

## CoLa mordenites steam resistant catalysts for the NO<sub>x</sub> SCR with CH<sub>4</sub>

Eduardo A. Lombardo\* and Laura Gutierrez

Instituto de Investigaciones en Catálisis y Petroquímica – INCAPE - (FIQ, UNL-CONICET),  
Santiago del Estero 2829, 3000 Santa Fe (Argentina)

\*nfisico@fiquis.unl.edu.ar.

### Introduction

A variety of metal cation-containing zeolites have been studied as HC-SCR catalysts. However, the low hydrothermal stability of these zeolites has impaired their practical application. In this vein, the combination of Co-zeolites with a noble metal (Pt or Pd) has been proposed to improve the zeolite water resistance; however, some deactivation proceeds after 50 h on stream [1-3]. On the other hand, it is well known that the incorporation of rare earth to Y zeolites increases its stability [4]. In this work, we have studied the effect of lanthanum addition to the mordenite system in order to improve the hydrothermal stability of CoHMordenite for the SCR of NO<sub>x</sub> with methane.

### Materials and Methods

The catalysts were prepared by ion exchange starting from Na-mordenite (Na-MOR), Si/Al= 6.5. The ion exchanged forms and Co,H-MOR were prepared following the procedure described in Gutierrez et al. [3]. Briefly, H-MOR was obtained contacting Na-MOR with a NH<sub>4</sub>NO<sub>3</sub> solution under reflux for 24 h at 100°C. An aliquot of H-MOR was exchanged with a solution of Co(CH<sub>3</sub>COO)<sub>2</sub> to obtain Co<sub>x</sub>H-MOR. An aliquot of CoHMOR was exchanged with lanthanum using a La(NO<sub>3</sub>)<sub>3</sub> solution and stirring during 36 h at 25°C. The solids named Co<sub>0.15</sub>LaHMOR-400 and Co<sub>0.16</sub>LaHMOR-500 were calcined at 400°C and 500°C prior to lanthanum exchange. The La content in all catalyst was ca. 1wt %. All catalysts before the catalytic tests and characterization were heated up in O<sub>2</sub> flow at of 2°C min<sup>-1</sup> to 400°C and kept at this temperature for 8 hours. The catalysts were characterized with TPR, Raman spectroscopy and FTIR. The reaction was carried out in a fixed-bed flow-through quartz reactor.

### Results and Discussion

Table 1 shows the conversions of NO and CH<sub>4</sub> obtained with fresh catalysts and after 400 h at 500°C under wet reaction stream. For the fresh catalyst (TOS=0), the incorporation of La decreased the NO conversion up to 30% and affects even more the methane conversion. A higher selectivity was obtained when the Co-exchanged zeolite was not calcined before the La exchange. After 400 hours on stream (TOS = 400) both the exchange order and the calcination of the Co-exchanged zeolite affected the hydrothermal resistance of the catalyst. Thus, Co<sub>0.42</sub>LaHMOR-500 is the best catalyst and even shows an increase of 33% in NO conversion after 400 h on stream.

The infrared study of CO adsorption on the calcined samples was performed. LaHMOR prepared by ion exchange showed a single band at 2188 cm<sup>-1</sup>. On the La/NH<sub>4</sub>MOR samples prepared by the impregnation, no CO band was observed. This might be a confirmation that La

is located at the lattice cation positions in the exchanged sample (LaHMOR). The Co containing mordenites invariably showed the CO-Co<sup>2+</sup> adsorption bands.

The TPR profiles show that La-containing solids which have been calcined after the Co exchange are the most stable ones since the transition metal neither migrates to occupy different lattice positions nor are cobalt oxides formed. The Raman spectra do not show the fingerprints of Co<sub>x</sub>O<sub>y</sub> species on the used bimetallic solids. On the other hand, the used cobalt catalysts not containing La or the La-Co solids without intermediate calcination show reduction peaks at low temperatures that are symptomatic of diminished interaction with the zeolite matrix and the 690 cm<sup>-1</sup> main band of Co<sub>3</sub>O<sub>4</sub> in the Raman spectra. Also in this case, the high temperature reduction peak moves to even higher temperatures indicating that the Co<sup>2+</sup> species migrates to less accessible lattice locations. These results suggest that the presence of lanthanum increases the hydrothermal stability of Co-mordenite when the rare earth is exchanged into the matrix after the active species (Co<sup>2+</sup>). This effect is enhanced when the CoHMOR is calcined at 500°C before the second metal exchange.

**Table 1. Catalytic activity<sup>a</sup>**

Catalyst <sup>b</sup>	TOS=0, T=500°C H <sub>2</sub> O=0%			TOS=400h, T=500°C H <sub>2</sub> O= 10%			Drop in Conversion (%)	
	C <sub>NO</sub> (%)	C <sub>CH<sub>4</sub></sub> (%)	S (%)	C <sub>NO</sub> (%)	C <sub>CH<sub>4</sub></sub> (%)	S	NO	CH <sub>4</sub>
LaHMOR	6	35	8.6	3	18	8	50	51
Co <sub>0.15</sub> HMOR	42	83	26	12	25	24	70	70
LaCo <sub>0.2</sub> HMOR	40	95	21	10	30	17	25	31
Co <sub>0.16</sub> LaHMOR	34	37	46	26	29	45	26	49
Co <sub>0.42</sub> LaHMOR-400	34	65	26	31	50	31	9	23
Co <sub>0.42</sub> LaHMOR-500	30	95	16	40	72	28	33 <sup>c</sup>	24

<sup>a</sup> Flow reactor; feed: 1000 ppm CH<sub>4</sub>, 1000 ppm NO, 2% O<sub>2</sub>; GHSV = 7500 h<sup>-1</sup>.

<sup>b</sup> The cobalt subscript shows its wt%.

<sup>c</sup> Increase in conversion.

### Significance

Increasing the hydrothermal stability of Co-zeolites would allow the use of these catalysts for NO<sub>x</sub> abatement in combustion gases from stationary and mobile sources.

### References

1. Ogura, M., Sugiura, M., Hayashi, Kikuchi, E., *Catal. Lett.* 42, 185 (1996).
2. Gutierrez, L., Boix, A., Petunchi, J., *Catal. Today* 54, 451 (1999).
3. Gutierrez, L., Ulla, M. A., Lombardo, M.A., Kóvacs, A., Lónyi, F. Valyon, J., *Appl. Catal. A: General*, 292, 154 (2005).
4. Bartlett, J. G., Cooney, R. P., and Kydd, R. A., *J. Catal.* 114, 53 (1988).