

Deoligomerization of paraffin wax to mineral oil with alumina supported zirconium complex catalyst

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The present study demonstrates the use of a homodinuclear macrocyclic Zr-Zr complex catalyst in the catalytic deoligomerization of paraffin waxes to mineral oil without any gases. The deoligomerization of waxes is commercially important process and it requires the breakage of C-C bond. Various heterogeneous catalysts reported in literature are known to produce more than 100 components consisting of noncondensable gases CO, CO₂, C₁ to C₆ alkanes, liquid products (C₇ to C₁₄), aromatics and several unsaturated compounds. The use of our catalyst, in the deoligomerization of waxes produce only liquid component and GC-MS analysis has been shown it to consist of octadecane, eicosane, tricosane, docosane, nonadecane and one alkene i.e. 1-hexacosene.

Keywords: Macrocyclic complex catalyst, Alkanes, Deoligomerization, Paraffin wax

In the modern context, wax is a plastic, slippery solid which is easy to melt but earlier this term was used to cover bees wax only. For industrial purposes, waxes are classified according to their origin sources such as mineral, vegetable, animal, insect and synthetic (or manufactured) waxes. The paraffin waxes are obtained from crude oil and approximately have molecular weights in the range of C₁₈ to C₆₅. Normally, these petroleum waxes are n-alkane type and can crystallize to give microcrystalline waxes which have large and flat plate type crystalline structure. Waxes can be converted into fuel oil and valuable chemicals by using degradation or cracking technologies. Waxes can be depolymerized or deoligomerized either by thermal treatment or by catalytic process but main drawbacks of using thermal procedure are wide product distribution and requirement of high temperatures, typically between 500 and 900°C. Catalytic cracking or deoligomerization reaction occurs at relatively low temperatures. The product yield and product distribution can be controlled potentially by selecting appropriate catalyst¹. In this paper, we have studied the deoligomerization of all paraffin wax to mineral oil having lower hydrocarbon at moderate temperature without any gas.

Literature reports the different studies on the depolymerization and cracking of waxes such as HDPE, LDPE and mixture of these two, n-heptane, polystyrene (PS), Fisher-Tropsch (or F-T) waxes.

Venkatesh *et al.*² studied the depolymerization of long chain alkanes and polyolefins (n-heptane, n-hexadecane, polypropylene, polystyrene) and Fischer-Tropsch waxes and reported that the hydrocracking and hydroisomerisation of alkanes over metal-impregnated anion-modified zirconium oxides (AZOs) is resulted to the formation of the higher yield of C₅-C₁₂ isoalkanes or a mixture of gases with high selectivities to isobutene and isopentane. Dupain *et al.*³ evaluated the potential of Fischer-Tropsch Synthesis (FTS) waxes as a feedstock for fluid catalytic cracking (FCC) with a once through microriser reactor operating under realistic conditions. A high gasoline fraction (70 wt%) having i-paraffins, n-olefins and i-olefins with a very low aromatics concentration was obtained. Due to the absence of sulfur and nitrogen in the feed extremely clean transportation fuels are obtained. The addition of ZSM-5 to an equilibrium catalyst allowed the production of significant amounts of light olefins, in particular propene (16 wt%) and butenes (15 wt%). Lee *et al.*⁴ investigated effect of Pd catalysts supported on SiO₂-Al₂O₃ xerogel (SA-X), prepared by impregnation technique on hydrocracking of paraffin waxes for the production of middle distillate. Authors reported that acidity of the catalyst is important factor for determining the catalytic performance in the hydrocracking of paraffin wax. Conversion of paraffin wax increased with increasing

the acidity of the catalyst. Arandes *et al.*⁵ studied the catalytic cracking of polyolefin pyrolysis waxes under conditions that mimic the operation of a catalytic cracking unit (FCC). Catalyst acidity had a significant effect on conversion and on yields and compositions of lumps (dry gases, LPG, gasoline and coke). The main effect of increasing catalyst acidity is an increase in coke content on the catalyst by decreasing the yield to dry gases. Due to the higher hydrogen transfer capacity, the gasoline obtained using the catalyst with higher acidity has a higher aromatic (especially C₆-C₈) and paraffinic content, and lower olefin content, being these two latter fractions less branched. Arandes *et al.*⁶ studied the effect of catalyst acidity and composition (mixtures of base catalyst and catalysts provided with HZSM-5 zeolite of different acidity) on the catalytic cracking of polyolefin pyrolysis waxes under standard conditions in a refinery FCC. The acidity of the catalysts had a relevant effect on hydrogen transfer capacity, which contributes to decreasing the concentration of olefins in the gases and in the gasoline. You *et al.*⁷ investigated the effect of silica modification on MF1, MOR and BEA zeolites catalyst in liquid-phase degradation of polyethylene wax to fuel oil and found that the degradation activities of poor catalyst were greatly enhanced due to the suppression of carbon deposit on the external surfaces. Lee *et al.*⁸ studied hydrocracking of paraffin wax in presence of a series of Pd/SiO₂-Al₂O₃ catalysts for the production of middle distillate (C₁₀-C₂₀). They also investigated the effect of SiO₂ on the conversion of paraffin wax also. Gamba *et al.*⁹ studied the hydrocracking of Fischer-Tropsch wax for obtaining high quality fuels from FT wax. They showed that isomerisation, an important reaction that took place during the hydroconversion process. The amount and the type of the isomers in the produced fuels heavily influenced both cold flow properties and cetane number. You *et al.*¹⁰ studied the catalytic liquid-phase degradation of polyethylene wax into fuel oil using mordenite catalysts with various Si/Al molar ratios prepared by dealumination.

The paraffin wax was purchased from market. The GC-MS of the paraffin wax was carried out and is reported in Fig. 1. In this, the product content is from C₂₁-C₃₉ and various peaks in it correspond to the components in it. The hetero-complex catalyst prepared in this study was used for deoligomerization of waxes to produce mineral oils and was shown to have maximum of only 6 components with the molecular size between C₁₈ to C₂₆.

Experimental Section

Preparation of homodinuclear macrocyclic Zr-Zr complex

First of all, 2,6-diformyl-4-methylphenol needed for formation of a cyclic complex was prepared following the procedure given in the literature¹¹. The three-step reaction for forming the cyclic complex with the zirconium is given in Fig. 2 (a) and the procedure of its preparation is discussed below.

Step I: N, N-dimethylformamide (50 mL) was added to 2,6-diformyl-4-methylphenol (1.95 g, 0.012 moles) at 40°C. It was followed by drop wise addition of (0.5 mL, 0.006 moles) of 1, 3 diaminopropane with stirring. To this solution, zirconium oxichloride (2.5 g, 0.006 moles) is added and the solution was stirred till all the zirconium oxichloride dissolves completely (step I of Fig. 2 (a)). The solution was kept as such for 1 h and then diethyl ether (50 mL) was added. Resulting precipitate was filtered and dried.

Step II: The dried precipitate obtained in step I was dissolved in 30 mL of methanol and to this solution, (0.9 g, 0.0045 moles) of zirconium oxichloride dissolved in methanol with stirring (step II of Fig. 2 (a)). After 1 h, diethyl ether (50 mL) was added and within 30 min olive green precipitate obtained which was filtered and dried.

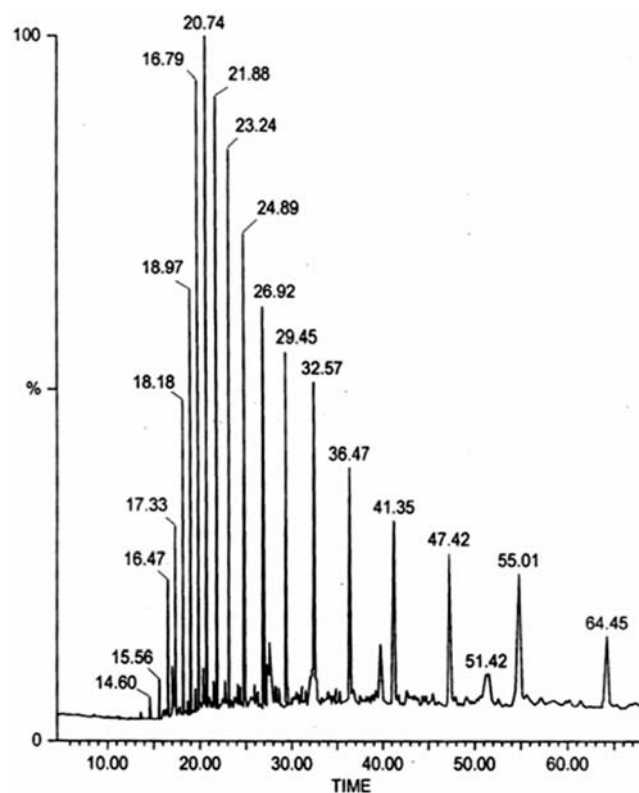


Fig. 1 — GC-MS of paraffin wax

Step III: Olive green precipitate obtained in step II was dissolved in 30 mL of methanol and to this, a solution of 1,3 diaminopropane (0.3 mL) was added drop wise with stirring. The solution was kept for 30 min and then diethyl ether (50 mL) was added to it (step III of Fig. 2 (a)). A precipitate obtained which was filtered from the solution and dried.

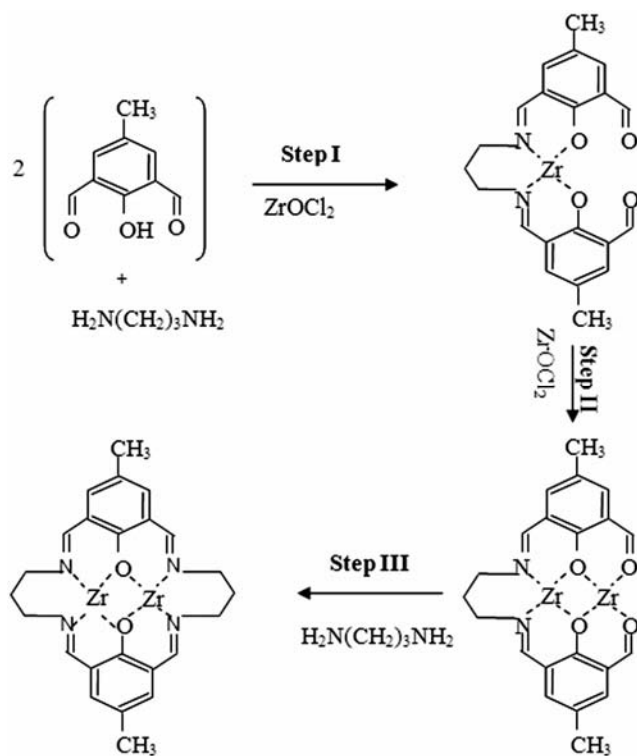


Fig. 2(a) — Synthesis of homodinuclear macrocyclic zirconium complex

Preparation of the supported complex catalyst

The final catalyst was prepared on alumina support. Alumina, after drying at $500^\circ C$, has been shown to have a number of hydroxy groups on its surface¹² these can be schematically represented as Al_2O_3-OH . Phenyl-isocyanate was prepared according to literature¹² by reacting benzoyl chloride with sodium azide at $0^\circ C$ in benzene medium (reaction 1 of Fig. 2 (b)). Obtained liquid and solid phases were separated and the liquid formed was actually phenylisocyanate. Dried alumina was reacted with phenylisocyanate for 4 h at ambient conditions (reaction 2 of Fig. 2 (b)). The carbamated alumina 3.0 g formed was combined with 50 mL of 1,2-dichloroethane in the presence of $ZnCl_2$ (5 mg) at $80^\circ C$ for 12 h. In this reaction chloride ion of dichloroethane reacted with hydrogen of carbamated alumina not with the hydrogen of aromatic ring (as shown in (reaction 3 of Fig. 2 (b)). The product was washed and dried. The complex prepared was dissolved in methanol and reacted with the modified alumina at $60^\circ C$ for 4-6 h in the presence of a lewis acid catalyst $ZnCl_2$ as shown in (reaction 4 of Fig. 2 (b))¹². The alumina catalyst thus obtained had the Zr-Zr complex molecularly bound to the support and has been schematically represented by $Al_2O_3-ZrZrC_6H_4$.

Characterization of the final catalyst

FTIR analysis of catalyst

The infrared spectrum of the catalysts represent the absorption and transmission of lights and is used to confirm the presence of the functional groups and components in the molecule ($C=O$, $C=N$, OH , Cl^- etc.).

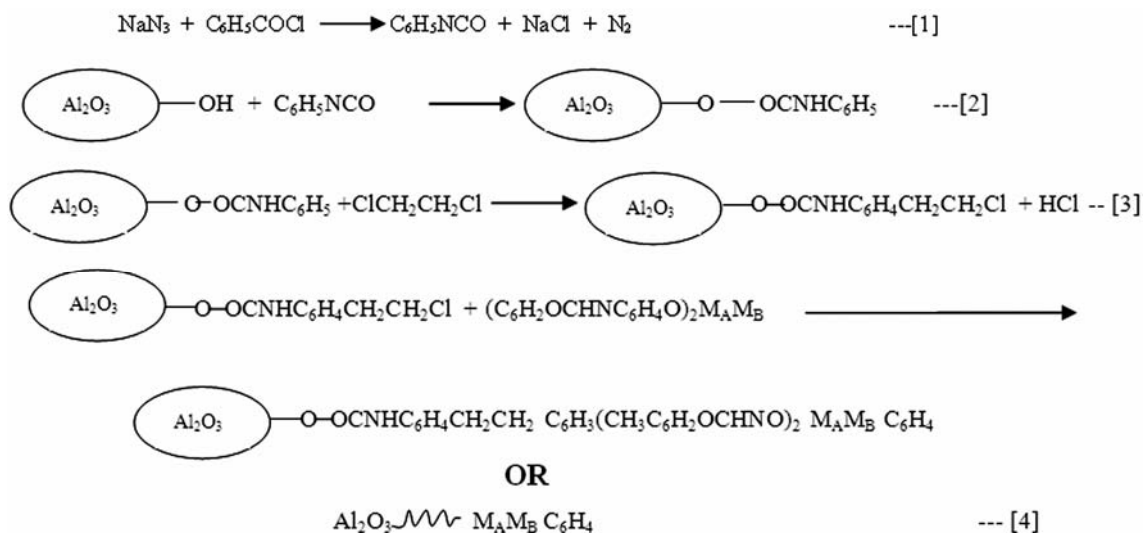


Fig. 2(b) — Preparation of heterogeneous complex catalyst

The FTIR analyses (Bruker vector 22) have been carried out in the range 4000–400 cm^{-1} . The samples were ground with KBr pellet (at about 1–3% by weight) and then pressed to 1 mm thick film. The loading of the complex on the support has been confirmed by the FTIR of the catalyst. The FTIR spectrum of alumina support after modification by isocyanate groups and reaction with 1, 2-dichloroethane is shown in Fig. 3(a). The presence of C-Cl at 728.27 cm^{-1} and –CONH at 1607.60 cm^{-1} confirms the presence of chloride and isocyanate groups. In the FTIR spectrum, the presence of OH group is seen at 3450 cm^{-1} . The FTIR of the final catalyst prepared by covalent bonding of the complex to the modified alumina shows the bonding of the complex at the Cl group, where the peak for -Cl has disappeared (shown in Fig. 3 (b) where [Zr-Zr] complex is loaded on alumina).

Temperature effect

The catalyst was exposed to temperature of 300, 400, 500, 600 and 700°C for 24 h for each temperature and their FTIR's were taken and given in Fig. 3(c). It was seen that the peak at frequency 3466 cm^{-1} for -OH was reduced in intensity which was because for high temperatures, there was a desorption of moisture giving a loss of –OH groups at 3466 cm^{-1} . As the temperature was increased beyond 400°C, the C=N bond at 1532 cm^{-1} appeared to reduce in intensity and after 600°C it disappeared indicating the breakage of this bond first. The efficacy of this catalyst was tested for reaction and was found to work very well up to 350°C. The TG study of the final catalyst suggests that the desorption of the complex starts at 300°C, but results implies that the complex bonded on the surface does not break or change its molecular structure upto 600°C.

Catalytic cracking of paraffin wax

The catalytic cracking reaction of paraffin wax was carried out in batch reactor made of stainless steel of 500 mL volume. The reactor was equipped with pressure gauge to monitor pressure in the reactor, a thermocouple to measure the temperature inside the reactor, gas delivery system and provision for sampling. An on/off temperature controller was used for controlling the temperature with a chrome alloy thermocouple for temperature sensing. 100 gram of wax is fed into the reactor along with 2 g of catalyst. The reactor was then closed and allowed to heat upto the desired temperature limit for reaction. In our case

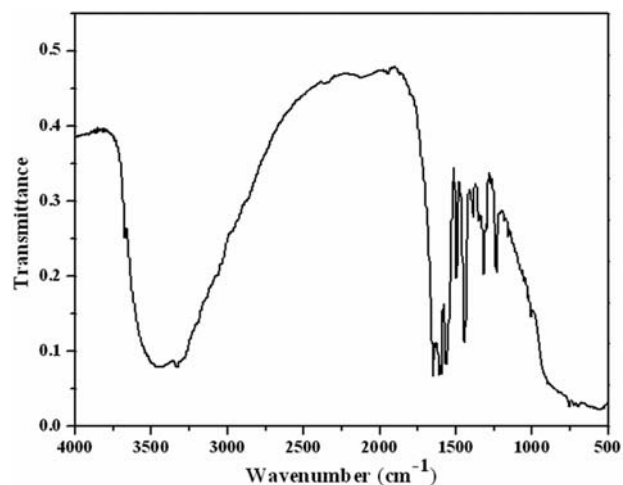


Fig. 3(a) — FTIR spectrum of alumina after reacting with 1,2 dichloroethane

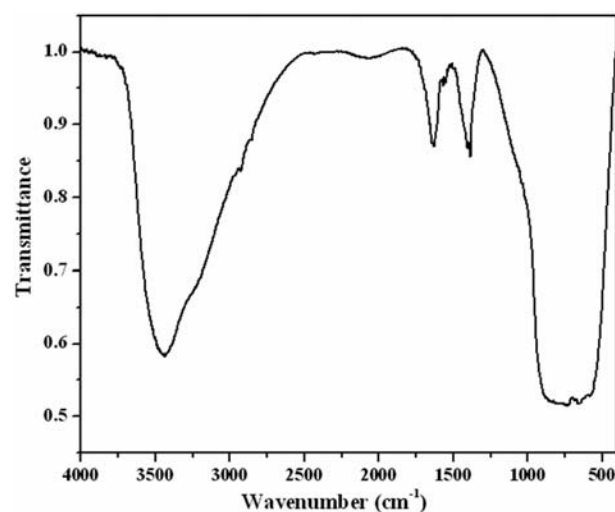


Fig. 3(b) — FTIR spectrum of [Zr-Zr]/Al₂O₃

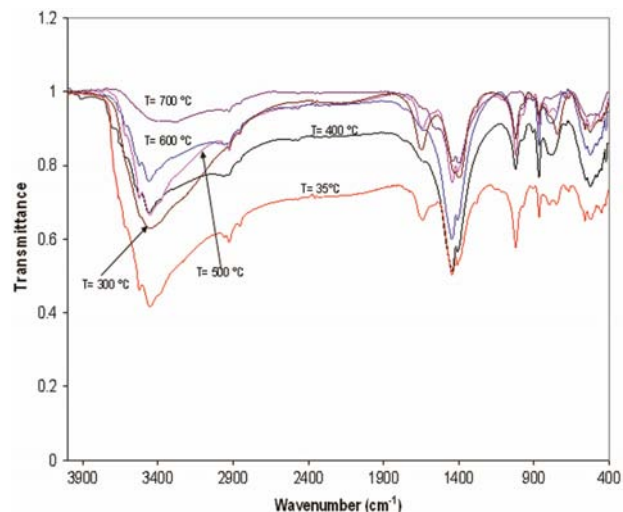


Fig. 3(c) — FTIR spectrum of the [Zr-Zr] complex catalyst at different temperatures for 24 h

the reaction is carried out in the temperature range of 300-450°C using $[Zr-Zr]/Al_2O_3$.

Results and Discussion

For cracking reaction, the catalyst and the wax (in ratio 2:100) were charged in the reactor to examine the effect of reaction time. The reactor was run for fixed times, the heating was stopped and the entire product was withdrawn. The product, thus formed, was oil and subjected to chromatographic analysis by HP-5ms, capillary column. The detailed gas chromatograph for GC-MS analysis is also given in Fig. 4 using the same HP-5ms column. On this particular diagram, we have also given the names of the components as obtained from MS analysis included in this appendix.

The paraffin wax was purchased from market and its GC-MS was carried out as shown in Fig. 1. It clearly shows that there are 22 products, components in it while the MS analysis shows 22 products ranging from C_{19} - C_{41} . The GC-MS analysis of the product for different times shows that the products clearly consist of three alkanes viz., Octadecane $C_{18}H_{38}$, Eicosane $C_{20}H_{42}$ and Tricosane $C_{23}H_{48}$. The role of the catalyst has not only been in reducing chain length of the wax, but also leads to considerable narrowing down of molecular weight distribution compared to the starting material of Fig. 1. Initially, the wax had 22 components where as after cracking, the oily product obtained, had only three alkanes. The results of Fig. 5 show that the concentration of each component continues to rise and the concentration of tricosane is higher than that of octadecane in reaction mixture. This figure also shows that lower molecular species are being formed for short time only but after 5 h of reaction, it attain equilibrium value which does not change.

The catalytic cracking of paraffin wax depends upon the temperature and in Fig. 6 we show the results at 350°C and one additional product docosane $C_{22}H_{46}$ is generated in addition to the earlier products octadecane, eicosane and tricosane. At this temperature, the amount of octadecane is the highest and the amount of eicosane is the lowest in the oily product formed. In addition to this, we see the formation of docosane, eicosane, tricosane reach an equilibrium value at 5 h while the octadecane reaches equilibrium value after 6 h of reaction, which for higher reaction times does not change very much. The important point that should be observed is with the increase in temperature, lower molecular weight

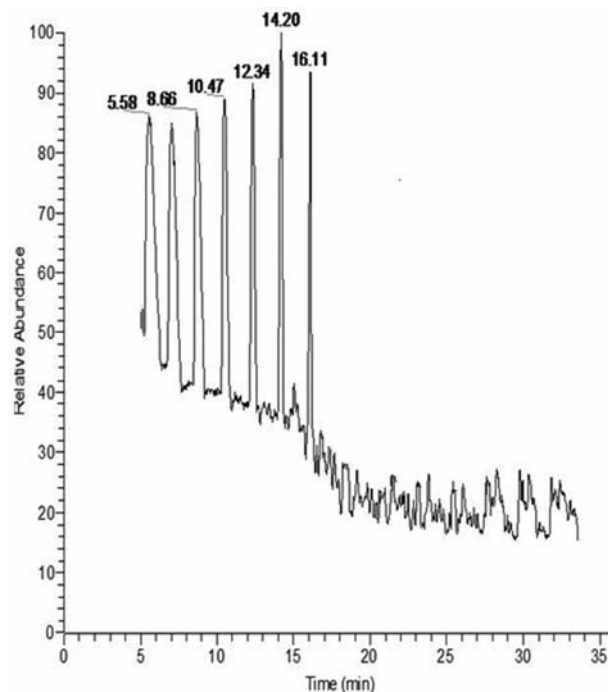


Fig. 4 — GC-MS of product obtained from wax

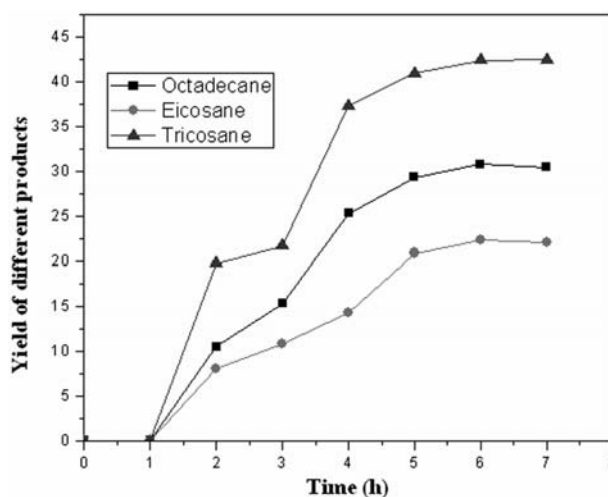


Fig. 5 — Yield of different products from the catalytic cracking of paraffin wax at 300°C using $[Zr-Zr]/Al_2O_3$

component are formed in larger percentage which is consistent by the general observation that with the increase in temperature, the oily product becomes thinner. In Fig. 7, the temperature has further been increased to 400°C and we find the formation of new component nonadecane $C_{19}H_{40}$ with the concentration of docosane as the highest. In Fig. 8 we increased the temperature to 450°C and we find that there is one additional component, 1-hexacosene $C_{26}H_{52}$ formed in smaller yields and its formation reaches equilibrium

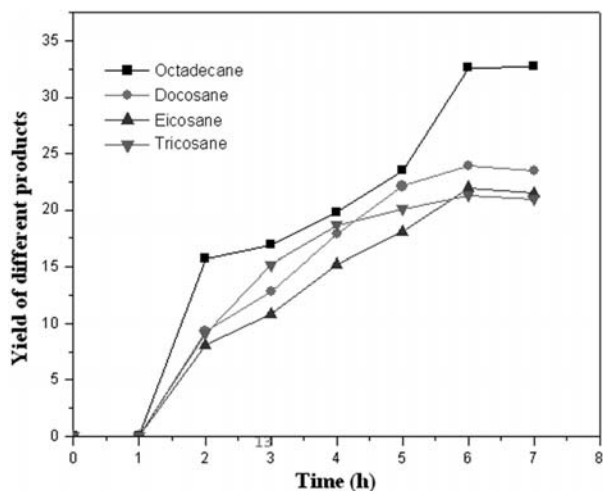


Fig. 6 — Yield of different products from the catalytic cracking of paraffin wax at 350°C using $[Zr-Zr]/Al_2O_3$

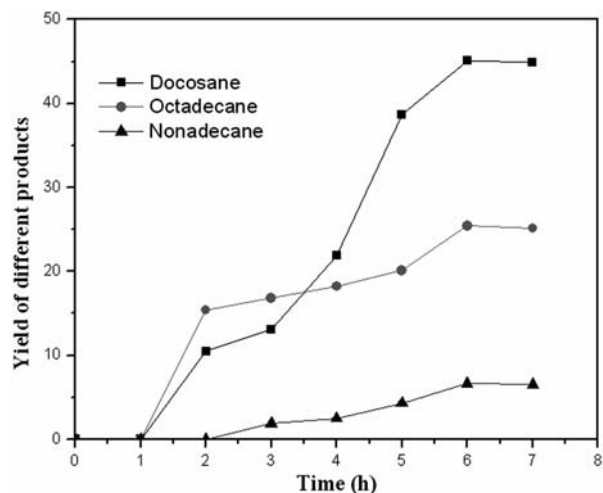


Fig. 7 — Yield of different products from the catalytic cracking of paraffin wax at 400°C using $[Zr-Zr]/Al_2O_3$

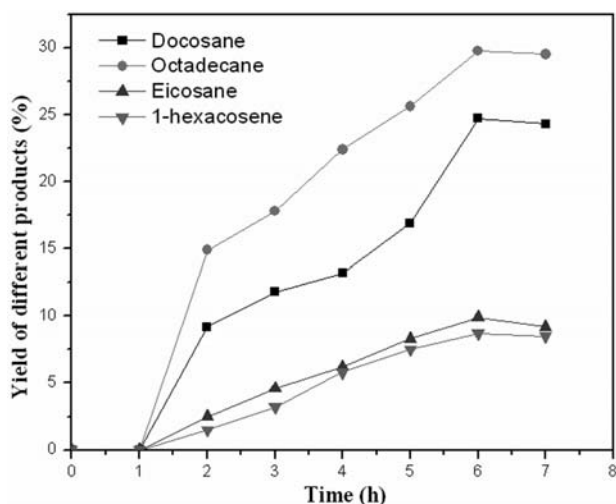


Fig. 8 — Yield of different products from the catalytic cracking of paraffin wax at 450°C using $[Zr-Zr]/Al_2O_3$

after 6 h of reaction. It is thus seen that the reaction temperature is an extremely important variable and in cracking reaction, the product is alkanes predominantly for short reaction times while for higher reaction temperature, long chain alkenes are also formed.

It appears that the disappearance of low molecular weight components of wax do not break while larger molecular weight components get deoligomerized. As a result, the overall molecular weight distribution of the formed product becomes narrow; eventually product consists of 3-4 components, suggesting that the reaction must be occurring very fast towards the formation of nearly constant molecular weight. If this chemical reaction is done beyond 450°C, there is lot of diesel like C_8-C_{15} components and we assumed that the profit of producing oily products more. We have avoided temperature beyond 450°C in our study to form oily products.

In this paper, the focus of the work is to deoligomerize paraffin wax to mineral oils using the complex catalyst and study the product distribution. The product distribution that we find is extremely narrow, selective and specific.

Conclusion

The deoligomerization of waxes is commercially important process and it requires the breakage of C-C bond. Various heterogeneous catalysts reported in literature are used for the catalytic cracking of waxes in presence of oxygen, produce more than 100 components consisting of noncondensable gases CO , CO_2 such as C_1 to C_6 alkanes, liquid products (such as C_7 to C_{14}), aromatics and several unsaturated compounds. By the use of our catalyst $[Zr-Zr]/Al_2O_3$, in the deoligomerization of waxes produce only liquid component and GC-MS analysis shown it to consist of octadecane, eicosane, tricosane, docosane, nonadecane and one alkene i.e. 1-hexacosene. The temperature range for this catalyst is 300-450°C as at the temperature below 300°C the wax remained unaffected. On operating the reactor batch wise, the reactor pressure rises and the final pressure p_0 has great influence on the product distribution. As this p_0 is increased the product is less viscous and lower molecular compounds are produced in larger amount.

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