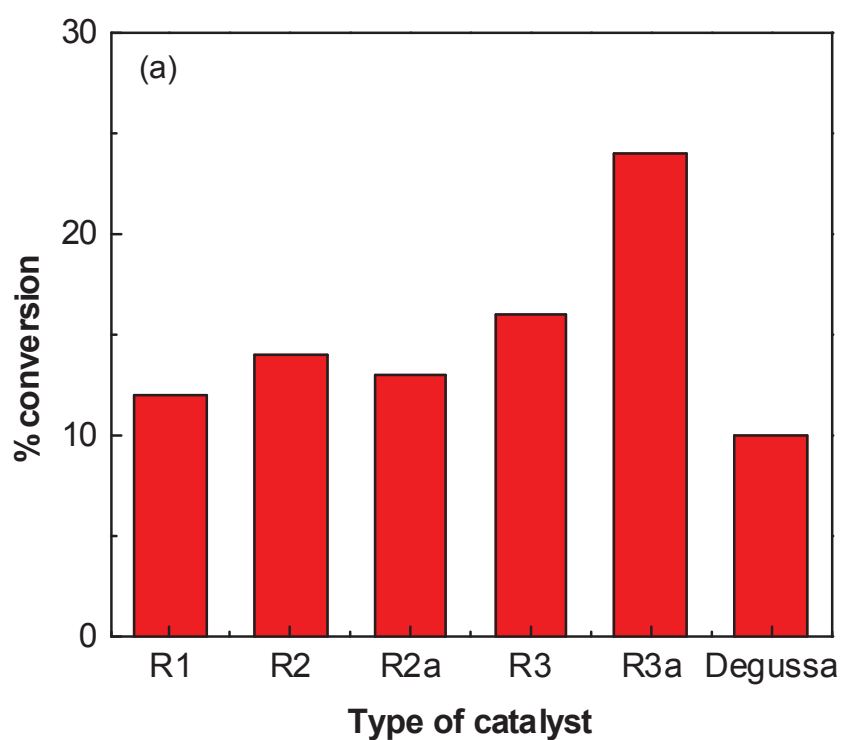


Figure 4.3: Epoxidation of cyclohexene catalyzed by synthesized TiO₂ samples and Degussa P-25 catalyst

These results suggest that in general:

(i) Pure phase anatase catalysts having mesoporous structure are better suited for epoxidation reaction.

(ii) The mixed phase catalysts R2 and R2a showed lower conversion than the pure anatase phase catalysts. This does not appear to be due to surface area/ porosity, as these samples had almost similar surface area and even larger average pore diameter. The higher activity could be due to favourable porosity in the pure anatase R3a which gave only one distinct porosity peak, unlike others.

(iii) R1 is a mixed phase catalyst synthesized without the use of thiourea. It showed lowest activity among the synthesized catalysts. This suggests the favourable effect of sulphur in case of S-doped catalysts of type R2 and R3 prepared by using thiourea. It may also be noted here (Table 4.1) that the higher activity of the S-doped catalysts is generally associated with much lower particle size.

(iv) The significantly poor activity of the Degussa P-25 could be due to absence of mesopore structure, low surface area as well as presence of rutile phase that resulted in low catalytic performance. Even if the effect of rutile phase is not yet clearly understood, the less degree of hydroxylation of the rutile structure rather than the anatase, may be considered as a probable drawback in the formation of peroxotitanium complex during epoxidation process [18-20].

It is also clear from Table 4.2, that all the synthesized samples showed higher selectivity to cyclohexene epoxide formation generally $\geq 40\%$. This is significantly higher than that of Degussa P-25 (which showed $\sim 30\%$ selectivity). It is reported in literature that selectivity to epoxide is often very low due to epoxide ring opening and formation of other products [4].

Figure 4.4 gives the details of product distribution of the cyclohexene epoxidation reaction. The catalysts R2 and R3a in particular showed formation of cyclohexene oxide selectivity beyond 50%.

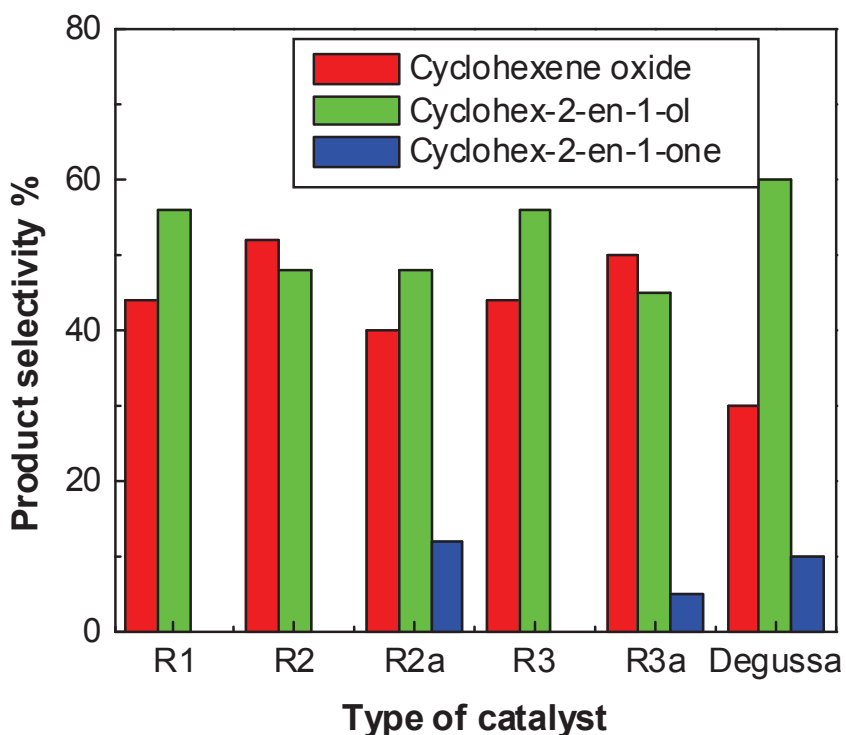
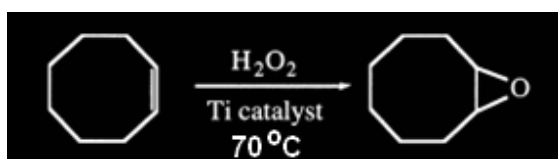


Figure 4.4: Product distribution of catalytic epoxidation of cyclohexene

b) Epoxidation of *cis*-Cyclooctene

The epoxidation of *cis*-cyclooctene reaction (scheme 4.2) was performed in a round bottom flask fitted with a condenser, under atmospheric pressure in air as described in section 4.3a.



Scheme 4.2: Epoxidation of *cis*-Cyclooctene

Conversion of *cis*-cyclooctene is defined as the weight percentage of *cis*-cyclooctene consumed. The selectivity to a product is expressed as the amount of a particular product divided by the amount of total products and multiplied by 100.

Table 4.3: Epoxidation of *cis*-cyclooctene over various TiO₂ samples

Sr. No.	Code	Method	Phase (% Anatase)	<i>cis</i> -Cyclooctene Conversion (%) ^a	% selectivity Cyclooctene oxide
1	R1	TiCl ₃ : HNO ₃	52	16	88
2	R2	TiCl ₃ (HNO ₃):Tu (1:2)	82	18	81
3	R2a	TiCl ₃ (HNO ₃):Tu (1:4)	34	17	79
4	R3	TiCl ₃ (HNO ₃):Tu:Oa (1:2:1)	100	20	89
5	R3a	TiCl ₃ (HNO ₃):Tu:Oa (1:4:1)	100	28	100
6	Degussa P-25		84	15	70

^a Reaction conditions: *Cis*-cyclooctene (mmol) = 3, H₂O₂ (mmol) = 3, acetonitrile (g) = 1.87, catalyst (g) = 0.05, reaction temperature (°C) = 70, time = 12 h.

The trends in catalytic activity for epoxidation of cyclooctene were similar to that of cyclohexene as summarized in Table 4.4.

Table 4.4: Activity of different catalysts for epoxidation of cyclohexene and *cis*-cyclooctene

Catalysts	R3a	R3	R2	R2a	R1	Degussa P-25
Cyclohexene activity	24	16	14	13	12	10
Cyclooctene activity	28	20	18	17	16	15

It was seen that all the catalysts showed higher activity for cyclooctene conversion than cyclohexene conversion for example, R3a which shows 24 % conversion of cyclohexene, showed 28 % conversion of cyclooctene.

It is also interesting to note that R3a not only showed higher activity among the S-doped samples but it also gave 100 % selectivity to cyclooctene oxide.

The selectivity profiles of all the TiO₂ samples investigated for epoxidation of cyclooctene are presented in Figure 4.5.

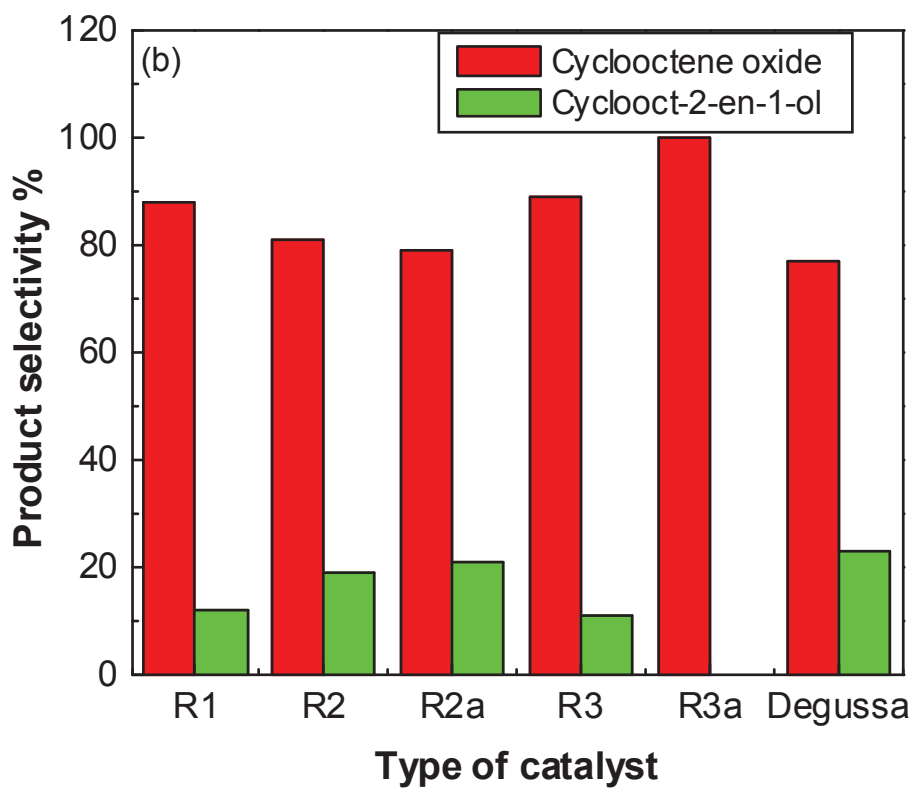


Figure 4.5: Product distribution of catalytic epoxidation of *cis*-cyclooctene

4.3.1. Pyridine adsorption IR spectra

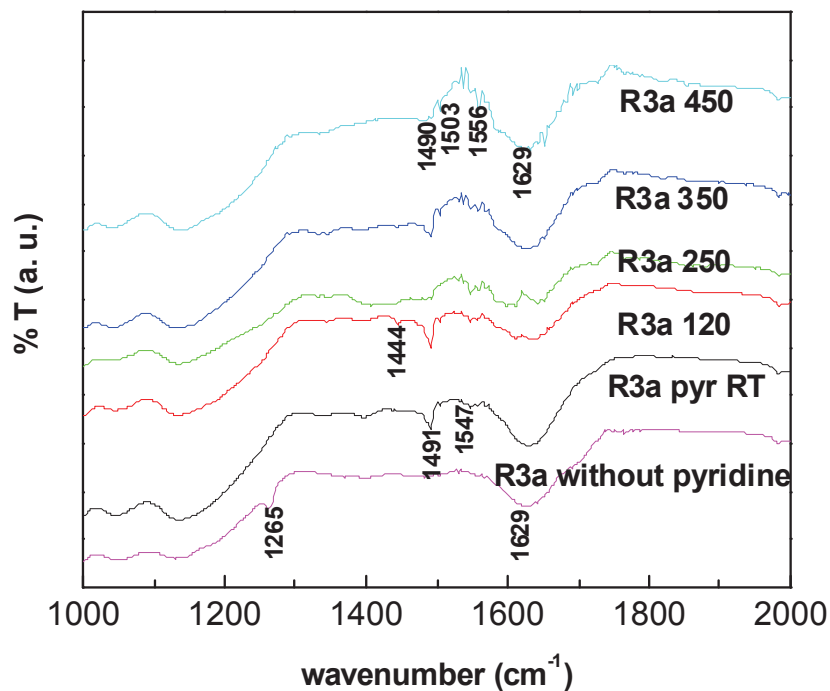


Figure 4.6: IR spectra of pyridine adsorbed on R3a

Pyridine was used as a probe molecule to characterize the type of acid sites, Lewis or Bronsted by infra red spectroscopy. Adsorption of pyridine is known to give *ir* absorptions corresponding to the acid sites as shown in Table 4.5.

The intense band at 1444 cm⁻¹ is attributed to the presence of strong Lewis acid sites (Ls) [21-23]. The weak band at 1556 cm⁻¹ indicates the presence of Bronsted acid site due to the presence of pyridinium ion PyH⁺ [21,24].

The band observed at 1490 cm⁻¹ [21,23,24] is the combination band and has contributions from both Bronsted and Lewis acid sites.

As can be seen from the Figure 4.6, the acidity in sample R3a is due to the presence of Lewis and Bronsted acid sites.

Table 4.5: IR absorption frequencies following adsorption of pyridine on various catalysts

<i>ir</i> frequencies (cm ⁻¹)	Assignments
1217 w	Ls (strong Lewis acid sites)
1450 vs	Ls
1485 w	L + B combination peak
1570 vw	B
1605 vs	Ls

Where w-weak, vw-very weak, vs-very strong

With the increase in temperature from ambient to 450 °C the intensities of the Lewis and Bronsted acid peaks are not lost indicating the presence of strong Lewis and Bronsted acid sites, as evident from the presence of 1490 cm⁻¹ band which is seen even at 450 °C (Figure 4.6). This peak is also consistently present in similar FTIR profiles of catalysts R2, R2a and R3, thus confirming the important role of both Bronsted and Lewis acid sites in these samples, for the epoxidation reactions. The low activity of the undoped sample R1 could be attributed to the lack of active acid sites as evident from Figure 4.7.

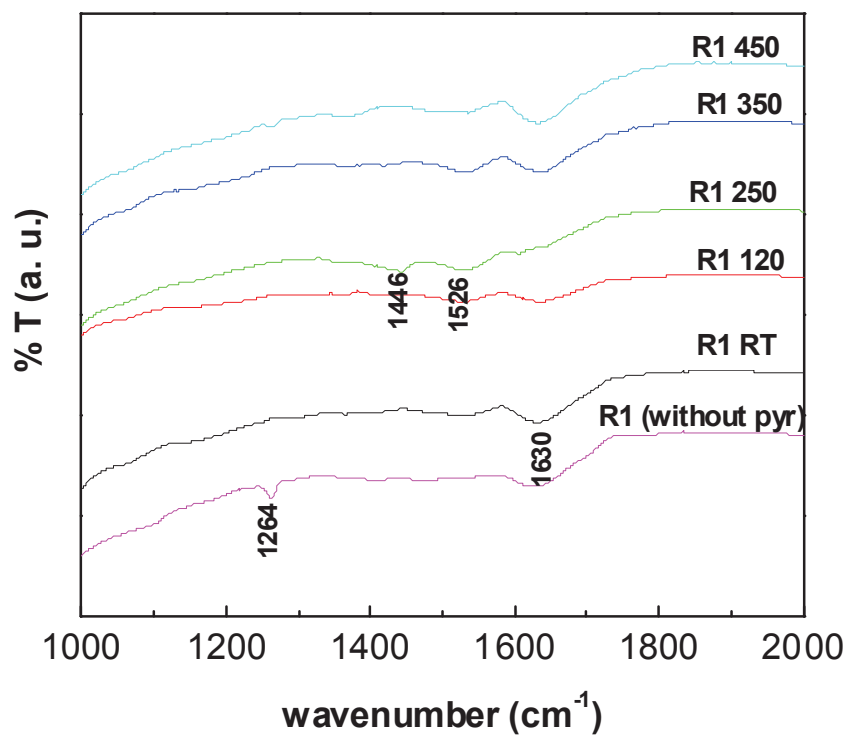


Figure 4.7: IR spectra of pyridine adsorbed on R1

4.4. Conclusions:

- (i) Pure phase anatase catalysts having mesoporous structure are better suited for epoxidation reaction.
- (ii) The higher activity in case of R3a (anatase TiO₂) could be due to favourable porosity which gave only one distinct porosity peak, unlike others.
- (iii) The higher activity of the S-doped catalysts in comparison to the undoped sample may be due to the favourable effect of Sulphur and much lower particle size of the synthesized samples.
- (iv) The significantly poor activity of the Degussa P-25 could be due to absence of mesopore structure, low surface area as well as presence of rutile phase that resulted in low catalytic performance.
- (v) It was seen that all the catalysts showed higher activity for cyclooctene conversion than cyclohexene conversion

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