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# Investigation of the Catalytic Degradation of Dotriacontane over the Diluted Forms of Mordenite, Ultra Stable Zeolite Y and ZSM-5 in Fluidized Bed Reactor

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Dotriacontane was degraded over the diluted forms of zeolites (ZSM-5), ultrastable zeolite Y(USY) and mordenite (MORD) using laboratory fluidized bed reactor (FBR) operating at 360°C. The degradation of dotriacontane resulted in the production of gaseous hydrocarbons vaying in the range of $C_1$–$C_8$. Experiments carried out with the diluted forms of zeolites gave good yields of volatile hydrocarbon with different selectivities in the final products depending on the type of zeolite used in the degradation.

## INTRODUCTION

Industrial waste can cause serious pollution but also could be regarded as a cheap and abundant source of chemicals and energy. Most industrial wastes are disposed of by landfill or incineration resulting in the loss of their energy content. Therefore, conversion of waste materials such as waxed paper, lubricating oil and paraffin wax which have dotriacontane as the main component[1], to useful chemical feed stocks may be promising as a solution to their growing environmental problems and as a viable alternative to fossil fuel[2].

Possible technologies for the conversion of waste to useful products have attracted research in the area of thermal degradation. Workers in Japan have developed a dual fluidised bed process for obtaining medium quality gases from municipal solid waste.[3, 4] Thermal cracking of waste polymer using fluid beds has been piloted on a significant scale.[5–8] However, the thermal degradation of polymer to low molecular weight materials has a major drawback in that a very broad product range is obtained. In addition, these processes require high temperature, typically more than 500°C and even up to 900°C. Suitable catalysts can have the ability to control both the product yields and product distribution from high molecular weight material degradation as well as to reduce significantly the reaction temperature, potentially leading to a cheaper process with more valuable products.

Papers studying the catalytic process using adiabatic batch and fixed bed reactors on the effect of the operation are numerous[9–14] dealing with experimental parameters including temperature, contact time, conversion and product distribution. Unfortunately, studies concerning fluidised bed reactors in catalytic pyrolysis are few.[15, 16]

This paper describes the catalytic degradation of dotriacontane using diluted forms of zeolites, ZSM-5, mordenite (MORD) and ultrastable zeolite Y (USY) in a fluidized bed reactor (FBR) to investigate the products distribution and to achieve different product selectivities.

## EXPERIMENTAL

Dotriacontane was investigated over three different diluted natural zeolites including ZSM-5 [(Si/Al = 17.5, pore size (5.5 × 5.1 Å)], mordenite [(Si/Al = 7, pore size (6.5 × 7.0 Å)] and ultrastable zeolite Y [(Si/Al = 6.2, pore size (7.4 Å)]. The diotriacontane (n-$C_{32}H_{66}$) was used as pellets and the diluant used was ludox ($SiO_2$, 40% suspension).

The catalysts were dilute with ludox which is a pure silica suspension in water (40% $SiO_2$) containing no alumina. Ludox possesses no acid sites and no catalytic activity and it is therefore an ideal diluent for the targeted zeolites. Mixture of 30% zeolite catalyst (3 g zeolite and 17.5 g ludox) were prepared by heating the ludox/zeolite mixture to 60–80°C with slow stirring using a stirrer hot plate till the solution became thin sticky. This was done to ensure that water was evaporated gently to prevent any damage to the catalyst. Once a significant amount of water evaporated, the solution became noticeably viscous and was transported to an oven for drying at 110°C. The resulting dry mixture was then pelleted using a press (force applied 5 tons) and gently ground and sieved to give particles ranging from 120 to 180 μm.

The catalyst (2–3 g) had to be activated before addition to the reactor. This was done in the laboratory by heating the catalyst under a flow of nitrogen (50 mL/min). The samples were heated at 2°C/min to 120°C, held for 2 h at this temperature, then heated 2°C/min to 450°C and held for 4 h. After the activation, the catalyst was preserved at 250°C under a continuous flow of nitrogen.

**Preparation of dotriacontane:** Dotriacontane needed to be treated before use. It was heated in a beaker until melting, then it was poured on a glass surface. After cooling, small pellets were prepared by cutting the alkane using a blade. Then, these pellets were sieved to particles in the range 125–185 μm.

**Reactor design and operation:** The reactor consisted of a 400 mm long pyrex glass tube with sintered distributor (10 mm id) in the middle section where the fluidized bed rests (Fig. 1). The reactor temperature (360°C) was maintained by using digital electronic controller to control the temperature of a three-zone furnace. The temperatures of the three zones were measured using thrermocouples and the effective temperature control of the fluidised bed was maintained.

The carrier gas used was high purity nitrogen. The flow to the reactor (499 mL/min) was controlled by a needle valve and preheated in the bottom zone of the furnace before entering the reaction zone. A flow meter was used to measure the flow rate at the start and the end of each run. The supply system consisted of a feeder which was connected to an inert gas supply (nitrogen or argon), so that dotriacontane could fall into the fluidized catalyst bed. A typical run involves 0.8 g of the activated catalyst poured into the reactor, and 40% (w/w) dotriacontane/catalyst was added.

The gaseous products were collected in sample Tedlar gas bags of 15 L capacity (1–10 min, 11–20 min) and automated sample valve system with 16 loops, each 5 $cm^3$ in volume (spot samples) at 1, 2, 3, 5, 8, 11, 15 min. Each run lasts for 30 min; at the end of each run, a small amount of residue was analysed by elemental analysis.

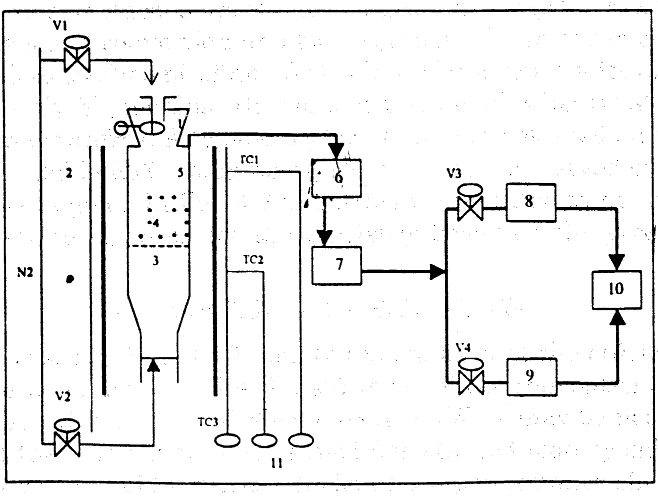

Fig. 1. Schematic diagram of catalytic fluidized bed reactor system: 1. Feeder, 2. Furnace, 3. Sintered distributor, 4. Fluidized catalyst, 5. Reactor, 6-Condenser, 7. Flowmeter, 8. Spot samples box, 9. Gas bag, 10. G.C., 11. Digital furnace controller.

The gaseous products were analysed using a Varian 3400 Chromatograph equipped with a Thermal Conductivity Detector (TCD) and a Flame Ionisation Detector (FID) which was used in this work. The GC was fitted with a Plot $Al_2O_3$/KCl fused silica capillary column (50 m × 0.32 mm id), which allows the separation of $C_1$–$C_8$ hydrocarbons. The column temperature was 110°C (isothermal), and the detector temperature was 270°C. The injection temperature was 250°C and the injection volume was 50 mL. The carrier gas of the GC is helium gas. A calibration mixture containing 1% of $C_1 - C_8$ hydrocarbons in nitrogen, was used to identify and quantify the gaseous products.

The amount of gas was calculated based on the sum of individual components, which were determined quantitatively by gas chromatography. Two types of GC analyses were carried out. Time average samples (0–10 min and 10–20 min) and spot samples (at 1, 2, 3, 5, 8, 11, 15 min). The spot samples were also used to plot the hydrocarbon production as a function of time. The calculations were performed using an Excel spreadsheet on a PC.

## RESULTS AND DISCUSSION

**Product formation rate:** Degradation of dotriacontane over the three catalysts used in this work shows that the rate of production was very fast. Fig. 2 shows the amount produced with time as a percentage. It is clear that the maximum yield was after 1 min for both MORD and ZSM-5, and slightly slower at 2 min for USY. Moreover, in degradation of dotriacontane, it was found that the course of reaction was finished very quickly. For both USY and MORD, the reaction was finished after eight minutes, showing no significant amounts produced after that time, whereas, for ZSM-5, the reaction was completed within the first 5 min.

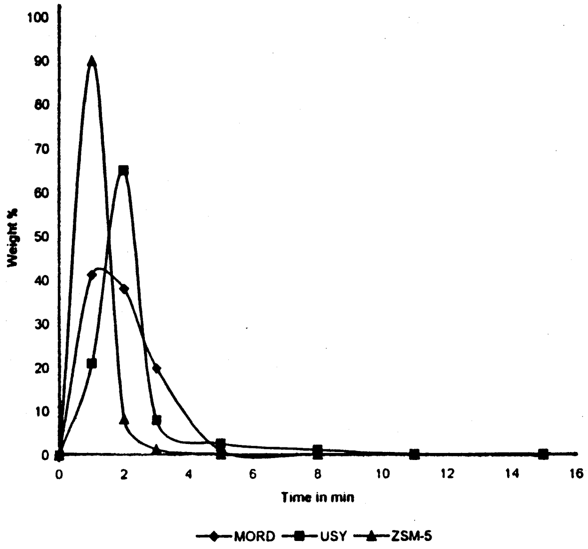

Fig. 2. Product yield with time for the degradation of dotriacontane over the diluted catalysts MORD, USY and ZSM-5

**Product ratios and mass balances:** Because of the nature of dotriacontane, there were some difficulties in using the fluidised bed reactor leading to plugging of the reactor which resulted in a low product yield and relatively low mass balances. Some modifications were needed such as reducing the flow rate to 499 mL/min for MORD and replacing the feeder system with a more suitable one (a necked stopper funnel) in order to achieve better results. After modifications it was possible to get better mass balances. As shown in Table-1, the mass balance is improved; however the product ratios were still low. The low product yield is observed due to the low amount of dotriacontane reacted because most of the amount fed stuck to the walls of the reactor and delivery resulted in a low reacted amount. Since these amounts were taken into considerating in calculation the mass balances, values were much more higher than the values of product ratios.

Mass balance % = weight of products × 100/weight of reactants.

TABLE-1
MASS BALANCE AND CONVERSION RATIOS FOR DOTRIACONTANE

| Catalyst | USY | MORD | ZSM-5 |
|---|---|---|---|
| Mass balance | 81% | 77% | 88% |
| Product ratio | 34% | 31% | 44% |

**Product stream variations with catalysts:** The products of degradation of dotriacontane varied in the range of $C_1 - C_8$ with no significant amounts of aromatic products. From Table-2, the results show that the distribution of the gaseous products is a significant amount over the range $C_3 - C_8$ for the three catalysts. It also shows that an increase in the amounts of $C_6$, $C_7$ and $C_8$ occurred with dotriacontane. Fig. 3 shows the distribution of the products for the degradation of dotriacontane as a function of carbon number.

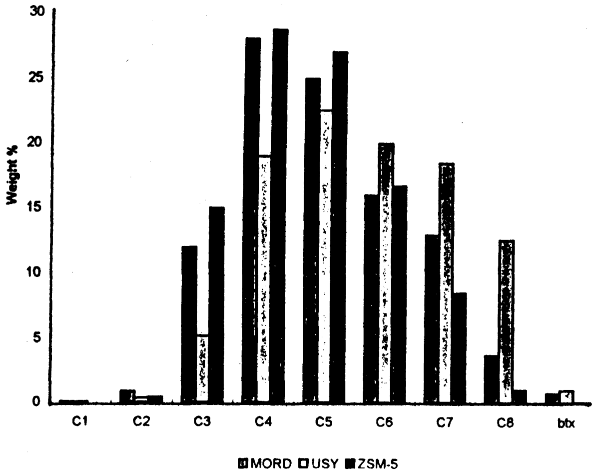

Fig. 3. Product stream distributions for the degradation of dotriacontane over the diluted catalysts as function of carbon number.

**Olefin/paraffin ratio (=/–):** The olefin/paraffin ratios for the degradation of dotriacontane over the diluted USY, ZSM-5 and MORD catalysts are reported in Table-3 and the ratios are in the order: ZSM-5 > MORD > USY. These results depend on the type of pore structure and Si/Al of these catalysts. Because bimolecular reactions are sterically hindered in ZSM-5, the higher olefin/paraffin ratios were observed for ZSM-5 whereas the lower values were observed for USY. This is expected since USY has less restrictive framework structures (12 pore opening and large internal supercages) and less Si/Al than MORD and ZSM-5, allowing bulky bimolecular reactions, yielding a lower olefin/paraffin ratio. Alkene/alkane ratios for mordenite ratios were between ZSM-5 and USY and this is expected since MORD with a 12 ring channel system is more accessible than the 10 ring channel system of ZSM-5.

TABLE-2
THE PRODUCT STREAM DISTRIBUTION FOR DEGRADATION OF DOTRIACONTANE (WEIGHT %)

| Product | MORD | USY | ZSM-5 |
|---|---|---|---|
| $CH_4$ | 0.03 | 0.02 | 0.00 |
| $C_2H_6$ | 0.03 | 0.05 | 0.00 |
| $C_2H_4$ | 0.85 | 0.30 | 0.40 |
| $C_3H_8$ | 8.00 | 1.25 | 2.90 |
| $C_3H_6$ | 3.80 | 4.03 | 12.00 |
| Butanes | 18.00 | 12.30 | 6.24 |
| i-$C_4H_{10}$ | 12.80 | 10.50 | 2.20 |
| n-$C_4H_{10}$ | 5.50 | 1.70 | 4.00 |
| Butenes | 9.70 | 6.90 | 22.60 |
| *trans*-2-Butene | 1.80 | 2.12 | 5.80 |
| 1-Butene | 0.84 | 0.98 | 2.80 |
| *iso*-Butene | 5.88 | 2.33 | 10.00 |
| *cis*-2-Butene | 1.19 | 1.46 | 3.88 |
| Pentanes | 12.20 | 16.00 | 5.44 |
| i-$C_5H_{12}$ | 10.26 | 14.60 | 1.65 |
| n-$C_5H_{12}$ | 1.95 | 1.42 | 3.80 |
| Pentenes | 12.88 | 6.60 | 21.60 |
| i-$C_6$ | 7.14 | 14.21 | 2.00 |
| $C_6H_{14}$ | 0.00 | 1.50 | 2.50 |
| Hexenes | 9.40 | 4.65 | 14.80 |
| $C_7H_{16}$ | 5.70 | 15.40 | 2.56 |
| Heptenes | 7.55 | 3.10 | 5.98 |
| i-$C_8$ | 2.60 | 11.65 | 0.43 |
| Octenes | 1.20 | 1.15 | 0.60 |
| btx* | 0.75 | 1.00 | 0.02 |

*btx = benzene, toluene and xylene

TABLE-3
OLEFIN/PARAFFIN RATIOS FOR DEGRADATION OF DOTRIACONTANE OVER THE DILUTED CATALYSTS MORD, USY AND ZSM-5

| Catalyst | USY | MORD | ZSM-5 |
|---|---|---|---|
| Olefins/paraffin | 0.5 | 1.0 | 4.0 |

**Iso-butane(i-$C_4$) and butene($C_4^=$):** The change in the yield of i-$C_4$ and $C_4^=$ with time gives information about the deactivation of the catalysts throughout the course of reaction. Fig. 4 shows the i-$C_4$ and $C_4^=$ yields with time during the degradation of dotriacontane over the three diluted catalysts. As expected, for ZSM-5, no change is observed in the i-$C_4$ and $C_4^=$ indicating no significant deactivation. For MORD, a decrease in the yields of i-$C_4$ and a slight increase in the yields of $C_4^=$ were observed. A decrease in the i-$C_4$ yields for USY was observed; however, there was a trend for increase in the yields of $C_4^=$. These results are to be expected due to the differences in the structure and type of each catalyst.

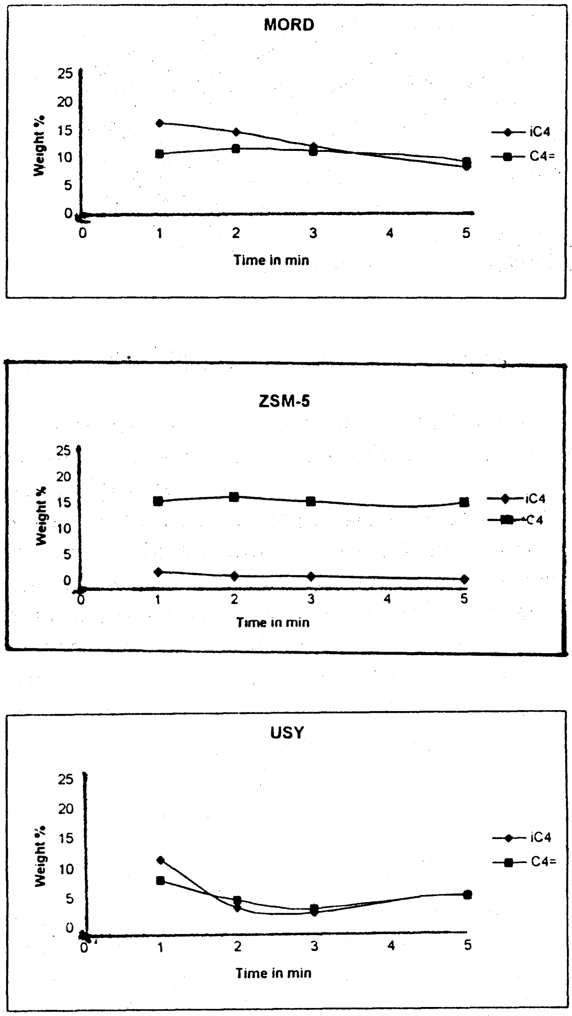

Fig. 4. i-$C_4$ and $C_4^=$ yields with time for the degradation of dotriacontane over the diluted catalysts MORD, USY and ZSM-5.

TABLE-4
COKE % FOR THE DEGRADATION OF DOTRIACONTANE OVER THE DILUTED CATALYSTS, ZSM-5, MORD AND USY AS DETERMINED BY ELEMENTAL ANALYSIS

| Catalyst | ZSM-5 | MORD | USY |
|---|---|---|---|
| Coke (wt %) | 0.35 | 0.70 | 1.25 |

**Coke formation:** The coke percentages for the residue of the degradation of dotriacontane were determined by elemental analysis. The coke formation was found in the order USY > MORD > ZSM-5. As expected, these results are shown in Table-4 and they are consistent with the type of the pore system of the zeolites. Coke is a by-product of secondary reactions, and these secondary reactions are sterically hindered in ZSM-5 more than in MORD and in USY.

## Conclusion

Catalytic degradation compared with thermal degradation could reduce the temperature of reaction and give more selective products. The degradation of dotriacontane was studied over the diluted forms of zeolites ZSM-5, USY and MORD. The behaviour of the catalysts was influenced by their type and nature of their pore sizes and their Si/Al ratio. The suitable catalyst for treatment could be chosen according to the aim of treatment and preferred products.

## REFERENCES

1. T.W. Solomons, Organic Chemistry, 4th edn., p. 136 (1988).
2. M. Lee, *Chem. in Britain,* **31,** 515 (1995).
3. M. Kagayama, M. Igraashi, J. Fukada and D. Kunii, Thermal Conversion of Solid Wastes and Biomass, ACS Symposium Series 130, Washington, D.C., p. 527 (1980).
4. M. Igrashi, Y. Hayafune, R. Sugamiya and Y. Nakagawa, *J. of Energy Resour. Technol.*, **106,** 377 (1984).
5. W. Kaminsky, B. Schlesselmann and C. Simon, *J. Anal. Appl. Pyrolysis,* **32,** 19 (1995).
6. W. Kaminsky, *Adv. in Polym. Technol.*, **14,** 337 (1995).
7. J. Conesa, R. Front, A. Marcilla and A.N. Garcia, *Energy and Fuel,* **8,** 1238 (1994).
8. S.F. Sodero, F. Berruti and A. Behil, *Chem. Eng. Sci.*, **51,** 2805 (1996).
9. G. Audisio, F. Bertini, F.L. Beltrame and P. Carniti, *Makromol. Chem. Macromol. Symp.*, **57,** 191 (1992).
10. H. Okita, R. Nishiyma, Y. Tochihara, T. Mizuhima, N. Kakuta, Y. Morioko, A. Ueno, Y. Namiki, S. Tanifuji, H. Kato, R. Nakayama and T. Kuroyanagi, *Indo. Eng. Chem. Res.*, **32,** 3112 (1993).
11. Y. Ishihara, H. Nanbu, K.O. Said, T. Ikermura, T. Takeuse and T. Kuroki, *Fuels,* **72,** 1115 (1993).
12. A.R. Songip, T. Masuda, H. Kuwahara and K. Hashimoto, *Applied Catalysis, B: Environmental,* **2,** 153 (1993).
13. R.C. Mordi, R. Fields and J. Dwyer, *J. Anal. Appl. Pyrolysis,* **29,** 45 (1994).
14. S. Hardman, S.A. Leng and D.C. Wilson, Eur. Patent Appl. 567292, 20.04.93, BP Chemical Limited, 9 pp.
15. D. Kunii and O.Levenspiel, Fluidization Engineering, 2nd Edn., Butterworth-Heinemann (1991).
16. G. Audisio, A. Silvani, P.L. Beltrame and P. Carniti, *J. Anal. Appl. Pyrolysis,* **7,** 83 (1984).

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