

Effect of lanthanum on the performance of Pt-Sn/Al₂O₃ Reforming catalysts. The impact of Al^{IV} species on metal-support interaction

Ignacio Contreras¹, Harry Bitter², Krijn P. de Jong², and Tomás Viveros^{1,*}

¹ Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa, Av. San Rafael Atlixco N. 186, 09340 México D.F. Tel. +52(55) 58044925

² Inorganic Chemistry and Catalysis Group, Utrecht University, Sorbonnelaan 16, 3584CA Utrecht, the Netherlands, tel, +31 302537400

*tvig@xanum.uam.mx

Introduction

Lanthanum has appeared as an alternative to decrease the deactivation and modify the selectivity of bimetallic PtSn/Al₂O₃ reforming catalysts [1, 2]. However, its impact is yet unclear, and its effect seems to be dependent on the preparation method used to introduce it in the system. By conventional wet impregnation lanthanum seems to decrease the platinum activity in three orders of magnitude due to the stabilization of platinum into Pt²⁺ [2]. But, if lanthanum is added to alumina by sol-gel method, that catalyst becomes more active showing higher resistance to deactivation and lower benzene production [1]. This work is focused to elucidate the effect of the Al^{IV} coordination on the acid/base properties of the support, to determine the changes in the metal-support interaction, and consequently on the catalytic behavior of Pt particles.

Materials and Methods

The sol-gel method was used to introduce La³⁺ into alumina matrix. The prepared support was impregnated conventionally either with a solution of H₂PtCl₆ or H₂PtCl₆ + SnCl₂ to produce mono and bimetallic catalysts. All catalysts were designed with 1 wt% of Pt and 0.6wt% of Sn in the case of bimetallic catalysts. The catalytic behavior and deactivation were evaluated in the *n*-heptane reforming at 1 atm and different temperatures to obtain the activation energies. A detailed characterization was also carried out, using physical adsorption of N₂, TPD of NH₃ and CO₂, ²⁷Al MQMAS-NMR, CO chemisorption, CO-FTIR and HRTEM measurements.

Table 1. Chemistry and catalytic properties of the catalysts.

Catalyst	Al ^{IV} /Al ^V ratio ^a	Acid/base site ratio ^a	Pt dispersion		TOF, s ⁻¹	Ea, KJmol ⁻¹
			CO chem	TEM		
Pt/Al ₂ O ₃	11.20	10.07	81.4	80.0	1454	51.02
Pt/Al ₂ O ₃ -La ₂ O ₃ -5	5.88	5.97	86	82.1	-	-
Pt/Al ₂ O ₃ -La ₂ O ₃ -15	5.40	4.57	81.6	80.1	1662	55.33
PtSn/Al ₂ O ₃	-	-	80.4	81.5	1504	61.89
PtSn/Al ₂ O ₃ -La ₂ O ₃ -15	-	-	82.2	79.5	2015	46.72

a: data's referred to the support after its calcination at 600°C. TOF obtained at 380°C.

Results and Discussion

The result of MQMAS NMR, TPD and those of the catalytic test are shown in table1. Besides the resonance lines attributed to tetrahedrally (Al^{IV}) and octahedrally (Al^V) coordinated aluminum, the MQ MAS NMR ²⁷Al spectra showed an extra line which was assigned to pentacoordinated Al (Al^V), which explains the decrease of the Al^{IV}/Al^V ratio shown

in table1. The coordinatively unsaturated Al ions (Al^V) are produced due to La and the sol-gel synthesis, which suggest that strongly distorted shells of Al^V are potential strong Lewis acid centers or they generate such sites upon calcination. Nevertheless, TPD results show a decrease of the acid/base ratio alumina with the presence of lanthanum. TPD profiles also showed that the desorption of the trace molecules used to determine the acidity and basicity is carried out at higher temperature, which indicates that La induces stronger acidity. Thus, lanthanum modifies the acid/base properties of the support, and seems to be responsible for changes in the catalytic properties of supported Pt particles. Therefore, TOF is highly influenced by lanthanum (reaction at 380 °C), which agrees with the decrease of the activation energy (Ea). According to Mojet et al. [3] the acid/base properties of the support influence the electronic properties of the supported metal particles, fact that is in line with the results shown in figure 1. This figure clearly shows the increase of the backdonation signal with lanthanum, which implies a higher electronic density at the surface. Actually, the shift of the linear signal to low wavenumbers also reveals changes in the electronic properties of platinum. Indeed, this figure shows the suppression of the bridge signal when tin is present; these results can be interpreted as evidence of the dilution of platinum atoms with tin, phenomena referred normally as geometric effect, which is related with the changes in the selectivity to aromatics.

Significance

This work elucidates the influence of Lanthanum on the performance of catalysts for the Catalytic Reforming Process, and demonstrates its impact decreasing the undesirable benzene production.

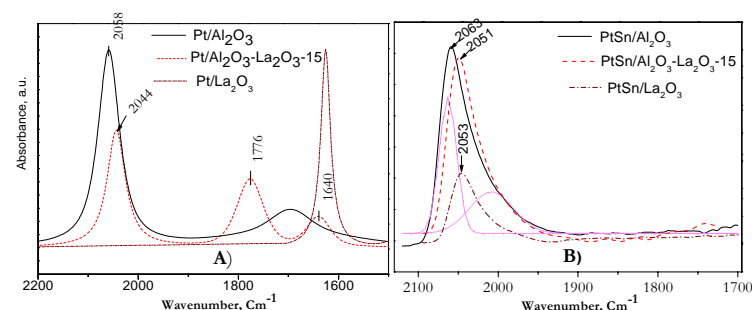


Figure 1. CO-FTIR analysis on A) monometallic Pt-base catalysts and B) bimetallic PtSn catalysts as function of the support.

References

- Contreras, I., Viveros, T. *Proceeding of the European Congress of Chemical Engineering* 6 T2-13p, 2061 (2007).
- Del Angel, G., Bonilla, A., Navarrete, J., Figueroa E.G., and Fierro, J. L. G., Acosta, D. *R. J. Catal.* 219, 63 (2003).
- Mojet, B.L., Ramaker, D.E, Miller, J.T., Koninsberger, D.C., *J. Catal.*186, 373 (1999).