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Reforming of *n*-hexane in presence of [1,2-bis(salicylidene amino)-phenylene]–zirconium complex chemically bound on modified silica gel support

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Abstract

The heterogeneous catalyst consisting of [1,2-bis(salicylidene amino)-phenylene]–zirconium complex chemically bound on modified carbamate silica gel was synthesised and the reforming of *n*-hexane was studied in a rocking type batch reactor system. The isomerization and cyclization of *n*-hexane occurs in presence of this catalyst at low temperatures (120–190 °C) with high conversion (72%) in an atmosphere of nitrogen. The analysis of the reaction products suggests the occurrence of isomerization (forming 2-methylpentane (2-MP) and 3-methylpentane (3-MP)) and cyclization (forming methyl cyclopentane (MCP) and cyclohexane (CH)). There is no formation of dibranched isomers and of aromatization reaction (forming benzene and toluene), dehydrogenation reactions (forming alkenes) and cracking reactions (forming C_1–C_5 compounds).
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1. Introduction

In recent years, catalytic reforming of *n*-alkanes has been gaining importance due to the restrictions imposed on the use of tetraethyl lead (TEL) as an additive for upgrading the octane number of gasoline. This reaction allows transforming *n*-alkanes (C_4–C_8) having low octane number, into *iso*-alkanes and dehydrocyclized products having considerably improved octane numbers. Commercially, these reactions are generally carried out in hydrogen environment (15–70 atm) and the process is known as hydro-reforming. The commonly used reforming catalysts are noble metal (Pt is the most common metal) supported on alumina which works in the temperature range of 350–500 °C [1]. The overall reaction for *n*-hexane for this catalyst has been shown to consist of four competing reactions, viz. cracking (forming C_1–C_5 compounds), isomerization (forming monobranched isomers 2-methylpentane (2-MP) and 3-methylpentane (3-MP) and dibranched isomers

2,2-dimethylbutane (2,2-DMB) and 2,3-dimethylbutane (2,3-DMB)), dehydrocyclization (MCP and cyclohexane) and aromatization reactions (forming benzene and toluene).

Traditional Pt/Al$_2$O$_3$ (working between 260 and 315 °C) catalyst are prepared by physical absorption of salts of platinum on the alumina or zeolite support and by adding HF or HCl at the stage of catalyst formation are known to give higher hydrocarbon conversion [2]. The hydroconversion (i.e., reaction carried out in presence of H$_2$) of *n*-pentane and *n*-hexane in presence of this catalyst leads to the products formed by cracking, isomerization and dehydrocyclization reactions and the yield of *iso*-alkanes increase and approaches close to equilibrium values [2]. Platinum on sulphated zirconia has been found to be active in alkane isomerization in the temperature range 127–287 °C and for *n*-hexane isomerization, the product formed consisted of $<C_6$, dimethylbutanes and methylpentanes with high selectivity for the isomerized products (80–100%) [3]. Binary oxides of titanium and zirconium (having both acid and base site) are also used as support and it was observed that there was a profound effect on the specificity of various reaction products formed [4]. Bimetallic catalyst have also been used in which the second metal (Re, Rh, Ir, Sn)

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is absorbed onto Pt/Al_2O_3 and this catalyst shows an improvement in the overall conversion of *n*-hexane [2,5]. The Pt/Al_2O_3, Sn/Al_2O_3 and $Pt/Sn/Al_2O_3$ catalysts (Pd has also been used instead of Pt) have also been used in the reforming of *n*-heptane and the addition of tin is known to enhance aromatization, inhibit hydrocracking and isomerization and decrease coke formation [6,7]. The $Pt/Sn/Al_2O_3$ has also been modified by gold, iridium and palladium and tested for *n*-octane reforming and the modified catalyst showed a slight increase in activity [8]. The use of hydrogen form of zeolite, HMCM-22 catalyst (having no metal) and has been found to give more cracking products during *n*-hexane reforming [9]. Among the solid super acids, sulphated zirconia (Lewis and Bronstead acid sites are present) has the highest acid strength and isomerizes *n*-butane in presence of hydrogen to *iso*-butane and *n*-pentane to *iso*-pentane [10].

In this work, we have synthesised a zirconium metal complex with [1,2-bis(salicylidene amino)-phenylene] and bound it chemically to carbamate modified silica gel support. The catalyst thus prepared was found to work very well at mild reaction conditions (120 °C) in presence of nitrogen giving an overall conversion of 72%. The products formed were identified using gas chromatography–mass spectroscopy (GC–MS) analysis and was shown to consist of 2-MP, 3-MP, MCP and cyclohexane suggesting that there was no formation of dibranched materials in isomerization reaction and an absence of cracking, dehydration and aromatization reactions. The catalyst demonstrates high specificity and is more selective for isomerized products than cyclized products.

2. Experimental section

2.1. Materials and methods

The *n*-hexane 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 synthesised [11] and the reaction steps are given below.

2.1.1. Preparation of carbamated modified silica gel

Silica gel (20 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 [12] was separated and washed with distilled water several times. Phenyl isocyanate (as confirmed by its IR and ^{13}C NMR) 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 ([13], p. 686) and this is utilised 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^{-1}, –NH group at 1599 cm^{-1}, C=O at 1647 cm^{-1}). 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 [14].

2.1.2. Preparation of zirconium complex [15]

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 zirconium oxychloride (15 g, 0.046 mmol) was 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 at 3053 cm^{-1} and $<$ C=N group at 1640 cm^{-1}.

2.1.3. Preparation of modified carbamated silica gel-supported zirconium complex catalyst

The carbamate groups of the modified silica gel (20 g) was reacted with dichloroethane (50 ml) by refluxing (60 °C) it in presence of a Lewis acid, $ZnCl_2$ catalyst (5.0 mg, 0.037 g mol) for 2 h. The FTIR of the product showed the alkyl group –CH$_2$ at 2940 cm^{-1} and the chloride group at 749 cm^{-1} on the silica gel, confirming that the reaction has occurred. As a result of this reaction, the support material (modified silica gel) now has –CH$_2$CH$_2$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)) 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 bound to the modified silica gel. The FTIR of the catalyst shows aliphatic and aromatic –CH at 2935 and 3025 cm^{-1}, C=O group at 1635 cm^{-1}, –OH group at 3437 cm^{-1} and C–N group at 1040 cm^{-1} and the absence of the chloride group. If we represent hydroxyl group of the silica gel molecule as Si–OH, then the formation of the catalyst can be written as shown in Fig. 1.

To prove that the complex is chemically bonded to the modified silica gel, we have carried out similar reactions with a lower homologue molecule, *t*-butanol. In the first step, phenyl isocynate is reacted with *t*-butanol and its FTIR shows phenyl group –CH at 3035 cm^{-1}, aliphatic –CH$_2$ group at 2940 cm^{-1}, –NH group at 1599 cm^{-1} and C=O group at 1647 cm^{-1}. In the next step, it is reacted with dichloroethane and its FTIR shows the presence of C1 group at 780 cm^{-1}. The final step consists of binding the complex
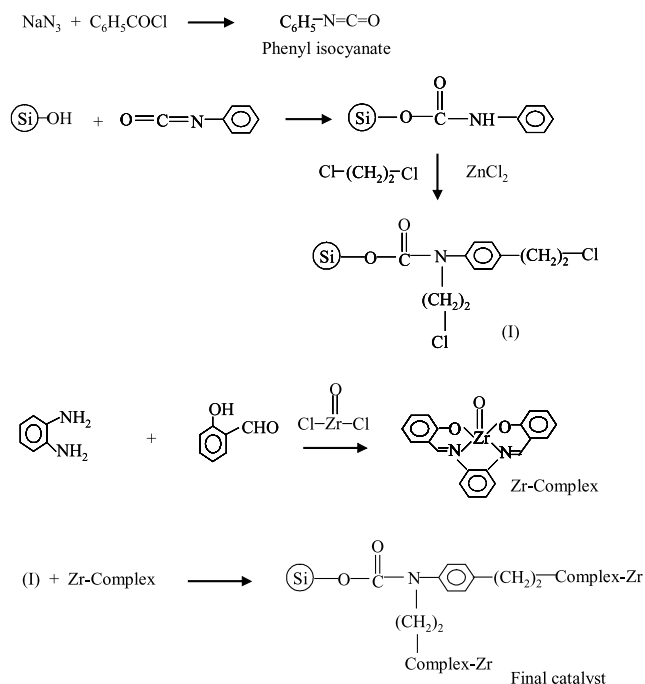
Fig. 1. Reaction scheme for the synthesis of [1,4-bis(salicylidene amino)-phenylene]–zirconium complex chemically bound on modified silica gel support.

with the carbamated *t*-butanol compound and the FTIR of the final product shows the reduction of the peak corresponding to the C1 group, thus confirming the chemical binding of the complex.

2.1.4. Catalyst characterization

The stability of the catalyst was measured by the thermogravimetric analysis (TGA) using Stanton Redcroft instrument at a heating rate of 10 °C/min under N_2 atmosphere and the catalyst was found to be stable upto 360 °C and the complex breaking occurs at 382.88 °C (Fig. 2). The XRD analysis of the zirconium complex as well as the final catalyst was carried out and it was found that both were
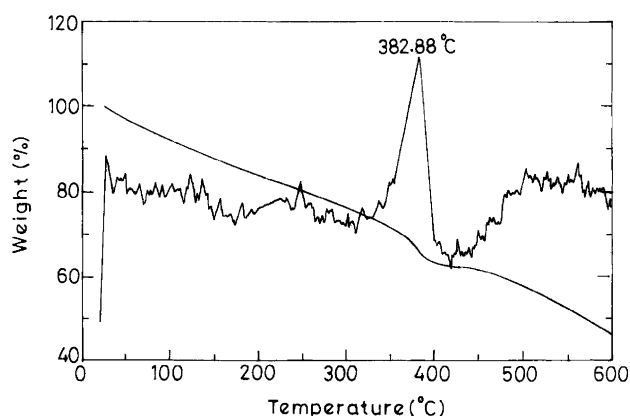

Fig. 2. Thermogravimetric analysis of the fresh zirconium complex catalyst with heating rate 10 °C/min under N_2 atmosphere.

amorphous in nature and the complex was present on the surface of the catalyst.

2.2. Reaction procedure

The reforming 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. An on–off controller was used for controlling the temperature with a chrome alloy thermocouple for temperature sensing. The reactor was initially charged with 100 ml *n*-hexane and 0.5 g of catalyst, then heated to the required temperature for the desired residence time in nitrogen environment. The products obtained after reaction were analysed by gas chromatography (GC) using a capillary column fused silica capillary column 0.25 mm × 50 m with flame ionisation detector and the gas chromatography mass spectroscopy (GC–MS) 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 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 was 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 catalyst as well as the one after 100 h of use, using scanning electron microscopy (SEM) analysis. The metal concentration was found to be 3.5% and was constant.

3. Results and discussion

The conversion and product distribution as a function of reaction time (2–12 h) and reaction temperature (120–190 °C) were studied. The gas chromatograph of the products of one of the runs (at 190 °C temperature and 8 h reaction time) is given in Fig. 3 and it shows a total of five major peaks. The identification of these compounds has been done by the GC–MS analysis and matching their mass spectra with those given in the literature. Peak 1 has been identified as 2-MP, peak 2 as 3-MP, peak 3 as hexane, peak 4 as MCP and peak 5 as cyclohexane. Adding pure components to the product and taking its GC again further authenticated these components. The results for the variation of conversion of *n*-hexane and selectivity of the products with reaction time keeping the temperature constant at 160 °C has been shown in Figs. 4 and 5, respectively. It appears that the reaction has almost attained equilibrium in less than 2 h as the conversion remains at a steady value of ∼72% in the time interval chosen for the study. The catalyst was found to be more selective towards the formation of 2-MP, 3-MP and MCP while cyclohexane was formed in considerably small amount. Low selectivity of cyclohexane has been explained
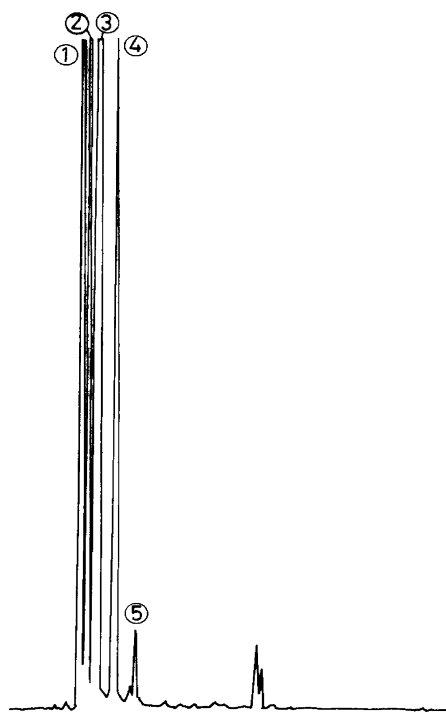
Fig. 3. Gas chromatograph of the product mixture.

to occur because the adsorbed MCP requires high energy for transformation into cyclohexane. The study shows that the selectivity of cyclohexane and MCP increases while 2-MP and 3-MP decreases with increase in reaction time.

The variation of the conversion of *n*-hexane and selectivity of the products with temperature was studied in the temperature range 120–190 °C keeping the reaction time constant (8 h) was studied and the results are shown

in Figs. 6 and 7, respectively. The conversion remains at around 72% in the temperature range studied but the amount of unidentified products increases at 190 °C indicating the possibility of cracking reactions occurring at and beyond this temperature. It was also observed that there is a little variation in the selectivity of the products in the temperature range studied and a high conversion of 71.6% was achieved at a low temperature of 120 °C. In our earlier study, we reported modified silica gel supporting cobalt catalyst and we found that the selectivity of 2-MP and 3-MP decreased while the selectivity of MCP and cyclohexane increased with increase in the reaction temperature in the temperature range studied (150–200 °C) [16]. This result is shown in Fig. 6 using dotted lines. The silica embedded *t*-butyldimethyl silyltriflouromethane sulfonate catalysts have recently been reported and this catalyst (operating in the temperature range 20–80 °C) gave selectivity of 10.5% to 2-MP, 6% to 3-MP, 42% to MCP and 41% to cylohexane [17]. Cyclohexane (30.3%) and MCP (25.3%) were the major products when reforming of hexane was done in presence of sulphated zirconia at 120 °C [18]. For this catalyst, cracked products (7.3%) were also formed at this temperature along with small amounts of monobranched (2-MP, 3-MP) and dibranched (2,2-DMB, 2,3-DMB) isomers.

In the commercial catalytic (Pt/Al$_2$O$_3$ or Pt/Rh/Al$_2$O$_3$) reforming reaction the selectivity of the isomerization, cyclic and aromatic compounds are not high due to the formation of several cracking products and these reactions are carried out at high temperatures (350–500 °C) in presence of hydrogen gas. In case of our catalyst aromatization and cracking reactions do not occur as the reactions are carried out at very low temperatures and only isomerized products (2-MP, 3-MP) and cyclized products (MCP and cyclohexane) are
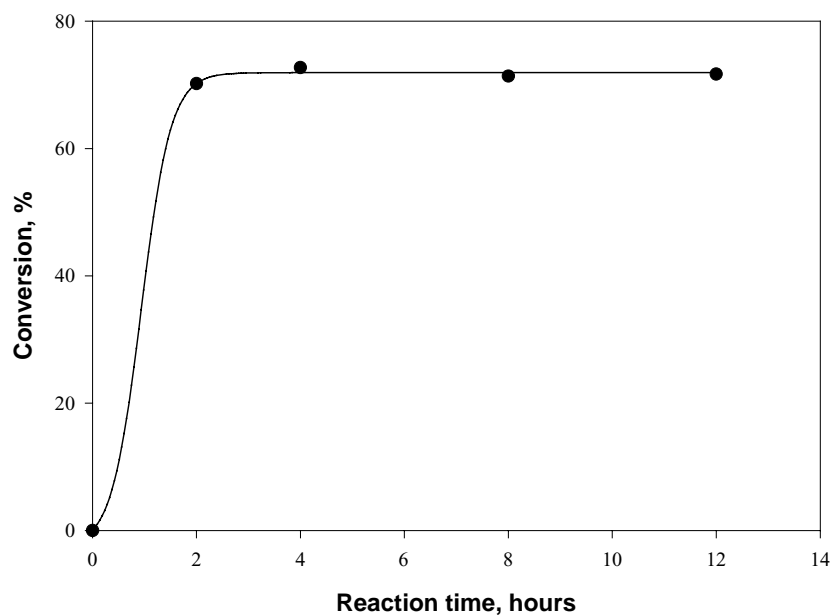

Fig. 4. Effect of reaction time on the overall conversion of *n*-hexane.
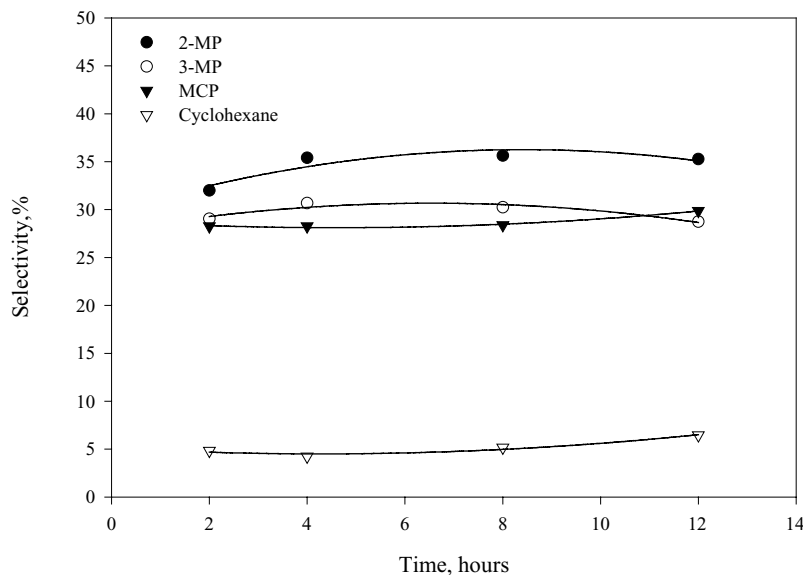
Fig. 5. Effect of reaction time on the selectivity of the products formed.

formed. Dibranched isomers were not formed as they are generally formed at higher temperatures and the yield of the isomerized products was greater than the yield of the cyclized products at all temperatures and for all reaction time. The high selectivity for *n*-hexane isomerization is a good characteristic of the reforming catalysts for production of high octane value reformate containing less aromatic compound and the formation of isomerized products indicates the acidic nature of our catalyst.

In metal-catalyzed isomerization low molecular weight hydrocarbons (C_4 and C_5 alkanes) undergoes isomerization predominantly through simple bond shifts (through carbanion intermediate). In this regard, the formation of α,α,γ-triadsorbed species (as in Anderson Avory Mechanism) and adsorbed cyclopropane species (as in Muller and Gault mechanism) have been proposed for isomerization. The metal-catalysed isomerization of *n*-hexane has been proposed to occur through C_5 adsorbed cyclic mechanism. According to this, hexane first undergoes 1,5-dehydrocyclization and is then adsorbed on the metal site. Depending upon the ring cleavage, the branching may occur at the second or third carbon of the chain. Other
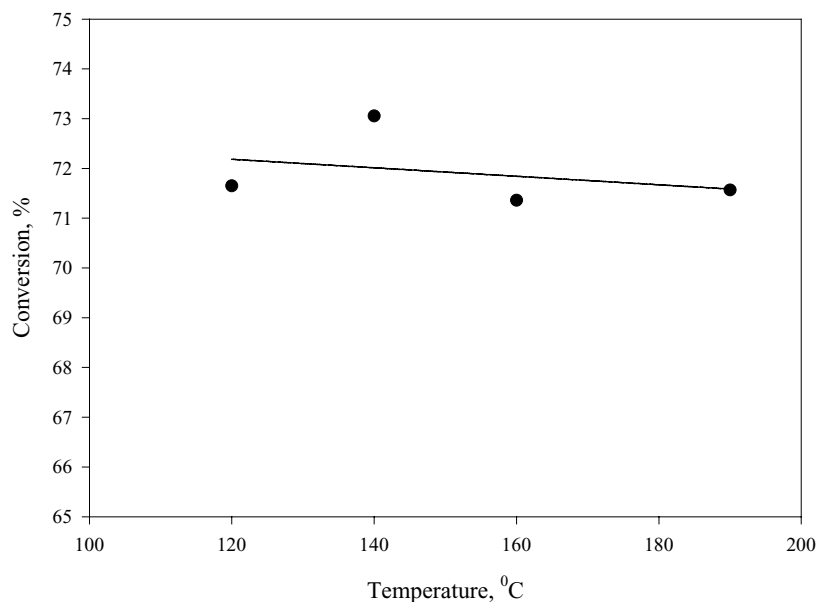

Fig. 6. Effect of reaction temperature on the overall conversion of *n*-hexane.
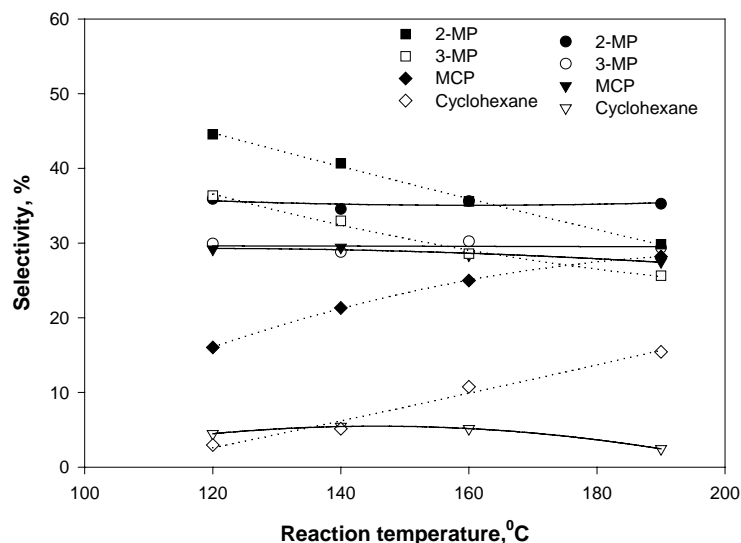
Fig. 7. Effect of reaction temperature on the selectivity of the products formed by the Zr catalyst (solid line) compared with the Co catalyst (dotted line).

adsorbed species that have also been suggested in literature are shown in Fig. 8 [19]. Isomerization progresses through a bond shift as well as cyclic mechanism and with the increasing molecular weight of the reactant, the contribution of the latter becomes more significant.

In the catalyst reported in this work, the potential site of radical generation could be metal centered or ligand centered [20]. Since the zirconium metal exhibits single oxidation state, the isomerization reaction is likely to have occurred at the terminal phenyl group of the ligand. The analysis of the reaction products indicates that the isomerization reaction has occurred both by bond shift and cyclic mechanism. A possible overall reaction observed in our experiment (consistent with literature) is shown in Fig. 9. The acidity of the ligand site terminal phenyl group is enhanced by the complexation with zirconium and the hexane carbonium ion is formed first which then undergoes
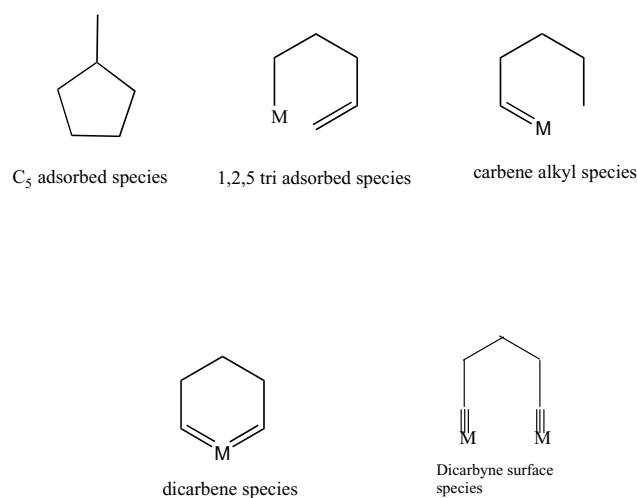

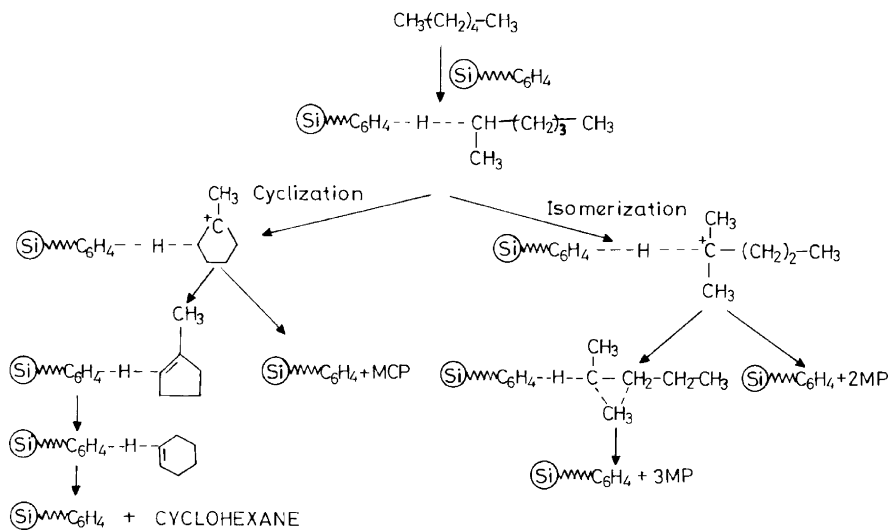Fig. 8. Probable surface intermediate in the isomerization mechanism.

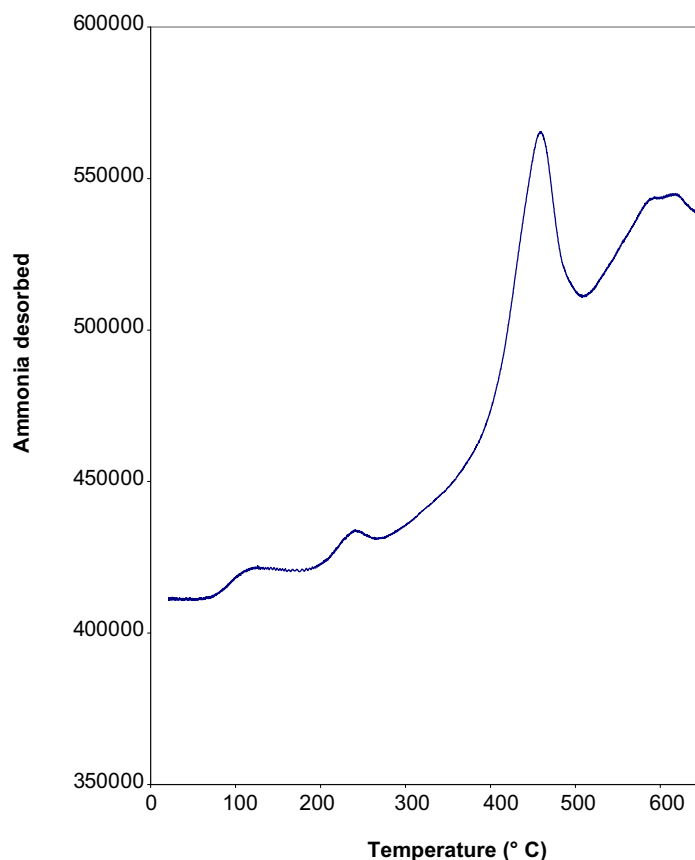

Fig. 9. Proposed mechanism for the reforming of n-hexane.

Fig. 10. Temperature-programmed desorption of NH$_3$, the final catalyst.

reactions through cyclization mechanism as well as bond shift mechanism. The branched isomers are produced by the bond shift mechanism while the cyclization mechanism gives rise to an adsorbed MCP species, which leads to the formation of MCP and cyclohexane.

In order to measure the acidity of the catalyst methods used are chemical titration, XPS, FTIR and thermal techniques [21]. The temperature-programmed desorption (TPD) of ammonia is one of the methods belonging to the latter in which the acidity is measured through desorption of
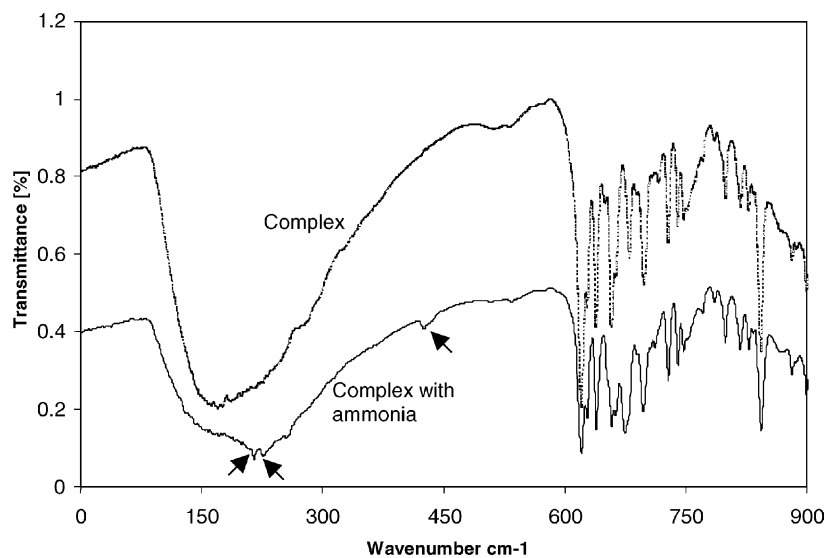
Fig. 11. FTIR of the complex before and after saturation with ammonia. The peaks marked with an arrow are the additional peaks due to ammonia adsorption.

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. 10 gives the TPD and is seen to exhibit two weak desorption peaks (at 117 and 242 °C temperature) and two major peaks (at 457 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. 11) are found to be different in the 2000–35,000 cm^{-1} range and the latter exhibits at least two additional peaks indicating that the complex has at least two kinds of acid sites.

4. Conclusion

We prepared a complex of zirconium with [1,2-bis(salicylidene amino)-phenylene] and chemically bound it to the modified silica gel support. The binding between the two has been demonstrated through modifying a small homologous compound *t*-butanol, which was chemically modified similarly.

The catalyst thus prepared has been used for isomerization of *n*-hexane. The reaction is found to occur at considerably lower temperature and pressure and the product distribution (as determined by the GC–MS analysis) is entirely different from those obtained from catalysts reported in literature. The active site in our catalyst could be metal centered or ligand centered and the isomerization reaction studied in this work suggests the latter. The product formations have been explained through a mechanism (consistent with literature) involving the bond shift and cyclization of the adsorbed species.

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