

# Oxidation of adamantane by urea hydroperoxide using vanadium complex anchored onto functionalized Si-MCM-41

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## Abstract

A tetradentate complex 3-[*N,N'*-bis-3-(salicylidenamino)ethyl]triamine] vanadium(IV), VO(Salten) was grafted onto MCM-41 through a covalently linked organic moiety. This covalently anchored complex was characterized by FTIR, X-ray diffraction, thermogravimetric and differential thermogravimetric (TG–DTA) and BET measurements. The structure of the support was retained after anchoring the complex. Based on the spectroscopic evidences it was envisaged that the complex retains its structure inside the channels and it hangs like a pendant inside MCM-41. This anchored complex allowed the catalytic oxidation of adamantane using urea hydroperoxide (UHP) as the oxidizing agent at 60 °C and atmospheric pressure. The reaction conditions have been optimized towards maximum conversion by varying different parameters. No leaching of the complex was observed after the reaction.

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**Keywords:** Covalently anchored vanadium complex; Functionalized Si-MCM-41; Oxidation; Adamantane; UHP

## 1. Introduction

Metal complexes have been recognized as potential catalysts for the oxidation of hydrocarbons. The desire of higher TON and reusability of the catalyst have led to the development of heterogenizing metal complexes in microporous materials such as zeolite-Y [1–3]. However due to the size restrictions in zeolite-Y the encapsulation of large complexes is difficult, as it imposes some geometrical restrictions on the complexes to accommodate it and makes it difficult for substrates to diffuse and access the active sites and for products to diffuse out of the pores [4,5]. Hence the focus has been shifted to mesoporous materials having bigger pores and higher surface area [6,7]. Since direct immobilization of such complexes onto the mesoporous support is not advantageous due to the possibilities of leaching, the anchoring of these metal complexes through an organic spacer to the support is preferred. These inorganic–organic hybrid materials offer great scope for the

development of new catalysts [8–12]. Brunel has reported immobilization of large number of complexes inside the channels of these materials [13]. The amine functions of triazocyclonane (TACN) was reacted with the epoxy groups of MCM-41 grafted (3-glycidyoxypropyl)-trimethoxy silane and was used to anchor 2-hydroxyalkyl-substituted TACN ligands to MCM-41 and its manganese complex was used for the epoxidation of styrene with H<sub>2</sub>O<sub>2</sub> [14]. Similarly ruthenium(II) mesotetrakis(4-chlorophenylporphyrin) was anchored on to the walls of MCM-41 modified with 3-aminopropyl triethoxysilane and was used for the alkene oxidation by TBHP [15].

Adamantane has been used in the literature as a model to probe into the mechanistic aspects of C–H activation reactions [16–21]. Bartoli et al. have reported the hydroxylation of adamantane with H<sub>2</sub>O<sub>2</sub> using iron polynitroporphyrins as catalyst [22]. In this paper we report the synthesis and characterization of Si-MCM-41 modified with 3-chloropropyl triethoxysilane and further covalently anchoring VO(Salten) complex onto it. The heterogenized complex is used in catalytic studies of the oxidation of adamantane using anhydrous urea hydroperoxide (UHP) as oxidizing agent. The results obtained with the immobilized catalyst is compared

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with those obtained with the corresponding homogeneous catalyst.

## 2. Experimental

### 2.1. Materials

Tetraethylorthosilicate (TEOS), cetyltrimethylammoniumbromide (CTAB), 3-chloropropyl triethoxysilane (CPTES), salicylaldehyde, di-ethylene triamine,  $\text{VOSO}_4$  and adamantane were obtained from Aldrich. Tetramethylammonium hydroxide (TMAOH), urea and  $\text{H}_2\text{O}_2$  were obtained from Merck. All the solvents were of AR grade and were procured from SD Fine Chemicals, India and were distilled and dried before use.

### 2.2. Synthesis

#### 2.2.1. Si-MCM-41

Si-MCM-41 was synthesized using standard procedure. In a typical procedure TMAOH (12.08 g) in 100 ml distilled water was added under constant stirring to 20.8 g

of TEOS and the mixture was allowed to stir for 1 h. Then a solution of CTAB (27.33 g) in 98 ml water was added dropwise. The composition of the resultant gel was  $\text{SiO}_2:0.33\text{TMAOH}:0.55\text{CTAB}:60\text{H}_2\text{O}$ . This mixture was stirred overnight. The gel was transferred to a Teflon-lined autoclave and kept at  $100^\circ\text{C}$  for 5 days. The solid Si-MCM-41 obtained was filtered, washed and dried at  $100^\circ\text{C}$  in air and then calcined at  $550^\circ\text{C}$  for 8 h in nitrogen and then kept at this temperature for 6 h in air. XRD and TEM (JEOL model 1200 EX) have confirmed the hexagonal mesoporous MCM-41 structure.

#### 2.2.2. Synthesis of Cl modified MCM-41 (Cl-Si-MCM-41)

Cl-Si-MCM-41 was prepared using similar procedure reported in the literature [11]. In a typical surface modification process Si-MCM-41 was activated (3 g,  $150^\circ\text{C}$ ) under vacuum and was refluxed in dry toluene (50 ml distilled over freshly cut sodium and dried over zeolite-A) with CPTES (3 g) for 3 h under argon atmosphere. The separated solid was washed with diethyl ether and Soxhlet extracted with 250 ml dichloromethane yielding 4.85 g of covalently anchored 3-chloropropyl triethoxysilane moieties Cl-Si-MCM-41 (Fig. 1(a)).

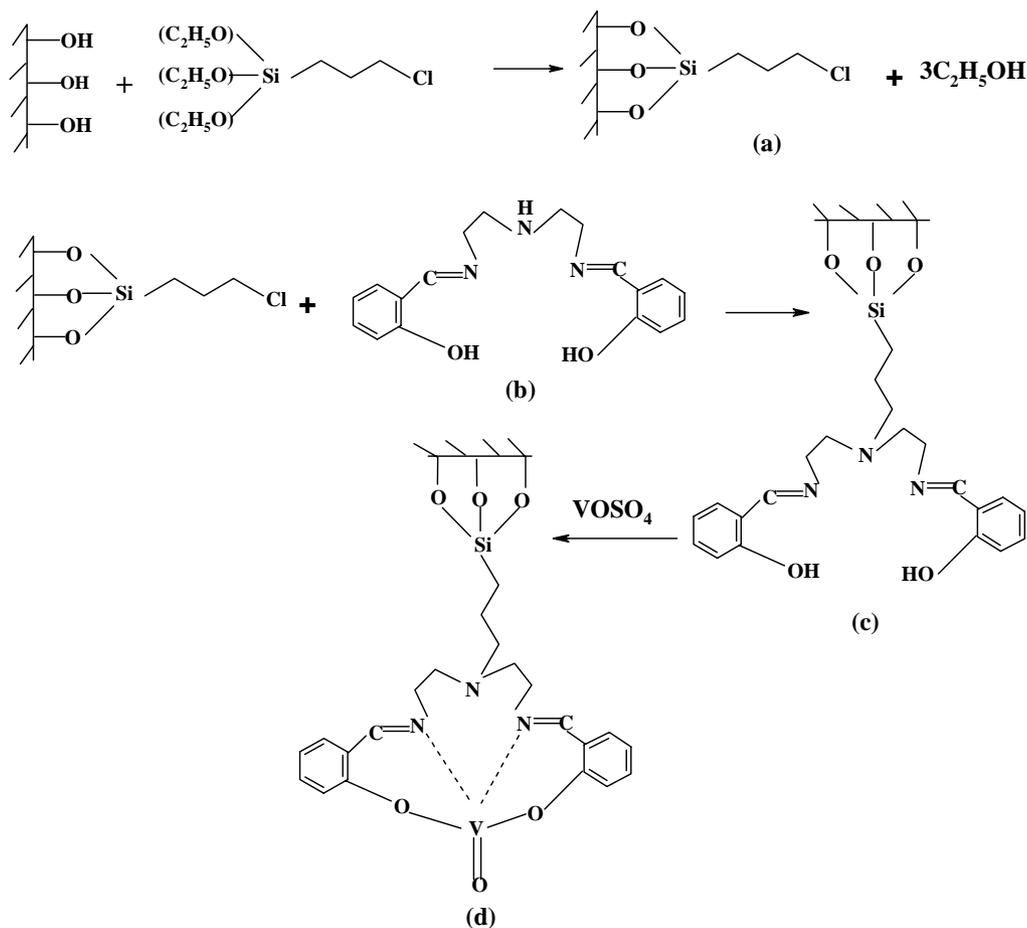


Fig. 1. Synthesis of Si-MCM-41-VO(Salten).

### 2.2.3. Synthesis of Salten = 3-[N,N'-bis-3-(salicylidenamino)ethyltriamine]

The ligand Salten Fig. 1(b) was prepared using similar procedure reported in the literature [23]. To an ethanolic solution of salicylaldehyde, a solution of diethyltriamine in ethanol was added in the ratio of 2:1 and the resulting yellow colored solution was allowed to reflux for 3 h. The excess of solvent was removed under vacuum and a dark yellow colored oily product was obtained.

### 2.2.4. Synthesis of vanadium Salten (VO(Salten))

VO(Salten) was prepared using a similar procedure reported in the literature [23]. In a typical procedure to an ethanolic solution of VOSO<sub>4</sub> (1.25 g in 50 ml ethanol) the ligand Salten (1.55 g in 5 ml ethanol) was added. The blue colored solution immediately turned green. After refluxing for 2 h the solid was filtered and recrystallized in ethanol.

### 2.2.5. Immobilization of VO(Salten) over Cl-Si-MCM-41

To a suspension of freshly dried Cl-Si-MCM-41 (1 g) in dry toluene (40 ml) a solution of Salten ligand (0.1 g) in dry toluene (10 ml) was added and the resulting solution was refluxed for 3 h. The yellow colored solid was separated, Soxhlet extracted with anhydrous toluene to remove the unreacted Salten ligand adsorbed on the external surface of Cl-Si-MCM-41 and vacuum dried for 24 h. The ligand gets attached to the Si-MCM-41 through the spacer by the nucleophilic displacement of chloride of Cl-Si-MCM-41 by the basic amino group of the ligand (Fig. 1(c)). Then to a suspension of this solid (1 g) in dry ethanol (40 ml) a solution of VOSO<sub>4</sub> (0.1 g) in dry ethanol (25 ml) was added. The solution immediately turned green indicating the formation of a vanadium complex. This was refluxed for 3 h. The green solid was separated by filtration, was dried and Soxhlet extracted with dry ethanol and acetonitrile to remove any unreacted vanadium from the surface. The vanadium content in Si-MCM-41-VO(Salten) was estimated to be 0.8 wt.% by AAS.

### 2.3. Characterization procedures

The C, H and N analysis of “neat” VO(Salten) was done on a Carlo Erba (model EA 1108) elemental analyzer. An atomic absorption spectrometer (AAS; Hitachi model Z-8000) estimated the vanadium content in the sample. The X-ray diffraction measurement of the covalently anchored complex was carried out using a Rigaku Miniflex diffractometer with Cu K $\alpha$  radiation. The thermogravimetric and differential thermogravimetric (TG–DTA) analyses of the neat and encapsulated VO(Salten) complexes were recorded on a Rheometric Scientific (STA 1500) analyzer. The textural properties Si-MCM-41, Cl-Si-MCM-41 and Si-MCM-41-VO(Salten) catalysts were determined from N<sub>2</sub> adsorption isotherms measured on an Omnisorb 100

CX Coulter instrument. The FTIR spectra of the samples were recorded on a Shimadzu (model 8201 PC) spectrophotometer.

### 2.4. Catalytic activity studies

A known amount of substrate (1.36 g adamantane), catalyst (“neat” VO(Salten) = 3 mg and Si-MCM-41-VO(Salten) = 50 mg), UHP = 1.88 g and acetonitrile = 40 g were taken in a 100 ml round bottom flask immersed in an oil bath and fitted with a water cooled condenser. The reactions were conducted at 60 °C. The progress of the reactions was monitored by withdrawing the samples at different times and analyzing them by a gas chromatograph (Shimadzu 14B; FID detector; SE-52 packed column). The identities of the products were confirmed by GC-MS (Shimadzu GC-MS QP 5000).

## 3. Results and discussion

### 3.1. Characterization

#### 3.1.1. XRD

Fig. 2 shows the XRD patterns of Si-MCM-41, Cl-Si-MCM-41 and Si-MCM-41-VO(Salten). XRD pattern of Si-MCM-41 (Fig. 2a) shows a very intense peak assigned to reflections at (1 0 0) and two additional peaks with low intensities at (1 1 0) and (2 0 0) reflections, respectively, which can be indexed to hexagonal lattice. Some loss in the intensities of the peaks was observed upon modification with 3-CPTES (Fig. 2b) which shows that though there is some

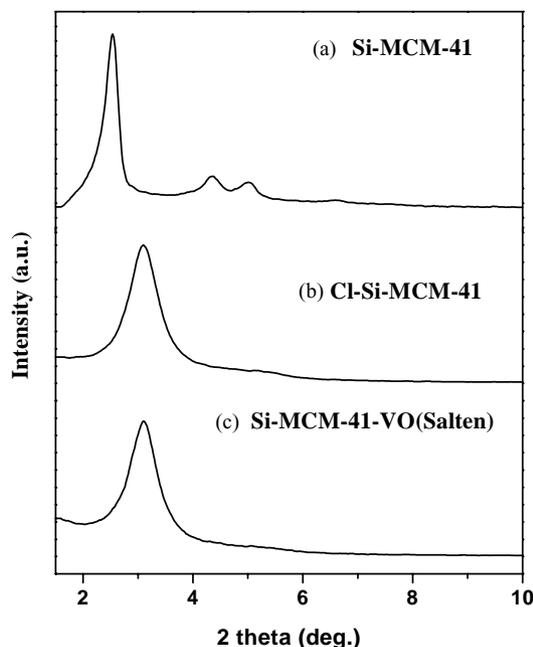


Fig. 2. XRD patterns of (a) Si-MCM-41; (b) Cl-Si-MCM-41; (c) Si-MCM-41-VO(Salten).

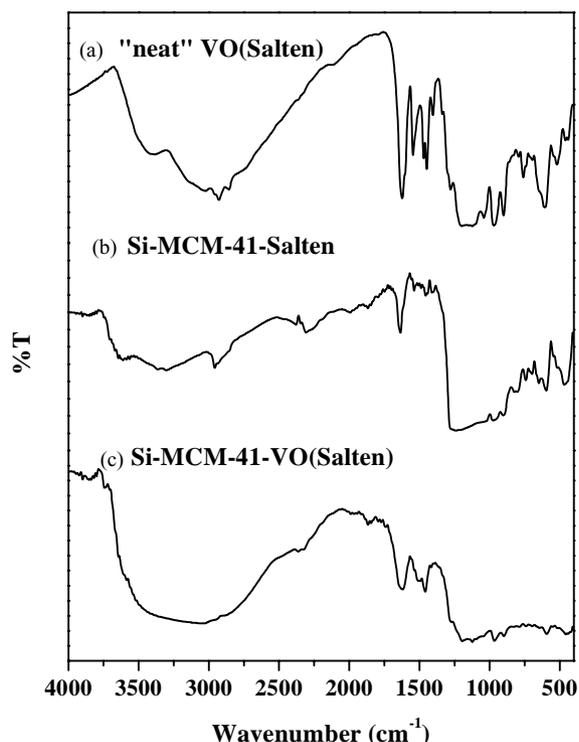


Fig. 3. FTIR spectra (a) “neat” VO(Salten); (b) Si-MCM-41-Salten; (c) Si-MCM-41-VO(Salten).

reduction in the crystallinity of Si-MCM-41, the mesoporosity of Si-MCM-41 is retained. No further loss in the intensity of the peak at (100) reflection was observed on immobilizing VO(Salten) complex onto Si-MCM-41-VO(Salten) (Fig. 2c). However the peaks at (110) and (200) reflections were not observed upon modification.

### 3.1.2. FTIR

The FTIR spectra (Fig. 3) confirms the formation and integrity of VO(Salten) complex inside the channel of Si-MCM-41. In the spectra of the immobilized complex the bands due to VO(Salten) are weak due to their low concentration and are masked by Si–OH bands. The assignments of a few representative bands for “neat” VO(Salten) and immobilized VO(Salten) are 1623 and 1624 (C=N), 1449 and 1455 (C=C) and 1376 and 1394 (C=O). The marginal shift in the positions of the bands corresponding to C=N, C=C and C=O is due to immobilization of the complex.

### 3.1.3. Thermal analysis

The thermal decomposition of the Si-MCM-41-VO(Salten) complex was observed in two steps. The former (<100 °C) is due to desorption of water while the latter is due to decomposition/combustion of Salten complex. The decomposition of VO(Salten) takes place in a temperature range in Si-MCM-41-VO(Salten) complex at 350–600 °C.

### 3.1.4. Sorption studies

The textural properties (surface area and pore size) of the immobilized complex were determined from the N<sub>2</sub>-sorption studies carried out at liquid nitrogen temperature. On modifying Si-MCM-41 with 3-CPTES the surface area of Si-MCM-41 decreased from 1000 to 850 m<sup>2</sup>/g and the pore size reduced from 3 to 2.4 nm. Upon immobilizing VO(Salten), a further reduction in the surface area from 850 to 700 m<sup>2</sup>/g and pore size from 2.4 to 1.6 nm was observed. The reduction in the surface area and pore size is due to the lining of the walls of Si-MCM-41 with the organic moieties. Similar trend has also been observed previously [24].

### 3.2. Catalytic activity

The catalytic oxidation of adamantane was investigated in non-aqueous medium using urea hydroperoxide as the oxidant and with “neat” VO(Salten) and Si-MCM-41-VO(Salten) complex. The two major products obtained were 1-adamantanol and 2-adamantanone (Fig. 4). Tembe et al. have reported similar product pattern for adamantane oxidation [25]. The kinetics data were interpreted using the initial rate approach model. The kinetic investigations results revealed a first order reaction rate dependence with the catalyst and substrate and half-order dependence with the oxidant. The reaction conditions have been optimized towards maximum conversion by varying different parameters.

#### 3.2.1. Effect of oxidants

The effect of different sources of the oxidizing agents on the conversion of adamantane (wt.%) and product selectivity (wt.%) was studied (Table 1) for comparison keeping other parameters (adamantane:UHP mole ratio, temperature, catalyst concentration and solvent) constant. It is observed that the adamantane conversion in the case of UHP is more than that of TBHP and aqueous H<sub>2</sub>O<sub>2</sub>. As evident from the table that air and TBHP are not good oxidants in the case of

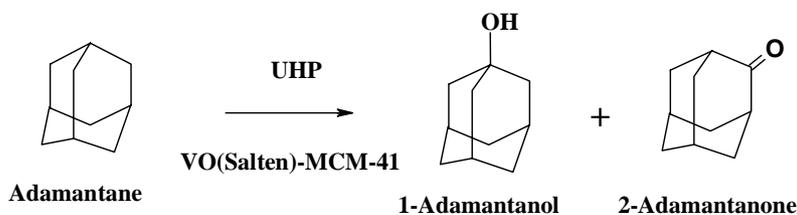


Fig. 4. Reaction scheme for oxidation of adamantane.

Table 1  
Effect of different oxidants on the oxidation of adamantane

| Oxidant                       | Conversion (wt.%) | Product selectivity (wt.%) |                |        |
|-------------------------------|-------------------|----------------------------|----------------|--------|
|                               |                   | 1-Adamantanol              | 2-Adamantanone | Others |
| UHP                           | 22.7              | 55.6                       | 43.2           | 1.2    |
| H <sub>2</sub> O <sub>2</sub> | 14                | 61.7                       | 38.3           | Nil    |
| TBHP                          | 2                 | 75                         | 25             | Nil    |
| O <sub>2</sub> (air)          | Nil               |                            |                |        |

Reaction conditions: catalyst wt.% = 50 mg, adamantane:oxidant (mol/mol) = 1:2, temperature = 60 °C, solvent (acetonitrile) = 40 g and reaction time = 2.5 h.

adamantane oxidation. In the case of aqueous H<sub>2</sub>O<sub>2</sub> the conversion was found to be lower than that of solid UHP. This is because of the slow release of hydroperoxide from the urea hydroperoxide adduct [26]. The reaction stops almost after 3 h. due to the complete consumption of peroxide.

### 3.2.2. Effect of UHP concentration

In Fig. 5 the effect of adamantane:UHP mole ratio on the adamantane conversion as a function of reaction time is plotted. The conversion increases with time with the increase in the mole ratio of adamantane:UHP and almost attains a steady-state after 2 h. This increase in conversion becomes marginal beyond adamantane:UHP ratio 1:5 and no signifi-

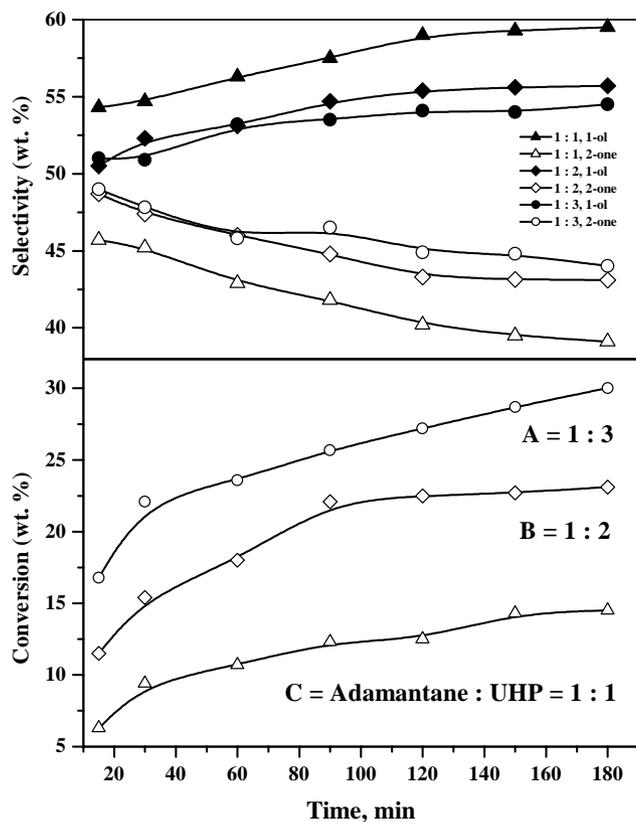


Fig. 5. Effect of adamantane to UHP mole ratio on the oxidation of adamantane. Reaction conditions: catalyst = Si-MCM-41-VO(Salten) = 50 mg, temperature = 60 °C, acetonitrile = 40 g and reaction time = 3 h.

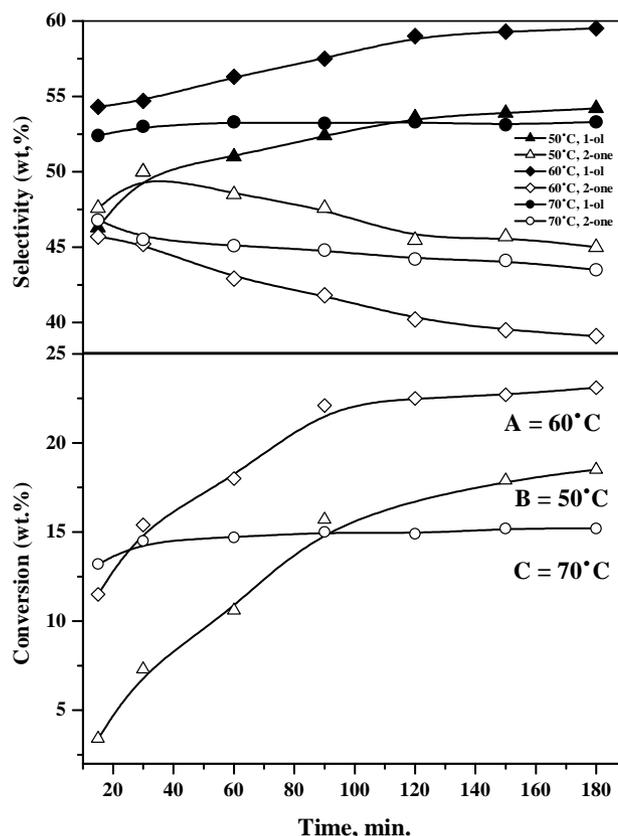


Fig. 6. Effect of reaction temperature on the oxidation of adamantane. Reaction conditions: catalyst = Si-MCM-41-VO(Salten) = 50 mg, adamantane = 1.36 g (10 mmol), UHP = 1.88 g (20 mmol), acetonitrile = 40 g and reaction time = 3 h.

cant change in the selectivity is observed with the increase in the ratio.

### 3.2.3. Effect of temperature

The effect of temperature on the adamantane conversion and selectivity is shown in Fig. 6. The adamantane conversion first increases linearly with time up to 90 min in the temperature range of 50–60 °C. This is because of the slow decomposition of UHP and thus making hydroperoxide available for a longer time. On further increasing the temperature (70 °C) there is a sudden increase in conversion up to 15 min and then it attains a steady-state. This may be due to the fast decomposition of UHP since the stability of urea hydroperoxide adduct decreases on increasing the temperature which facilitates the faster decomposition of peroxide. Therefore from Fig. 6 it is clear that increasing the temperature above 60 °C does not enhance the percentage conversion of adamantane using UHP as oxidant.

### 3.2.4. Effect of catalyst concentration

Fig. 7 depicts the effect of catalyst concentration on the oxidation of adamantane. The amount of catalyst was varied in the range of 25–75 mg. It is observed that an increase in the catalyst concentration with respect to adamantane

Table 2

Catalytic activities of “neat” and Si-MCM-41-VO(Salten) in oxidation adamantane with UHP<sup>a</sup>

| Catalyst (weight in mg)   | Adamantane oxidation |                  |                            |                |        |
|---------------------------|----------------------|------------------|----------------------------|----------------|--------|
|                           | Conversion (wt.%)    | TOF <sup>b</sup> | Product selectivity (wt.%) |                |        |
|                           |                      |                  | 1-Adamantanol              | 2-Adamantanone | Others |
| VO(Salten) (3)            | 5                    | 31               | 56                         | 42.4           | 1.6    |
| Si-MCM-41-VO(Salten) (50) | 22                   | 141              | 55.7                       | 43.2           | 1.1    |

<sup>a</sup> Reaction conditions: adamantane = 1.36 g (10 mmol), UHP = 1.88 g (20 mmol), acetonitrile = 40 g, temperature = 60 °C, reaction time = 2 h.

<sup>b</sup> TOF: mole substrate oxidized per mole of metal per hour.

resulted in an increase in the conversion of adamantane initially, and then attained a steady-state after 1 h of the reaction time. This could be because of the decomposition of peroxide by the catalyst. This clearly suggests that large amount of catalyst is not required for adamantane oxidation.

### 3.2.5. Effect of immobilization

Oxidation of adamantane was also carried out using “neat” VO(Salten) containing the same amount of vanadium as in the case of immobilized complex. The results are stated in Table 2. It is evident from the table that the conversion increases on immobilizing the complex. Earlier studies reveal

that the “neat” vanadium(IV) complexes of Schiff bases like Salen tends to form oxo-bridged dimer in solution [4,27,28] thus inhibiting the catalytic activity. Therefore in the present study it is evident that the higher conversions for adamantane is because the VO(Salten) molecules are isolated and well separated from each other since they are anchored to the walls of MCM-41. The reactions did not proceed in the absence of VO(Salten). Also no reaction took place over Si-MCM-41 and Cl-Si-MCM-41.

From the above study it is evident that the reaction rate enhances in the beginning with time and then becomes constant after 2 h. The conversion of adamantane attains a maximum level after 3 h. A conversion of 23% and a selectivity of 56 and 43% are obtained with the immobilized catalyst.

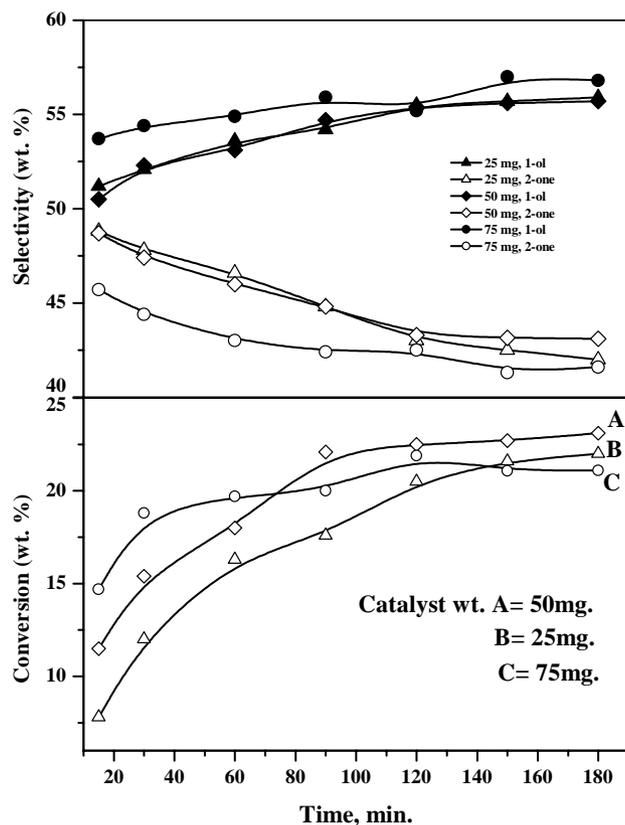


Fig. 7. Effect of catalyst concentration on the oxidation of adamantane. Reaction conditions: adamantane = 1.36 g (10 mmol), UHP = 1.88 g (20 mmol), temperature = 60 °C, acetonitrile = 40 g and reaction time = 3 h.

## 4. Conclusion

A significant increase in the conversion of adamantane was observed on anchoring the complex inside the mesoporous of Cl-Si-MCM-41. The conversions were low in the case of homogeneous complex compared to that of immobilized complex. The formation of catalytically inactive  $\mu$ -oxo-bridged complexes with “neat” VO(Salten) complex has been speculated as the cause of catalyst deactivation. When UHP was used as an oxidant for adamantane oxidation a significant increase in the conversion was observed compared to the use of aqueous H<sub>2</sub>O<sub>2</sub>. This is because of the slow release of peroxide from the urea-hydroperoxide adduct. These inorganic-organic hybrid materials have proved to be efficient catalysts as the active species are covalently bound to the support and place no restrictions on the pore size.

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