Silica gel supported [1,4-bis(salicylidene amino)-phenylene] vanadium oxo complex catalyst for the oxidation of *n*-heptane using molecular oxygen

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Abstract

A complex of vanadium with nitrogen containing ligand, vanadium(II) [1,4-bis(salicylidene amino)-phenylene] vanadium oxo, has been covalently bonded on chemically modified silica gel, which serves as a catalyst for the oxidation of *n*-heptane in presence of molecular oxygen. The reaction occurs at low temperature (at 150 °C, 200 psi and reaction time of 480 min) and the nine major reaction products formed have been identified by the GC–MS analysis. Most of the products are substitution products of *n*-heptane and 2-heptanol (~38.1%) is formed with high specificity with very little acid (~8.0%). The product distribution is completely different from those reported in literature and suggests that heptane in presence of this catalyst undergoes negligible cracking or isomerization reactions at this temperature.
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Keywords: [1,4-bis(Salicylidene amino)-phenylene] vanadium oxo complex; *n*-Heptane; GC–MS analysis

1. Introduction

In the oxidation of alkanes using molecular oxygen, one generally faces the following two problems. The first one is the chemoselectivity arising because the formed products are more reactive towards oxygen compared to the reactants. The second one faced is the regioselectivity because of which the radicals and the electrophilic acids tend to attack various –CH bonds on it with different energetic. For example, tertiary and secondary bonds form more stable radicals compared to primary –CH bonds [1]. In addition to this, alkanes do not have orbitals of sufficiently high energy, accessible for chemical reaction and normally they required either very reactive oxidizing agents or extreme reaction conditions or both. For hydrogen peroxide as oxidizing agent, one needs low temperatures and several experiments of oxidation of alkanes using solid catalyst have been reported [2–7]. However, there are only few reported for molecular oxygen as the oxidizing agent [8–12] and high temperatures and pressures are required. Under these conditions, in addition to the oxidation reaction, alkanes also undergo thermal cracking, isomerization, dehydrogenation, dehydrocyclization, alkylation, metathesis, oligomerization and polymerization [13]. The most notable among the catalysts is the metal (Co, Mn, Fe) loaded on aluminophosphate zeolite [14] catalyst which gives oxidation of pentane, hexane and octane giving their alcohols and ketones without cracking. With these catalysts, however, the reaction is reported to stop at low conversions and the deactivation phenomena has been explained through metal leaching and/or pore blocking.

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Heptane has been subjected to cracking (catalytic, homogenous or steam pyrolysis) to give mostly alkenes such as ethylene, propylene and butylene [15]. These processes require high temperature and calcium oxide supported over alumina (CaO/Al_2O_3) is used as one of the most common catalysts which lowers the reaction temperature and suppresses the coke formation. On using zeolite catalyst (H-MCM-22, H-ZSM-5 and H-ferrierite), the selectivity of a given alkene formation has been increased [16–19]. In presence of pure oxygen using zeolite catalyst (SAPO-5 and 11, BEA and MCM-41) [20], heptane was found to undergo partial oxidation along with cyclization forming heptanone and heterocyclic compounds. Some of the compounds reported to have formed are 2,3- and 4-heptanones, 2-methyl-5-ethyl-furan, 2,6-dimethyl-pyran, 1-hepten-4-ol and two branch dienes.

In this paper, a non-zeolite catalyst has been reported in which [1,4-bis(salicylidene amino)-phenylene] vanadium oxo complex has been covalently bonded to carbamate modified silica gel support. The oxidation of *n*-heptane using this catalyst has been carried out and the reaction products were identified by the GC–MS analysis, which shows that it gives entirely different product distribution. The compounds formed are (2-heptanone, 18.9%; 4-heptanone, 7.3%; 2-heptanol, 38.1%; trans-3-hepten-2-one, 5.1%; 2-octanol, 3.1%; 1-heptanol, 5.7%; octanoic acid, 5.3%; heptaldehyde, 7.3%; and heptanoic acid, 2.9%). The study of these products suggests that the heptane undergoes negligible cracking, ionization reaction or cyclization giving mostly substituted products. The catalyst has been tested up to 300 h of reaction with negligible leaching of vanadium metal complex as confirmed by atomic absorption spectroscopy (AAS).

2. Experimental

2.1. Materials and methods

The *n*-heptane (99.9%, bp 98 °C) used in our study was obtained by fractionating LR grade chemicals. The catalyst loaded with [1,4-bis(salicylidene amino)-phenylene] vanadium oxo complex has been synthesized according to the literature [21] in a four steps

scheme. In the first step, the complexing agent was prepared according to reference [22] in which the *o*-phenylenediamine (10.8 g, 0.1 g mol) is reacted with salicylaldehyde (24.4 g, 0.2 g mol) by condensation reaction at room temperature in absolute ethanol (25 ml). The reaction mixture was stirred for about 3 h and a yellow precipitate of the product appears, which is filtered and dried. The VO^{2+} complex was prepared in the second step, the complexing agent formed as earlier (3.0 g, 9.5 mmol) was reacted with vanadyl sulfate (3 g, 12.9 mmol) dissolved in 100 ml of acetonitrile. The reaction mixture was refluxed at 80 °C for 2 h and the precipitate of vanadium complex was formed. The precipitate was once again washed with acetonitrile and dried at 80 °C. In the third step, silica gel (5 g) was washed with distilled water, then with acetone and dried at 80 °C under vacuum [23]. This was then refluxed with 50 ml of HCl (35%) in a flask for 4 h and was separated and washed with distilled water several times with its FT-IR given in (Fig. 1a). Benzoyl isocyanate was prepared by the reaction of sodium azide, (16.8 g, 0.26 g mol) with an equivalent number of moles of benzoyl chloride (35 g, 0.26 g mol) in a benzene medium (20 ml) at 0 °C. The reaction mass separates into two phases, the liquid phase was filtered and was reacted with 5 g of silica gel. The reaction mass was stirred at 40 °C for 6 h and the carbamate bonds on the silica gel was confirmed by FT-IR (Fig. 1b), with aromatic –CH at 3030 cm^{-1}, –NH group at 1599 cm^{-1}, C=O at 1693 cm^{-1}. The extent of reaction was estimated by determining the amine group concentration on silica gel (0.26 meq/g) using butyl amine method [23]. In the final step, carbamate modified silica gel (2 g) from the third step is refluxed for 2 h at 80 °C with dichloroethane (50 ml) in presence of a Lewis acid catalyst $ZnCl_2$ (5 mg). The concentration of chloride groups on the silica gel was determined by the gravimetric test and its FT-IR is given in Fig. 1c, with alkyl group –CH$_2$ at 2940 cm^{-1} and –Cl group at 749 cm^{-1}. This was then refluxed with the complex in the presence of a Lewis acid to get the final catalyst (FT-IR given in Fig. 1d).

The oxidation reactions were performed in high-pressure stainless steel catalytic reactor. An autoclave-rocking reactor having capacity of 500 ml, gas delivery, and sampling line was employed for oxidation of *n*-heptane. An on/off controller was used for
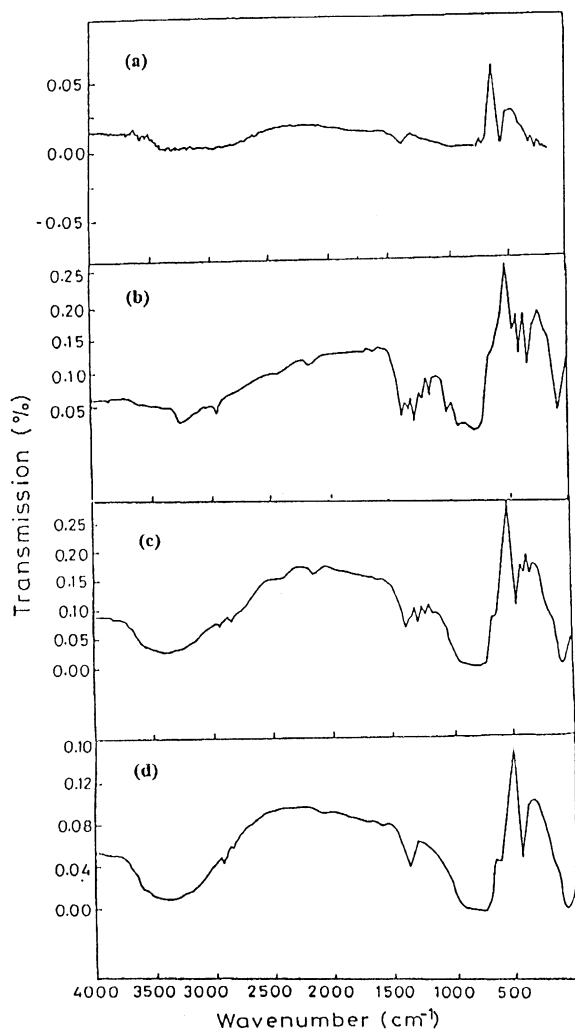
Fig. 1. FT-IR spectrum of (a) pure silica gel (b) silica gel with carbamate bound group (aromatic –CH at $3030 \, cm^{-1}$, –NH group at $1599 \, cm^{-1}$, C=O at $1693 \, cm^{-1}$) (c) carbamated silica gel with dichloroethane (shows alkyl group –CH$_2$ at $2940 \, cm^{-1}$ and chloride group at $749 \, cm^{-1}$) (d) silica gel supported vanadium metal complex catalyst (aliphatic and aromatic –CH at 2940 and $3030 \, cm^{-1}$, C=O group shifted to $1644 \, cm^{-1}$, at $1509 \, cm^{-1}$ with the absence of chloride group).

controlling the temperature with a chrome alloy thermocouple for temperature sensing. The catalyst was originally green in color, which after the oxidation reaction turned into brown in color and the catalyst was separated by the filter paper and distilled to remove unreacted *n*-heptane.

3. Results and discussion

Experiments on functionalization of *n*-heptane have been conducted at constant temperature ranging between 100 and 200 °C batchwise. After charging heptane, the reactor was pressurized by commercial oxygen and the reactor placed inside the rocking oven. The reactor pressure first rises due to heating and subsequently falls very slowly due to chemical reaction with oxygen by as much as 10% of the highest value and the pressure reported in this work is the average value of these. To demonstrate the oxidation occurring in presence of the catalyst only, the oxidation reaction was first carried out without the catalyst for as long as 12 h at 200 °C temperature and we found that there was no product formation. After ensuring this, the catalyst was introduced into the reactor and the strong smell at end of the oxidation initiated the formation of the product.

As a result of the chemical reaction, the catalyst showed a change in color from dark green to brown. The most of the unreacted *n*-heptane (the distillate shown as pure material by IR) was distilled at 110 °C and the residue (4.3 ml, after 8 h of the reaction) was collected. This was subjected to the GC–MS analysis (GC given in Fig. 2) and it was shown to consist of 2-heptanone (18.9%) as peak (1), 4-heptanone (7.3%) as peak (2), 2-heptanol (38.1%) as peak (3), trans-3-hepten-2-one (5.1%) as peak (4), 2-octanol (3.1%) as peak (5), 1-heptanol (5.7%) as peak (6), octanoic acid (5.3%) as peak (7), heptaldehyde (7.3%) as peak (8) and heptanoic acid (2.9%) as peak (9). Further distillation of the residue at 180 °C got completely distilled, indicating negligible loss of metal from the catalyst and this was later confirmed by atomic absorption experiments.

The temperature effect on the oxidation reaction of *n*-heptane was examined for reaction temperatures varying from 100 to 200 °C. The percentage yield increased very slowly from 1.26% at 100 °C to 5.22% at 200 °C with 1.91% at 125 °C, 3.87% at 150 °C and 4.67% at 175 °C. Beyond this temperature, slight amount of unidentifiable black material was formed and as result, the reaction temperature was never allowed to go beyond this value. The effect of oxygen pressure on the oxidation reaction of *n*-heptane was studied by carrying out experiments at different oxygen pressures at 150 °C temperature, in
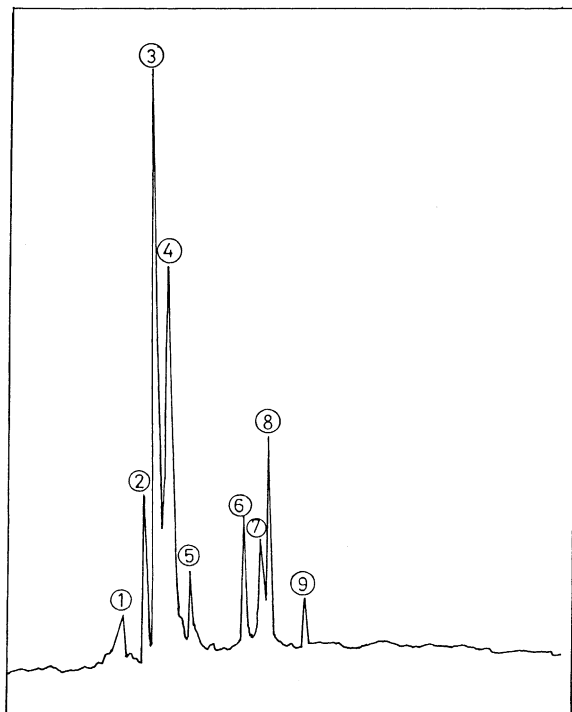
Fig. 2. Gas chromatogram of the product shown as 2-heptanone (18.9%) as peak (1), 4-heptanone (7.3%) as peak (2), 2-heptanol (38.1%) as peak (3), trans-3-hepten-2-one (5.1%) as peak (4), 2-octanol (3.1%) as peak (5), 1-heptanol (5.7%) as peak (6), octanoic acid (5.3%) as peak (7), heptaldehyde (7.3%) as peak (8) and heptanoic acid (2.9%) as peak (9).

presence of the catalyst. On application of the pressure, some oxygen goes to the solution in heptane and the dissolved oxygen plays an important role in the oxidation. On further increasing the reaction pressure (130–285 psi), the solubility of oxygen increases giving higher heptane conversion (1.44% at 130 psig, 2.69% at 160 psig, 4.26% at 240 psig and 4.67% at 285 psig). At 285 psi the maximum conversion is seen to be 4.67% and further increase in pressure (350 psi) does not change the final conversion attained. We have varied the amount of support bound vanadium catalyst (2.16% at 0.5 g, 3.88% for 1.0 g, 4.28% for 1.5 g and 4.53% for 2.0 g) and we find that the conversion does not change beyond 2.0 g. The catalyst is likely to play a dual role in the initiation and termination reaction steps and this may be responsible for this observation of the amount of the catalyst dependent kinetics. The conversion increases with reaction time

(0.76% at 6 h, 3.88% at 8 h, 4.14% at 10 h, 5.98% at 12 h and 7.99% at 24 h) as expected and the yield of these compounds increases with increase in reaction time. Initially the yield increases rapidly but for long times approaches an asymptotic value (7.99% at 30 h). The atomic absorption spectroscopy (AAS) of the catalyst was used to estimate the amount of metal on the silica support. In the fresh catalyst, vanadium metal was observed to be 0.048% and after 100 h of catalytic reaction, the vanadium metal is found to reduced to 0.044%. However, the catalyst activity was not affected adversely as observed from the final conversion attained in a given reaction time.

The freshly prepared vanadium loaded silica gel catalyst has strong green color. This indicates the presence of VO^{2+} ion and shows its characteristic EPR spectrum at room temperature (Fig. 3). Experiments have shown that no reaction occurs in absence of the silica gel catalyst or in presence of free vanadium complex. It was further observed that the green color of the catalyst becomes brown after the reaction in presence of molecular oxygen. This implies that all VO^{2+} species on the catalyst (green colored, EPR active) are oxidized to VO^{3+} oxo–peroxo [24–27], because the latter does not give any EPR spectrum. This also suggests that in the hydroxylation of *n*-heptane, the oxo and peroxo groups of the loaded catalyst must be involved. The catalyst seems to play a dual role in the initiation as well as termination steps of the accepted reaction mechanism [28,29] of functionalization of alkanes using vanadium. The oxidation of heptane with molecular oxygen in presence of the vanadium catalyst could occur through (a) auto oxidation of free radicals, (b) the metal ion followed by reoxidation of the reduced metal, or (c) catalytic
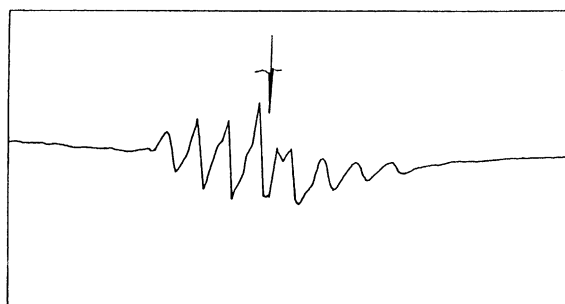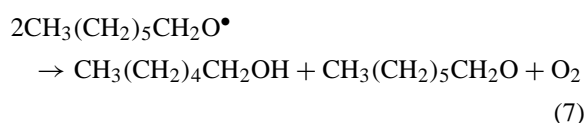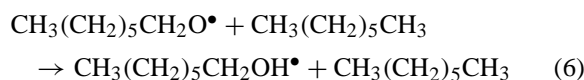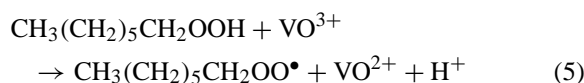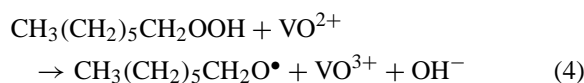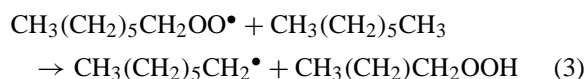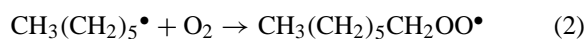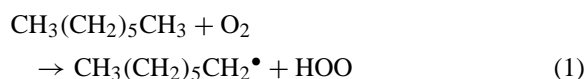

Fig. 3. The EPR of the freshly prepared vanadium catalyst, the used catalyst is EPR silent.

oxygen transfer. In order to show that the reaction is not occurring via free radical mechanism, we carried out the oxidation of *n*-heptane in presence of free radical initiator, like for example benzoyl peroxide (BPO) and found negligible effect on the initial slow phase or the final conversion reached. In addition to this, we also carried the oxidation reaction in presence of free radical scavengers like, hydroquinone and once again found no effect upon the final conversion reached. The proposed mechanism for the oxidation reaction using the support vanadium catalyst [30] can be written in Eqs. (1)–(7) given below:

$$CH_3(CH_2)_5CH_3 + O_2$$
$$\rightarrow CH_3(CH_2)_5CH_2{}^\bullet + HOO \tag{1}$$

$$CH_3(CH_2)_5{}^\bullet + O_2 \rightarrow CH_3(CH_2)_5CH_2OO^\bullet \tag{2}$$

$$CH_3(CH_2)_5CH_2OO^\bullet + CH_3(CH_2)_5CH_3$$
$$\rightarrow CH_3(CH_2)_5CH_2{}^\bullet + CH_3(CH_2)CH_2OOH \tag{3}$$

$$CH_3(CH_2)_5CH_2OOH + VO^{2+}$$
$$\rightarrow CH_3(CH_2)_5CH_2O^\bullet + VO^{3+} + OH^- \tag{4}$$

$$CH_3(CH_2)_5CH_2OOH + VO^{3+}$$
$$\rightarrow CH_3(CH_2)_5CH_2OO^\bullet + VO^{2+} + H^+ \tag{5}$$

$$CH_3(CH_2)_5CH_2O^\bullet + CH_3(CH_2)_5CH_3$$
$$\rightarrow CH_3(CH_2)_5CH_2OH^\bullet + CH_3(CH_2)_5CH_3 \tag{6}$$

$$2CH_3(CH_2)_5CH_2O^\bullet$$
$$\rightarrow CH_3(CH_2)_4CH_2OH + CH_3(CH_2)_5CH_2O + O_2 \tag{7}$$

In the above mechanism, the initiation step (Eq. (1)) is typically very slow, and once the free radicals are formed, these quickly react with dissolved oxygen to form peroxy radical (Eq. (2)). In this reaction, the main role of the vanadium metal ions is to catalyze the formation of the intermediate hydroperoxide ($C_7H_{13}OOH$) as in Eqs. (3)–(5). As a result of this, vanadium metal ions generate chain-initiating radicals, which gives the formation alcohols as an oxidation products according to Eqs. (6) and (7). However, experimental results for this catalyst (i.e. low percentage of ketone formation) show that Eq. (6) is the dominating step.

4. Conclusion

We concluded on the basis of earlier discussion that the oxidation reaction of *n*-heptane in presence of silica gel supported [1,4-bis(salicylidene amino)-phenylene] vanadium oxo complex is the new novel supported catalyst and the metal does not leach out for at least 300 h of experimentation, the results are shown below:

1. The product distribution is entirely different. Nine main compounds are identified and 1-heptanol as well as 2-heptanol are the major (44%) compound with the ratio of heptanol to heptanone is 6:4.
2. Catalyst has been tested up to 300 h of reaction with negligible leaching of vanadium metal.
3. Increase in temperature and the amount of catalyst increased the conversion of product.
4. Increase in presence of oxygen increased the conversion due to higher solubility of oxygen in the medium.

Since the yield of the product formed by the unsupported metal complex in the reaction is very small, it appears that the support is playing an important role in catalyzing the oxidation of *n*-heptane.

Acknowledgements

References

[1] O. Reiser, Oxidation of weakly active C–H bonds, Angew-Chem. Int. Ed. Engl. 33 (1) (1994) 69–72.
[2] G.B. Shulpin, G.V. Nizova, Formation of alkylperoxide in presence in the oxidation of alkanes by H_2O_2 catalyzed by transition metal complexes, React. Kinet. Catal. Lett. 48 (1992) 333–336.
[3] T. Tagaw, Liquid phase oxidation of benzene to phenol over supported iron salts, J. Catal. 78 (1993) 201–210.
[4] S. Murakashi, Y. Oda, T. Naota, N. Komiya, Aerobic oxidants of alkanes and alkenes in the presence of aldehydes catalyzed by copper salts, Chem. Soc., Chem. Commun. 2 (1993) 139–140.

[5] A.K.S. Sinha, V. Shanker, Low-temperature catalyst for total oxidation of *n*-hexane, Ind. Eng. Chem. Res. 32 (6) (1993) 1061–1065.

[6] R. Raja, G. Shanker, J.M. Thomas, New catalyst of aerobic selective oxidation of hydrocarbons: Mn(III) and Co(III)—containing molecular sieves for the epoxidation of alkanes, Chem. Commun. (1999) 829–830.

[7] Z. Wang, E. Martell Arthur, R.J. Motekaitis, Hydroxylation of alkanes by molecular oxygen with dinuclear Fe(II) macro cyclic complexes catalysts, Chem. Commun. (1998) 1523–1524.

[8] S. Murahashi, Y. Oda, J. Naota, T. Kuwabara, Ruthenium catalyst cytochrame P-450 type oxidation of alkanes with hydroperoxides, Tetrahedron Lett. 34 (1993) 1202–1299.

[9] M. Hartman, S. Ernst, Selective oxidation of linear alkanes with molecular oxygen on molecular sieve catalysts—a breakthrough, Angew-Chem. Int. Ed. 39 (2000) 888–890.

[10] P.A. Shapley, N. Zhang, J.L. Allen, D.H. Pool, H.C. Liang, Selective alcohol oxidation with molecular oxygen catalyzed by Os–Cr and Ru–Cr Complexes, J. Am. Soc. 122 (2000) 1079–1091.

[11] M.C. Capel-Sanchez, J.M. Compos-Martin, J.L.G. Fierro, M.P. Frutos, A.P. De Polo, Effective alkene epoxidation with dilute hydrogen peroxide on amorphous silica-supported titanium catalysts, Chem. Commun. (2000) 855–856.

[12] A. Kumar Jr., S.K. Das, A. Kumar, Formation of benzene catalyzed by polymer-bond vanadyl acetoacetonate, J. Catal. 166 (1997) 108–110.

[13] G.A. Olah, A. Molnar, Hydrocarbon Chemistry, 3rd ed., Wiley, New York, 1995, pp. 10–27.

[14] J.M. Thomas, R. Raja, G. Shanker, G. Bell Robert, Molecular sieve catalyst for selective oxidation of linear alkanes by molecular oxygen, Nature 398 (1999) 227–230.

[15] K.K. Pant, D. Kunzaru, Catalyst pyrolysis of *n*-heptane: kinetics and modeling, Ind. Eng. Chem. Res. 36 (1997) 2059–2065.

[16] T. Komatsu, H. Ishihare, Y. Fukui, T. Yashima, Selective formation of alkenes through the cracking of *n*-heptane on Ca^{2+} exchanged ferrierite, Appl. Catal. Part A: Gen. 214 (2001) 103–109.

[17] K.I. Alhumaizi, V.M. Akhmedov, S.M. Al-Zahrani, S.H. Al-Kuowater, Low temperature hydrocracking of *n*-heptane over Ni-support catalysts: study of global kinetics, Apl. Catal. Part A: Gen. 219 (2001) 131–140.

[18] D. Meloni, D. Martin, M. Guisnet, Acidic and catalytic properties of H-MCM-22 zeolites-2. *n*-Heptane cracking activity selectivity and deactivation cocking, Appl. Catal. Part A: Gen. 215 (2001) 67–79.

[19] Y. Wang, A. Zhang, Q. Xu, R. Chen, Characterization of titanium modified USY zeolites and their catalytic performance on *n*-heptane cracking, Appl. Catal. Part A: Gen. 214 (2001) 167–177.

[20] D. Stokylova Chanv Cher., H.T. Lechert, C.P. Bezouhanova, Oxidation conversion of *n*-heptane over molecular sieves, Appl. Catal. 203 (2000) 121–126.

[21] G.S. Mishra, A. Kumar, Preparation of heterogeneous vanadium (VO^{2+}) catalyst for selective hydroxylation of cyclohexane by molecular oxygen, Catal. Lett. 81 (2002) 113–117.

[22] C.A. Root, C.R. Hoeschele Cornman, J.W. Kamf, V.L. Pecoraro, Structural and spectroscopic characterization of dioxo vanadium(V) complex with asymmetric schiff base ligands, 32 (1993) 3855–3861.

[23] B.E. Leach, A Text Book—Applied Industrial Catalysis, vol. 3, Academic Press, London, 1984.

[24] S. Siggia, Quantitative Organic Analysis, vol. 558, 3rd ed., Wiley, New York, 1963.

[25] S.K. Das, A. Kumar, S. Nandrajog, A. Kumar, Polymer support VO^{2+} schiff base catalyst for hydroxylation of benzene, Tetrahedron Lett. 36 (1995) 7909.

[26] H. Mimoun, L. Sausaine, E. Daire, M. Postal, J. Fisher, R. Weiss, Vanadium(V) peroxo complexes. New versatile bismimetric reagents for epoxidation of olefins and hydroxylation of alkanes and aromatic hydrocarbons, J. Am. Chem. Soc. 105 (1983) 3101–3110.

[27] G.S. Mishra, A. Kumar, Catalytic oxidation of alkanes using molecular oxygen with supported vanadium complex, Chem. Con., India 1 (2000) 41–45.

[28] S. Kulkarni, M. Alurker, A. Kumar, Polymer support with schiff functional groups supporting cobaltous palmitate as oxidation catalyst for oxidation, Appl. Catal. Part A: Gen. 142 (1996) 243.

[29] B.K. Das, J.H. Clark, A novel immobilized cobalt(III) oxidation catalyst, Chem. Commun. (2000) 605–606.

[30] R. Gopinathan, B.K. Patel, A catalytic oxidative esterification of aldehydes using V_2O_5–H_2O_2, 2 (5) (2000) 77–579.