Plasma Catalytic Conversion of Hexane in a Dielectric Barrier Discharge

A. Ağıral1, C. Boyadjian2, K. Seshan2, L. Lefferts2, J. G. E. (Han) Gardeniers1

1Mesoscale Chemical Systems, MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands
2Catalytic Processes and Materials, University of Twente, Enschede, The Netherlands

Abstract: A plasma catalytic reactor based on dielectric barrier discharge has been developed for oxidative cracking of hexane with Li/MgO catalyst at atmospheric pressure. Effect of temperature, oxygen concentration, helium flow, MgO support and Li/MgO catalysts on the conversion of hexane, selectivity and yield values of olefins is reported.

Keywords: Plasma catalysis, dielectric barrier discharge, hexane, MgO, Li, olefin synthesis.

1. Introduction

Ethylene and propylene are building blocks for chemical industry due to enormous demand for these olefins with a growth rate of 4% predicted for the coming years. In the future, it is expected that higher growth rate of propylene will be in demand compared to ethylene. However, current process technologies are unlikely to satisfy demand for olefin yields. Steam cracking of hydrocarbon feedstock (ethane to naphtha) at temperatures of 700 - 900°C is the major route for the production of light olefins. Steam cracking is highly endothermic reaction, requiring substantial amount of energy input and producing coke which inhibits heat transfer. One of the potential alternatives to steam cracking is catalytic oxidative cracking since oxidation is exothermic with minimized coke formation and energy required for cracking can be generated internally. Moreover, atmospheric pressure non-thermal plasma technology introduces efficient chemical activation routes to break thermodynamic limitations. In plasma catalytic reactors, cold plasma can provide high electron temperature and impact of energetic electrons with the reactant molecules can create active species at ambient gas temperatures.

The purpose of this work is to investigate the oxidative cracking of hexane in an alternating current barrier discharge reactor in the presence of Li/MgO catalyst to instantly produce olefins at elevated temperatures. Effects of plasma and catalyst parameters in the conversion, product selectivities and yields are explained on the basis of oxidative radical mechanism.

2. Experimental

Fig. 1 shows the schematic representation of plasma catalytic reactor. Discharge was generated between high voltage wire electrode and the grounded metal foil around the quartz tube. 6 kV peak AC voltage with 50 kHz frequency is used to generate the plasma. Power spent on the supply is 10 W. Unless stated otherwise, 100 ml/min total flow rate was used with gas mixture ratio of 10% hexane, 8% oxygen and the rest is helium. The discharge gap was filled with a packed bed of nonconducting catalyst particles. The mean free path of electrons is too small in the micro pores for the existence of a discharge. The advantage of packed bed plasma catalytic reactor is that it possesses the most optimized catalyst support area to plasma volume ratio. The discharge generated in the voids of the bed, very near to the catalyst surface. Furthermore, dielectric reactor wall makes the plasma current almost independent of the gas mixture and spark formation is inhibited. It is the most optimized combination of continuous flow plasma and catalytic technology.

Mg(OCH3)2 solution (Aldrich), methanol (Merck) and LiNO3 (Aldrich) were used as catalyst precursor materials. Pure hexane (Fluka) was used for catalytic experiments. Shortly, Li/MgO catalysts were prepared by mixing a methanol solution containing Mg(OCH3)2 (0.4M) and the required amount of LiNO3 (to obtain 1 wt.% Li/MgO) with a solution of water in methanol (0.8 M) at room temperature to form a sol and this sol mixture was allowed to stay for 24 h for gelation. The gel was dried at 50°C in vacuum for 7 h and calcined at 500°C in air for 1 h. BET surface area of the catalyst was found as 75 m²/g. The catalytic tests were carried out in a quartz reactor of 4 mm internal diameter and the catalyst bed (10 mm length) was packed between two quartz-wool plugs. A thermocouple outside the quartz tube reactor was used to control the temperature of the furnace. An elaborate micro-GC system allows full analysis of C1-C8 hydrocarbons both paraffins and olefins.
3. Results and Discussion

Fig. 2 shows the change in the plasma conversion of hexane when the temperature increased from 400°C to 600°C without any catalyst material in the empty reactor. Molar conversion of hexane increased from 27% to 33% when the temperature was increased from 400°C to 600°C, respectively. Main reactions that are responsible for plasma hexane cracking are electron impact dissociation of hexane and oxidative cracking with highly excited oxygen radicals. Assuming that the plasma activation was not affected by the temperature, difference in the conversion could be attributed to homogeneous gas phase activation via hydrogen abstraction by gas phase diatomic oxygen, forming HO₂⁻ radicals at 600°C. Since gas phase thermal initiation of radicals starts (Eq. 1) starts

\[ \text{C}_6\text{H}_{14} + \text{O}_2 \rightarrow \text{C}_6\text{H}_{13}^- + \text{HO}_2^- \]  

significantly above 575°C, increasing temperature to 600°C led to an increase in the homogeneous activation of hexane independent of plasma. Electron impact dissociation of hexane is complex process. It is believed that initial reactions involved in the plasma dissociation of hexane are dissociative excitation with high energy electrons and oxygen radicals leading to hexyl radicals (C₆H₁₃), hydrogen molecules (H₂) and methyl radicals (CH₃) since these are the direct products from cracking of C-C and C-H bonds.

\[ \text{C}_6\text{H}_{13}^- \rightarrow \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9, \text{C}_5\text{H}_{11}, \text{C}_6\text{H}_{13} \] (formation of hydrocarbon radicals with electron impact processes)  

\[ \text{O}_2^- \rightarrow \text{O}(^3\text{P}), \text{O}(^1\text{D}) \] (formation of excited oxygen radicals)  

Eq. [2-4] shows the main processes responsible for hexane conversion taking place in the discharge. The hexyl radicals that were fragmented during the initial dissociation processes are believed to follow dissociation patterns which form olefins subsequently.

\[ \text{O} (^3\text{P}, ^1\text{D}) + \text{C}_6\text{H}_{14} \rightarrow \text{Radicals} \] (oxidative cracking with radicals generated in the discharge)  

Fig. 3 shows how conversion changes with increasing from 0 percent to 8 percent at 600°C at atmospheric pressure. As the oxygen ratio increased from 0 to 8 percent, conversion of hexane increased from 7 to more than 30 percent. This fact shows that during plasma cracking, an increase in the amount of oxygen radicals can alter the conversion significantly. The primary event in the plasma oxidative cracking of hexane is the electron impact excitation of molecular oxygen yielding atomic oxygen in the ground O(^3P) and excited O(^1D) states. In the presence of hexane, excited atomic oxygen can open

O(^3P)+ \text{C}_6\text{H}_{14} \rightarrow \text{O} \text{ radicals}
new cracking pathways.

Fig. 4 Effect of oxygen concentration on non-catalytic plasma hexane conversion.

Fig. 5 shows the effect of oxygen on corresponding product selectivities. Formation of oxygenates were not observed due to the high temperature in the reaction conditions (600°C). As the conversion increased, total selectivity to olefins slightly decreased, however overall yield increased. Maximum olefin yield was obtained as 15% at 8% oxygen ratio. Further increase in the oxygen ratio did not increase the olefin yield since the ratio of energy spent on cracking hexane decreased and further decomposition of olefins by the activated oxygen radicals could take place.

Fig. 6 Effect of oxygen concentration on non-catalytic plasma hexane conversion.

In the course of experiments, helium was used as the diluent gas. However, it has two significant effects on the plasma processing. The first one is that it changes the residence time of the processing gas in the active discharge region and secondly it can help to activate the hexane molecules through energy exchange between highly excited helium species. Fig. 6 shows how the conversion changes with different flow rates of helium during the oxidative plasma cracking of hexane at 600°C at atmospheric pressure. Increasing the helium flow rate decreased the residence time of hexane in the plasma reactor and therefore conversion decreased considerably.

Fig. 7 shows the effect of helium flow rate on product selectivities during non-catalytic plasma hexane conversion. Lower selectivities were observed when the helium flow rate decreased. This can be explained by the fact that although the conversion decreased with increasing flow rate, since the number of excited helium species increased, they could accelerate combustion reactions due to energy transfer to the oxygen and hydrocarbon radicals. This can be seen in the increase of selectivity of CO$_x$ products. Since the ratio of energy spent on hexane conversion decreased with increasing helium content then less energy was spent on dissociating hexane with increasing helium content.

To prove the existence of plasma catalytic effect of Li/MgO catalyst for olefin production during oxi-cracking of hexane, plasma conversion experiments were carried out in the presence of MgO support. MgO is the basic oxide support for the Li/MgO catalyst. MgO particles were filled in the plasma region and conversion and yield values were compared with 3 different cases as shown in Fig. 8 and Fig. 9. Pure plasma conversion experiments were carried out in the presence of SiO$_2$ particles. Assuming that SiO$_2$ does not show any catalytic activity and
represents the same geometric structure in the reactor with the catalyst, it was used as a model particle filling.

Fig. 7 Effect of helium flow rate on product selectivities during non-catalytic plasma hexane conversion.

Fig. 8 shows that plasma+MgO gave higher hexane conversion than plasma (SiO$_2$) case. It may be due to different permittivity values of these two dielectric materials. Changes in permittivity may slightly change the accumulation of charges in the plasma before the breakdown and more streamers could be formed at the contact point of particles. Comparing the yield values in Fig. 9, there is no change in the yield of olefins. These results show the fact that there is no synergistic effect of plasma catalysis with MgO support for olefin synthesis. In the case of Li/MgO+plasma catalytic experiment, hexane conversion reached the maximum value around 50 % with highest yield of olefins.

These data show that there is plasma catalytic synergistic effect observed with Li/MgO catalyst which can give 30 % olefin yield. Li/MgO can facilitate activation of hexane. Amount of oxygen were kept far below stoichiometry for complete combustion of hexane to minimize this reaction route. [Li$^+$O$^{-}$] type defect sites are responsible for catalytic activity of Li/MgO catalyst and then hydrocarbon activation can occur via a radical mechanism involving homolytic scission of C-H bonds. Oxygen of [Li$^+$O$^{-}$] defect sites on the catalyst surface selectively abstracts a hydrogen from hexane, forming [Li$^+$OH$^{-}$] on the surface and releasing a hexyl radical to the gas phase:

$$C_6H_{14} + O^{-} \rightarrow C_6H_{13}^* + OH^{-}$$  \[5\]

Further reactions with hexyl radicals take place in the gas phase. In the presence of plasma, activated species such as excited oxygen radicals may regenerate [Li$^+$O$^{-}$] sites and form new type of chain propagators to activate hexane. In addition to surface activation, excitation of hexane to hexyl radicals by high energy electron impact can accelerate the homogeneous gas phase radical mechanism.

Fig. 9 Comparison of olefin yields in the presence of MgO support and Li/MgO catalyst with plasma.

4. Conclusions

A plasma catalytic reactor based on dielectric barrier discharge is designed for oxidative cracking of hexane. Hexane can be converted to valuable olefins in the presence of plasma and Li/MgO catalyst. Lowering process temperature in the plasma reactor results in coupling of hydrocarbon radicals producing heavier hydrocarbons which can be interesting for upgrading hexane. Increasing oxygen ratio and residence time in the plasma gives higher conversion values for hexane. Plasma catalytic effect has been observed with Li/MgO at 600°C giving 30% olefin yield.