

# Catalytic Oxi-Cracking as a Route to Olefins – Efficient Mo-Li/MgO Catalysts for Hexane Conversion

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## Introduction

Oxidative catalytic cracking of naphtha range hydrocarbons is conceptually a promising alternative to steam cracking for the production of light olefins. Efforts in the last years to develop efficient catalysts have not shown promise; the rates and olefin selectivities achieved are insufficient for commercialization. Recent work in our laboratories shows sol-gel synthesized Li/MgO catalyst as promising catalysts for the oxidative conversion of propane to propylene [1]. In this paper we investigate oxidative cracking of hexane over modified Li/MgO catalysts and look at the possibility (i) to enhance hydrogen abstraction, which is the rate limiting step in oxidative conversion and (ii) to maximize propylene selectivities (as against ethylene from steam cracking)

## Materials and Methods

Li/MgO catalysts as such and modified with MoO<sub>3</sub> were prepared. For the preparation of the Li/MgO, a solution of Mg(OCH<sub>3</sub>)<sub>2</sub> in methanol (0.4M) containing LiNO<sub>3</sub> (in appropriate amounts to obtain 1 wt%) was mixed with water in methanol (0.8M) at room temperature and allowed to stay for 24hrs for gelation. Dried gels were calcined at 500 °C in air for 1 hr. Modified Mo-Li/MgO was prepared by wet impregnation of Li/MgO with a solution of ammonium molybdate. The modified catalyst was then dried at 50 °C in vacuum for 7 hours and calcined at 600 °C for 5 hours.

Catalytic tests were carried out at atmospheric pressure and isothermal conditions in a fixed-bed reactor. An alumina tubular reactor of 4mm internal diameter was used and tests were carried out in the temperatures in the range between 425 – 600 °C. Powder catalysts were pressed, crushed and sieved to the particle size of 0.425-0.6 mm. The catalyst bed (10mm length) was packed between two quartz-wool plugs. An alumina rod of 3mm internal diameter was placed below the catalytic bed to block the post catalytic volume and minimize homogenous gas reactions. Total feed of 100ml/min was used. The feed consisted of 10% of hexane vapor, 8 mol% O<sub>2</sub> and balance helium.

## Results and Discussion

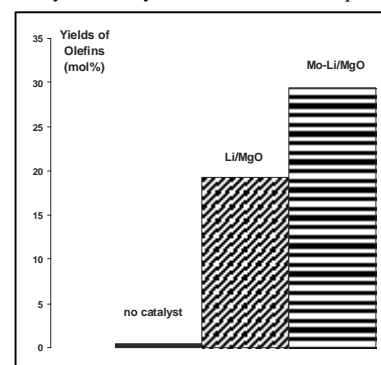
Li/MgO shows activity for hexane cracking at temperatures as low as 425 °C, however olefin selectivities improve with temperature indicating that catalytic oxidative cracking of hexane is heterogeneously initiated homogenous reaction involving radical chemistry in gas phase. At a reaction temperature as low as 575 °C, 28mol% of hexane conversion has been achieved with 61mol% selectivity to light olefins and 25mol% to CO<sub>x</sub>. Co-feeding of oxygen helps to increase hexane conversions, operate in an autothermal mode and inhibit coke formation. However, excess oxygen in the feed enhances deep oxidation reactions via the catalyst surface. CO<sub>2</sub> produced during reaction has a negative effect on catalyst activity; due to surface carbonate formation however addition up to 5mol% of CO<sub>2</sub> to

the feed improves selectivity to light olefins by minimizing secondary deep oxidation reactions via the catalyst surface.

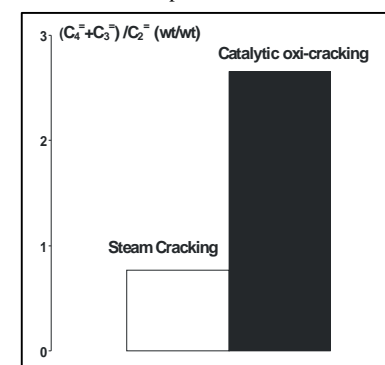
Two strategies to improve activity of the catalyst are (i) to introduce a redox activity (Li/MgO has no redox properties) to facilitate hydrogen abstraction from hexane forming hydroxyl groups, and (ii) to minimize the influence of the carbonate build up on Li and MgO.

Incorporation of 5% monolayer coverage of MoO<sub>3</sub> improves the activity tremendously, maintaining high olefin selectivities. These improvements are translated in higher yields of light olefins at same experimental conditions (figure 1). The advantage of maximizing higher olefin (C<sub>3</sub><sup>=</sup>, C<sub>4</sub><sup>=</sup> compared to C<sub>2</sub><sup>=</sup>) selectivities as compared to steam cracking is significant, as seen from Figure 2.

In order to understand the role of molybdenum oxide structures on the catalytic activity, the following are studied (i) varying Mo loadings to provide monomeric to oligomeric Mo species (ii) their characterization by XRD and Raman spectroscopy and (iii) structure catalytic activity correlations. These aspects will be discussed in the presentation.



**Figure 1.** Yields of olefins over Li/MgO and Mo-Li/MgO (0.5wt%Mo, 1wt%Li). Reaction conditions: 100ml/min, 10% C<sub>6</sub>H<sub>14</sub>, 8% O<sub>2</sub>, balance He, 575 °C



**Figure 2.** Ratios of (C<sub>4</sub><sup>=</sup> + C<sub>3</sub><sup>=</sup>)/C<sub>2</sub><sup>=</sup> for steam cracking of hexane at 700 °C [2] and catalytic oxi-cracking of hexane over Mo-Li/MgO (0.5wt%Mo, 1wt%Li) at 575 °C

## Significance

Steam cracking, the major process for production of light olefins, is an energy consuming process and most likely fails to meet the current environmental regulations. Moreover, yields of propylene from this process are not sufficient to meet the market demands. Through oxidative catalytic cracking process we intend to lower reaction temperatures, minimize coking and gain more control over product distribution increasing propylene to ethylene ratio.

## References

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