

## The Effect of Lanthanum on the Acid-base Properties of Al<sub>2</sub>O<sub>3</sub> as Support for Catalytic Reforming Catalysts

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### Introduction

Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts used in the Catalytic Reforming Process (CR) are bifunctional. The support plays an important role in cracking and isomerization reactions. In fact, according to the generally accepted CR reaction pathway, benzene and coke production are the major problems of the process. It has been reported that modifications of the support with Zr<sup>4+</sup>, Ti<sup>4+</sup> or La<sup>3+</sup> affect both the selectivity and the catalyst deactivation [1]. Lanthanum seems to be one of the most promising additives because it provides high benzene inhibition and resistance to deactivation [2]. However, its effect on the catalytic properties is still unclear. The aim of this work is to provide more detailed characterization of the support and correlate it with the PtSn catalysts behavior.

### Materials and Methods

Alumina and the mixed oxide of Al<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub> were prepared by the sol-gel method and La<sub>2</sub>O<sub>3</sub> was synthesized by precipitation [3]. Aluminum tri-sec-butoxide (Strem, 98%) and lanthanum nitrate (Strem, 99%) were used as material precursors. Once the dry gels were synthesized, they were calcined at 520°C during 6 h using a 3 °C/min heating rate. The materials were analyzed by N<sub>2</sub> physisorption at liquid nitrogen temperature (Quantachrome), X-ray diffraction (Siemens, D-50), Electron Diffraction (Carl Zeiss, EM-910), MAS-NMR (Bruker, ASX-300), NH<sub>3</sub> and CO<sub>2</sub> TPD and FTIR thermo-desorption of pyridine.

### Results and Discussion

Table 1 summarizes the results of the effect of lanthanum over the textural and acid-base properties of the solids. By N<sub>2</sub> physisorption type IV isotherms, mesoporous materials with high surface areas were observed.

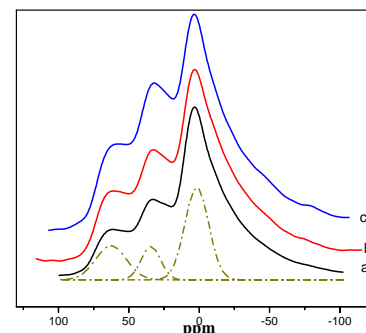
**Table 1. Textural and Acidity-Basicity Properties of the Supports**

Sample	N <sub>2</sub> Physisorption			Acidity-Basicity Properties		
	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore volume (cc/g)	Pore diameter (Å)	Temperature Programmed Desorption		
				Acid site density (mole NH <sub>3</sub> /m <sup>2</sup> ) X10 <sup>4</sup>	Base site density (mole CO <sub>2</sub> /m <sup>2</sup> ) X10 <sup>6</sup>	Ψ
Al <sub>2</sub> O <sub>3</sub>	327	1.26	156	2.72	2.70	10.07
Al <sub>2</sub> O <sub>3</sub> -La <sub>2</sub> O <sub>3</sub> -5	345	1.00	115	2.32	3.88	5.97
Al <sub>2</sub> O <sub>3</sub> -La <sub>2</sub> O <sub>3</sub> -15	355	0.82	93	1.99	4.35	4.57
La <sub>2</sub> O <sub>3</sub>	30	0.23	330	3.11	8.03	3.87

Al<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-5: with 5 wt% of La<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-15: with 15 wt% of La<sub>2</sub>O<sub>3</sub> and ψ: acid/base site ratio

The surface area is increased with lanthanum content, reaching its maximum at 15% of La<sub>2</sub>O<sub>3</sub> content. Acid site density is diminished, while the base site density is increased with the introduction of lanthanum (ψ, Table 1). Furthermore, the higher base site density (15 wt% of La<sub>2</sub>O<sub>3</sub>) is in agreement with the inhibition of benzene and resistance of the deactivation of the PtSn/Al<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-15 reported by Contreras et al. [2]. By pyridine desorption FTIR it was determined that alumina has mainly Lewis acid sites although a small signal attributed to Brönsted acid sites was present up to 200°C. For mixed oxide solids, when the wt% of La was increased, the strength of the Lewis acid sites decreased and the strength of the Brönsted acid sites increased.

By X-ray diffraction it was determined that at 520°C these materials were amorphous. In contrast, the Electron Diffraction patterns suggested that there are micro-domains perfectly crystallized. The existence of one phase of lanthanum aluminate in the mixed oxides was determined, LaAl<sub>11</sub>O<sub>18</sub> (33-699 JCPDS card) could be responsible for the change in the acid-base properties of the support. Figure 1 shows the effect of lanthanum on the spheres of coordination of the Al<sup>3+</sup>. A decrease of aluminum in octahedral environment Al<sup>VI</sup> (3.5 ppm) as well as an increase of the pentahedrally coordinated Al<sup>V</sup> (32 ppm) as a function of the lanthanum content was observed. These changes in the spheres of coordination of Al can be attributed to the introduction of lanthanum to the framework of Al<sub>2</sub>O<sub>3</sub>.



**Figure 1.** Al<sup>27</sup> MAS-NMR spectra of the materials after 520°C treatment a) Al<sub>2</sub>O<sub>3</sub>, b) Al<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-5 and c) Al<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub> -15 and the dash dot line is deconvolution of the peaks.

### Significance

This work explains how lanthanum contributes to overcome both benzene formation and catalyst deactivation, the main problems of the Catalytic Reforming Process.

### References

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