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## NO REDUCTION WITH C<sub>3</sub>H<sub>8</sub> ON Co/Al<sub>2</sub>O<sub>3</sub> CATALYST. EFFECT OF O<sub>2</sub> CONCENTRATION

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### Abstract

The selective catalytic reduction (SCR) of NO by propane in excess oxygen-containing gas mixture was studied on Co/Al<sub>2</sub>O<sub>3</sub> catalyst. The oxygen concentration is very important for the reaction. The NO conversion to N<sub>2</sub> without oxygen is 3% at 800 K and when the O<sub>2</sub> concentration is raised up to 8% the NO conversion reaches its maximum value of 60% at 800 K. Characterization results by TPR and UV-Vis spectroscopy show that in the catalyst, species strongly interacting with tetrahedral and octahedral Co<sup>2+</sup> ions in the support are present.

*Keywords:* NO reduction, C<sub>3</sub>H<sub>8</sub>, Co/Al<sub>2</sub>O<sub>3</sub>

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## INTRODUCTION

Several papers on selective catalytic reduction of nitric oxide by hydrocarbons (HC-SCR) have appeared since the 90's. Most of the active catalysts known to date are zeolite [1-7] and nonzeolitic catalysts [8-19], as well as metal oxides with or without transition metals. It has been shown that alumina-based catalysts, such as Co-Sn/Al<sub>2</sub>O<sub>3</sub> [17], Ag/Al<sub>2</sub>O<sub>3</sub> [16], Pt/Al<sub>2</sub>O<sub>3</sub> [20], Cu/Al<sub>2</sub>O<sub>3</sub>, Ni/Al<sub>2</sub>O<sub>3</sub>, Co/Al<sub>2</sub>O<sub>3</sub> [12] are efficient and stable catalysts for NO reduction with hydrocarbons. Among them, Co/Al<sub>2</sub>O<sub>3</sub> has recently attracted much attention being stable in the presence of SO<sub>2</sub> and water [21]. The preparation method, cobalt loading, cobalt source, calcination temperature and alumina source are the critical variables for the activity.

In this work a cobalt catalyst supported on alumina was prepared and characterized. The influence of the oxygen concentration on both reactions NO reduction to  $N_2$  and propane combustion was analyzed.

## EXPERIMENTAL

### Catalyst preparation

The cobalt catalyst was prepared by impregnating 2 g of support ( $\gamma$ -alumina) in 500 cm<sup>3</sup> of an aqueous solution of  $Co(NO_3)_2$  in ammoniacal medium, at room temperature under constant stirring for 6 h. The nominal concentration for this catalyst was 1.5%. After impregnating the support the material was washed and dried at 373 K. The calcination was carried out in a muffle from room temperature to 1273 K and maintaining this temperature for 2 h.

### Catalyst characterization

The cobalt content was determined by Atomic Absorption Spectroscopy (AAS) using an ILL equipment utilizing samples that were calcined at lower temperature (600°C for 2 h) to avoid the strong metal-support interaction occurring when the precursor was calcined at 1273 K making the material disintegration difficult for its subsequent analysis.

The superficial area of catalysts was determined in a Micromeritics Accusorb 2100E equipment using the BET method for its estimation.

The metal-support interaction was studied by temperature-programmed reduction (TPR) using a conventional equipment constructed in this laboratory. A  $H_2/N_2$  mixture was fed with 10% hydrogen concentration using a heating rate of 10 K/min up to a final temperature of 1273 K.

In order to obtain more information about cobalt species present in the catalyst, diffuse reflectance spectroscopy analyses were carried out in a Varian Super Scan 3 equipment. Spectra of catalysts finely milled were recorded between 300 and 800 nm using alumina as reference.

### NO reduction with $C_3H_8$

Catalytic reactions were evaluated in a fixed-bed reactor made of quartz (id = 0.8 cm) and heated electrically. The temperature measured by means of a thermocouple of the K type in contact with the catalytic bed. The reaction mixture was obtained from four feed lines controlled individually: NO/He,

C<sub>3</sub>H<sub>8</sub>/He, O<sub>2</sub>/He and He to close the balance at 1 bar. The standard reaction feed was 50 mL/min of 1500 ppm NO, 2000 ppm C<sub>3</sub>H<sub>8</sub> and variable concentration (0-8%) of O<sub>2</sub> corresponding to a space velocity of about 8600 h<sup>-1</sup>.

Reaction products were monitored with a Shimadzu model GC-8A gas chromatograph provided with a TCD detector. The separation of products was performed with a concentric CTRI column of Altech. This system permits the identification and quantification of O<sub>2</sub>, N<sub>2</sub>, N<sub>2</sub>O, CO<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, CO and NO.

The conversions for the NO reduction reaction were calculated in terms of N<sub>2</sub> production as  $X_{N_2} = 2[N_2]/[NO]$ . The propane conversion due to hydrocarbon combustion with oxygen was calculated as  $X_{CO_{2comb}} = (1/3 [CO_2] - 1/2.5 [N_2])/[C_3H_8]$ , where [N<sub>2</sub>], [CO<sub>2</sub>] are gas-phase concentrations after reaction and [NO], [C<sub>3</sub>H<sub>8</sub>] are feed concentrations. The carbon balance was always better than 98% and no other N-containing compound, as N<sub>2</sub>O, was detected.

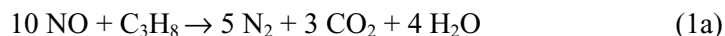
## RESULTS AND DISCUSSION

### Catalyst characterization

The catalyst is a brilliant blue material with 63 m<sup>2</sup>/g of superficial area and 1.68 g of cobalt content for each 100 g of material (AAS). UV-Vis spectra showed a triplet at 540, 580 and 625 nm, which represents tetrahedral Co<sup>2+</sup> ions. The 480 nm signal was attributed to octahedral Co<sup>2+</sup> ions [22]. Yan *et al.* [21] postulated this last cobalt species as the active site for NO oxidation to NO<sub>2</sub>. The TPR diagram of the Co1.5Al catalyst did not show any reduction signal when the experiment was carried out up to 1273 K. These results indicate the presence of species strongly interacting with the support. Bulk cobalt aluminate starts its reduction at 1173 K.

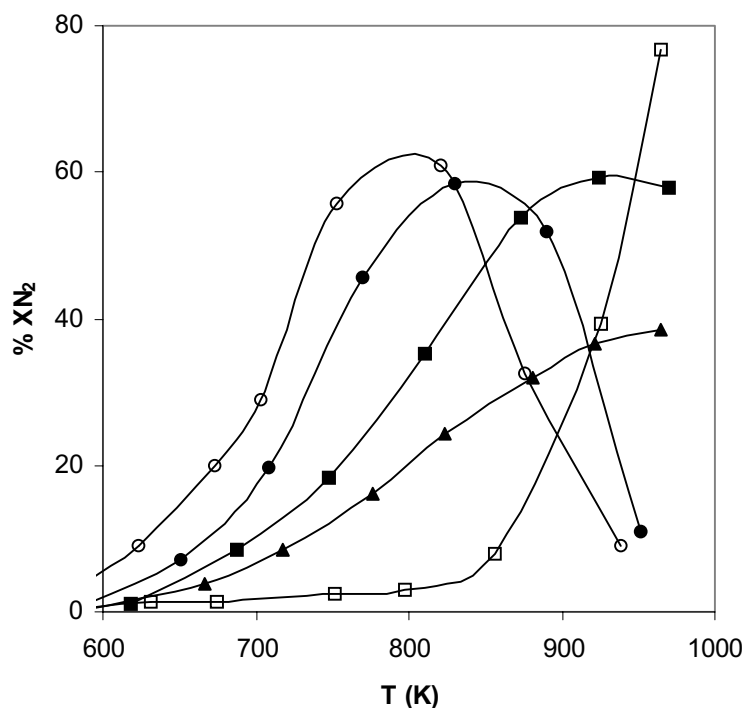
### NO reduction with C<sub>3</sub>H<sub>8</sub>

Figure 1 shows the NO conversion to N<sub>2</sub> for the Co1.5Al1000 catalyst in the temperature range studied (600-1000 K). When NO reduction with propane takes place without oxygen the reaction can be represented by the following stoichiometry:



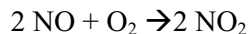
The catalyst shows activity for NO reduction of nitric oxide with and without oxygen. The oxygen effect is very important since it increases NO

reduction to  $N_2$  in all the concentration range studied (0.6% to 8% of oxygen). For example, at 800 K the NO conversion without oxygen is 3% while for a 8% oxygen concentration the conversion is 60%.



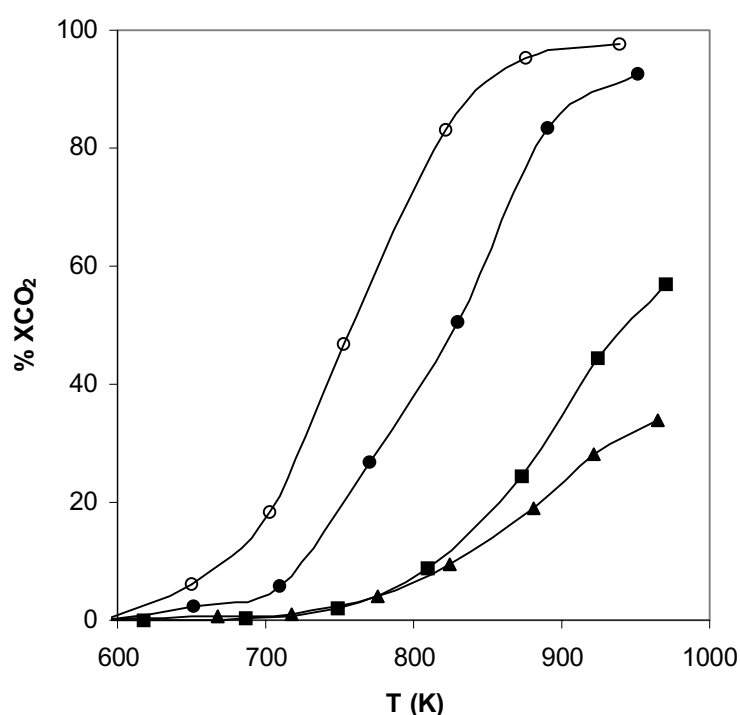
**Fig. 1.** NO conversion to  $N_2$  at the following  $O_2$  concentrations (%):  $\circ$  8,  $\bullet$  2,  $\blacksquare$  0.8,  $\blacktriangle$  0.61 and  $\square$  0; 1500 ppm of NO and 2000 ppm of  $C_3H_8$

There is some consensus that the initial step of NO reduction is the NO catalytic oxidation to  $NO_2$  which then reacts with propane giving  $N_2$ .



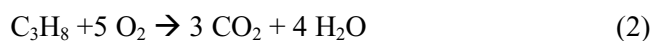
The oxidation of NO to  $NO_2$  is favored with the increase of oxygen concentration and consequently the  $N_2$  generation rate is also enhanced [10-12,14,23-24].

The reduction of NO without oxygen requires a temperature of more than 230° with respect to the experiment with 8% oxygen to achieve about 10% conversion, reaching 77% conversion at 965 K. The NO reduction by C<sub>3</sub>H<sub>8</sub> without oxygen takes place at higher temperatures. Similar results were found by Meunier and Ross on a low-load silver-alumina catalyst using propane as reducing gas [14].



**Fig. 2.** C<sub>3</sub>H<sub>8</sub> conversions to CO<sub>2</sub> at the following O<sub>2</sub> concentrations (%): ○ 8, ● 2, ■ 0.8 and ▲ 0.61; 1500 ppm of NO and 2000 ppm of C<sub>3</sub>H<sub>8</sub>

Figure 2 shows the results of propane conversion to CO<sub>2</sub> produced only by the secondary reaction of propane combustion (eq. 2) that occurs in parallel with NO reduction to nitrogen.



From the analysis of data obtained it is possible to observe that propane conversion to  $\text{CO}_2$  in presence of NO is noticeably affected by oxygen. Propane combustion increases in the whole temperature range tested (600-1000 K) when the oxygen concentration in the feed is increased. When the oxygen concentration is increased by one order of magnitude from 0.8 to 8%, the propane conversion grows from 12 to 83% at 820 K.

The increase of oxygen concentration, besides increasing the NO conversion to  $\text{N}_2$ , produces also a temperature decrease at which the conversion is maximum. Thus, for example, for 8% oxygen the maximum conversion is obtained at 800 K, while for 0.6% oxygen the maximum conversion is not achieved within the temperature range studied. The increase of oxygen concentration increases the combustion rate (eq. 2) so the main reaction (eq. 1) is affected to a higher extent at lower temperature.

Results obtained using a 8% oxygen feed show that at 820 K NO conversion to  $\text{N}_2$  is 60% and propane conversion to  $\text{CO}_2$  by the secondary reaction of propane combustion is 83%. Thus, from the 2000 ppm of propane used as feed, 1660 ppm is consumed in the propane combustion, leaving 340 ppm for the hydrocarbon reduction. According to the stoichiometry of the reaction (eq. 1b) with 340 ppm of propane it would be possible to reduce 1700 ppm of  $\text{NO}_2$ , which would mean 100% theoretical conversion. The experimental value is 60% and this indicates that for 820 K the reaction (eq. 1b) is not complete. On the other hand, if results obtained at 940 K are analyzed, propane conversion by the combustion reaction is 97.7%, with residual 2.3% propane. This means that 46 ppm is available for the reduction of 230 ppm nitric oxide, thus the maximum conversion possible with the residual propane would be 15% and the experimental one is 9%. Similar results are obtained by analyzing the experiment at 876 K. The decrease of NO conversion from 876 K is produced by the lack of hydrocarbon for the reduction.

## CONCLUSIONS

The catalyst shows activity for NO reduction by propane with and without oxygen. When increasing the oxygen concentration in the feed the NO conversion to  $\text{N}_2$  increases and the maxima of conversion are shifted toward lower temperatures. The activity increase with oxygen concentration is postulated to be due to the formation mechanism of  $\text{NO}_2$  with subsequent reduction by hydrocarbon.

In this reaction system, propane combustion appears as a secondary reaction that consumes hydrocarbon. As the oxygen concentration is increased the combustion reaction is accelerated. This fact also produces a strong decrease of the hydrocarbon concentration, and so the  $\text{NO}_2$  reduction in a catalytic way is not favored.

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