

Selective Oxidation of Linear Alkanes by a Schiff Base Ligand [1,4-bis(Salicylidene Amino)-Phenylene] Vanadium (VO²⁺) Complex Bonded on Modified Silica Gel Support¹

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Abstract—A Schiff base complex from vanadium (VO²⁺) has been successfully immobilized by chemical reaction on an isocyanate modified silica gel support. This catalyst proves to be an active heterogeneous catalyst for the selective oxidation of *n*-pentane and *n*-hexane in the presence of molecular oxygen at moderate temperatures (150°C) and pressures (~20 atm). The products were identified by GC/MS analysis, and the product distribution was found to be entirely different from that reported in the literature. The oxygenated compounds formed from *n*-pentane are mostly mesaconic acid (COOH(CH₃)C=CHCOOH) while those from *n*-hexane are alcohols (2-methyl-2,4-pentanediol, 1-hexanol, and 1,6-hexanediol), ketones (2-hexanone), and acids. As analyzed by thermogravimetric analysis, the catalyst was seen to be stable up to 393°C and the atomic absorption study shows a negligible leaching of the catalyst.

1. INTRODUCTION

Alkanes are the most abundant and least expensive hydrocarbon feedstock available. They are relatively unreactive (due to their high ionization energy, *pK_a* values, and low electron affinity) and, in forming their oxidative products (alcohol, aldehyde, ketones, and acids), the challenge facing the researcher is selectivity [1–3]. Oxidation of alkanes at low temperatures can be carried out in the presence of solid catalysts using hydrogen peroxide as the oxidizing agent [4]. This has the advantage of preserving the molecular structure (i.e., absence of isomerization reaction), but commercially, oxidation using molecular oxygen is more attractive proposition. This normally requires high temperature, pressure, and suitable catalysts, and, at these conditions, the molecule can undergo additional reactions, viz., cracking, isomerization, dehydrogenation, cyclization, and dehydrocyclization [5, 6]. In fact, this property has been utilized industrially through catalytic reforming [7–10] (using Pt/Al₂O₃ catalyst at 350°C) and, during this reaction, *n*-hexane forms lower alkanes by cracking (methane, ethane, propane, butane, etc.), mono-branched materials through isomerization (2- and 3-methyl pentanes, etc.), cyclized alkanes through dehydrocyclization (methyl cyclopentane, cyclohexane, etc.), olefins by dehydrogenation (ethylene, propylene, etc.). The oxidation of *n*-pentane (in the temperature range of 300–500°C) is carried out industrially using vanadyl pyrophosphate and vanadium–molybdenum–phosphorus oxide [11–13] catalyst, and the reaction product consists of a mixture of phthalic and

maleic anhydride. In order to improve selectivity further, catalysts having higher acidic properties and redox properties have been used and these are 1,2-molybdo-vanado phosphoric acid and cesium salts of 1,2-molybdo-vanado phosphoric acid.

The oxidation of *n*-hexane (as well as *n*-pentane and *n*-octane) in the presence of oxygen has been carried out in the temperature range of 150–200°C by Thomas *et al.* [14] in which there is no isomerization or cracking. The catalyst tested was cobalt and manganese deposited on aluminophosphate zeolite (Co-AlPO₄) and the product (formed in small amount) consisted of various alcohols, acids, aldehydes, and ketones of *n*-hexane. Sometimes it is desired to promote combustion using a catalyst and, for this, LaM₀₃ (M = Mn, Fe, Co) perovskite [15] (in the temperature range of 200–350°C) and PtNi/Al₂O₃ (operating in the temperature range of 350–500°C) have been used [5].

In this paper, we report a nonzeolite heterogeneous vanadium catalyst supported on carbamate modified silica gel. We have used this for the oxidation of *n*-pentane and *n*-hexane (and analyzed the products using GC/MS analysis). The analysis showed similar level of conversion as that observed by Thomas *et al.* for *n*-hexane oxidation.

2. EXPERIMENTAL

The *n*-pentane (b.p., 36°C) and *n*-hexane (b.p., 69°C) used in our study were obtained by fractionating LR grade chemicals. The catalyst loaded with [1,4-bis(salicylidene amino)-phenylene] vanadium oxo complex

¹ This article was submitted by the authors in English.

was synthesized according to the literature [16], and the reaction steps are given below.

2.1. Preparation of VO^{2+} complex [17, 18]. The complexing agent [1,4-bis(salicylidene amino)-phenylene] was prepared by the condensation reaction of *p*-phenylenediamine (10.8 g, 0.1 g mol) with salicylaldehyde (24.4 g, 0.2 g-mol) at room temperature in absolute ethanol (25 ml). The reaction mixture was stirred for about 3 h, and a yellow precipitate of the product appeared, which was filtered and dried. This complexing agent (3.0 g, 9.5 mmol) was reacted with vanadyl sulfate (3.0 g, 12.9 mmol) dissolved in 100 ml of acetonitrile. The reaction mixture was refluxed at 80°C for 2 h, and a green colored precipitate of vanadium (VO^{2+}) complex was formed (IR spectrum shows the aliphatic and aromatic –CH group at 2927 and 3053 cm^{-1} , respectively, $>\text{C}=\text{N}$ isocyanate at 1640 cm^{-1} , and –OH group at 3610 cm^{-1}). The precipitate was once again washed with acetonitrile and dried at 60°C.

2.2. Preparation of carbamate modified silica gel. Silica gel (5.0 g) was washed with distilled water, then with acetone, and dried at 60°C under vacuum. This was then refluxed with 50 ml of HCl (35%) in a flask for 4 h, and the hydroxylated silica gel [19] was separated and washed with distilled water several times. Phenyl isocyanate (see [20, p. 656] as confirmed by its IR and ^{13}C -NMR) was prepared by the reaction of sodium azide (16.8 g, 0.26 g-mol) with an equivalent number of moles of benzoyl chloride (35.0 g, 0.26 g-mol) in a benzene medium (20 ml) at 0°C. The reaction mass separated into two phases, the liquid phase was filtered. This was readily reacted with a hydroxyl group (see [20, p. 686]) with 5.0 g of silica gel. The reaction mass was stirred at 40°C for 6 h, and the carbamate bonds on the silica gel were confirmed by FTIR (aromatic –CH at 3027 cm^{-1} , –NH group at 1595 cm^{-1} , C=O at 1690 cm^{-1}). The extent of the reaction was estimated by determining the amine group concentration (0.26 meq/g) on silica gel using butyl amine method [21].

2.3. Formation of chemically bound vanadium oxo complex catalyst. The carbamate modified silica gel (2.0 g) was refluxed for 2 h at 80°C with dichloroethane (50 ml) in the presence of a Lewis acid catalyst ZnCl_2 (5.0 mg). The concentration of chloride groups on the silica gel was determined by gravimetric analysis, and the FTIR spectrum of the modified silica gel showed an alkyl group – CH_2 at 2935 cm^{-1} and a –Cl group at 746 cm^{-1} . The vanadium complex was dissolved in absolute ethanol and was subsequently refluxed in the presence of ZnCl_2 catalyst with the modified silica gel suspended in it for 3 h. It gave a green color silica gel. Its FTIR is shown, the disappearance of the chloride group suggests the binding of the metal complex.

The vanadium metal content on the catalyst was determined by atomic absorption spectroscopy (AAS) analysis. Thermogravimetric analysis (TGA) was carried out by Stanton Redcroft Instrument at a heating

rate of 10°C/min under N_2 atmosphere and the stability of the bound VO^{2+} species of the catalyst analyzed by EPR (E-Line Century Series EPR Spectrometer Model 109, X-band).

2.4. Oxidation reaction procedure. The oxidation reactions were performed in high-pressure stainless steel catalytic reactor. An autoclave-rocking reactor having a capacity of 500 ml, gas delivery, and sampling line was employed for the oxidation of alkanes. An on/off controller was used for controlling the temperature with a chrome alloy thermocouple for temperature sensing. After charging the material, the reactor was pressurized by pure 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.

The catalyst was originally green in color, which, after the oxidation reaction, turns brown in color. After carrying out the oxidation reaction, the catalyst was separated by the reaction product filter paper and distilled to remove unreacted alkane. The product of the oxidation was analyzed by gas chromatography using a capillary column (fused silica capillary column 0.25 mm × 50 m film thickness 0.25 μm) with a flame ionization detector and the products were identified by the GC/MS (Shimadzu QP-2000) instrument.

3. RESULTS AND DISCUSSION

Experiments on the functionalization of *n*-pentane and *n*-hexane have been carried out at constant temperatures (varying between 110–200°C for *n*-hexane and 130–200°C for *n*-pentane) and the results are summarized in Tables 1 and 2. To demonstrate the activity of the catalyst for both *n*-pentane and *n*-hexane, the oxidation reaction was first carried out without the catalyst and then in the presence of the complex alone. We found that there was no product formation in either of these cases. After ensuring this, the catalyst was introduced into the reactor and the strong smell at the end of the oxidation indicated the formation of the product.

3.1. Catalytic oxidation of *n*-pentane using molecular oxygen. The vanadium catalyst oxidizes *n*-pentane, and the product can be separated by fractional distillation. In an exercise to identify the product, 100 ml of *n*-pentane were reacted in the presence of the supported catalyst at a temperature of 150°C and pressure of 27.89 atm for 12 h of reaction time. As a result of the reaction, the catalyst showed a change in color from dark green to brown. After the chemical reaction, the distillate was shown to be entirely *n*-pentane and the remaining material was identified by GC/MS analysis. The GC chromatograph of the product is shown to consist of mesaconic acid (selectivity of 92.3% as seen from Fig. 1) as the only major product. Several other

Table 1. Oxidation reactions of *n*-pentane in the presence of vanadium oxo complex catalyst

Sample no.	Temperature, °C	Reaction pressure, atm	Time, h	Catalyst concentration, g	Oxygen, mol	Conversion, %
1	150	27.89	12.0	0.5	0.017	1.80
2	150	27.89	12.0	1.0	0.017	2.22
3	150	27.89	12.0	1.5	0.017	2.32
4	150	27.89	12.0	2.0	0.017	2.40
5	110	16.7	12.0	1.0	0.017	0.50
6	130	20.74	12.0	1.0	0.017	0.57
7	170	34.69	12.0	1.0	0.017	2.40
8	200	40.82	12.0	1.0	0.017	2.55
9	150	27.89	8.0	1.0	0.017	1.00
10	150	27.89	16.0	1.0	0.017	2.43
11	150	27.89	20.0	1.0	0.017	2.67
12	150	27.89	24.0	1.0	0.017	2.80
13	150	14.96	12.0	1.0	0.011	0.60
14	150	22.80	12.0	1.0	0.013	2.79
15	150	32.99	12.0	1.0	0.020	3.10
16	150	37.75	12.0	1.0	0.024	3.13

Table 2. Oxidation reactions of *n*-hexane in the presence of vanadium oxo complex catalyst

Sample no.	Temperature, °C	Reaction pressure, atm	Time, h	Catalyst concentration, g	Oxygen, mol	Conversion, %
1	130	14.96	5.0	1.0	0.083	4.1
2	140	15.98	5.0	1.0	0.083	4.9
3	150	16.62	5.0	1.0	0.083	8.1
4	160	21.08	5.0	1.0	0.083	8.7
5	170	24.83	5.0	1.0	0.083	9.6
6	200	27.21	5.0	1.0	0.083	10.0
7	150	6.46	5.0	1.0	0.066	5.2
8	150	7.48	5.0	1.0	0.075	5.9
9	150	16.67	5.0	1.0	0.091	8.6
10	150	17.68	5.0	1.0	0.096	9.0
11	150	16.32	1.0	1.0	0.083	3.0
12	150	16.32	2.0	1.0	0.083	5.7
13	150	16.32	7.0	1.0	0.083	8.5
15	150	16.32	9.0	1.0	0.083	8.7
16	150	16.32	5.0	0.5	0.083	2.3
17	150	16.32	5.0	1.5	0.083	8.9
18	150	16.32	5.0	2.0	0.083	9.2

compounds were formed in minor amounts (below 1.0%).

In the study of the oxidation of *n*-pentane, the reaction temperature was varied from 110 to 220°C at 27.89 atm pressure. Beyond 200°C, there was a slight charring of the reactant and, as a result of this, 150°C (the amount of the catalyst as 1.0/(100 ml pentane)) was found to be the optimal condition for the *n*-pentane oxidation reaction. At 150°C, the product conversion is 2.22% for 12 h of reaction time, and, as can be seen from Table 1, it increases to 2.80% for 24 h of time of reaction. In Fig. 1 we have plotted selectivity as a function of temperature, and we find that, for mesaconic acid ($C_5H_6O_4$), it first increases sharply, but, for higher temperatures, there is a gradual fall. With an increase in temperature, the total amount of waste product, on the other hand, is reduced. The pressure effect has been studied by keeping the reaction temperature as 150°C and residence time 12 h. It may be recalled that, at high pressure, some oxygen goes to the solution, which reacts with *n*-pentane and this way the dissolved oxygen plays an important role in the oxidation reaction. On increasing the reaction pressure from 14.96 to 37.75 atm, the solubility of oxygen increases giving a higher conversion of *n*-pentane (Table 1). We observed that, at 37.75 atm, the maximum conversion is seen to be 3.13% and further increasing the pressure does not change the final conversion attained. We have varied the amount of the vanadium catalyst (0.5 to 2.0 g), and we found the conversion changed from 1.80 to 2.40%. For a variation of the residence time from 8 to 24 h, as expected, the conversion (Table 1) of product increases from 1.00 to 2.80% rapidly but, for a long time, approaches an asymptotic value.

3.2. Catalytic oxidation of *n*-hexane using molecular oxygen. The majority of the unreacted *n*-hexane (the distillate shown as pure *n*-hexane by IR and 1H -NMR) was distilled at 150°C, and the residue (8.1 ml in 100 ml, after 5.0 h) was collected. This was subjected to GC/MS analysis, and it was shown to consist of 2-methyl-2,4-pentanediol (23.8%), cyclohexane (10.3%), 2-hexanone (1.8%), 1-hexanol (51.6%), 2,5-hexanedione (1.8%), and 1,6-hexanediol (2.4%). Several compounds were formed in minor amounts, and they constituted only about 8.3% of the total product formed. On further distilling the residue at 180°C, there was no residue remaining.

The effect of temperature on the oxidation reaction of *n*-hexane was examined for reaction temperatures varying from 130 to 200°C. The percentage conversion increased slowly from 4.1% at 130°C to 10.0% (Table 2). Beyond a temperature of 170°C, a slight amount of unidentifiable black material was formed, and, as a result, the reaction temperature was never allowed to go beyond this value. In Fig. 2, we have plotted the selectivity of various products formed as a function of temperature. It can be seen that it first rises, and, beyond 150°C, they all attain asymptotic values. The

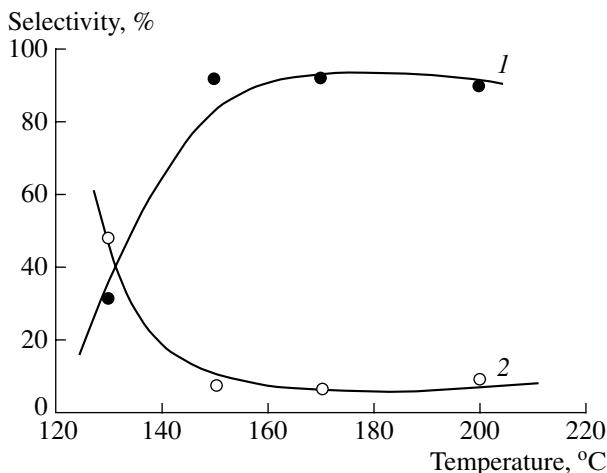


Fig. 1. Effect of temperature on the selectivity of the oxidative products formed by *n*-pentane oxidation: (1) mesaconic acid, (2) unidentified products.

effect of oxygen pressure on the oxidation reaction of *n*-hexane was studied by carrying out experiments at different oxygen pressures at a temperature of 150°C, in the presence of the catalyst. On application of higher pressure, for the same reason, oxygen goes to the solution in hexane and the dissolved oxygen participates in the oxidation. On further increasing the reaction pressure (6.46 to 17.68 atm, Table 2), the solubility of the initial oxygen increases giving a higher hexane conversion. At 17.68 atm, the maximum conversion is seen to be 9.0% and a further increase in pressure produces no change in the final conversion attained. The conversion increases with reaction time as expected. We have varied the amount of support bound vanadium oxo catalyst concentration, and we found that the conversion does not change beyond 2.0 g of the catalyst.

3.3. Characterization. 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 0.073%, and, after 300 h of catalytic reaction, the vanadium metal is found to reduce to 0.054%. 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 a strong green color. This indicates the presence of VO^{2+} ion (g value = 2.00035) and shows its characteristic EPR spectrum at room temperature (Fig. 3). Experiments have shown that no reaction occurs in the absence of the silica gel catalyst or in the presence of free vanadium complex. It was further observed that the green color of the catalyst becomes brown after the reaction in the presence of molecular oxygen. This implies that all VO^{2+} species on the catalyst (green colored, EPR active) are oxidized to VO^{3+} oxo-peroxy [22, 23], because the latter does not give any EPR spectrum. This also suggests that, in the hydroxylation of alkane, the oxo and peroxy groups of the loaded cata-

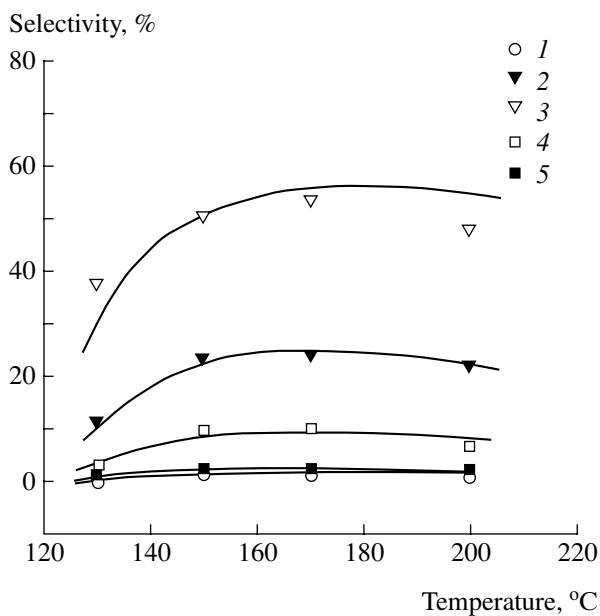


Fig. 2. Effect of temperature on the selectivity of the oxidative products formed by *n*-hexane oxidation: (1) 2,5-hexanedione, (2) 2-methyl-2,4-pentanediol, (3) 1-hexanol, (4) cyclohexane, (5) 1,6-hexanediol.

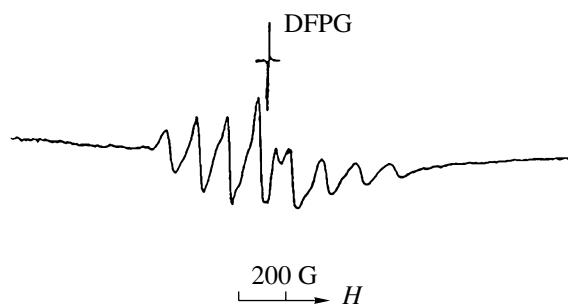


Fig. 3. The EPR of the freshly prepared vanadium catalyst.

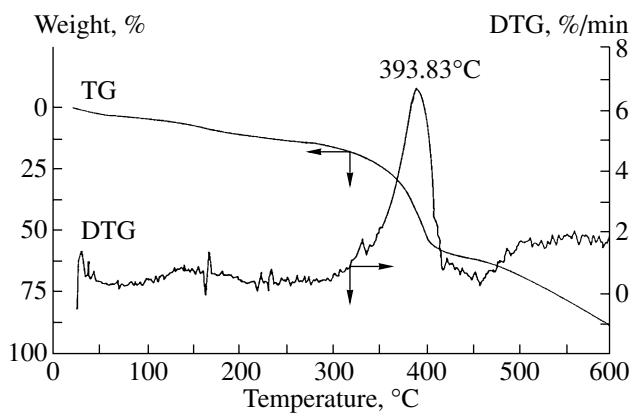


Fig. 4. TGA analysis of the fresh silica gel supported vanadium metal complex catalyst.

lyst must be involved. In order to assess the stability of the supported catalyst, we determined its TGA, and the results are shown in Fig. 4. We find that the catalyst is stable up to 200°C and began to break at 393.83°C.

The catalyst seems to play a dual role in the initiation as well as termination steps of the accepted reaction mechanism [1, 24–26] of the functionalization of alkanes using vanadium. The oxidation of alkane with molecular oxygen in the presence of the vanadium catalyst could occur through (a) autoxidation of free radicals, (b) the metal ion followed by reoxidation of the reduced metal, or (c) catalytic oxygen transfer. In order to show that the reaction is not occurring via a free radical mechanism, we carried out the oxidation of *n*-octane in the presence of a free radical initiator, like, for example, benzoyl peroxide (BPO), and found only a negligible effect on the initial slow phase or the final conversion reached. In addition to this, we also carried the oxidation reaction in the presence of free radical scavengers like hydroquinone and once again found no effect upon the final conversion.

4. CONCLUSIONS

We concluded on the basis of the above discussion that the oxidation reaction of liner alkanes (*n*-pentane and *n*-hexane) in the presence of silica gel supported [1,4-bis(salicylidene amino)-phenylene] vanadium oxo complex is the novel supported catalyst for the oxidation reaction. During the reaction, metal does not leach out for at least 300 h of experimentation and the catalyst is stable under the reaction condition. The product distribution is entirely different in all the cases, and only mesaconic acid (92.3%) as a major product is formed in the pentane oxidation. In the *n*-hexane oxidation, the major product of 1-hexanol (51.6%) is obtained. Increasing the temperature, pressure, time, and the amount of catalyst increased the conversion of product formed, and it appears that the support is playing an important role in catalyzing the oxidation of alkanes.

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