



Review

An alumina-supported homonuclear macrocyclic zirconium complex for reformation of *n*-hexane

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Abstract

The homonuclear macrocyclic complex involving zirconium on both sites is prepared starting from 2,6-diformyl-4-methyl-phenol and 1,2-phenylenediamine, and is chemically bound to carbamate-modified alumina. The UV-Vis spectrum shows the presence of the metal on the catalyst surface. The TGA of the catalyst suggests that the catalyst is stable up to 250 °C. Reformation of *n*-hexane has been carried out in its presence under nitrogen atmosphere at considerably low temperature and pressure (423 K, 27 atm). We obtained a high conversion of 72% and the GC-MS of the product showed the forming of 2-methylpentane (2MP), 3-methylpentane (3MP), methylcyclopentane (MCP) and cyclohexane (CH). Experimental results reveal that there are no dehydrogenation (forming alkenes), dehydrocyclization (forming benzene or toluene), and cracking (forming C₁–C₅ compounds) reactions and a mechanism forming the products has been suggested.

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Keywords: Heterogeneous catalysis; *n*-Hexane; Homonuclear macrocyclic complex; Reformation

1. Introduction

Normal alkanes obtained by distillation of petroleum crude are relatively unreactive due to high ionization potential and low electron affinity [1]. These are normally burnt and due to stringent requirements of environmental protection, the chemical processes are now being designed to modify these to branched alkanes and aromatic compounds for efficient burning. The process of converting linear alkanes to branched ones is called reformation and heterogeneous catalysts used for this have proved to be a major tool that determines the quality of the product. During reformation, some of the reactions that compete with each other are isomerization (giving branched molecules), dehydrogenation (giving alkenes and hydrogen), cracking (giving lower alkanes), cyclization (giving cyclic compounds like methylcyclopentane (MCP) and cyclohexane (CH)) and dehydrocyclization (giving benzene and toluene) [2]. When the reformation is carried out in the presence of

hydrogen, it is called hydroforming and the alkene formed is hydrogenated during this process.

The most common commercial reformation catalyst is platinum salt physically adsorbed on silica, alumina or zeolite. Various methods of loading metal on a given support are physisorption, chemisorption, encapsulation, etc. [3–6] and these catalysts have the following two functions. The acid function is provided by the solid supports like Al₂O₃, silica or zeolite and the metallic function is provided by the noble metals like Pt. The Pt-hydrogen-mordenite and chlorinated alumina catalysts are commercially used for the reformation of C₅ and C₆ alkanes. Yashima et al. [7] studied Pt loaded zeolite catalysts for *n*-hexane reformation in the temperature range of 400–600 K and a maximum conversion of 76% was obtained at 548 K. The products obtained were dimethylbutanes (BMB), methylpentanes (MP) and some cracking products. Katrib et al. [8] studied hydroreformation of *n*-hexane with MoO₃ supported on TiO₂. The conversion was studied in the range 500–673 K and was found to increase with temperature but selectivity decreased from 90.9% at 600 K to 69.5% at 673 K. This is due to dominant cracking reactions occurring at high temperatures. Guevara-Franco et al. [9] used sulphate-mixed oxide of alumina and zirconia for *n*-hexane isomerization at 523 K and

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maximum conversion obtained was 18.5%. Patrylak et al. [10] studied the isomerization of *n*-hexane over natural zeolites containing palladium. The conversion varied from 17 to 79.5% in the temperature range 523–573 K.

In our work, we have prepared a functionalised alumina with phenylisocyanate and then reacted with dichloroethane. To this, we bonded the homonuclear macrocyclic zirconium metal complex chemically. As a result of this, the thermal stability of the catalyst was found to improve considerably. The catalyst thus formed was characterised by FTIR spectroscopy for confirming the modification of alumina, UV-Vis absorption spectroscopy, TGA analysis, BET surface area and TPR measurements. The reformation reaction of *n*-hexane has been studied at different temperatures and reaction times and the product formed has been analysed by gas chromatography mass spectroscopy (GCMS).

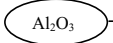
2. Experimental

2.1. Preparation of 2,6-diformyl-4-methylphenol

The 2,6-diformyl-4-methylphenol needed for cyclic complexing agent is prepared following the procedure given in [11]. The NMR spectrum of the dialdehyde prepared by us shows singlets at 11.42 (phenolic), 10.2 (aldehydic), 7.74 (aromatic) and 2.36 ppm (methyl), is consistent with that of the assigned structure and matches with that given in [11]. The reactions forming the cyclic complex with the zirconium is given in Fig. 1 (step (4)) and the procedure of its preparation is discussed below.

- ZrL' : To 50 ml of *N,N*-dimethylformamide at 40 °C, 2,6-diformyl-4-methylphenol (0.95 g, 0.012 mol) is added. 1,2-phenylenediamine (0.65 g, 0.006 mol) is added to this solution. To this solution, zirconium oxychloride (1.93 g, 0.006 mol) is added and the precipitate of ZrL' complex formed is filtered, washed with diethyl ether and dried. The FTIR spectrum shows the presence of functional groups C=N at 1690 cm^{-1} and C=O at 1614 cm^{-1} and C_6H_5O at 1223 cm^{-1} .
- $ZrZrL'$: The zirconium oxychloride (2.74 g, 0.008 mol) is dissolved in methanol (20 ml) at ambient temperature and ZrL' (2.74 g, 0.008 mol) prepared earlier is added. The solution is stirred for 0.5 h and the crystals of the complex appear. These are collected by filtration and washed with diethyl ether and dried. The FTIR spectrum of this complex show C=O at 1618 cm^{-1} and C=N at 1508 cm^{-1} and C_6H_5O at 1224 cm^{-1} .
- $ZrZrL$: The $ZrZrL'$ (2 g) is dissolved in 30 ml of methanol and 0.336 g of 1,2-phenylenediamine (0.336 g) is added. The crystals that appear are collected by filtration and washed with diethyl ether and dried. The FTIR spectrum shows only C=N at 1512 cm^{-1} and no C=O peak appears as it forms C=N with 1,2-phenylenediamine.

2.2. Preparation of the catalyst

The alumina after drying at 500 °C has been shown in Refs. [12,13] to have a number of hydroxyl groups on its surface and these can be schematically represented as  — OH. Phenylisocyanate is prepared according to Ref. [14] by reacting benzoyl chloride with sodium azide at 0 °C in presence of benzene (step (1) of Fig. 1). The liquid and solid phases obtained are separated and the liquid formed (phenyl isocyanate) is reacted with the dried alumina for 4 h at ambient conditions (step (2) of Fig. 1). The FTIR spectrum shows —NH group at 3337 cm^{-1} , C=O at 1650 cm^{-1} and —OH at 3466 cm^{-1} . The carbamated alumina (3 g) is reacted with 50 ml of 1,2-dichloroethane in the presence of $ZnCl_2$ (5 mg) at 80 °C for 2 h (step (3) of Fig. 1). The product is washed and dried, and its FTIR spectrum show —N=C=O at 2341 cm^{-1} and C—Cl at 694 cm^{-1} . The complex prepared in Section 2.1 (shown in Fig. 1) is dissolved in methanol and reacted with the modified alumina at 60 °C for 4–6 h in the presence of a Lewis acid catalyst $ZnCl_2$ (step (5) of Fig. 1) [15,16]. The alumina catalyst thus obtained is washed and dried.

In order to confirm that the complex is indeed chemically bonded with the modified alumina, we have also carried out the similar bonding of the complex with small molecular weight compound like *t*-butanol. In the first step, phenylisocyanate is reacted with *t*-butanol. Its FTIR shows the phenyl group —CH— at 3035 cm^{-1} and aliphatic —CH₂— at 2940 cm^{-1} . In the next step, it is reacted with dichloroethane and its FTIR shows presence of —Cl at 780 cm^{-1} . The final step consists of binding the complex with the carbamated *t*-butanol compound. The FTIR of the final product shows the reduction of peak corresponding to the Cl group, this way suggesting that the Zr—Zr complex is attached to the carbamate-modified *t*-butanol.

2.3. Reaction studies

Reformation of *n*-hexane is studied in a batch reactor with the catalyst prepared in Section 2.2. In this study, we have varied the reaction times (from 1 to 6 h) and temperatures from 423 to 473 K. The reactions have been carried out in nitrogen environment. The products obtained are analysed by gas chromatography mass spectroscopy.

3. Characterization of the catalyst

3.1. Thermo-gravimetric analysis (TGA)

Thermo-gravimetric analysis is conducted to determine the thermal stability of the catalyst. About 10–15 mg of the catalyst is taken and the weight loss is measured in the temperature range 323–1253 K in an inert atmosphere. A sharp decrease in mass has been observed at 523 K indicating

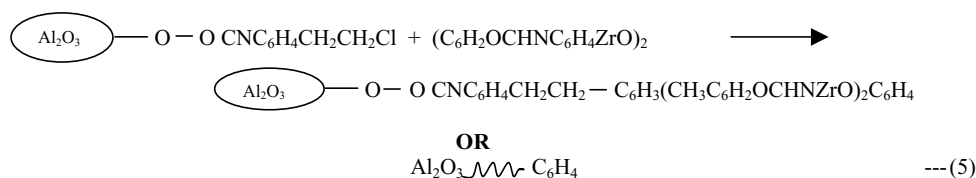
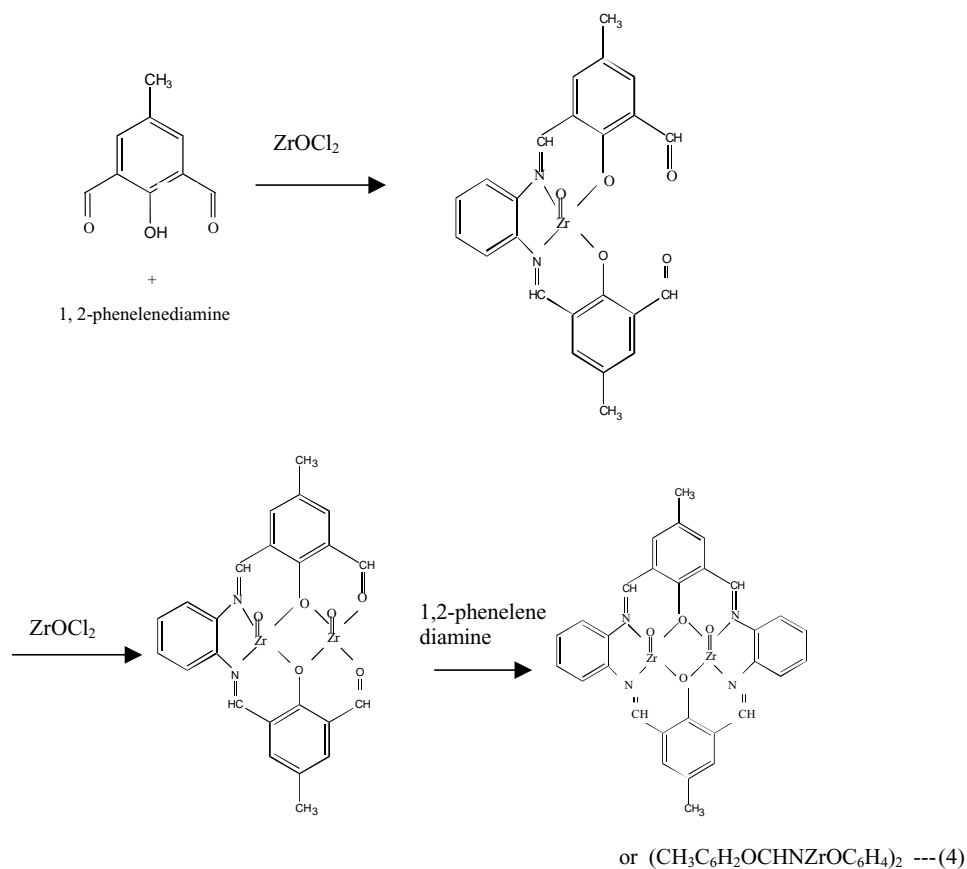
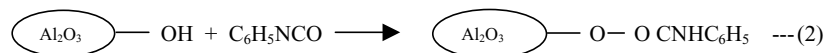


Fig. 1. Steps of preparation of catalyst.

the breakage of the complex bonded to the catalyst at this temperature.

3.2. Surface area measurement

The surface area is measured on a Coulter SA2100 instrument and is analysed by the BET method. The surface area of alumina was found to be $226 \text{ m}^2 \text{ g}^{-1}$ while that of the fresh catalyst was $138 \text{ m}^2 \text{ g}^{-1}$ and it is seen that the surface area of the alumina decreases by 38% after the complex is

chemically bound to alumina. The surface area of the catalyst further decreased after 10 h reaction to $75 \text{ m}^2 \text{ g}^{-1}$ possibly due to the blocking of pores by the reaction products, but does not change further (tested for 100 h of reaction).

3.3. UV-Vis absorption spectroscopy

The UV-Vis spectrum of the homonuclear zirconium complex was observed in the range 270–1100 nm and is shown in Fig. 2. The bands in the range 500–600 nm can be as-

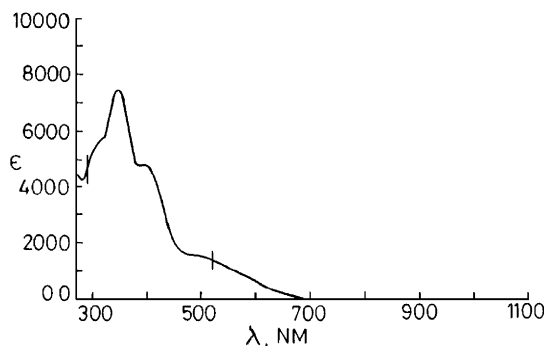


Fig. 2. UV-Vis spectrum of the homonuclear macrocyclic complex.

signed to that of ligand-to-metal charge transfer transition [17].

3.4. Leaching of the catalyst

To check if the leaching of the catalyst occurred, we followed filtration method described in [3]. First, we carried out the reformation reaction of *n*-hexane with the catalyst for 8 h. After the reaction, the catalyst was removed and the reaction was carried out for another 8 h at same conditions of temperature and pressure. Both the reaction products were analysed by gas chromatography and they showed no difference in the amount of compounds formed and their selectivity.

3.5. Temperature-programmed reduction

The TPR technique is used to find the reducing conditions of a substance. In this, the sample is introduced in a tube and a reducing gas (5% H₂ in an inert gas) is flowed over the sample and heated up to 1100 °C. A thermal conductivity detector monitors the reaction between the sam-

ple and reducing gas and the temperature signal is recorded. The TPR measurements are made on a micromeritics Pulse ChemiSorb 2705 instrument.

4. Results and discussion

The products obtained by reformation of *n*-hexane using our catalyst have been identified using GCMS as 2-methylpentane (2MP), 3-methylpentane (3MP), methylcyclopentane and cyclohexane. This indicates that there is no cracking, dehydrocyclization or dehydrogenation reactions taking place at the reaction conditions studied. The overall conversion of *n*-hexane was found to be 72% at 423 K and 27 atm and the variation of the conversion with reaction time is shown in Fig. 3. The selectivity of 2MP is 25.5% and increased slightly with reaction time. For 3MP and MCP the selectivity is 28.3 and 35.9%, respectively, and there is no considerable difference in selectivity with reaction time. The selectivity of CH is 5.2% as shown in Fig. 4. Using our catalyst, the selectivity of MCP is more than that of CH, which shows the methylcyclopentene carbonium ion favours the formation of MCP as compared to that of CH. Some catalysts like sulphated zirconia reported in the literature showed formation of higher compositions of CH and di-branched isomers like (2,2- and 2,3-DMBs) are also formed [18] whereas they are completely absent in our analysis. As the temperature is increased the overall conversion also increased from 58% at 423 K to 72% at 473 K. The selectivity of 2MP increased, while that of 3MP remained constant and for both MCP and CH, the selectivity decreased with temperature (Fig. 5). Our previous work done with Schiff base cobalt complex catalyst also gave 74% conversion of *n*-hexane at 150 °C and 16 atm [16] but selectivities for isomerised compounds, 2-MP (44.57%) and 3-MP (36.35%) was higher and that for the MCP (16.03%)

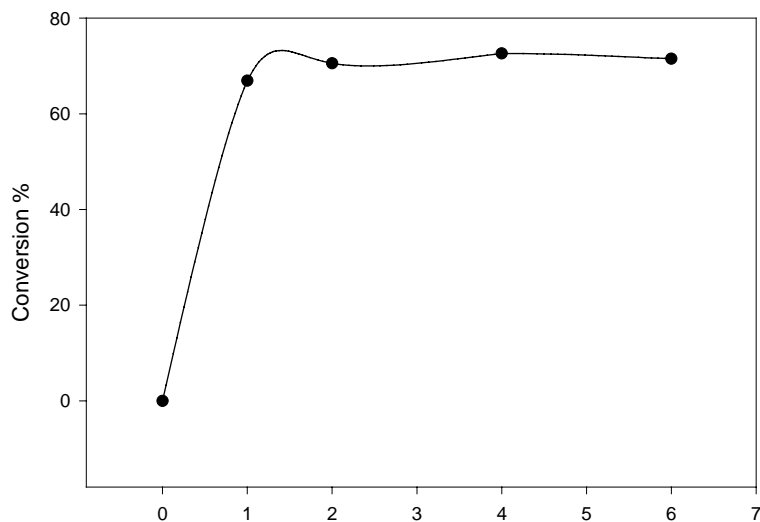


Fig. 3. Conversion of *n*-hexane with time.

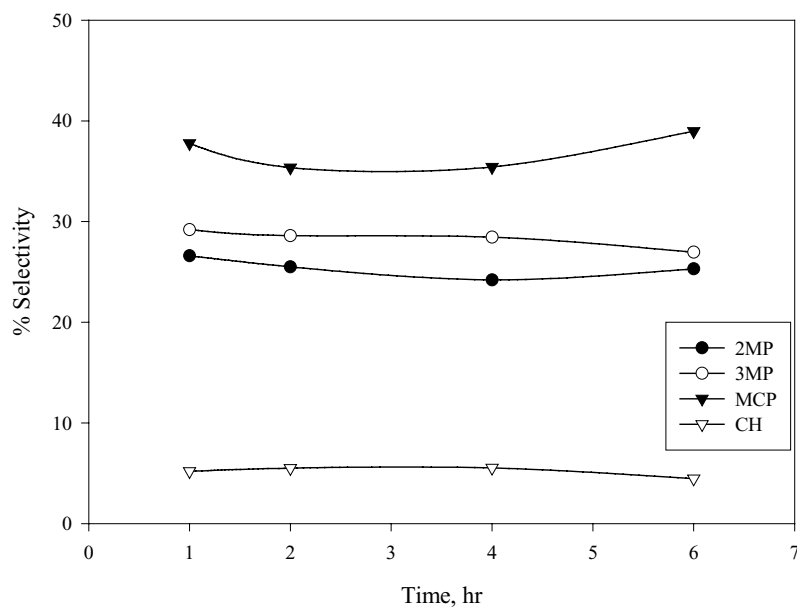


Fig. 4. Selectivity of products with time.

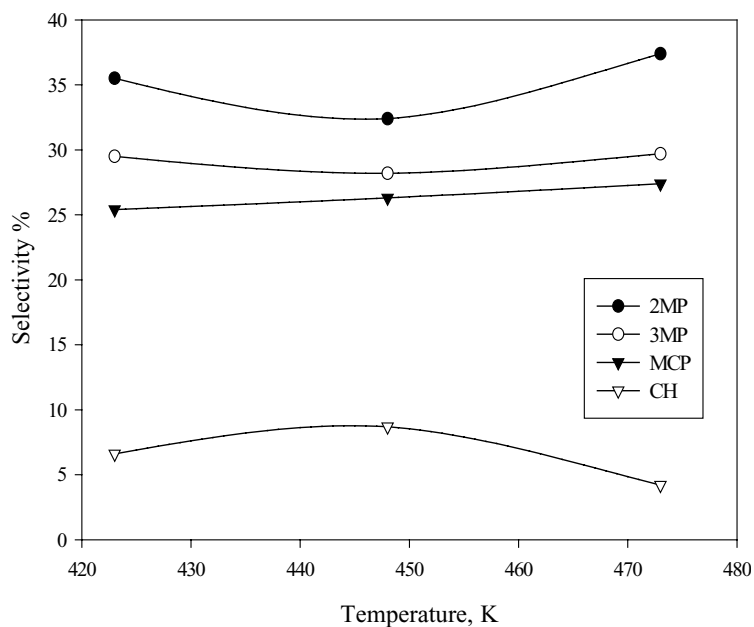


Fig. 5. Effect of temperature on selectivity.

was lower with no CH formed. In our case, the MCP selectivity is also high compared to that of the Schiff base cobalt complex catalyst.

Low molecular weight hydrocarbons (C_4 and C_5 alkanes) undergo reformation predominantly through simple bond shifts (through carbanium intermediate). The metal catalysed reformation of n -hexane occurs differently and form a C_5 -adsorbed cyclic intermediate. According to this, hexane first undergoes 1,5 dehydrocyclization to form MCP and is then adsorbed on the metal site. Depending on the position

of the ring cleavage, the branching may occur at the second or the third carbon of the chain. The isomerization progresses through a bond shift as well as a cyclic mechanism and with the increasing molecular weight of the reactant [19], the contribution of the latter becomes more significant.

In our catalyst, we have a homonuclear macrocyclic zirconium complex which is bonded to the modified alumina surface (shown in Fig. 1). In this, the potential site of reaction could be metal centered or ligand centered [20–23]. The analysis of the reaction products suggests that the reformation

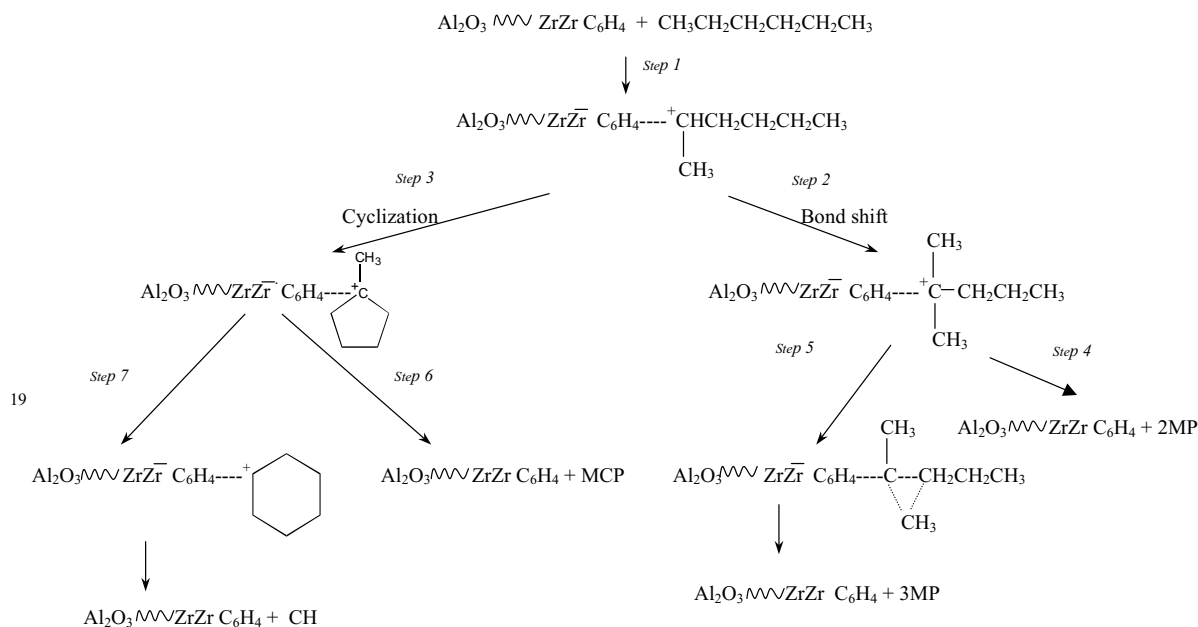


Fig. 6. A plausible reformation mechanism of *n*-hexane using homonuclear macrocyclic zirconium complex bound to carbamated alumina.

tion has occurred both by bond shift and the cyclic mechanism at the metal site of the complex. A possible overall reaction observed in our experiments (consistent with the literature) is shown in Fig. 6. In this figure, in step (1), the complexation is shown to occur at the second carbon atom of hexane [18,23,24]. The complexed hexane molecule could undergo either a bond shift (as in step (2)) or a cyclization reaction (as in step (3)). The complex formed in step (2) can then form either 2-methyl pentane (as in step (4)) or 3-methyl pentane (as in step (5)). During the cyclization step, the complex molecule could form methyl cyclopentane (as in step (6)) or cyclohexane (as in step (7)).

5. Conclusions

The formation of the zirconium homonuclear macrocyclic complex has been confirmed by the FTIR analysis and the UV-Vis absorption spectroscopy. The bonding of the complex to the modified alumina has been demonstrated through carrying out similar reactions with *t*-butanol. The TGA analysis shows that the catalyst is stable up to 250 °C.

The reformation of *n*-hexane has been carried out in the environment of nitrogen using our catalyst. The reaction occurred at low temperature and pressure and the major compounds were 2MP, 3MP, MCP and CH. The product selectivity was high for 2MP, 3MP and MCP as compared to that of CH and has been explained to occur because the adsorbed MCP requires high energy for transformation to CH. The comparison with the other catalysts existing in the literature (sulphated zirconia and Pt/zeolite), the product distribution obtained using our catalyst is entirely different.

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