



# Oxidation of *n*-heptane with molecular oxygen using heterogeneous catalyst formed by covalently binding [1,2-bis(salicylidene amino)-phenylene] zirconium complex to modified silica gel

K.S. Anisia, A. Kumar\*

*Department of Chemical Engineering, Indian Institute of Technology, Kanpur 208016, India*

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## Abstract

A heterogeneous catalyst consisting of [1,2-bis(salicylidene amino)-phenylene] zirconium complex chemically bonded to carbamate-modified silica gel catalyst has been synthesized and the oxidation of *n*-heptane using molecular oxygen was studied in a batch reactor system. The study was conducted in the temperature range of 160–200 °C. The product distribution was found to be entirely different from that reported in literature. Cyclohexanone was the only oxygenated product formed, the rest being isomerized products of hexane and heptane (2-methylpentane, methylcyclopentane, 4-methyl, 1-pentene and toluene). Experiments suggest that in the oxidation of heptane carried out in this work, reforming reaction occurred first and cyclohexane formed undergoes oxidation to give cyclohexanone. The thermogravimetric analysis (TGA) shows that the catalyst starts breaking only beyond 383 °C.

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## 1. Introduction

Selective and partial oxidation of hydrocarbons to oxygen-containing compounds (alcohols, aldehydes, ketones and acids) is extremely important and useful for the chemical industry. Terminally oxidized hydrocarbons serve as potential feedstocks for the chemical and pharmaceutical industry. However, these reactions represent a challenge because alkanes are relatively unreactive due to their high ionization energy,  $pK_a$  values and low electron affinity and in forming their oxidative products, their selectivity is usually quite low [1–3]. With respect to chemoselectivity, the initial product of alkane oxidation is often more reactive towards the oxidant compared to the alkane itself. Another problem faced is regioselectivity because of which the radicals and the electrophilic reagents prefer-

entially attack tertiary over primary and secondary –CH bonds [4].

Controlled partial oxidation is easier to achieve with sacrificial oxidants such as hydrogen peroxide [5], alkylhydroperoxide or iodosylbenzene [6] than with molecular oxygen or air, although from an economic point of view, the use of the latter is preferred. This normally requires high temperature, pressure and suitable catalysts and at these conditions, alkanes generally undergo additional reactions, viz. cracking, isomerization, dehydrogenation, alkylation, metathesis, oligomerization and polymerization [7–9]. For hydrogen peroxide as the oxidizing agent, one needs low temperatures and several experiments of oxidation of alkanes using solid catalyst have been reported [10–13].

There are few studies on the oxidation of *n*-heptane. Non-catalytic oxidation occurs at high temperature (277–877 °C) and pressure of 1–40 atm with low selectivity (products being methanol, methane, ethene, ethylene, acetylene, acetaldehyde, ethylene oxide, propane, butene, 1-butene, 1-hexene, 1-heptane and many unidentified compounds) [14]. Molecular sieves (SAPO-5, SAPO-11, BEA,

\* Corresponding author. Tel.: +91 512 2597195; fax: +91 512 2590104.

*E-mail address:* [anilk@iitk.ac.in](mailto:anilk@iitk.ac.in) (A. Kumar).

MCM-41) have been used for partial oxidation in the temperature range 300–400 °C and the products formed are a mixture of heterocyclic compounds (2-methyl-5-ethyl furan and 2,6-dimethyl pyran), heptanones, 4-methyl-1,4-hexadiene, 2,4-dimethyl-1,3-pentadiene and 1-hepten-4-ol [15]. Other reactions involving *n*-heptane are hydrocracking using Ni-supported ZSM-5 zeolite (in temperature range of 160–200 °C) and cracking using MCM-22 catalyst (in temperature range of 450–550 °C) [16,17]. Catalytic pyrolysis of *n*-heptane giving alkenes in larger proportion has also been reported [18] and catalytic reforming on Pt/Al<sub>2</sub>O<sub>3</sub>, Sn/Al<sub>2</sub>O<sub>3</sub> in hydrogen atmosphere in the temperature range of 350–550 °C has been studied [19]. The study shows the formation of hydrocracking products (formation of C<sub>1</sub>–C<sub>6</sub> compounds) and aromatized products (benzene and toluene).

In this paper, we report a heterogeneous catalyst formed by bonding a well-defined coordinated complex on a carbamate-modified silica gel support and this catalyst was used to study heptane oxidation in the temperature range of 160–200 °C. The reaction products formed were identified by gas chromatography–mass spectroscopy (GC–MS) analysis (Shimadzu QP-2000, GC column ULBAN HR-1, fused silica capillary—0.25 m × 50 m) and it was found that the product distribution in this case was entirely different. From the analysis of the reaction products, it appeared that isomerization (forming 2-methylpentane), cyclization (forming methylcyclopentane, 4-methyl-1-pentene), cracking (forming C<sub>6</sub> products) and aromatization (forming benzene and toluene) reactions occurred and the cyclohexane thus formed was oxidized to cyclohexanone.

## 2. Experimental

### 2.1. Material and methods

The *n*-heptane used in our study was obtained by fractionating the LR grade chemicals (Ranbaxy Chemicals, India). The catalyst loaded with [1,2-bis(salicylidene amino)-phenylene] zirconium complex has been synthesized and the reaction steps are given below.

- (i) *Preparation of carbamated modified silica gel:* Silica gel (20.0 g) was washed with distilled water, and 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 [20] was separated and washed with distilled water several times. Phenyl isocyanate (as confirmed by its IR and <sup>13</sup>CNMR) was prepared by the reaction of sodium azide (35 g, 0.538 g mol), with an equivalent number of moles of benzoyl chloride (76 g, 0.54 g mol) in dry benzene medium (20 ml) at 0 °C with constant stirring. The reaction mass separates into two phases; the liquid phase was filtered and was reacted with 20.0 g of silica gel. Phenyl isocyanate reacts readily with hydroxyl and amine groups (p. 686 in [21]) and this is utilized in functionalizing silica gel. The reaction mass was stirred at 40 °C for 6 h and the carbamate bound on the silica gel was confirmed by FTIR (aromatic –CH at 3025 cm<sup>-1</sup>, –NH group at 1599 cm<sup>-1</sup>, C=O at 1647 cm<sup>-1</sup>). The extent of reaction (0.26 meq./g) was estimated by determining the amine group concentration on silica gel using the standard butyl amine method [22].
- (ii) *Preparation of zirconium complex*[23]: The complexing agent [1,2-bis(salicylidene amino)-phenylene] was prepared by the condensation reaction of *o*-phenylenediamine (11 g, 0.1 g mol) with salicylaldehyde (24.5 g, 0.2 g mol) in absolute alcohol solvent (100 ml) for 3 h. After the completion of the reaction, a yellow precipitate of the product was formed, which was filtered and dried. In the next step, this (3.0 g, 9.5 g mol) and equivalent moles of zirconium oxychloride were dissolved in acetonitrile (100 ml) solvent. The solution was then refluxed (80 °C) for 2 h and after the completion of the reaction, an orange colour precipitate of the zirconium complex was formed. The complex was washed several times with acetonitrile for purification and dried at 80 °C. The IR spectrum of the complex shows aromatic –CH group 3053 cm<sup>-1</sup> and >C=N group at 1640 cm<sup>-1</sup>.
- (iii) *Preparation of modified carbamated silica gel-supported zirconium complex catalyst:* The carbamate group of the modified silica gel (20 g) was reacted with dichloroethane (50 ml) by refluxing (60 °C) it in presence of a Lewis acid, ZnCl<sub>2</sub> catalyst (5.0 g, 0.037 g mol) for 2 h. The FTIR of the product showed the alkyl group –CH<sub>2</sub> at 2940 cm<sup>-1</sup> and the chloride group at 749 cm<sup>-1</sup> on the silica gel, confirming that the reaction had occurred. As a result of this reaction, the support material (modified silica gel) now has –CH<sub>2</sub>CH<sub>2</sub>Cl groups possibly attached to the phenyl and the secondary amine groups of the carbamate and the chloride groups of these react with the zirconium metal complex [formed in step (ii) earlier] dissolved in acetonitrile. This was subsequently refluxed (80 °C) for additional 3 h to give the desired heterogeneous [1,2-bis(salicylidene amino)-phenylene] zirconium complex chemically bonded to the modified silica gel. The FTIR of the catalyst shows aliphatic and aromatic –CH at 2935 cm<sup>-1</sup> and 3025 cm<sup>-1</sup>, C=O group at 1635 cm<sup>-1</sup>, –OH group at 3437 cm<sup>-1</sup> and C–N group at 1040 cm<sup>-1</sup> and the absence of the chloride group. If we represent hydroxyl group of the silica gel molecule as  $\text{Si}-\text{OH}$ , then the formation of the catalyst can be written as shown in Fig. 1.

To prove that the complex was chemically bonded to the modified silica gel, we have carried out similar reactions with a lower homologue molecule, *t*-butanol. In the

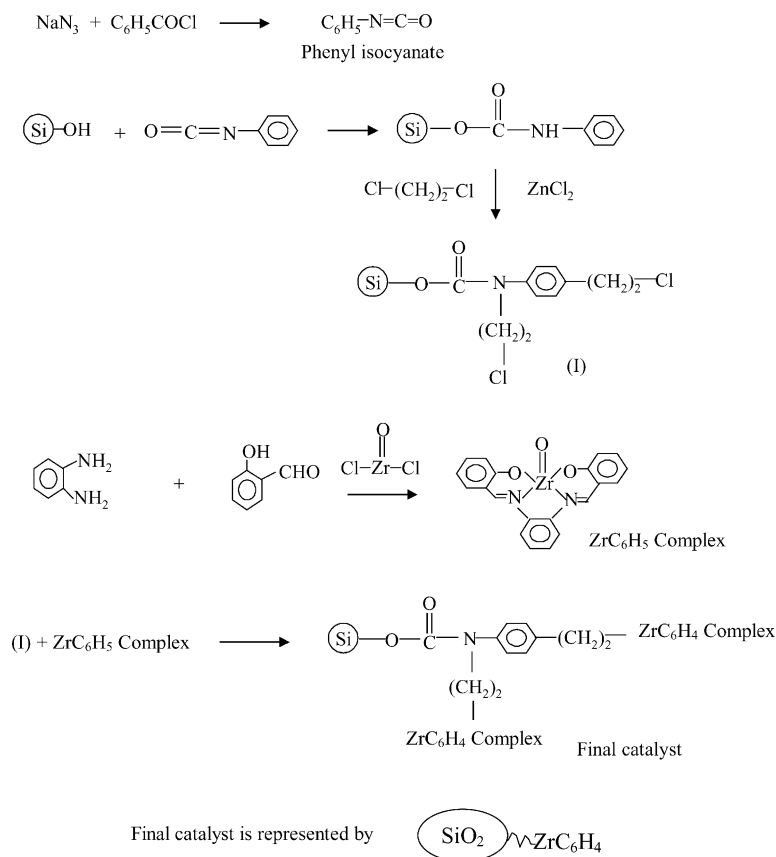


Fig. 1. Reaction scheme for the synthesis of [1,2-bis(salicylidene amino)-phenylene] zirconium complex chemically bound on modified silica gel support.

first step, phenyl isocyanate was reacted with *t*-butanol and its FTIR shows phenyl group  $-\text{CH}$  at  $3035 \text{ cm}^{-1}$ , aliphatic  $-\text{CH}_2$  group at  $2940 \text{ cm}^{-1}$ ,  $-\text{NH}$  group at  $1599 \text{ cm}^{-1}$  and  $\text{C}=\text{O}$  group at  $1647 \text{ cm}^{-1}$ . In the next step, it was reacted with dichloroethane and its FTIR shows the presence of Cl group at  $780 \text{ cm}^{-1}$ . The final step consisted of binding the complex with the carbamated *t*-butanol compound and the FTIR of the final product shows the reduction of the peak corresponding to the Cl group, thus confirming the chemical binding of the complex.

The stability of the catalyst was measured by the thermogravimetric analysis (TGA) using Stanton Redcroft Instrument at a heating rate of  $10^\circ\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere and the catalyst was found to be unstable only beyond  $382.88^\circ\text{C}$  (given in Fig. 2).

## 2.2. Reaction procedure

The oxidation reactions were performed in a high-pressure stainless steel batch reactor. An autoclave-rocking reactor having capacity of 250 ml, gas delivery and sampling line was employed for the reaction. The reactor was initially charged with 100 ml *n*-heptane and 0.5 g of catalyst, and then heated to the required temperature for the desired residence time in presence of molecular oxygen (initial reactor pressure of 100 psi was applied). An on/off controller was used

for controlling the temperature with a chrome alloy thermocouple for temperature sensing. The products obtained after reaction were analyzed by gas chromatography using a fused silica capillary column,  $0.25 \text{ mm} \times 50 \text{ m}$  tube, with flame ionization detector and the products were identified using gas chromatography–mass spectroscopy, which was carried out using a Shimadzu QP-2000 instrument. To find out if the catalyst was free from metal leaching, a reaction was run; the catalyst was filtered from the reaction mixture after 4 h and the reaction mixture was left to react in identical conditions

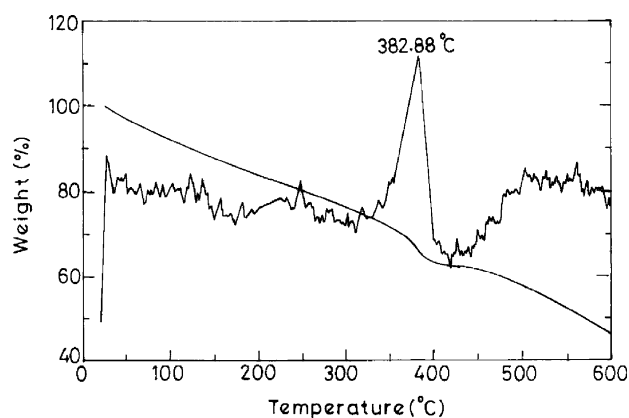


Fig. 2. Thermogravimetric analysis of the fresh zirconium complex catalyst with heating rate  $10^\circ\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere.

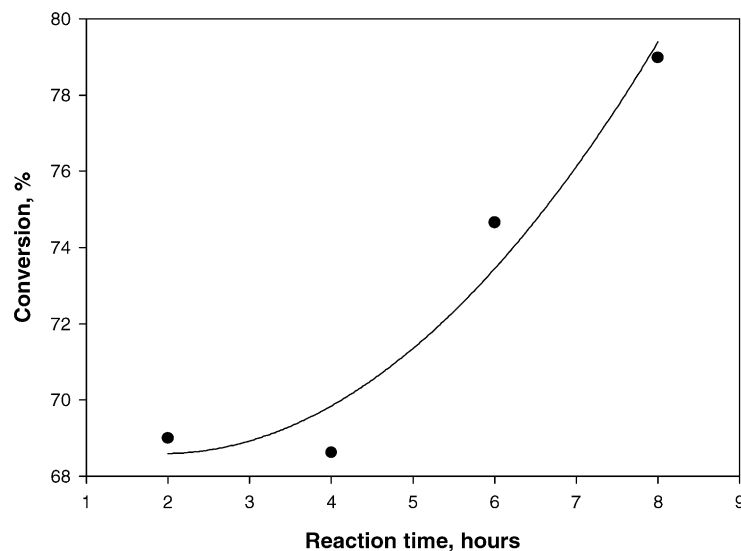


Fig. 3. Effect of reaction time on the overall conversion of *n*-heptane.

in the absence of the catalyst for the same reaction time. The overall conversion was monitored using the GC before and after the catalyst was filtered out. As no more conversions were observed after the removal of the catalyst, we concluded that there was no leaching of the catalyst. As a further confirmation, we determined the metal content of the fresh as well as the one after 100 h of use using SEM analysis and the metal concentration was found to be constant (3.5%).

### 3. Results and discussion

The conversion and product distribution as a function of reaction time (2–12 h) and reaction temperature

(160–220 °C) were studied. The gas chromatograph of the product shows a total of six major peaks. The identification of these compounds was done by the GC–MS analysis and their mass spectra of the compounds was matched with those given in the literature. Peak 1 has been identified as 2-methylpentane, peak 2 as methylcyclopentane, peak 3 as 4-methyl-1-pentene, peak 4 as heptane, peak 5 as cyclohexanone and peak 6 as toluene. Adding pure components to the product and taking its GC again further authenticated these components. The results for the variation of conversion of *n*-heptane and selectivity of the products with reaction time keeping the temperature constant at 200 °C has been shown in Figs. 3 and 4, respectively. The conversion was found to be 69% for 2 h reaction time, which increases to 79%

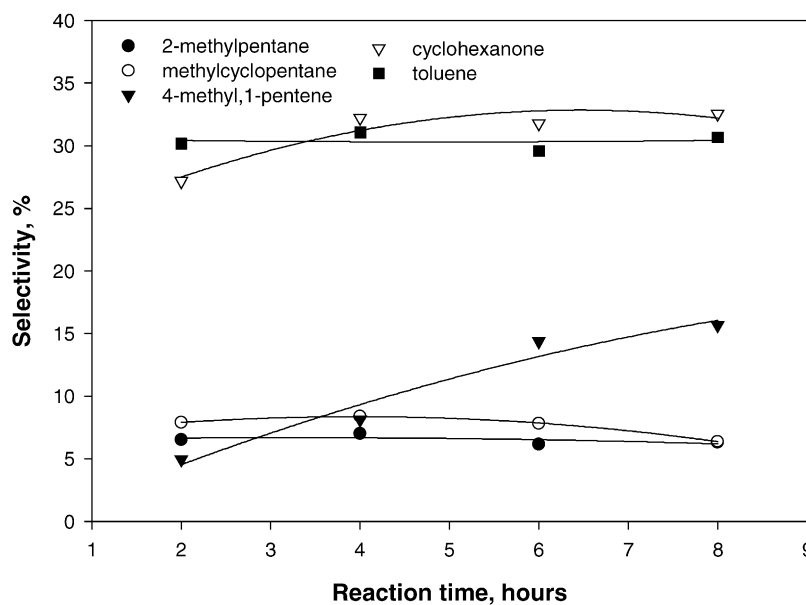


Fig. 4. Effect of reaction time on the selectivity of the products formed.

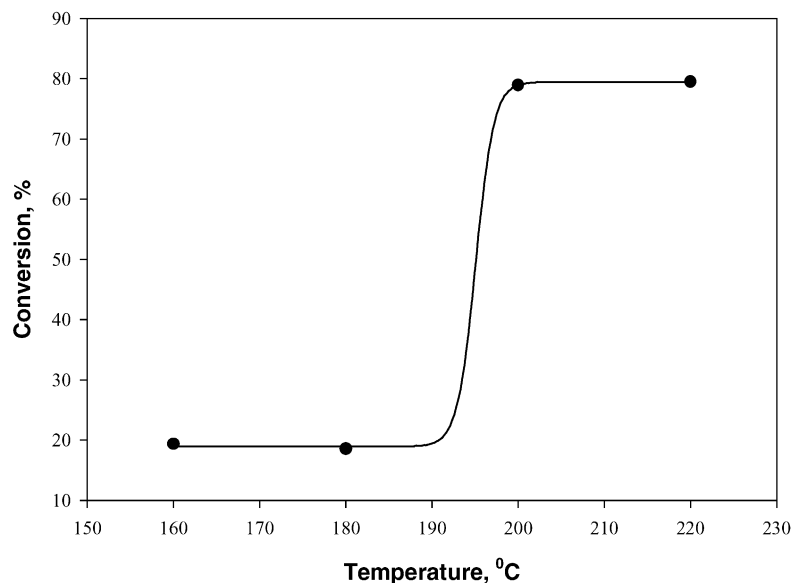


Fig. 5. Effect of reaction temperature on the overall conversion of *n*-heptane.

when the reaction time was increased to 8 h. The selectivity of the products formed also increased with increase in reaction time. The catalyst was more selective towards the formation of cyclohexanone and toluene, with cyclohexanone being the only oxygenated product formed. A large number of products were formed in very small amount (less than 1%), which remained unidentified. The mass spectra of these compounds were not obtained owing to their low concentration in the reaction product.

The variation of the conversion of *n*-heptane and selectivity of the products with temperature was studied in the temperature range 160–220 °C, keeping the reaction time

constant (8 h), and the results have been presented in Figs. 5 and 6, respectively. The conversion increases with increase in reaction temperature and significant reaction occurs only at and beyond 200 °C. It is only 19.4% at 160 °C while it rises to 79.5% at 220 °C. The selectivity of the products also shows an increase with increase in reaction time and at all temperatures, cyclohexanone was formed with the highest selectivity.

In our earlier study, we reported a similar catalyst but having cobalt complex bonded to the modified silica gel. The products formed were 4-heptanone, 2-heptanone, 2-heptanol, heptanoic acid in the oxidation of *n*-heptane

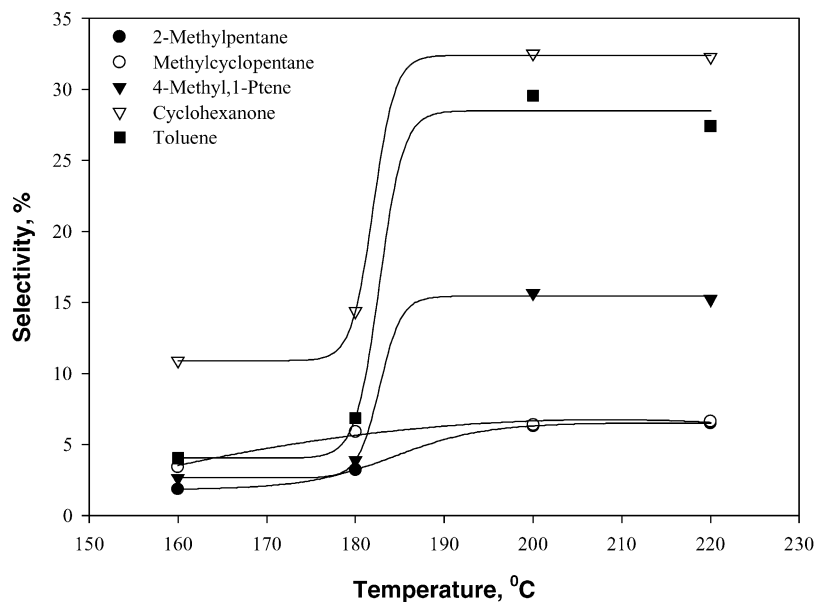


Fig. 6. Effect of reaction temperature on the selectivity of the products formed.

in presence of oxygen and there was no cracking, aromatization, cyclization and dehydrocyclization reactions [24]. The overall conversion also increased with increase in reaction time but was considerably lower (9.5% at 200 °C) when compared to zirconium complex catalyst (79% at 200 °C). When chemically bound vanadium catalyst was used, the oxygenated products formed were 2-heptanone, 4-heptanone, 2-heptanol, *trans*-3-hepten-2-one, 2-octanol, 1-heptanol, octanoic acid, 2-octanol, 1-heptanol, heptaldehyde and heptanoic acid but the overall conversion was still lower (4.67% at 150 °C) [25].

Transition metal complex-catalyzed alkane oxidation has been proposed to occur through mechanism involving the formation of alkyl hydroperoxide intermediate. To detect the presence of alkyl hydroperoxide (ROOH), the literature has suggested the use of an excess of triphenylphosphine (PPh<sub>3</sub>) to reduce these to alcohols [26]. The reduced sample is then expected to have alcohols, which are confirmed by the GC. In our case, the original sample did not have any alcohol and the chromatogram of the reduced sample did not show any extra peak corresponding to an alcohol, which suggests the reaction might have proceeded through some other mechanism.

In our catalyst, we have heteromolecular salen complex containing zirconium, which is bonded to silica gel. In this, the potential site of reaction could be metal centered or ligand centered [27]. In Fig. 7, we give a plausible metal-centered reaction mechanism, which would give the observed product distribution. In this figure, the second

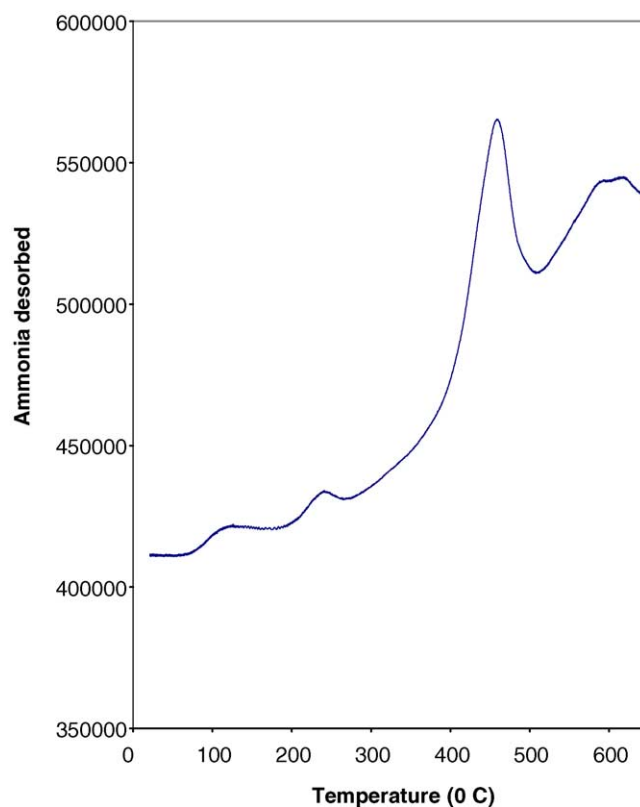


Fig. 8. Temperature-programmed desorption of NH<sub>3</sub>, the final catalyst. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

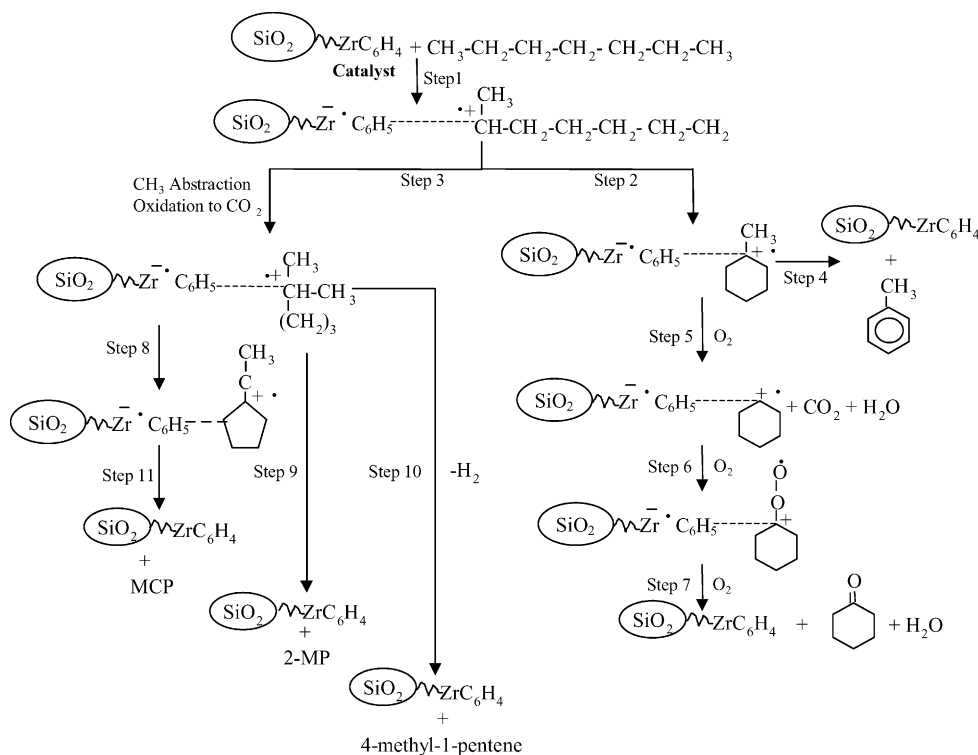


Fig. 7. A plausible metal-centered mechanism giving the product distribution obtained in this work.



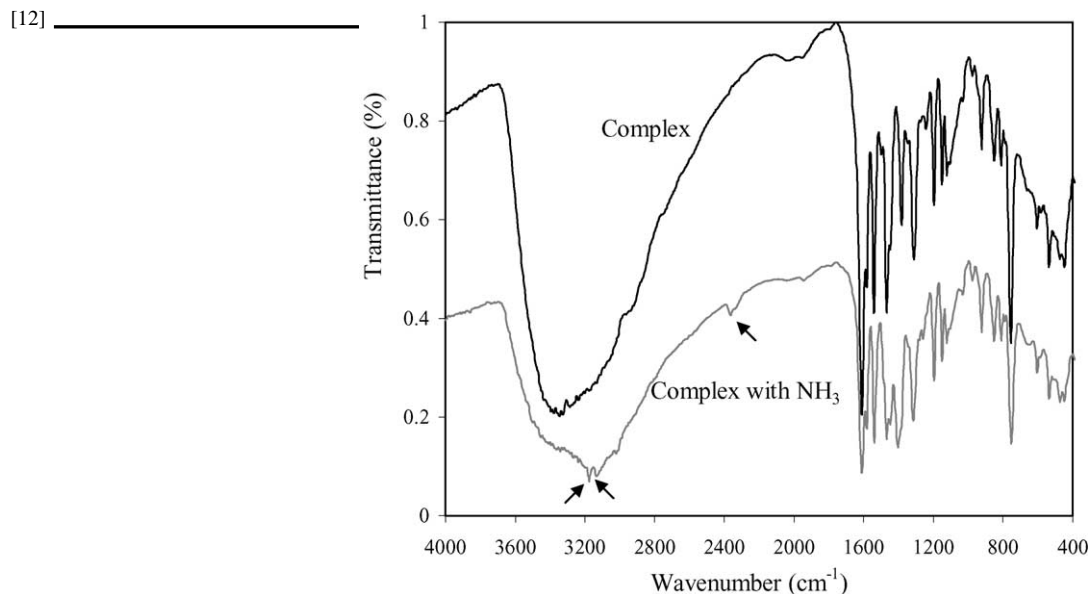


Fig. 9. FTIR of the complex before and after saturation with ammonia. The peaks marked with an arrow are the additional peaks due to ammonia adsorption.

carbon of *n*-heptane is shown to complex with the catalyst (in step 1) [28,29]. This can further cyclize, forming methyl cyclohexane cation radical (in step 2). This, being an active species, can either give rise to the formation of toluene (in step 4) or lose a methyl group through oxidation (in step 5) [19]. The cyclohexyl cation radical formed in this step adds on an oxygen molecule (as given in [30] in the oxidation reaction) that eventually gives rise to a molecule of cyclohexanone (in step 7). As opposed to this, the adsorbed heptane could lose a methyl group [19,31] (as in step 3) and then cyclize to form methyl cyclopentane cation radical (in step 8) to give methylcyclopentane (in step 11) finally. The complex species formed in step 3 can also lose hydrogen to form 4-methyl-1-pentene or undergoes isomerization to form 2-methylpentane.

In order to assess the acidity of the catalyst, methods reported in the literature have been chemical titration, XPS, FTIR and thermal techniques [32]. The temperature-programmed desorption (TPD) of ammonia is one of the methods belonging to the latter class in which the acidity is measured through desorption of ammonia with increasing temperature. In our experiment, 0.1 g of the final catalyst was saturated with 1.5 ml (introduced in 15 pulses) ammonia into the flowing helium at 150 °C. Fig. 8 gives the TPD and is seen to exhibit two weak desorption peaks (at 117 °C and 242 °C temperature) and two major peaks (at 457 °C and 602 °C temperature). The TGA data suggest the breaking of the complex beyond 382 °C, which means that the peak of the TPD at 457 °C may have combined gas release due to degradation of the complex. This peak at 602 °C of the TPD spectrum also suggests that the complex may have broken in two stages, one at 457 °C and the other at 602 °C. We have also taken an FTIR of the complex and the catalyst before and after saturating with ammonia. The

spectrum of the complex before and after the adsorption of ammonia (given in Fig. 9) is found to be different in the 2000–3500 cm<sup>-1</sup> range and the latter exhibits at least two additional peaks, indicating that the complex has at least two kinds of acid sites.

#### 4. Conclusion

In this work, we prepared a heterogeneous catalyst by chemically binding [1,2-bis(salicylidene amino)-phenylene] zirconium complex to the modified silica gel support. This catalyst has been used to study the oxidation of *n*-heptane using molecular oxygen. It gives a conversion of 79% at temperatures around 200 °C, giving an entirely different product distribution. A metal-centered mechanism has been suggested to explain the observed product distribution.

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