

# Bi-Component MoO<sub>3</sub>-CeO<sub>2</sub> Catalyst Supported on Ytria Stabilized Alumina Aerogel: Textural, Structural and Surface Properties, as well as Catalytic Activities for the ThermalCatalytic Cracking (TCC)

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## Introduction

ThermoCatalytic Cracking (TCC) is a newly developed process [1] for the production of light olefins such as ethylene and propylene, which are considered the backbone of the petrochemical industry. This process employs supported metal mixed oxides (i.e. MoO<sub>3</sub>-CeO<sub>2</sub>) based catalysts, which operate in the presence of steam at high temperature. It is well known that the physicochemical and catalytic properties of supported metal oxides catalysts are influenced by many factors, however the nature of the catalyst support is one of the most important. Therefore, evaluating the thermal stability and hydrothermal stability of the catalyst supports as well as their influence on the dispersion and the structure of active components, and consequently the catalytic activities, are of paramount importance for the TCC process. In our previous publication [2], we have investigated the silica-alumina with high silica loading (86.0 wt.% SiO<sub>2</sub> and 14.0 wt.% Al<sub>2</sub>O<sub>3</sub>) as a support for both mono- and bi-component MoO<sub>3</sub>-CeO<sub>2</sub> catalysts. It was found that silica-alumina showed a weak metal-support interactions that lead to the segregation of the active MoO<sub>3</sub> phase and consequently low TCC activities, due to low concentration of basic surface hydroxyl groups and low isoelectric point (IEP). Conventional alumina was also investigated as a potential support for the TCC process. It was found that its efficiency as an effective catalyst support for the TCC process was hindered by its poor thermal and hydrothermal stability at high temperature [3]. On the other hand, yttria doped alumina aerogel that was prepared by sol-gel method using supercritical drying technique, showed much more improved thermal and hydrothermal stability [3]. The main objective of the present work is to further investigate the superiority of yttria doped alumina aerogel as a catalyst support. In particular, its influence on the textural, structural and surface properties as well as catalytic activities of mono- and bi-component MoO<sub>3</sub>-CeO<sub>2</sub> based catalysts for the TCC process.

## Materials and Methods

The methods of catalyst preparation were reported in previous papers [1-3]. The main catalyst active species were molybdenum and cerium, obtained by co-impregnation of ammonium molybdate hexahydrate and cerium (III) nitrate tetrahydrate onto a mesoporous support. The supports studied were conventional  $\gamma$ -alumina, undoped alumina aerogel, and yttria doped alumina aerogel with different amounts of yttria. The various catalyst systems were characterized by diverse techniques such as BET Nitrogen adsorption-desorption, X-ray diffraction (equipped with a search-match software), Laser Raman spectroscopy (LRS), Thermal analysis (DTA/TGA), Isoelectric point measurement (for the catalyst support), and <sup>1</sup>H MAS solid-state NMR. Catalytic performances in the cracking of n-hexane were evaluated using the experimental set-up, catalyst testing and reaction product analysis procedures as reported elsewhere [1,2].

## Results and Discussion

Textural, structural, thermal analysis and other surface properties results of mono-component MoO<sub>3</sub> catalysts loaded onto different supports have demonstrated interesting and significant findings. MoO<sub>3</sub> was highly dispersed on yttria doped alumina aerogel compared to other studied support, as evident from the presence of higher population of dispersed molybdate species (i.e. isolated tetrahedral and polymeric octahedral species), and the delay in the segregation of MoO<sub>3</sub>. It can be inferred from these results that the support-metal interactions (SMI) are quite strong. Isoelectric point (IEP) measurements (Fig.1) have clearly showed the incorporation of Y<sub>2</sub>O<sub>3</sub> into alumina aerogel has succeeded in shifting the IEP to higher values (i.e. IEP of undoped alumina aerogel = 8.16, whereas IEP of 10.0 wt.% Y<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> = 8.60). <sup>1</sup>H MAS NMR spectra have also indicated that the doping alumina aerogel with Y<sub>2</sub>O<sub>3</sub> (which is highly basic in character and has IEP = 9.15) has led to the creation of newly basic surface hydroxyl groups.

Mono-component CeO<sub>2</sub> catalysts have also shown an improved physical properties when loaded onto yttria doped alumina aerogel. This was evident from the significant improvements in the dispersion of CeO<sub>2</sub> crystallites. The results have shown that the transition between the bulk and the dispersed ceria phases was shifted to higher ceria loadings, when using yttria doped alumina aerogel as a support. Furthermore, the ceria crystallites, which were present in the bulk phase had much smaller sizes. This could be attributed to the possible formation of solid-solution between CeO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub>. Calculation of the CeO<sub>2</sub> cubic unit cell parameters supports that possibility. Similar findings were also observed with bi-component MoO<sub>3</sub>-CeO<sub>2</sub>.

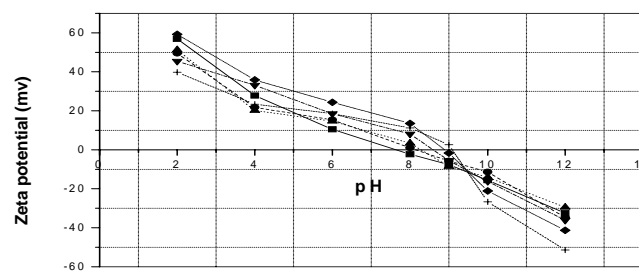


Figure 1: Zeta potential curves of dispersed particles versus pH of aqueous solutions for pure Y<sub>2</sub>O<sub>3</sub> (+), conventional alumina (■), undoped alumina aerogel (●), 2.5 wt.% (▲), 10.0 wt.% (▼) and 20.0 wt.% (◆) yttria doped alumina aerogel (Y<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>)

## Conclusion

Textural, structural, thermal analysis and other surface properties results of mono- and bi-component MoO<sub>3</sub>-CeO<sub>2</sub> catalysts loaded onto different supports led to one explicit conclusion. It can be stated unambiguously that yttria doped alumina aerogel is by far the most effective catalyst support compared to conventional alumina and undoped alumina aerogel. It is anticipated that the catalytic activities were also positively influence by using yttria doped alumina aerogel.

## References

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